High-throughput Screening of Coke Resistant Catalyst with Thermal Barcodes

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ABSTRACT

Deactivation of fluid catalytic cracking (FCC) catalysts is mainly associated with carbonaceous deposits or coke formation. Coke yield is a key measurement of catalyst performance and often used in catalyst selection. Many factors influence the coke formation such as structure and composition of catalyst, and operating conditions, thus a large parameter space will have to be explored to identify the best coke resistant catalyst as well as optimum operating condition to minimize coke formation. However, the existing methods for heterogeneous catalyst evaluations are limited by low throughput, meaning each time only one catalyst or one experiment condition can be tested. Barcodes have been used ubiquitously to tag products, but common barcodes that are attached on exteriors of packages are not suitable for catalyst evaluation. There is an unmet need to develop a new type of barcodes that can be used to label each catalyst bead, and a group of catalysts will then be able to be evaluated simultaneously to save time and effort.

The main objective of my research was to establish a high-throughput catalyst evaluation system based on thermal barcodes, in which a selected panel of phase change nanoparticles (PCM) was embedded into catalyst pellets. Owing to sharp melting peak of phase change nanoparticles and large temperature range of thermal analysis, the labeling capacity of thermal barcodes was greatly increased to over millions, sufficiently to evaluate a large number of catalysts in one batch of reaction. The thermal barcodes have been used to test coke formation for catalyst evaluation. After reaction, coke formation was tested by thermo-gravimetric analysis and the thermal barcode was decoded with a differential scanning calorimeter (DSC). Items like heat transfer, interaction among catalyst and PCM particles, and gas diffusion have been studied to exam the feasibility of the high-throughput screening method.
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1.0 INTRODUCTION

Fluid catalytic cracking (FCC) is one of the most important conversion processes used in petroleum refineries. It is widely used to convert high-boiling, high-molecular weight hydrocarbon fraction of petroleum crude oils to valuable gasoline and olefin gases.\textsuperscript{1-3} FCC reactions are catalyzed with heterogeneous catalysts at high temperature. In FCC process, the reversible deactivation of FCC catalysts has been mainly associated with carbonaceous deposits or coke formation.\textsuperscript{4-6} Coke formation during catalytic reaction blocks access to catalytic active sites, cause hydrocarbon/heat loss. Costs to industry for catalyst regeneration, replacement, and even plant shutdown can be billions of dollars every year. Therefore, coke yield is an important measurement of FCC catalyst performance and one key criterion in catalyst selection.

Many factors can influence coke formation such as the natures and structures of catalytic species and supporters, and operating environment (temperature and pressure).\textsuperscript{7} Coke formation on catalyst can be decided simply by using thermogravimetric analysis (TGA), where coke is burned into gaseous carbon dioxide with measurable weight loss.\textsuperscript{8} A large number of experimental parameter spaces will have to be explored in order to identify the best catalyst and operating environment to reduce coke formation. To achieve high analysis efficiency, high-throughput screenings (HTS) technologies have already been used in catalyst selection area. Infrared thermography was used to evaluate catalyst activity by detecting catalytic reaction heat. More complex catalyst evaluation testing unit was built based on mass spectrometry (MS) detector. 48 catalyst samples were tested simultaneously in three different reaction conditions. Various gases (such as NO\textsubscript{x}, SO\textsubscript{2}, CO, CH) can be brought into the high-throughput but expensive testing unit.
Phase change materials (PCM) nanostructures with sharp thermal peaks in differential scanning calorimetry (DSC) can serve as barcode for objective of interest. Particles of nanoscale size can mix with the objective homogeneously to enhance the detection sensitivity. Sharp melting peaks and large thermal scanning range of phase change nanoparticles enable the barcoding capacity of thermal barcodes to be greatly increased to over millions. Thus, the main objective of my research is to establish a high-throughput catalyst evaluation system based on thermal barcodes, in which a selected panel of phase change nanoparticles are embedded into catalyst pellets (Figure 1). Large barcoding capacity and high sensitivity of the thermal barcode enable to evaluate a large number of catalysts in one batch of reaction. After reaction, the amount of coke will be determined by thermogravimetric analysis (TGA) and the thermal barcode will be decoded with a differential scanning calorimeter (DSC). The research is described in more detail as follows.

Figure 1. Proposed idea: label each catalyst pellet.\textsuperscript{10}
**Part 1** was to design and generate thermal barcodes for heterogeneous catalysts. Ten kinds of PCM with melting temperature between 600 and 1000 °C have been identified after analyzing materials availability, melting temperatures, cost and toxicity. These materials were made into nanoparticles by surfactant assisted ball mill. Large labeling capacity was achieved by combining ten kinds of PCM particles to produce 1023 (2^{10} - 1) kinds of thermal barcodes. Silica encapsulation helped to prevent the interaction between PCM and catalyst particles. Metallic components were loaded on support by ion exchange to form catalyst. The catalysts mixed with PCM nanoparticles and binder, following by drying, calcination, and extrusion, to form uniform catalyst pellets. The optimal catalyst/binder ratio was determined by mechanical compression and TGA tests.

**Part 2** was to evaluate catalyst coke formation ability with high-throughput. Each type of catalyst has a predetermined unique barcode was created. The reactant (hydrocarbon or ethanol) was delivered with a flow of nitrogen to pass through a large number of catalysts in one bath at 850 K. After reaction, these catalysts underwent DSC-TGA detection. TGA was used to test the amount of coke and DSC was to decode the thermal barcode to know catalysts composition. Catalyst pellets with different metal species, concentration, size, and support types, were placed in one fixed bed reactor to process reactions. Specifically, coke dispersion along pellet radius direction was studied to find out how the pellet structure influencing cokes dispersion.

**Part 3** was to establish high-throughput screening method. Nanoparticles with small size (eg: 10 nm) have different melting behavior from the bulk one. Thus size-dependent melting behavior of particles was studied to select particles size. Heat transfer inside pellet was studied because thermal insulated SiO₂ will retard heat transfer among PCMs.
particles. Then interaction among catalyst and PCMs was studied via XRD analysis. Finally, kinetic items of the system were studied. PCMs particles embedding and pellets formation changed the internal diffusion of gas reactants.
2.0 LITERATURE REVIEW

2.1 Coke formation on catalyst

Crude oil refinery reactions over heterogeneous catalyst are accompanied by the formation of heavy and low-boiling-point byproducts that deposit on the external surface and the inner pore of the catalyst. These deposit byproducts with carbon species as main components are called coke.\cite{6,11,12} Coke can form from a wide range of hydrocarbons and alcohols. Coke formation leads to a loss over time of catalytic activity, which is a problem in catalyst industry. Costs to industry for catalyst regeneration, replacement, and even plant shut down can be billions of dollars every year. Therefore, coke yield is an important measurement of catalyst performance and one of the key criteria in catalyst selection and catalyst performance optimization. Factors influence coke formation on heterogeneous catalyst can be various: reaction temperature, pressure, time, metal concentration, hydrocarbon flow rate and ration.\cite{5,13,14} Thus efforts have been made by researches to explore how these factors influencing coke formation on catalyst.

2.1.1 Crude oil refinery

Crude oil contains a lot of long chain hydrocarbons, which need to be transferred to useful product, such as gasoline.\cite{15} This process is called crude oil refinery. Cracking and reforming are two main reactions during refinery. Cracking is to break long chain to short one, and reforming is to transfer normal hydrocarbon to the one with high-octane (Figure A). Cracking and reforming are free radical reactions occurring at high temperature and high pressure.\cite{16} If catalyst was applied in reaction, it can decrease activation energy required for reaction, thus decrease reaction temperature and pressure.
to save energy (Figure B). Catalyst also have specific pore size to select product with specific molecule structure, thus to improve reaction selectivity (Figure C).

Figure 2. Cracking and reforming reactions in crude oil refinery (A), catalyst decreases activation energy (B), catalyst improves reaction selectivity (C).  

2.1.2 Heterogeneous catalyst

In industry, heterogeneous catalyst is applied in the oil refinery, which has a different phase with the reactant and product. The main benefit of using heterogeneous catalyst is that they can be separated from a reaction mixture in a straightforward way, such as filtration or being taken away directly. Industrial heterogeneous catalysts are mostly zeolites, metallic oxides and porous carbons with metallic species supported. Catalyst metal is active site for undergoing reaction. The support provides good mechanical strength and disperses metallic component well (Figure 3A). To have sufficient contact with the catalyst, reactants are usually volatized to gaseous phase. Thus, expensive catalysts can be recovered easily and effectively, which is an important factor to be considered in industrial processes. Industrial catalysts are usually made into pellets. Centimeter level catalyst pellets are packed at the reaction tower with reactant go through
them (Figure B).\textsuperscript{20}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{Industrial heterogeneous catalyst composition (A) and catalyst pellets (B).\textsuperscript{20}}
\end{figure}

### 2.1.3 Coke formation steps

Breaking of C-H bond leads to byproduct coke, which is carbon species depositing on catalyst (Figure 4A). Coke can be formed from a wide range of hydrocarbons, including small species such as propene and big one like heteroatomic molecules.\textsuperscript{21, 22} The main component of the coke is carbon, which can be amorphous ($<400$ °C), crystalline ($500$ °C - $600$ °C), or graphite ($>800$ °C) (Figure 4B). Coke on catalyst covers catalyst metals and blocks the access of gas reactant to active sites (Figure 4C). Hydrocarbons thus don’t reach active sites and process thermal decomposition directly without aim products, which lead to waste of hydrocarbon and energy. Coke on catalyst can be removed by regeneration, which is oxidation reaction of hydrocarbon under high temperature. However, if catalyst reacted with carbon species to form carbide, it will deactivate permanently.
Figure 4. Coke formation (A), species (B), and consequence (C). Hydrocarbon first flows in and adsorbs on the surface of active site (Figure 5A and 5B). Then processing thermal decomposition to break bonds. As a result, hydrogen gas leave with carbon depositing on the surface (Figure 5C). The carbon on surface will gradually form solid solution with metal nanoparticles at high temperature (Figure 5D). Thus carbon gradually dissolves into the metal. When the concentration of carbon reach super saturated, it starts to diffuse and nucleate (Figure 5E). As time going, the carbon nucleates gradually to accumulate on the surface, which grows into carbon nanomaterials (Figure 5F).
2.1.4 Factors influence coke formation

Parameters influence coke formation can be ascribed into three aspects: reaction gas, metal-support interaction, and nature of catalyst compositions (Figure 6). Although there are hundreds and thousand of hydrocarbons, reactants influence coke formation simply because they can be ascribed to several types: long chain, short chain, aromatic one etc. Effects about catalyst composition nature have been studied widely to select right catalyst for reaction in industrial.\textsuperscript{24-26} Among all catalyst composition studied, the most complex is metal and support interaction. With the same surface area and porosity, iron support on SiO\textsubscript{2} and iron support on Al\textsubscript{2}O\textsubscript{3} can have different activity for catalyzing the growth of carbon nanotube based on ethanol as carbon resource. Different interaction between iron particles and support lead to different iron particles size and dispersion. There are a lot of research about how reaction temperature, pressure, time, metal concentration, hydrocarbon flow rate and ration influence the interaction between metal and support. Thus, having a systematic study of factors affecting coke formation is necessary. A high-throughput screening method is proposed to solve this problem.

![Figure 6. Factors affect coke formation in heterogeneous catalysis.](image-url)
2.2 High-throughput screening methods

High-throughput screening (HTS) is a method for scientific analysis widely used in the relevant fields of biology and chemistry. Combining robotics, data processing and control software, liquid handling devices, and sensitive detectors, HTS allows researchers to quickly conduct millions of biochemical analysis tests. HTS has also been used in catalyst screening area to optimize catalyst. In this section, recent catalyst high-throughput screening technologies will be reviewed first. Use phase change nanoparticle as thermal barcode to do labeling will be explained as followed. This PCM nanoparticles barcoding system established will be used as a high-throughput screening tool.

2.2.1 Catalyst high-throughput screening

Catalysts were place at reactor and heated by laser rapidly and accurately (Figure 7A). Gaseous reactants went through the reaction tube and arrived at the surface of catalyst directly to undergo reaction. After reaction, the products were detected via gas chromatography – mass spectrometry. The product CO$_2$ concentration tested was marked with various colors as shown in Figure 7B. The CO$_2$ concentration increases as color turning form cold to warm. The catalyst test is an ultra-fast process as laser heating and GC-MS detection. It takes only one minute for single catalyst pellet to under reaction.
Infrared thermography technology was used to detect heat emission from reaction to achieve high-throughput screening.\textsuperscript{31,32} For simple reactions with large reaction heat (eg: \(2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}; \Delta H = -482 \text{ kJ/mol}\)), catalytic activity can be tested by measuring the heat exchange in reaction process. In Figure 8A, catalyst pellets loaded with various metals were placed on reactor, which covering with infrared transparent BaF\(_2\) window. Hydrogen gas was used to purge the system first. Then oxygen gas was introduced, following by temperature scanning to initiate reaction. The difference in catalytic activity resulted in a difference in reaction heat, which could be detected by infrared thermography. In-situ detection result was shown in Figure 8B. The reaction conversion reached highest at 5 minutes. Then the conversion decreased as the color turning from warm to cold. This method can only be applied to simple reaction with evident reaction heat. Heat exchange difference between pellets should be significant enough to be detected by infrared thermography.
A much more complex high-throughput screening system has been brought into catalysis area (Figure 9A).\textsuperscript{34-36} The heart of the testing unit was the reactor (Figure 9B). The reactor composes of multiple cells, where catalyst powders were placed with reactants gases going through (Figure 9C). The products are detected by mass spectrometry. The 49\textsuperscript{th} hole is for reference, while the left 48 holes are for sample evaluation. Three valves can be set to three different reaction conditions. Under each reaction condition, 16 samples can be evaluated simultaneously. In sum, 48 samples can be evaluated simultaneously under three different reaction conditions (Figure 9D). Thus, high-throughput screening can be achieved. This testing unit was designed by BASF Company to evaluate emission control catalysts with reactants like NOx, CO, SO\textsubscript{2}, and CH. The high-throughput method has become a reliable approach for rapid screening of both reaction parameter spaces, as well as materials properties relevant for exhaust gas catalyst development.
2.2.2 Phase change nanoparticles as thermal barcode

Solid/liquid phase change materials usually melt at fixed temperature, thus they can generate evident melting peaks at fixed temperature in differential scanning calorimeter. If DSC is used as decoding method, thus solid/liquid phase change materials can be used as a kind of tagged method as they generating thermal signal at fixed temperature. Therefore, solid/liquid phase change materials, such as paraffin/fatty acid or metal/alloy can be applied in this tagged method. However, to tag aim product, the thermal barcode cannot be picked up easily, otherwise they will be changed or discarded. Thus these phase change materials were made into nanoparticles and tagged to aimed product. After being make into nanoparticles, these material will show a sharp melting peak during linear thermal scan in differential scanning calorimetry (DSC). A panel of nanoparticles with discrete melting temperatures can be mixed, and distinguished from each other in a single thermal scan. One melting peak can be seen as one bar; therefore, the series of melting peaks is described as thermal barcode.
The thermal barcode has large labeling capacity. For a normal DSC machine, the half peak width of metallic nanoparticles (i.e., metal and eutectic alloy) can be smaller than 0.6°C at thermal ramp rate of 1°C/min. If thermal scan is in the 100-700°C range, the maximal number of melting peaks that can be resolved will reach 1,000 based on spectral resolution, which means 1,000 different types of nanoparticles (of distinct melting peaks) can be simultaneously detected in one thermal scan.\textsuperscript{38,39}

Labeling capacity can be further enhanced by alloy formation.\textsuperscript{40} Metal nanoparticles have sharp melting peaks, but a limited number of metals in the periodic table can be used to make nanoparticles due to availability and safety issues (Figure 12A). Most metals form eutectic alloys that go directly from solid to liquid phases without a pasty stage, and can be treated as pure metals.\textsuperscript{41} The compositions and melting temperatures of each mixture (alloy) can be determined by calculation of phase diagram (Figure 12B). Nanoparticles of eutectic alloy composition have single sharp melting peaks, and composition-dependent melting temperatures. Based on the combination law of phase diagram, ten different metals can form 45 types of binary alloys, 120 types of ternary eutectic alloys, 210 types of quaternary eutectic alloys and so on. The total number of codes derived from Pascal’s triangle reaches 1,023 (Figure 12C). Large labeling capacity makes the thermal barcode a tool for high-throughput screening potentially.
2.3 Thermal properties of phase change material (PCM) nanoparticles

Water is a common phase change material. As energy being input, ice melts to water, which further evaporates to steam. When heat is released, the steam condenses to water, which then solids to ice (Figure 10). Phase change materials can undergo solid-liquid, liquid-vapor, or solid-vapor transitions at certain temperatures, storing or releasing large amounts of energy in this process. Liquid-gas change is not practical for thermal storage due to the large volumes or high pressures required to store the gaseous materials. The solid-solid phase changes are typically very slow, rare, and have low heat of transformation. Thus, the commonly used phase change process is the solid-liquid, which has been widely used in energy storage area. In this section, definition and classification of solid-liquid phase change materials will be introduced first. Then main thermal
properties of PCM will be discussed individually. Finally, PCM nanoparticles preparation by mini-emulsion and ball mill will be explained, respectively.

![Figure 11. Phase change process of water.](image)

2.3.1 PCM Classification

Many materials undergo solid/liquid phase transitions at certain temperatures. Solid-liquid PCMs that commonly used in engineering include salt hydrates, organic solids, metals and alloys, as well as metallic oxides and ceramics.

Early efforts in the development of latent storage materials used inorganic PCMs. Inorganic PCMs are salt hydrates.\textsuperscript{42,43} Molten salts (fluoride, chloride, and nitrate) have high melting point and large fusion heat; therefore, they can be used as heat transfer fluids as well as for thermal storage. Besides, salt hydrates are usually non-flammable, low-cost, and readily available. Regular table salt (NaCl) has a melting point of 800\textdegree C and a heat of fusion of 0.52 kJ/g. Molten chloride salts are often used as baths for some alloy product heat treatments in industry, e.g. annealing of steel. However, the colloid process of molten salts process is not well established due to solubility of salt in water, and salt may generate corrosive gas byproducts by thermal decomposition at high temperature. The disadvantages of inorganic PCMs lead to the study of organic PCMs.
Organic PCMs have a number of characteristics to make them superior. They are not only more chemically stable than inorganic substances and melting congruently without evident supercooling, the organic PCMs are also more compatible with other building materials.\textsuperscript{44, 45} Commonly used organic solids include paraffin waxes and fatty acids. Paraffin waxes and fatty acids can be extracted from petroleum products and plants, respectively, and both can be mass-produced at low cost.\textsuperscript{46} Depending on carbon numbers and polarity of the molecules, the melting temperatures of organic solids can cover a wide temperatures range. Organic solids have large latent heat in the range of 100 to 200 J/g, which is about one order of magnitude higher than those of metallic materials. They are chemically stable and inert to ambient environment, and have been used widely in thermal energy storage. However, due to be flammable, harmful fumes generation on combustion, low melting points and high solubility in organic solvents, organic solids are not good candidates for some high-temperature chemical applications.

Metals and alloys can undergo solid-liquid phase change as melting.\textsuperscript{47-49} The melting point ranges from tens to more than one thousand census degree and the latent heat ranges from 20 to 500 kJ/kg. The melting temperature is dependent on the atomic number (for metal) and composition (for alloy). Most metals form eutectic alloys that go directly from solid to liquid phases without pasty stage, and can be treated as pure metals. During melting, metals absorb heat without temperature rise based on Gibbs phase rule. If the dimension of metal is small enough, the melting time will be negligible due to high thermal conductivity of metal. Therefore, metals nanoparticles have sharp melting peaks in DSC. Low melting point alloys such as Sn-Pb alloy are widely used in solder industry while high melting point alloys like steel can be used in building industry.
Ceramics usually have very high melting point (more than 800 °C) and large fusion latent heat (over 1000 kJ/kg). Because of the high melting point, ceramics are not considered as phase change materials in most cases. Besides, solid-solid phase change before totally melting makes the phase change process to be complex. However, ceramics can be good candidates for applications that need to tolerate high temperature.

2.3.2 Thermal properties of PCM

Commonly used thermal properties measurements include DSC, TGA, and SDT (simultaneous DSC/TGA). DSC is often used to determine the melting temperature and latent heat of fusion of materials, while TGA is often used to determine materials mass loss during temperature increasing. Using SDT can achieve a simultaneously measurement of sample’s heat flow and weight change.50

Generally speaking, there are two kinds of DSC: power compensated DSC and heat flux DSC. Energy input is constant for power compensated DSC while heat flux is constant for heat flux DSC. In my research, power compensated DSC was applied and the working mechanisms were studied (Figure 11A). As the energy input is constant, the heat flux difference between sample and reference can be tested. Time derivative of the heat flux is the heat flow. The heat flow difference between the samples and the reference is:

\[
\Delta \frac{dH}{dt} = \left( \frac{dH}{dt} \right)_{\text{sample}} - \left( \frac{dH}{dt} \right)_{\text{reference}}
\]  

(1)

The difference can be either positive or negative. In an endothermic process, heat is absorbed; therefore, heat flow to the sample is higher than that to the reference. Hence \( \Delta dH/dt \) is positive. In an exothermic process, such as crystallization, some cross-linking process, oxidation reactions, and some decomposition reactions, the opposite is true and
dH/dt is negative. DSC analyzes a small quantity of sample (1–10 mg). DSC measures heat flow associated with phase transition and chemical reaction as a function of temperature. The temperature of both the sample and reference are increased at a constant heating or cooling rate. Figure 11B was the melting curve of indium particles in DSC. Thermal properties can be obtained from the DSC measuring results. Slope of the baseline is the heat capacity of materials. Temperature where solid-liquid phase change beginning is the melting point. Latent heat can be calculated from the peak area. Slope of the melting part of the peak is the solid thermal conductivity.

![Diagram of DSC working mechanism](image)

**Figure 12.** Power-compensated DSC working mechanism (A) and melting curve of indium (B).

TGA (Thermo gravimetric analysis) is used to determine selected characteristics of materials that exhibit either mass loss or gain due to decomposition, oxidation, or loss of volatiles. Fourier transform infrared spectroscopy and mass spectrometry are coupled with the gas analysis. Commonly, the TGA weighs a sample continuously as it is heated to temperatures of up to 1200 °C. As the temperature increases, various components of the sample will decompose and each will result in mass change that can be measured. Results are plotted with temperature on the X-axis and mass loss on the Y-axis, and the data can be adjusted using curve. Oxidation happens at the temperature increasing process, and oxidative mass losses are the most common observable losses in TGA.
2.3.3 Synthesis of PCM solid nanoparticles

Decrease of particles size results in specific surface area increasing and more heat to be exchanged in unit time. Thus, there are sharp melting peaks with short melting time in DSC test. However, nanoparticle’s melting point and fusion latent heat will not change if their sizes are higher than the thermodynamic threshold size. Hydrated salt and organic nanoparticles have low melting points and unstable thermal property. Therefore, following PCM nanoparticle discussion will focus on metal/alloys and ceramic oxides.

Some metals and alloys nanoparticles can be synthesized by mini-emulsion method.\textsuperscript{51, 52} Take the mini-emulsion synthesis of bismuth nanoparticle for instance. With high boiling point PAO (poly-a-olefin) as solvent (250 °C), bismuth powders can be heated to the temperature near their melting point (271 °C). Under high shear stress stemming from mechanical stirring, the soft bismuth powders can be cut into small nanoparticles and stabilized by PAO. The sizes of the final products are believed to be the result of a balanced interplay between several parameters, especially the concentration of precursors and stirring rate.\textsuperscript{53}

Nanoparticles of ceramics and high melting point materials (such as Al\textsubscript{2}O\textsubscript{3}, Mg\textsubscript{2}Si and TiSi\textsubscript{2}) are hard to synthesize from chemical methods mentioned above. Ball milling is considered as a simple and general method. Ball milling is a process where a powder mixture placed inside is subjected to high-energy collision from the balls. This method could successfully produce fine and dispersed well nanoparticles.

In ball milling process the rotation directions of the bowl and disc are opposite, the centrifugal forces are alternately synchronized. Thus friction resulted from the collision between milling balls and powder mixture, powder and powder, powder and
inner wall of the bowl. In the milling process, the alternatively press stress lead to
deformation of powder particles surface and these particles further break into smaller
ones. The appearance of plastic deformation made the particle is difficult to be ground
into smaller one due to a balance between the press force and the tendency for the
particles to accumulate again. The minimum particles size for ball milling is about 1 um.
With surfactant assistant, particles can be ground to small size less than 100 nm.\textsuperscript{54}

2.3.4 Encapsulation of phase change nanoparticles

Molten liquid phase can move around and cause stability problems after solid-
liquid phase change. A common way to prevent liquid phase moving is to encapsulate
materials with non-melting materials. Encapsulation can reduce possible reaction with
outside environment, increase heat transfer area, and control material volume changes as
phase change occurs. The PCM remains well shaped and can be used directly requiring
no support or even coating. Meanwhile, the encapsulated PCM exhibits excellent
mechanical stability under cyclic cooling–heating conditions. Phase change materials are
usually encapsulated into silica shell. Silica was deposited by the hydrolysis of
Tetraethyl-orthosilicate (TEOS) or 3-Aminopropyltriethoxysilane (APTES).\textsuperscript{55}
Specifically, TEOS/APTES is added in an ethanolic suspension of PCM nanoparticles,
followed by dropwise addition of ammonium hydroxide. Encapsulated nanoparticles are
washed by ethanol for several times.
3.0 EXPERIMENTAL SECTION

3.1 Synthesis of PCM nanoparticles

Phase change materials used in the research are metal/alloy, inorganic salt and ceramics having fixed melting points. These solid/liquid phase change materials can be made into nanoparticles via mini-emulsion and surfactant assisted ball milling. These PCM nanoparticles were further encapsulated with silica layer by hydrolysis of APTES.

3.1.1 Mini-emulsion

In Mini-emulsion process, metal/alloy powders are heated to the temperature above their melting points under strong shear force.\textsuperscript{56, 57} Thus, the metal droplets can be cut into smaller size and be stabilized by surfactant. Most of the low melting point metallic nanoparticles can be synthesized using this method by selecting appropriate solvent, reaction temperature, stirring rate/sonication power and surfactants. In the case of bismuth that has a melting point of 271.5 °C, emulsification is carried out by boiling certain amount of bismuth powder in PAO (polyalphaolefin) at 200°C or higher overnight with magnetic stirring under the protection of N\textsubscript{2}. The diameters of bismuth nanoparticles obtained depend on boiling time and size of starting materials (powder). When the reaction time increases from 2 to 48 hours the diameters of nanoparticles decreases from 165 to 85 nm (Figure 12).\textsuperscript{58} The relationship between nanoparticle size and reaction time can be fitted to Taylor’s formula:

$$r_p = W_e \times \sigma / (\mu_c \times \lambda)$$  \hspace{1cm} (2)

Where: \(r_p\) = the nanoparticle radius, \(W_e\) = Weber number, \(\sigma\) = the interfacial tension between nanoparticles and PAO, \(\gamma\) = the shear rate, \(\mu_c\) = the viscosity of PAO.

3.1.2 Ball milling
Materials like Germanium (Ge) have melting temperature much higher than the boiling point of most solvents used in mini-emulsion method. These high melting point materials are hard to be sharped into nanoparticles with chemical method. One simple and general method is ball milling. The equipment used is PQ-N04 planetary ball mill produced by Across International Company. In the ball mill experiment, 5 gram of sample powders mix with 4 large and 8 small balls with ethanol as solvent. The volume of ethanol added should just submerge the powders and balls. Too much ethanol will weaken the grinding effect. The rotating speed is 400 rpm with 30 minutes running and 5 minutes rest for one turn. After 12 hours grinding, most large bulk in original powders can be ground into particles less than 1 um. Nano-sized particles were sieved by using a sieve of 200 meshes. Powder is hard to be ground into particles less than 1 um, under which particles tend to aggregate. However, if surfactants such as polyvinyl alcohol (PVA) were applied, powders can be ground into particles under than 100 nm.

3.1.3 Synthesis of silica encapsulated PCM nanoparticles

Silica encapsulated nanoparticles are synthesized via the hydrolysis of (3-Aminopropyl) triethoxysilane (APTES). 60 µl APTES is added in 3 ml ethanolic suspension of Germanium nanoparticles (5 µM), followed by dropwise addition of 15µl ammonium hydroxide (30%) at 30 °C. After reacting for 24 hours, encapsulated nanoparticles are washed by ethanol for several times.

3.2 Structure characterization

Nanoparticles have been characterized using a variety of techniques. An SDT (simulated DSC and TGA, TA instrument SDT Q600) is used to measure the weight loss due to coke decomposition and the melting temperatures of PCM nanoparticles in
nitrogen gas atmosphere at temperature ramp rate of 10 °C/min. A Zeiss (Ultra 55) SEM operated at 10 keV is used to image the morphology of nanoparticles. A TEM (JEOL 1011) operated at 100 kV is used to determine the structure of the nanoparticles. In order to prepare sample for TEM imaging, an ethanol drop containing nanoparticles is dropped on a copper TEM grid coated with carbon film. XRD analysis is carried out on a Rigaku 2500 diffractometer using Cu Kα radiation (40.0 kV and 30.0 mA) at step width of 2.0°/min. To collect XRD curves, nanoparticles are glued on double-sided tape and fixed on the XRD holder. The BET surface areas and pore volumes for all samples were obtained from results of N₂ adsorption at 77 K, which was performed by using a Quantachrome NOVA 2200e pore surface and pore volume analyzer. Before adsorption, all samples were degassed at 80 °C for 24h.

3.3 Creating thermal barcodes

Thermal barcodes are created by mixing objective PCM nanoparticles with certain weight ratio. Due to the large latent heat generated in the melting process, only a small amount of PCM nanoparticles needs to be added. The small size of nanoparticles makes them easy to be mixed homogeneously with the product. Then, the tagged product will be put in a small alumina pan to take DSC/TGA measurement. Temperature scanning function is used to decode the thermal barcode. Usually temperate scanning starts from room temperature with a heating rate of 10 °C/min.

3.4 Fabrication of tagged catalyst pellet

Catalyst was prepared by impregnation or ion exchange method. Specifically, catalyst metals were loaded onto the support first by soaking support powders into metal precursor (Fe³⁺) solution. The powders further underwent drying and calcination to active
all metallic active sites. Catalyst samples usually dry at 100 °C for 6 hours, and calcinate at 550°C for 3 hours. The pellets in the research were made by extrusion. Catalyst was mixed with barcode nanoparticle and binder powder homogeneously. Usually, binder used in the research was kaolin (Al₂Si₂O₅(OH)₄). Water was added into the powder (binder + catalyst + barcode) to make slurry-like mixture. The slurry mixture was filled into injector. The injector was pushed forward to exclude bubbles in the slurry. Finally, push the injector to the end to extrude a long rod of materials. Short-rod pellets were obtained by cutting the long-rod into many parts. The short rod like mixture was dried first, then underwent calcination to form robust pellet.
4.0 RESULTS AND DISCUSSION

4.1 Design and generate thermal barcodes for heterogeneous catalysts

Catalytic reactions with coke formation usually happen under high temperature (500 °C ~ 700 °C). Thus, PCM nanoparticles barcode inside catalyst pellets should have high melting point to endure high reaction temperature. In this section, a series of high-melting point materials was identified first. Surfactant-assist ball mill method was applied to grind the bulk materials into nanoparticles. The PCM nanoparticles were mixed with binder and catalyst to form pellet by extrusion. The mechanical property and coke formation ability of pellets were studied to determine the optimal catalyst/binder ratio.

4.1.1 Identifying a new set of metals with high melting point

For most coke formation catalytic reactions, the reaction temperatures can be as high as 600 °C. On the other hand, the highest working temperature for TGA is 1200 °C. Thus, the PCM are designed with melting temperature ranging from 700 to 1000 °C, and melting temperature interval of 10 °C or higher to avoid peak overlap. Materials selected should be stable both in preparation and evaluation process. No decomposition or evident solid/solid phase change before totally melting. Barcode materials should not react with catalytic active components (such as Fe, Co, Ni) as well. Finally, barcode materials should be feasible that means materials are not precious, rare, or toxic elements, and can be purchased easily. Based on above discussion, following materials have been selected to use as thermal barcode after forming nanoparticles: Bi$_2$Se$_3$ (710 °C), GeTe (725 °C), GeSe$_2$ (742 °C), SnTe (790 °C), Bi$_2$O$_3$ (817 °C), Bi$_2$S$_3$ (850 °C), SnSe (861 °C), SnS (882 °C), In$_2$Se$_3$ (890 °C), Ge (937 °C). Thermal properties of these materials can be found from literatures. The ten kinds of PCMs can form totally 1023 kinds of
barcodes. Therefore, this high-melting point PCM series has a large labeling capacity.

Table 1. Materials selected with melting point increasing

<table>
<thead>
<tr>
<th>Compound</th>
<th>Melting Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi₂Se₃</td>
<td>710</td>
</tr>
<tr>
<td>GeTe</td>
<td>725</td>
</tr>
<tr>
<td>GeSe₂</td>
<td>742</td>
</tr>
<tr>
<td>SnTe</td>
<td>790</td>
</tr>
<tr>
<td>Bi₂O₃</td>
<td>817</td>
</tr>
<tr>
<td>Bi₂S₃</td>
<td>850</td>
</tr>
<tr>
<td>SnSe</td>
<td>861</td>
</tr>
<tr>
<td>SnS</td>
<td>882</td>
</tr>
<tr>
<td>In₂Se₃</td>
<td>890</td>
</tr>
<tr>
<td>Ge</td>
<td>937</td>
</tr>
</tbody>
</table>

4.1.2 Nanoparticles by ball milling

Ball mill is a type of grinder used to grind and blend materials into smaller size. Germanium with a high melting point was studied for instance. Figure 13A shows the SEM image of germanium nanoparticles synthesized by ball milling without surfactant PVA. These nanoparticle are sieved with 200 meshes sieve, but particles still aggregate together. When surfactants are applied such as polyvinyl alcohol (PVA), powders were ground into particles under than 100 nm (Figure 13B). Surfactants act to stabilize nanoparticles to prevent aggregating. With surfactant, germanium nanoparticles are dispersed well with small size. Figure 13C is the TEM image of germanium nanoparticles generated with surfactant protected. It can be clearly seen that the nanoparticle has size around 50 nm -100 nm. In addition to germanium, other barcode materials like Bi₂Se₃, GeTe and Bi₂S₃ can also be ground into small nanoparticles.
4.1.3 Silica encapsulation

It is inevitable for the PCM particles reacting with catalyst particles or coke deposited. A shell of silica thus was designed to deposit around the PCM nanoparticles to act as protection effect. Germanium was studied as an example to show silica shell can be covered around PCM nanoparticles. The Ge nanoparticles ground from ball milling was sonicated and modified with (3-Aminopropyl) triethoxysilane (APTES) to become well dispersed in water. The APTES molecule can absorb on the surface of Ge nanoparticles via the lone pair oxygen electrons. Small amount (10µL) of ammonia hydroxide (30%) was added into the solution to accelerate the hydrolysis of APTES. The silica encapsulated germanium nanoparticles was shown in Figure 14A. The silica shell was 25nm - 50nm that was confirmed by HRTEM in Figure 14B. The component of the core-shell structure was confirmed by testing the energy dispersive spectrometry (EDS) in Figure 14C. The size of the core-shell nanoparticles was around 100 - 200 nm, which was confirmed by using dynamic light scattering (Figure 14D).
4.1.4 Catalyst pellets preparation

Catalyst powder was prepared by impregnation or ion exchange method. Specifically, metallic ions were loaded onto support first by soaking support powders in metal precursor (Fe³⁺) solution to process ion exchange. The product further underwent drying and calcination to produce metal nanoparticles as active sites. Catalyst samples were dried at 100 °C for 6 hours, and calcinated at 550 °C for 3 hours. Calcination is a thermal decomposition process, during which metallic salt will decompose and form metallic nanoparticles or metallic oxide nanoparticles.

To achieve high throughput screening, catalyst has to be made into small pellet. Pellet in the research was generated by extrusion. The catalysts were then mixed with PCM nanoparticles barcodes and binders to form slurry after adding of water. To form homogeneous mixture, the slurry was stirred under 500 rpm for half an hour. The
homogeneously mixed slurry was sent to extruder to form pellet, which still contained some water. The extruded pellet was dried at 100 °C for 2 hours to loss water, and calcinated at 550 °C for 3 hours to form robust pellet. Binder used in the research was kaolin (Al₂Si₂O₅(OH)₄). As a good binder material, kaolin has very similar chemical composition as most support, like silica, alumina, and zeolite, but very low coke deposition. To ensure good mechanical strength and catalytic activity, the ratio of catalyst (support) to binder or the percentage of binder was studied.

Figure 15A shows the catalyst pellets made with/without metallic salt loading. Figure 15B is the mechanical test of single pellet. In fixed-bed reactor, thousands of pellets are packed together to undergo reaction. The pellets thus are very likely to get pressed and broken. Stress as a function of compression distance for a single pellet was tested. The highest pressure or the stress the pellet can endure is 1.57 MPa. The strain is 0.0887/1.25 (height of pellet)=7.1%. Young’s modulus is (1570-0)/0.071=22.113MPa. As stress has the expression: pressure=ρgh, the height of catalyst tower can be calculated. The highest catalyst column was calculated to be 52 meters, which was much higher than the experiment design. Thus, a lot of pellets packed and tested in one experiment. The pellets were packed at reactor to undergo reaction. As catalyst samples were tagged by thermal barcode, many samples could be processed in one time without confusion. Thus, a lot of time and energy could be saved. Except accumulating with coke, no morphology changed after reaction for the pellets.
Figure 15. Pellets without catalyst loading (white) and pellets with various catalysts loading (colorful) (A), compression pressure as a function of distance for a single pellet (B)

4.1.5 Determine optimal percentage of binder

Catalyst powders were mixed with binder (kaolin) and PCM particles to undergo extrusion and to form pellets. Samples with various percentages of binder were generated to have their mechanical strength and coke deposition ability studied, thus to determine the optimal binder percentage. Samples were designed to contain 0 wt.%, 25 wt.%, 50 wt.%, 75 wt.% of binder. Pellets were taken to undergo catalytic experiment firstly. Then the coked pellets processed TGA test to determine the coke amount. When silica weight percentage increased from 0 wt.%, 25 wt.%, 50 wt.% and 75 wt.% to 100 wt.%, the coke deposition increases from 3 wt.%, 12 wt.%, 15 wt.% and 16 wt.% to 18 wt.. Increasing silica percentage from 50 wt.% to 75 wt.% generates no change on the coke amount.
Figure 16. TGA curves of coked pellets with various percentages of binder: 0% (pink), 25 wt.% (green), 50 wt.% (blue), 75 wt.% (red), 100 wt.% (black). Inset is coke amount calculated as a function of binder percentages.

The mechanical properties of pellet were measured as well. Figure 17A is the mechanical compression test of catalyst pellets as a function of binder percentage. All samples crashed before the compressed distance reaching 10% of the pellets height. The highest pressure is the stress while the slope of the peak is the Young’s modulus. The stress decreases with the increasing of silica percentage (Figure 17B black line). The Young’s modulus has also been calculated (Figure 17B blue line), which has opposite tendency with the stress. The higher percentage of binder, the more elastic of pellet, thus the higher stress can endure. The pellets with few binders are more likely to be bristling. Stress of the 50 wt.% sample was similar to that of the 25 wt.% one. Above all, the optimal percentage of binder was chosen to be 50 wt.% to have good mechanical strength and stable coke amount.
Figure 17. Mechanical compression test of catalyst pellets with various binder percentages: 0 wt.% (A-1), 25 wt.% (A-2), 50 wt.% (A-3) and 75 wt.% (A-4), stress and Young’s modulus calculated as a function of binder percentage (B).

4.2 Evaluate catalyst coke formation ability with high-throughput

Catalysts tagged by thermal barcodes can be prepared and evaluated in large volume. In this section the high-throughput screening system based on thermal barcodes was built. After reaction, coke amounts were determined by thermal gravimetric analysis and catalyst compositions were decoded by differential scanning calorimeter. Thermal signal generated by the PCM was analyzed to test the feasibility of thermal signal. Factors affected coke formations are studied in details. Coke deposition along radial direction of pellet was studied to understand the influence of pellet morphology on coke deposition. Further characterizations of carbon species were analyzed as well.

4.2.1 Build catalysis reactor

Catalytic reactor with fixed-bed design is shown in Figure 18. Catalyst pellets tagged with thermal barcodes were packed in a two ends-open glass cylinder (Figure 18A). The small glass cylinder has two ends opened to let gas flow go fluently. Glass
cotton was placed on two ends to fix pellets and work as buffer for gas flow. The small reactor was placed at the center of tube furnace (Figure 18B). The outside glass tube is to keep warm. During reaction, the tube furnace was closed (Figure 18C). The whole glass reactor was covered with thick asbestos tube furnace wall. The temperature of the catalyst bed was monitored with thermocouple and feedback electronics. Prior to reactant addition, the column was treated with a flow of pure nitrogen gas. Following this pre-treatment, we fed a mixture of nitrogen and reactant to the column. The column was kept at 850 K for the duration of the reaction. After reaction, the reactor was cooled to lower temperature (less than 373 K) to take out catalyst. Carbon accumulated on crucible need to be burned out with an after-reaction treatment. Finally, the reactor was cooled to room temperature to wait for next reaction. By calculation, it takes about 6 hours to complete the whole reaction process. If samples are tested one by one, 1200 hours will be consumed to test 200 samples. With thermal barcode being applied, reaction time will decrease to 12 hours assuming 100 samples were tested in one reaction.

Figure 18. Fixed bed reactor for high-throughput screening: inner side (A) and outside (B), tube furnace for reaction (C).

4.2.2 Build high-throughput screening method

After evaluation, catalysts pellets were taken out to process TGA-DSC detection.
TGA is used to determine coke amounts, and DSC is to decode PCM barcodes to know catalyst composition. In Figure 19 below, blue curves represent for weight loss due to coke decomposition while black curves refer to DSC decoding of PCM barcodes. Decoding from the DSC curves, the melting peaks in Figure 19 represent Bi$_2$Se$_3$ (A), SnTe (B), Bi$_2$S$_3$ (C), and Ge (D) nanoparticles, respectively. The four kinds of thermal barcodes are used to tag four catalysts samples: 10 wt.% Co/SiO$_2$, 5 wt.% Co/SiO$_2$, 10 wt.% Fe/SiO$_2$, 5 wt.% Fe/SiO$_2$, respectively. The coke amount and catalyst composition thus can be obtained simultaneously.

![DSC-TGA curves](image)

Figure 19. DSC-TGA curves of 10wt.%Co/SiO$_2$–Bi$_2$Se$_3$ (A), 5wt.%Co/SiO$_2$–SnTe (B), 10wt.%Fe/SiO$_2$–Bi$_2$S$_3$ (C), 5wt.%Fe/SiO$_2$–Ge (D).

Combining any two kinds of the PCMs (Bi$_2$Se$_3$/ SnTe / Bi$_2$S$_3$/ Ge) resulted in six more barcodes (Figure 20). The six barcodes were tagged with Fe catalyst with different concentrations (increase from 0.5 wt.% to 20 wt.%) to undergo catalytic reaction at
700 °C. After reaction, TGA-DSC was tested to determine coke deposition and catalyst composition.

![DSC-TGA curves of Fe catalyst at 700 °C with different concentration: 20 wt.% – Bi₂Se₃+SnTe (A), 15 wt.% – Bi₂Se₃ +Bi₂S₃ (B), 7.5 wt.% – Bi₂Se₃+Ge (C), 5 wt.% – SnTe+ Bi₂S₃ (D), 2.5 wt.% – SnTe +Ge (E), 0.5 wt.% – Bi₂S₃+Ge (F).](image)

Figure 20. DSC-TGA curves of Fe catalyst at 700 °C with different concentration: 20 wt.% – Bi₂Se₃+SnTe (A), 15 wt.% – Bi₂Se₃ +Bi₂S₃ (B), 7.5 wt.% – Bi₂Se₃+Ge (C), 5 wt.% – SnTe+ Bi₂S₃ (D), 2.5 wt.% – SnTe +Ge (E), 0.5 wt.% – Bi₂S₃+Ge (F).

New barcodes by combining three kinds of PCM (Bi₂Se₃+ SnTe + Bi₂S₃) were generated to tag SiO₂ catalyst (Figure 21A). Four more barcodes thus can be generated. Furthermore, combine four kinds of PCM (Bi₂Se₃+SnTe+Bi₂S₃+Ge) also generated new barcode to tag Al₂O₃ catalyst (Figure 21B). Above all, 15 (2⁴-1) kinds of barcode can be generated based on the four kinds of phase change material. Large labeling capacity of
the thermal barcode makes the high-throughput screening to be feasible.

![DSC-TGA curves](image)

**Figure 21.** DSC-TGA curves of SiO$_2$–Bi$_2$Se$_3$ + SnTe + Bi$_2$S$_3$ (A) and Al$_2$O$_3$–Bi$_2$Se$_3$+SnTe+Bi$_2$S$_3$+Ge (B) at 600 °C for 1 hour.

**4.2.3 Test factors influencing coke formation**

Usually soft coke (high H/C ratio) deposits on Pt or Pd metals and hard coke (low H/C ratio) deposits on the porous support in catalytic process. Both hard and soft cokes are responsible for deactivation. While coke on metals deactivates metals, coke also blocks support pores to prevent gaseous reactants reaching active sites. So heavy coke formation means the loss of activity, which is also one of the most important criteria for deactivation. The formation of coke (carbon species) involves many parameters, for example: hydrocarbon species, gas flow rate, temperature, reaction time, reactor geometry, catalyst species/concentration, support, and so on. In our research, fixed-bed reactor was designed to simulate industrial FCC process. Hydrocarbon species, temperature, reaction time, catalyst species/concentration, support are examined by using the PCM barcodes to optimize reaction condition.

Silica supported Fe, Co, Ce and Bi catalysts were tested to study their catalytic differences. All catalysts were prepared by impregnating precursors solutions (Fe(NO$_3$)$_3$, Co(NO$_3$)$_3$, Ce(NO$_3$)$_3$, Bi(NO$_3$)$_3$) with silica powders. The concentration of catalyst was 5...
wt.% of pellet. Following by drying, calcination and extrusion, the four kinds of catalyst pellets were taken to undergo coke deposition experiment simultaneously. TGA curves of the four coke deposited catalysts were measured in Figure 22A. Both Fe and Co were good candidates for coke formation, while Ce and Bi almost had no coke formed. In addition to catalyst species, catalyst concentration has also been studied in this research to know the optimal concentration for coke formation. Fe/SiO$_2$ catalysts with different concentrations (0.5 wt.%, 1 wt.%, 5 wt.%, 10 wt.%, 15 wt.%, 20 wt.%) had been designed to undergo catalytic reaction simultaneously. After reaction, these catalysts were tested TGA to determine coke deposition amount. Figure 22B shows the TGA curves of these coke deposited catalysts. The inset shows the coke amount calculated as a function of Fe concentration. Coke amount kept increasing as Fe increased from 0.5 wt.% to 10 wt.% but decreased as Fe concentration increased from 10 wt.% to 20 wt.% Therefore, 10 wt.% is the optimal concentration. Increasing Fe catalyst concentration results in more coke deposition. However, when the catalyst concentration is too high, Fe particles on silica tended to aggregate and form larger particles.$^{72}$ Large particles usually have smaller specific surface area, which lead to low reaction activity and low coke formation.$^{73,74}$

Figure 22. TGA curves of coked catalyst: Fe (red), Co (blue), Ce (black), and Bi (green) (A), TGA curves of coked catalyst with different Fe concentrations: 0.5 wt.% (brown), 1 wt.% (pink), 5 wt.% (blue), 10 wt.% (black), 15 wt.% (red) and 20 wt.% (green) (B).
Generally speaking, coke formation includes following steps: physically adsorption and thermal decomposition, solid solution formation, nucleation and growth. Figure 23A shows how ethanol molecule processes adsorption and thermal decomposition on the surface of active sites. Ethanol first adsorbs on the surface via the lone pair electrons of oxygen. Then the absorbed ethanol processes dehydrogenation, cleavage of C-C and C-O bonds to deposit carbon species. The reactions are free radical reactions. Enthalpy and activation energies required for ethanol processing thermal decomposition on iron nanoparticles were calculated and shown as the scheme in Figure 23B. Ethanol decomposes on different metals requiring different activation energies. Low activation energy enables the ethanol molecule to decompose and to deposit carbon species on catalyst easily.

Figure 23. Scheme of thermal decomposition of ethanol decomposing on Fe catalyst (A) and activation energies required (B).
Enthalpy required for ethanol adsorbing on various catalyst metals were shown in Figure 24A. The values were so similar that they made no difference for all metals listed. Activation energy required for C-H, C-O and C-C bonds cleavage on various metal catalysts were shown in Figure 24B. Pt, Pd and Cu have higher activation energy on all C-H, C-C and C-O bonds cleavage than Fe, Co and Ni. Thus hydrocarbon, such as ethanol, is more likely to thermally decompose and generate carbon atoms on Fe, Co and Ni than Pt, Pd and Cu.

![Figure 24. Binding energy of ethanol adsorbing on several catalyst metals. (A); activation energies of C-H bond (black), C-C bond (red) and C-O bond cleavage (blue) required for several catalyst metals (B).](image)

After thermal decomposition carbon atoms tend to dissolve into catalyst metals to form solid solution. To form solid solution with carbon, the catalyst metals should be melted at reaction temperature. Usually metals bulk like Fe, Co, Ni, Cu, Au and Si have very high melting points. However, catalyst metals tend to form nanoparticles supported on silica via the ion-exchange method and have small size less than 5nm. Small size nanoparticles have more surfaces exposed than the bulk material. The chemical bonds on the surface are easier to break than that on the bulk one. Therefore, nanoparticles with small size is more likely to melt than the bulk one. The actual melting point of catalyst
metals should be lower than the bulk one and can be calculated based on the size-dependent melting point depression equation:

\[
\frac{\Delta H_m}{T_m} \Delta T_m = \frac{2\gamma^{sl}V^s}{\gamma}
\]  

(3)

\(\Delta H_m\): Melting latent heat, \(T_m\): bulk materials melting point, \(\Delta T_m\): change of melting point, \(\gamma\): nanoparticles radius, \(V^s\): atomic volume of solid, \(\gamma^{sl}\): solid-liquid surface energy. By applying the particles size and other parameters, the decrease of melting point can be calculated. The melting points of Fe, Co, Ni, Au, Pt, Pd, Cu, Al and Si have been calculated based on 5 nm size nanoparticles and listed in Figure 25. Co and Ni have melting point around 800 °C. Pt, Cu and Si have melting point larger than 800 °C while Fe, Au, Pd and Al have melting points lower than 800 °C. Usually coke deposition reaction happens around 500 °C to 700 °C. Metallic nanoparticles (5nm) with melting point about 800 °C may be qualified for forming solid solution with carbon because the actual nanoparticles may smaller than 5 nm. Besides, the actual melting point of nanoparticles is largely influenced by their morphology especially when the particle is very small. Therefore, metal nanoparticles (5nm) with melting point below 800 °C were more likely to form solid solution with carbon than those have melting point above 800 °C.
Figure 25. Size dependent melting point calculated for several catalyst metals nanoparticles (5nm).

Phase diagrams of Fe, Co, Ni, Au, Pd and Al with carbon were studied to know carbon solubility and whether carbon in solid solution can further diffuse. The phase diagrams of Fe-C and Al-C were shown in Figure 26. Fe reacts with carbon to form eutectic mixtures, which are metastable to enable carbon diffusion (Figure 26B). Carbon solubility thus can be calculated based on the eutectic point in phase diagram. On the other hand, Al reacts with carbon to form stable compound, in which carbon cannot diffuse (Figure 26A). Thus coke cannot be generated.

Figure 26. Phase diagram of carbon-aluminum (A) and carbon-iron (B).

Figure 27A shows Fe, Co and Ni have higher carbon solubility than Au and Pd. On the other hand, carbon nucleation coefficients of these metals also were listed in Figure 27B. While $1.5 \times 10^{-11}$ m$^2$/s is good enough for carbon to nucleate in Fe, all of
the nucleation coefficients make no difference for these metals. Above all, low activation energy for thermal decomposition but high carbon solubility in forming solid solution enable the Fe, Co, Ni catalyst with high coke formation ability.

![Figure 27. Carbon solubility (A) and carbon nucleation coefficient (B) in several metals.](image)

Commonly used catalyst supports are graphite, silica, alumina, active carbon, alumina-silicate, etc. Catalyst supports influence catalytic reaction via the support structure and metal and support interaction. When the support is microporous structure (<2nm), the pore is too small for the coke molecule to go inside. Porous silica with a small pore size of 2 nm was taken into study. After reaction, the catalyst pellet was still white, which demonstrated no coke deposition on this catalyst. When the pore size increases to mesoporous (2-50nm), small carbon crystallite such as carbon nanotubes or nanofibers can form. As the pore size increase to macroporous (>50 nm) or larger, coke or graphite can deposit. The amount of deposited carbon species or coke is determined by the reaction condition and pore size. For a single pore, the amount of carbon deposited increases with the decrease of pore size, which can be described by the Young-Laplace equation:

\[ h = \frac{2ycos\theta}{\rho g} \]  

(4)

Where: \( h \) is the carbon or coke column, \( \gamma \) is the surface tension, \( \theta \) is the contact anger, \( \rho \) is
the density of coke, g is the gravity constant and a is the radius of silica pores. In this research, kaolin was tested to have low coke deposition. Thus, kaolin can be used as a binder.

On the other hand, different supports (Al₂O₃, SiO₂, TiO₂, kaolin—binder) with similar microstructure (specific surface area: 100 m²/g) were studied (Figure 28). 5 wt.% Fe was loaded on these supports by impregnation, following by drying, calcination and extrusion to form pellet. Then the pellets were brought to undergo catalytic reaction. Alumina was demonstrated to be a better support than silica and titanic oxide owing to the strong metal-support interaction, which allows high metal dispersion and thus a high density of catalytic sites. Such interaction prevents metal species from aggregating and forming unwanted large cluster that lead to graphite particles. Thus the interaction between support and catalyst determine the catalyst particles size and dispersion.

**Figure 28. DSC curves for coke formed on different supports: kaolin (red), TiO₂ (blue), SiO₂ (green), Al₂O₃ (black).**

The molecular structure of precursor has a detrimental influence on the coke growth. Aromatic hydrocarbons play an important role in the coke formation, more than saturated hydrocarbons and olefins. In this research, ethanol and cyclohexane were used as saturated and aromatic hydrocarbons to compare their coke formation ability. SiO₂,
Co/SiO$_2$ and Fe/SiO$_2$ catalysts have been tested both in ethanol and cyclohexane atmospheres to study the reactant influence (Figure 29). As there are two carbon atoms in ethanol molecules and four carbon atoms in cyclohexane molecules, the concentration of ethanol was set to be twice of that of cyclohexane. For all the three catalysts, cyclohexane resulted in a higher coke amount than ethanol. During reaction process, it is much easier for the straight hydrocarbon to decompose and to produce some small molecule items, like some gaseous ones. For the aromatic hydrocarbon, they are usually hard to decompose and large C/H molecules exist. Thus, coke can easily produce.$^{84}$

![Figure 29. TGA curves of coked catalysts (SiO$_2$ (sphere), Co/SiO$_2$ (square), Fe/SiO$_2$ (triangle)) on ethanol (black) and cyclohexane (red).](image)

Increasing temperature promotes decomposition and carbon generation. During coke formation reaction, hydrocarbon dissociated on metals to form C$_a$, an adsorbed atomic carbon; C$_a$ can react to C$_\beta$, a polymeric carbon film as temperature increasing. However, the more reactive, amorphous carbon formed at low temperature are converted at high temperature over a period of time to less reactive, graphitic forms.$^{85}$ Fe/SiO$_2$ catalysts were prepared and processed reaction under temperature from 400 °C to 700 °C
with an interval of 50 °C. Figure 30 shows the TGA curves of coke deposition on Fe/SiO$_2$ catalyst at different temperatures: 400 °C (black), 450 °C (purple), 500 °C (light blue), 550 °C (blue), 600 °C (green), 650 °C (yellow), 700 °C (pink). Inset is the temperature dependent coke percentage. No coke formed below 500 °C as the temperature was too low to form solid solution. Coke amount increases rapidly when temperature increasing from 500 °C to 600 °C due to rapid thermal decomposition. However, coke amount decrease slowly after 600 °C because the formation of unreactive graphite. 600 °C thus is the optimal temperature for coke depositing on Fe/SiO$_2$ catalyst.$^{86,87}$ The carbon species can also be determined from the decomposition temperature. Weight losing between 500 °C to 600 °C usually comes from the oxidation of crystalline carbon. Considering the catalyst is Fe/SiO$_2$, the carbon species may be carbon nanotubes.

![Figure 30. TGA curves of coke amount on Fe/SiO$_2$ catalyst under different reaction temperatures: 400 °C (black), 450 °C (purple), 500 °C (light blue), 550 °C (green), 600 °C (pink), 650 °C (yellow), 700 °C (blue). Inset is the coke percentage calculated as a function of reaction temperature.](image)

Influence of reaction time on coke formation was tested. Figure 31 shows the
TGA curves of coke formed on Co/SiO$_2$ catalyst with different reaction time: 5min (black), 20mins (red), 30mins (green), 45mins (yellow), 60mins (blue) and 90mins (pink). Inset is the coke percentage calculated as a function of reaction time. Reaction reaches a steady state quickly (less than 5mins). The coke amount increased almost linearly with reaction time in one hour. One hour later the coke deposition reached a platform. The reaction rapidly reaches steady state in beginning several minutes, thus the coke deposition was almost linear with the reaction time. Then the coke deposition was almost no increasing after one hour due to the stop of reaction. Therefore, the longest time for ethanol cracking reaction on Co/SiO$_2$ catalyst was one hour.

![TGA curves of Fe/SiO$_2$ sample with different reaction time: 5 min (black), 20 mins (red), 30 mins (green), 45 mins (yellow), 60 mins (blue) and 90 mins (pink). Inset is the coke amount on Fe/SiO$_2$ catalyst as a function of reaction time.](image)

**Figure 31.** TGA curves of Fe/SiO$_2$ sample with different reaction time: 5 min (black), 20 mins (red), 30 mins (green), 45 mins (yellow), 60 mins (blue) and 90 mins (pink). Inset is the coke amount on Fe/SiO$_2$ catalyst as a function of reaction time.

4.2.4 Coke dispersion along radial direction of pellet

It is assumed that coke deposition is not homogeneous along radial direction due to gas diffusion. The coke dispersion thus was studied along the radial direction. Scraping the cylinder pellet layer-by-layer resulted in the color shifts from dark black on
surface to dark brown in center (Figure 32). The color shift confirmed the change of coke deposition. Based on the above result, both experiment and calculation were done to estimate the dispersion of coke.

![Figure 32. The fifth (A), third (B) and first (C) layer of coked catalyst pellets.](image)

The coked catalyst pellet was scraped layer-by-layer with a layer thickness of 1 mm, to map the coke dispersion using TGA. The diameter of original coke deposited pellet was 1.4 mm. A few amounts of powders (less than 0.1mg) were scraped from the surface to ensure the diameter was still 1.4 mm. The coke amount for each layer thus can be calculated from the TGA test.

Coke dispersion can also be calculated. A steady-state mass balance exists for carbon species,

\[
D_A \frac{1}{r^q} \frac{d}{dr} \left( r^q \frac{dC_A}{dr} \right) - r_{surface} = 0
\]

(5)

With the boundary conditions:

\[
\frac{dc_j}{dr} = 0 \quad r = 0
\]

\[
C_j = C_{if} \quad r = R
\]

\(D_e\) is effective diffusivity, coefficient \(q\) is 1 for cylinder, \(r\) is the radial of cylinder, \(C_A\) is the concentration of reactant ethanol, \(r_{surface}\) is the surface reaction rate or reaction rate
excluding diffusion and adsorption. \( C_{jf} \) is the surface concentration of product coke (carbon), which can be deduced from TGA data of the first layer of coke. TGA shows the first layer of coke deposition is 15 wt.\%, thus the calculated surface concentration of coke \( C_{jf} \) is 0.0125 mol/g (Figure 33). Effective diffusivity \( D_e \) can be calculated by applying the microstructure data of catalyst pellets\(^90\),

\[
D_e = \frac{D_{AB} \phi \sigma}{\tau}
\]

where \( D_{AB} \) is the diffusivity in atmosphere for reactant, \( \phi \) is porosity, \( \sigma \) is construction factor, \( \tau \) is tortuosity. Carbon particles diffuse in atmosphere is \( 1.26 \times 10^{-7} \text{m}^2/\text{s} \); porosity of catalyst pellet calculated from BET measurement is 0.4; construction factor for silica catalyst pellets usually to be 0.3; tortuosity for silica catalyst pellets can be set to 3.0\(^{92}\). Finally, the calculated effective diffusivity of coke (carbon) is \( 0.5 \times 10^{-8} \text{m}^2/\text{s} \).

The rate of surface reaction is the rate excluding gas diffusion and adsorption, which can be measured experimentally. Catalyst powders rather than pellets were taken to process catalytic reaction as a function of time. The reaction time was set to 2 min, 5 min, 10 min, 30 min, 1 h, 1.5 h, and 2 h. Figure 33 is the TGA curves of coked catalyst powders. Inset is the coke amount as a function of time. The deposition rate can be calculated by differentiating the coke amount on time. Prior to one hour, the coke amount was in linear with reaction time due to steady state. When the time reached one hour, the reaction rate kept instant. The slope of the curve prior to one hour or the coke formation rate was calculated to be 0.0222 mol/(g)(min).
Figure 33. TGA of coke formed on catalyst powder as a function of reaction time. Inset is the coke percentage calculated as a function of reaction time.

Solving the equation with boundary conditions obtained the result: $C_A = Ar^2 + Br + C$ while $A = \frac{r_{\text{surface}}}{4D_e}$; $B=0$; $C = C_{ff} - \frac{R^2 r_{\text{surface}}}{4D_e}$ Inserting the $D_e$, $r_{\text{surface}}$, R into the A and C expression to generate the expression of $C_A$: $C_A = 0.0185r^2 + 0.00343$ (Figure 34A). The coke amount decreases as parabolic along the radial direction. On the other hand, coke formed on each layer was measured using TGA (Figure 34B). The weight loss percentage for each layer due to layer-by-layer scraping was described in Figure 34A with blue dots. The tendency of dots is similar to that of calculated curve, which exhibits the consistence of experimental and calculation results. The curve in Figure 34A thus can be used to estimate the coke dispersion along radial direction.
Figure 34. Coke amount on different layers (calculated result: curve, experimental result: dots); TGA curves of coke amount on different catalyst layers: 6th (yellow), 5th (blue), 4th (green), 3th (red), 2nd (black) and 1th (pink).

Figure 34A show how coke amount changes with pellets radius when the pellet was a rod. When the pellet is sphere or plate, the coke concentration can also be calculated. When pellet is plate (q=0), the equation 5 can be resolved and has the form: $C_A = \frac{R^2}{2D_e} - \frac{R^2}{2D_e}$. Similarly when pellet is sphere (q=2), the equation 5 can be resolved and has the form: $C_A = \frac{D_e}{6D_e} \frac{R^2}{2D_e} - \frac{R^2}{2D_e}$. Inserting the values of $D_e$, $r_{observed}$ and R into the above two expressions generate the results: $C_A = 0.037r^2 - 0.00563$ when pellet is plate (Figure 35A red curve) and $C_A = 0.01233r^2 - 0.00646$ when pellet is sphere (Figure 35A blue curve). Figure 35A shows the coke formation ability for the three kinds of shapes is: sphere > rod > plate.

The coke dispersion studied in Figure 34B has catalyst porosity of 0.4. When the porosity changes but still in mesoporous range, the coke amount along radius as a function of porosity can be calculated. Based on equation 5 coke amount as a function of radius and porosity can be expressed as: $C_A = \frac{7350}{\phi}r^2 + 0.0125 - \frac{0.0036}{\phi}$. Thus the value of $C_A$ can be calculated when the $\phi$ increasing from 0.1 to 0.9 (Figure 35B). Coke amount increases as porosity increasing. Thus catalyst with large porosity is easy to accumulate.
coke. The coke amount increases slowly when the porosity approaching to 1.

![Figure 35](image)

**Figure 35.** Coke amount calculated along radius (A – red: plate, black: rod, blue: sphere) as a function of pellet shape; coke amount calculated along radius as a function of pellet porosity (B – black: 0.1, red: 0.2, blue: 0.3, green: 0.4, pink: 0.5, yellow: 0.6, purple: 0.7).

### 4.2.5 Carbon species characterizations

After determining coke amount and catalyst composition, the coke or carbon species were processed further characterizations to have more understanding of the factors influencing coke formation. The morphologies of carbon species formed under different reaction temperatures have been detected by scanning electron microscope (SEM). No evident carbon species formed below 450 °C. Short rods carbon formed when temperature increased to 500 °C, which transformed to long rods carbon when temperature increased to 550 °C. Finally long wires carbon formed when reaction temperature increased to 650 °C. The morphology transition exhibited that high temperature (650 °C) promoting to the formation of long carbon fiber or tubes. Ethanol could undergo decomposition to generate carbon atom under 500 °C. But the carbon solubility under 500 °C was too low to form solid solution. 500 °C was long below the melting temperature of Fe catalyst. As the temperature was higher 500 °C, carbon started
to form solid solution with Fe, thus a few carbon materials diffused and generated. As temperature increased, the carbon solubility in Fe was faster than the carbon diffusion, thus long and regular carbon nanotube/fibers tended to form. When the temperature was higher than 800 °C, graphite rather than crystallite carbon generated and the amount of carbon nanotubes/fibers decreased.

Figure 36. Carbon nanomaterials on Fe/SiO$_2$ catalyst under different reaction temperature: (A) 400 °C, (B) 450 °C, (C) 500 °C, (D) 550 °C, (E) 600 °C, (F) 650 °C.

Further characterization was necessary to determine the microstructure of carbon species. Transmission scanning electron microscope (TEM) image (Figure 37 A) exhibited the structure was long fiber with small nanoparticles being encapsulated. High resolution TEM (HRTEM) further showed the fiber/tube structure was multi-wall, and the nanoparticles encapsulated was a different kind of material. According to the catalyst composition, the multi-wall structure was supposed to be carbon, and the nanoparticles encapsulated were assumed to be iron or iron oxide nanoparticles. Selected area diffraction for the Figure 37B area was taken to confirm the composition (Figure 37C). The bright solid ring was the diffraction ring of carbon, while the dispersed bright dots
were the diffraction of iron nanoparticles.

![Transmission electron microscopy image](image)

**Figure 37.** Transmission electron microscopy image (A), high-resolution transmission electron microscopy image (B), selected area diffraction (C) of carbon nanotubes.

Some materials have specific absorbance under infrared spectroscopy (FTIR). Silica has an absorbance peak at 1023 cm\(^{-1}\) (Figure 38A). After loading with iron, new absorbance peaks at 722 cm\(^{-1}\) and 3418 cm\(^{-1}\) appeared (Figure 38B). The new absorbance peak at 722 cm\(^{-1}\) was caused by the iron nanoparticles. A new peak at 1624 cm\(^{-1}\) ascribed to carbon nanotubes appeared after catalytic reaction (Figure 38C). The formation of carbon nanotubes influenced the absorbance of iron oxide nanoparticles as the peak at 722 cm\(^{-1}\) shifted to 702 cm\(^{-1}\). The peak shift confirmed that interaction between carbon species and iron nanoparticles.

![FTIR results](image)

**Figure 38.** FTIR results of SiO\(_2\) (A), Fe/SiO\(_2\) (B) and Fe/SiO\(_2\) covered with carbon nanotubes (C).

**4.3 Establish high-throughput screening method**
To establish high-throughput screening method, more issues needed to be studied in addition to evaluate catalyst coke formation ability with thermal barcode. Heat transfer as a function of PCM particles size and dispersion should be studied to determine particles size. Interaction among catalyst metals and PCM particles was studied as well to test the feasibility of silica shell. Finally, the change of gas diffusion in catalytic reaction due to formation of pellet and encapsulation of PCM particles was also tested.

4.3.1 Size dependent melting behavior

Generally speaking, nanoparticles have similar melting point as the bulk ones. However, melting point starts to descend dramatically with the reducing of particles size when particles size decreases to a certain number, such as 5 nm for gold nanoparticles. This phenomenon is called size dependent melting-point depression. Small size nanoparticles have more surfaces exposed than the bulk material. The chemical bonds on the surface are easier to break than that on the bulk one. Therefore, nanoparticles with small size is more likely to melt than the bulk one. In my research, phase change materials were made into nanoscale size, as small size nanoparticles cannot be distinguished by naked eye. However, if the nanoparticles are too small, the melting points can be largely different from the bulk one, which conflicts with the concept that the thermal barcode should have fixed melting points. Bismuth nanoparticles with three different sizes were selected to test the influence of particles size on melting point. Bismuth here was used to test the size-dependent melting point depression due to its easily size control. Three different kinds of bismuth nanoparticles were synthesized by using mini-emulsion method. Controlling reaction temperature and stirring speed can generate nanoparticles with different sizes. TEM images of three different sizes
nanoparticles were shown in Figure 39A (400nm), 39B (100nm), and 39C (20nm). Colloid solutions were dried to powders by freezing dry over night. The melting points of the nanoparticles powders were measured using DSC as 270.0°C (Figure 39D), 265.5°C (Figure 39E), and 245.5°C (Figure 39F). When the particles size decreased from 400 nm to 20 nm, the melting point reduced from 270.0°C to 245.5°C.

Figure 39. SEM images of bismuth nanoparticles of 400 nm (A), 100 nm (B) and 20 nm (C), DSC curves of bismuth nanoparticle with size of 400 nm (D), 100 nm (E), and 20 nm (F), respectively.

Size-dependent melting point can be calculated from the Gibbs-Thomson equation95. Figure 40 is the calculated size-dependent melting point change curve. The red points are the experimental results shown above. Three more melting points of particles with sizes of 500 nm, 750 nm and 1000 nm, were also measured and shown in Figure 40. These particles with specific size were synthesized by controlling reaction time and stir speed. The experimental results approach to the calculation curve. In the
curve, nanoparticles with a size around 100 nm have very similar melting point comparing to the corresponding bulk one. To be a thermal barcode, the nanoparticles melting point should be fixed. Thus nanoparticles with a diameter larger than 100 nm should be chosen to use as thermal barcode.

![Figure 40. Calculated melting point of bismuth nanoparticle as a function of size (black curve) and the corresponding experiment results (red points).](image)

4.3.2 Size-dependent melting time of PCM particles in pellet

Pellet is composed of PCM nanoparticles and catalyst powders. If the barcode particles were dispersed well in pellet, the structure can be simplified into multi-layer core-shell structure (Figure 41). In the simplified model, silica has lower thermal conductivity (1.0 W/m K) than the bismuth (10 W/m K) and can serve as thermal insulated layer. Heat flow transfers from outside bismuth shell to silica shell, and finally arrives the inner bismuth core. Due to the thermal conductivity difference, heat transfers fast in bismuth layer but slow in silica. If the silica shell thickness d is very small, the structure can be seen as one bismuth ball and one melting peak appears. If d is large, peak splitting appears as time is consumed for heat delay in the silica shell. The splitting peak will break into two peaks completely when d is large enough.
Bismuth particles with different sizes (100 nm, 2 µm and 20 µm) were synthesized by changing mini-emulsion temperature, stirring speed and surfactant amount (Figure 42A, 42B, 42C). The three different sizes of bismuth particles with equal mass were mixed with silica to form pellets. The smaller size of particles, the more homogeneously these particles mix with silica. DSC was used to study the melting temperature change of the three structures. The three melting peaks have similar melting points. The half peak widths are 0.8 °C (Figure 42D), 1.8 °C (Figure 42E), and 3.8 °C (Figure 42F) for the three kinds of particles, respectively. Thus the more homogeneous the PCM nanoparticles mixing with binder, the narrower (sharper) DSC peaks. As the peak width is determined directly by melting time, particles size thus was correlated with melting time by calculation below.

**Figure 41. Scheme of DSC signal affected by heat transfer**
Figure 42. SEM images of bismuth particles with sizes of 100 nm (A), 2 µm (B) and 20 µm (C). DSC curves of bismuth particles mixing silica with size of 100 nm (D), 2 µm (E) and 20 µm (F).

Set we have four kinds of bismuth particles: $r_1=250$ µm (bulk level), $r_2=10$ µm, $r_3=1$µm, and $r_4=0.05$ µm, respectively. The four kinds of nanoparticles are well dispersed in four pellets. The bismuth concentration keeps the same in each catalyst pellet. Based on the heat transfer model built above (Figure 41), the thickness of each PCM layer and silica layer in pellets can both be set to be the diameter of PCM particles. By calculation, there are 1, 31, 313 and 6229 layers of bismuth for 250 µm, 10 µm, 1µm and 0.05 µm particles, respectively.

The total heat transfer equation as following:

$$\frac{T_S-T_m}{R_{Total}} = 4\pi \rho_{Bi} Q_{Bi} r^2 \left(-\frac{dr}{dt}\right)$$

(7)

$T_S$: Surface temperature, $T_m$: melting temperature, $R_{Total}$: total thermal resistance, $\rho_{Bi}$: bismuth density, $Q_{Bi}$: bismuth latent heat, $r$: radius of pellets, $t$: melting time.

The time consumed can be calculated as following:
\[ \frac{T_e - T_m}{4\pi k_{Bi}Q_{Bi}} \, dt = -r^2 R_{total} \, dr \]  

To calculate the time consumed for heat transfer, the total thermal resistances need to be calculated, which is the function of the bismuth ball’s radius:

\[ R_{total} = \frac{1}{4\pi k_{Bi}} \left( \frac{1}{r} - \frac{1}{r_0} \right) + \frac{1}{4\pi k_{SiO2}} \left( \frac{1}{r_0} - \frac{1}{2r_0} \right) + \frac{1}{4\pi k_{Bi}} \left( \frac{1}{2r_0} - \frac{1}{3r_0} \right) + \frac{1}{4\pi k_{SiO2}} \left( \frac{1}{3r_0} - \frac{1}{4r_0} \right) + \ldots \]  

\( k_{Bi} \): Thermal conductivity of bismuth, \( k_{SiO2} \): thermal conductivity of silica, \( r_0 \): radius of PCM particles.

The melting time consumed for particles with different size were calculated and the results are listed in Table 2 as below.

<table>
<thead>
<tr>
<th>Particles</th>
<th>( r_1 )</th>
<th>( r_2 )</th>
<th>( r_3 )</th>
<th>( r_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius (um)</td>
<td>250</td>
<td>10</td>
<td>1</td>
<td>0.05</td>
</tr>
<tr>
<td>Time (s)</td>
<td>( 4.582 \times 10^{-2} )</td>
<td>( 5.823 \times 10^{-4} )</td>
<td>( 5.805 \times 10^{-6} )</td>
<td>( 1.465 \times 10^{-8} )</td>
</tr>
<tr>
<td>Lg radius</td>
<td>2.398</td>
<td>1</td>
<td>0</td>
<td>-1.301</td>
</tr>
<tr>
<td>Lg time</td>
<td>-1.3389</td>
<td>-3.235</td>
<td>-5.236</td>
<td>-7.834</td>
</tr>
</tbody>
</table>

The logarithm of melting time and radius in table 2 is described in Figure 43. The logarithm of melting time increases with the logarithm of particles size, which consists with the experimental results. Sharp thermal peak is good for thermal barcode because the thermal signal is evident and more peaks can be accommodated in certain temperature rang. Therefore, small nanoparticles have size around 100 nm to 200 nm were suggested as thermal barcode in the research.
4.3.3 Gas diffusion in catalyst pellet

For gas-solid heterogeneous catalysis, gaseous reactants need to undergo external and internal diffusions before adsorption and surface reaction. After surface reaction and desorbing from catalyst, gaseous products need to process internal and external diffusion as well.\(^9\) Internal diffusion refers to the diffusion of reactants or products from particle surface (pore mouth) to pellet interior. Internal diffusion usually takes much longer time than the external diffusion. Some catalysts with complex pore structure have internal diffusion even slower than surface reaction, of which the internal diffusion is the rate-determining step. The internal diffusion is influenced by catalyst pellet composition directly. The internal diffusion path thus will be changed after encapsulation of PCM nanoparticles and formation of compact pellet. The kinetic process of catalytic reaction (includes diffusion and surface reaction) can be described by thiele modulus \((\phi_n)\):

\[
\phi^2 = \text{surface reaction rate/diffusion rate}
\]  \(\text{equation 10}\)

The value of thiele modulus \((\phi_n)\) is a function of catalyst pellet’s microstructure parameters (surface area, porosity, density, tortuosity, and pellet radius), which is described in equations (11)(12). In our research, PCM nanoparticles encapsulation and
compact pellet formation will change the microstructure of catalyst pellets. Thus, the change of kinetic process can be calculated from change of pellets microstructure.

\[
\phi_n^2 = \frac{k_n R^2 S_a \rho_c c_A^{n-1}_{AS}}{D_e}
\]  \hspace{1cm} (11)

\[
D_e = \frac{D_{AB} \phi \sigma}{\tau}
\]  \hspace{1cm} (12)

Where: \( \phi_n \) is thiele modulus for reaction of \( n^{th} \) order, \( k_n \) is the reactive constant, \( R \) is the radius of catalyst pellets, \( S_a \) is the surface area of catalyst pellets, \( \rho_c \) is the density of catalyst pellets, \( C_{AS} \) is the concentration of reactants outside of pellets, \( D_e \) is the effective diffusion constant, \( D_{AB} \) is the diffusion constant in atmosphere, \( \phi \) is the catalyst pellet porosity, \( \sigma \) is the constriction factor, \( \tau \) is the catalyst tortuosity.

To test the influence of PCM particles and pellet formation on the gas diffusion, three samples were designed as following: catalyst powder, catalyst pellet and PCM particle tagged catalyst powder. Set the surface reaction rate is constant; the diffusion rate of all samples can be calculated from structure parameters. Encapsulation of PCM particles and formation of pellets will change structure parameters like: specific surface area, porosity, density and tortuosity, all of which have been listed in Table 3 below. For the three samples, diffusivity, construction factor, reactive concentration and constant are the same, all of which are not taken into consideration in the calculation. The factors that are different for the three samples are: specific surface area, porosity, density and tortuosity. All samples are the mixture of binder and silica with the ratio of 1:1. The microstructure of catalyst pellet was characterized by nitrogen gas adsorption (BET). Samples in the states of powder and pellet have been tested separately. Specific surface area and porosity of the two samples can be measured and obtained. Density was
obtained by dividing mass to effective volume of pellets. Tortuosity can be found from literature.\textsuperscript{92} The microstructure values for pellet and powder are described in Table 3.

### Table 3. Pellet and powder catalyst microstructure comparison

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density (kg/m(^3))</th>
<th>Porosity (%)</th>
<th>Specific surface area (m(^2)/g)</th>
<th>Tortuosity (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2)/binder= 1:1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catalyst powder</td>
<td>0.353×10(^4)</td>
<td>65.19%</td>
<td>408.532</td>
<td>1.25</td>
</tr>
<tr>
<td>Catalyst pellet</td>
<td>1.124×10(^4)</td>
<td>54.26%</td>
<td>341.767</td>
<td>1.31</td>
</tr>
<tr>
<td>Catalyst-PCM</td>
<td>0.371×10(^4)</td>
<td>63.22%</td>
<td>399.55</td>
<td>1.25</td>
</tr>
</tbody>
</table>

The gas diffusion rate in pellet was calculated to be 30% of that in powder (2.544×10\(^9\)/ 8.4956×10\(^9\)=0.3)\textsuperscript{98}. Thus formation of pellet decreased the gas diffusion largely. However, the gas diffusion rate in PCM tagged pellet was calculated to be 95% of that in bare pellet. Therefore, encapsulation of PCM thermal barcode has almost not changed the diffusion rate. No change of the kinetic process is due to the small amount of PCM particles (less than 5 wt.%).

#### 4.3.4 Catalytic effect of PCM

If PCM nanoparticles have catalytic activity, coke will deposit on them or react with them to form carbide. Metal nanoparticles encapsulated by a layer of coke tends to melt slower than the pure metal nanoparticles. The delay of heat transfer is due to coke layer encapsulation. In addition to the heat transfer delay, PCM nanoparticles are consumed to form carbide. The formation of carbide is irreversible, cause materials loss and lead to lower sensitivity in DSC test\textsuperscript{99}.

Based on the above discussion, PCM nanoparticles (eg: Bi\(_2\)Se\(_3\), Ge\(_2\)Sb\(_2\)Te\(_5\), Bi\(_2\)S\(_3\)
and Ge) were tested as catalysts under experiment conditions. Figure 44A shows the TGA curves for Bi$_2$Se$_3$ particles before and after catalytic reaction. The black curve is the weight loss of Bi$_2$Se$_3$, while the red curve is the weight loss of coke deposited Bi$_2$Se$_3$. The coke deposition on the PCM is less than 1 wt.% of the total materials mass, which is pretty low comparing to the coke deposition on catalyst (20 wt.% - 40 wt.%). The inset of Figure 44A shows the coke amount on several barcode materials. The low coke amount confirms that these barcode materials have limited catalytic ability.

If PCM formed carbide by reacting with carbon, the carbide part will not process phase change at melting point of the PCM. The difference of melting peak areas (before and after reaction) thus can be calculated to determine how much PCM barcode has already consumed to form carbide. DSC was tested for germanium particles before (red) and after (black) catalytic reaction (Figure 44B). The peak area difference between before and after reaction has been calculated for four kinds of materials (inset). No peak area difference is more than 1 wt.% of the PCM melting peak. Thus, no carbide formed for these barcode materials.
4.3.5 Mass effect of PCM

The sensitivity of thermal barcode depends on PCMs melting peak area, which is the heat release or adsorb during phase change process. The heat exchange during phase change process is in linear with the mass of PCM:

\[ Q = m \Delta H_m \] (13)

Where \( Q \): heat exchange in phase change process, \( m \): mass of PCM, \( \Delta H_m \): melting latent heat. Considering the minimum heat exchange in DSC is 0.1 mJ and the latent heat of germanium fusion is 36.94 kJ/mol, the minimum mass of germanium thus is 0.2 \( \mu \text{g} \). Although the theoretically minimum amount of PCM can be very small as being calculated above, the small amount like 0.2 \( \mu \text{g} \) cannot be recognized easily. Therefore, a large amount of PCM is added usually to generate large peak area that can be detected easily. But using too much PCM will lead to materials waste. So we look for the minimum amount of barcode that still generating evident thermal signal.
Melting peak changing with the mass of PCM was tested experimentally. Different amounts of catalyst sample tagged with germanium particles were processed DSC test, to study the thermal signal sensitivity as a function of samples mass (Figure 45A). The DSC peak became sharper as the germanium mass ratio increasing from 0.5 wt.% to 3.5 wt.% The germanium mass dependent melting peak area was calculated (Figure 45B). The melting peak area and barcode ratio were in good linear relationship, which confirmed the feasibility of this measurement. 0.5 wt.% may not be the minimum weight percentage of Ge. However the DSC signal is not very evident when the mass ratio of Ge is 0.5 wt.%. Therefore, 0.5 wt.% can be selected as the minimum amount of for germanium.

\[ PV = nRT \] (14)
Where P: pressure, V: volume, n: molar number, T: temperature. Thus, the germanium vapor concentration is $2.116 \times 10^{-6}$ mol/m$^3$. As the nitrogen flow rate is 100 ml/min, the germanium evaporation velocity is $2.116 \times 10^{-10}$ mol/min or $0.16 \times 10^{-7}$ g/min. Set material has the similar vapor pressure in temperature range [-20 °C, 20 °C] of melting point and material has to process heating and cooling process with a heat rate of 10 °C/min, totally 8 min is needed to process evaporation. Therefore, 1.7 nmol (0.13 µg) of germanium can be consumed each decoding process at the velocity of $2.116 \times 10^{-10}$ mol/min. The amount is so small that it is not necessary to worry about the PCMs evaporation.

The repeatability of PCM was studied by experiment. DSC of germanium tagged sample was tested repeatedly to see whether there are changes in peak shape and peak area (Figure 46). Inset is the peak area calculated as a function of repeated numbers. The melting peak of germanium still kept constant after repeating nine cycles. The peak area decreases with the increasing of recycling number. But the decrease can be ignored comparing to the mass of barcode materials. Thus the thermal barcode can be tested repeatedly.

![Figure 46. Multi-cycle DSC test of germanium particles in catalyst pellet.](image-url)
4.3.7 Interaction among PCM particles and catalyst

As for the PCM based high-throughput screening method, no interaction among catalytic metals and PCMs particles is assumed. However, formation of compact pellets and further calcination brings the catalyst metals and PCM particles to contact closely. Whether there is an interaction among catalytic metals and barcodes needs to be studied. X-ray diffraction results show the generation of new species or material’s microstructure change. Take the germanium nanoparticles tagged Fe/SiO$_2$ catalyst pellet for example. XRD pattern of three samples (Fe/SiO$_2$ catalyst; Ge particles; Fe/SiO$_2$/Ge pellet) were measured. Whether there is new species generated or microstructure change can be analyzed from XRD results.

XRD patterns of three samples (Fe/SiO$_2$ catalyst, Bi$_2$Se$_3$ particles, Fe/SiO$_2$/Bi$_2$Se$_3$ pellet) were measured to study the interaction between Bi$_2$Se$_3$ and Fe catalyst. Figure 47A are the XRD patterns for Fe/SiO$_2$ catalyst, Bi$_2$Se$_3$ particles, and Fe/SiO$_2$/Bi$_2$Se$_3$, respectively. The XRD pattern of Fe/SiO$_2$/Bi$_2$Se$_3$ is nearly the overlap of that for Fe/SiO$_2$ and Bi$_2$Se$_3$. Therefore, no new material is generated as no new peak appears after mixing Fe/SiO$_2$ and Bi$_2$Se$_3$. Similarly, the XRD patterns for Fe/SiO$_2$ catalyst, Ge particles and Fe/SiO$_2$/Ge pellet, and XRD patterns for Fe/SiO$_2$ catalyst, Bi$_2$S$_3$ particles and Fe/SiO$_2$/Bi$_2$S$_3$ pellet are shown in Figure 47B and 47C. For all of the three samples, no evident new peak was generated after mixing PCM particles and Fe/SiO$_2$ catalyst. Thus crystalline size and strain of the PCM and Fe species were studied to know if there was any change from interaction. The Fe/SiO$_2$/Bi$_2$Se$_3$ sample was taken as an example. The strain and crystalline size was calculated by applying the Williamson-Hall Method\textsuperscript{102,103}:

\[ \beta \cos \theta = \frac{\kappa \lambda}{\tau} + 4\varepsilon \sin \theta \]  

(15)
\( \beta \) is the half peak width (radians), \( \theta \) is the maximum peak location (radians), \( \lambda \) is the wavelength of radiation source (nm), \( \kappa \) shape factor (typically 0.9 can be 1 if completely spherical crystallites exist in samples), \( \varepsilon \) is the strain, \( \tau \) is the crystallite size (nm). We further set:

\[
\beta^* = \frac{\kappa}{\tau} + 2\varepsilon d^* = \frac{\beta \cos \theta}{\lambda} \tag{16}
\]

\[
d^* = \frac{2 \sin \theta}{\lambda} \tag{17}
\]

\( \beta^* \) was set as y-axis and \( d^* \) was set as x-axis to draw figure. Strain and crystalline size can be calculated from slope and intercept of the curve:

\[
\text{Slope} = 2 \varepsilon; \text{intercept} = \frac{\kappa}{\tau}
\]

Several main diffraction peaks in XRD were selected to calculate strain and crystallite size. For iron species, the value of \( \beta^* \) and \( d^* \) before (red points) and after (black points) mixing have been calculated based on equations (15) – (17), and described in Figure 47D. Similarly, the value of \( \beta^* \) and \( d^* \) for Bi\textsubscript{2}Se\textsubscript{3} before (red points) and after (black points) mixing have been shown in Figure 47E. These points can be linearly fitted to form line. Slope and intercept thus can be calculated to determine the change of crystallite size and strain after mixing. The calculated results were listed in Table 5.
Figure 47. XRD tests of FeO$_x$/SiO$_2$+Bi$_2$Se$_3$ (A), FeO$_x$/SiO$_2$ +Ge (B), FeO$_x$/SiO$_2$+Bi$_2$S$_3$ (C), microstructures calculated for FeO$_x$ (D) and Bi$_2$Se$_3$ (E) before (red) and after (black) catalytic reaction.

For the FeO$_x$/SiO$_2$+Bi$_2$Se$_3$ sample, the strain of Bi$_2$Se$_3$ kept the same as $5.6 \times 10^{-4}$ after mixing and the crystallite size increased from 35.184 nm to 50.173 nm. The strain of FeO$_x$ decreased from $13.3 \times 10^{-4}$ to $6.55 \times 10^{-4}$ after mixing and the crystallite size of FeO$_x$ increased from 13.95 nm to 20.01 nm after mixing. The crystallite sizes of both FeO$_x$ and Bi$_2$Se$_3$ were increased after mixing. The strains of both FeO$_x$ and Bi$_2$Se$_3$ were so small that we can think there is no change of strain after mixing. Similarly, the crystalline size increased but no strain changed after mixing for all materials in sample FeO$_x$/SiO$_2$+Ge and sample FeO$_x$/SiO$_2$+Bi$_2$S$_3$. Usually, grain size growing and sintering happen at
Tamman temperature. So the additive decreases the required annealing temperature. Even the temperature has not reached melting point, interaction may happen. Several reasons increase the tendency for the agglomeration of crystallite size to grow bigger one: formation of a ternary compound with high crystallite size, Ostwald ripening and doping.\textsuperscript{104-107} Formation of a ternary compound cannot be the reason for crystallite size growing because no new peak appears on the XRD patterns. Doping can change both crystallite size and strain. However, for all samples listed in the table we found, the crystallite strain has almost no change. Thus, doping cannot be reason for crystallite size change. Therefore, the growing of crystallite size is very likely coming from Ostwald ripening. Ostwald ripening is an observed phenomenon in solid solutions or liquid sols that small crystals or sol particles dissolve, and redeposit onto larger crystals or sol particles. Therefore, no interaction exists between catalyst and PCMs because Ostwald ripening usually happens among the same materials. During Ostwald ripening crystalline size increases without strain change. Thus, the silica shell round PCMs nanoparticles works well to prevent the interaction between catalyst and PCM nanoparticles.

<table>
<thead>
<tr>
<th></th>
<th>Pure</th>
<th>Bi\textsubscript{2}Se\textsubscript{3}/FeO\textsubscript{x}</th>
<th>Ge/FeO\textsubscript{x}</th>
<th>Bi\textsubscript{2}S\textsubscript{3}/FeO\textsubscript{x}</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_{\text{Bi}_2\text{Se}_3}$</td>
<td>$5.6 \times 10^{-4}$</td>
<td>$5.6 \times 10^{-4}$</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>$\varepsilon_{\text{Ge}}$</td>
<td>$12.45 \times 10^{-4}$</td>
<td>/</td>
<td>$5.4 \times 10^{-4}$</td>
<td>/</td>
</tr>
<tr>
<td>$\varepsilon_{\text{Bi}_2\text{S}_3}$</td>
<td>$7.2 \times 10^{-4}$</td>
<td>/</td>
<td>/</td>
<td>$8.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>$\varepsilon_{\text{FeO}_x}$</td>
<td>$13.3 \times 10^{-4}$</td>
<td>$6.55 \times 10^{-4}$</td>
<td>$12.7 \times 10^{-4}$</td>
<td>$9.021 \times 10^{-4}$</td>
</tr>
<tr>
<td>$\tau_{\text{Bi}_2\text{Se}_3(\text{nm})}$</td>
<td>35.184</td>
<td>50.173</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>$\tau_{\text{Ge}(\text{nm})}$</td>
<td>17.903</td>
<td>/</td>
<td>30.143</td>
<td>/</td>
</tr>
<tr>
<td>$\tau_{\text{Bi}_2\text{S}_3(\text{nm})}$</td>
<td>40.245</td>
<td>/</td>
<td>/</td>
<td>50.35</td>
</tr>
<tr>
<td>$\tau_{\text{FeO}_x(\text{nm})}$</td>
<td>13.9556</td>
<td>25.012</td>
<td>27.675</td>
<td>32.12</td>
</tr>
</tbody>
</table>
No interaction is assumed among any PCM nanoparticles as nanoparticles are encapsulated by silica. However, we cannot completely think that no interaction exists between any two PCM nanoparticle, as the formation of compact pellets and calcination. Therefore, X-ray diffraction also applied to exam the interaction among PCM particles. Any two of three thermal barcode samples: Bi\textsubscript{2}Se\textsubscript{3}, Ge and Bi\textsubscript{2}S\textsubscript{3}, were mixed homogeneously. After being extruded to form pellets and undergoing calcination, the pellets were crushed to powders and processed XRD detection. Figure 48 is the XRD patterns of Ge, Bi\textsubscript{2}Se\textsubscript{3} and the mixture (A), Bi\textsubscript{2}S\textsubscript{3}, Ge and the mixture (B), Bi\textsubscript{2}S\textsubscript{3}, Bi\textsubscript{2}Se\textsubscript{3} and the mixture (C). From all of the three XRD patterns, no new diffraction peak was found. Thus, no new materials formed by mixing any two materials. Similarly, Williamson-Hall method was applied to study the change of strain and crystallite size. Figure 48D are the $\beta^*$ and $d^*$ values of Ge from sample (Bi\textsubscript{2}S\textsubscript{3}+Ge), calculated from equations (15) – (17). The red points are values prior to mixing while the black points are values after mixing. These points were fitted into line to calculate slope and intercept, both of which can be used to calculate crystalline size and strain of Ge.
The crystalline size and strain values of Bi$_2$Se$_3$, Ge and Bi$_2$S$_3$ prior to and after mixing have been listed in Table 5. As the XRD peaks of Bi$_2$S$_3$ are too complex to be distinguished, only several main diffraction peaks were used to calculate crystallite size and strain change. For the three sets of samples, the crystalline size of catalyst and PCM increased after mixing. However, the strain for all materials were still so small that we can think there was no change of strain after mixing. As being discussed in the PCM and catalyst interaction section, Ostwald ripening is very likely to be the reaction for increasing crystallite size without strain change. That means no interaction exists for PCMs barcodes. Thus, the silica shell around PCMs nanoparticles works well to prevent interaction among any PCM barcodes.
Table 5. Crystallite size and strain calculated for any two mixtures of Bi$_2$Se$_3$/Ge/Bi$_2$S$_3$ samples

<table>
<thead>
<tr>
<th></th>
<th>Pure</th>
<th>Bi$_2$Se$_3$/Ge</th>
<th>Bi$_2$Se$_3$/Bi$_2$S$_3$</th>
<th>Ge+Bi$_2$S$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_{\text{Bi}_2\text{Se}_3}$</td>
<td>$5.6 \times 10^{-4}$</td>
<td>$10 \times 10^{-4}$</td>
<td>$6.15 \times 10^{-4}$</td>
<td>/</td>
</tr>
<tr>
<td>$\varepsilon_{\text{Ge}}$</td>
<td>$12.45 \times 10^{-4}$</td>
<td>$13.55 \times 10^{-4}$</td>
<td>/</td>
<td>$15.55 \times 10^{-4}$</td>
</tr>
<tr>
<td>$\varepsilon_{\text{Bi}_2\text{S}_3}$</td>
<td>$7.0 \times 10^{-4}$</td>
<td>/</td>
<td>$7.5 \times 10^{-4}$</td>
<td>$8.05 \times 10^{-4}$</td>
</tr>
<tr>
<td>$\tau_{\text{Bi}_2\text{Se}_3}(\text{nm})$</td>
<td>35.184</td>
<td>33.052</td>
<td>49.889</td>
<td>/</td>
</tr>
<tr>
<td>$\tau_{\text{Ge}(\text{nm})}$</td>
<td>17.903</td>
<td>35.686</td>
<td>/</td>
<td>28.055</td>
</tr>
<tr>
<td>$\tau_{\text{Bi}_2\text{S}_3}(\text{nm})$</td>
<td>42.575</td>
<td>/</td>
<td>50.322</td>
<td>49.625</td>
</tr>
</tbody>
</table>
5.0 Conclusion

Ten kinds of high melting-point materials have been identified as barcode materials for high-throughput screening, which were ground into nanoparticle using surfactant-assisted ball milling. The nanoparticles with sizes around 100 nm were further encapsulated with a layer of silica to form silica encapsulated PCM nanoparticles with diameter between 100 nm – 200 nm. The formation of silica shell was confirmed by TEM and EDX. Catalyst powder was synthesized by ion exchange with metallic precursor, following by drying and calcination. The catalyst powder was mixed with binder (kaolin) and PCM nanoparticles to undergo extrusion and form pellet. Coke formation ability and mechanical property of pellets were measured to determine the optimal binder ratio as 50 wt.%.

Fixed-bed catalytic reactor was build with a large amount of catalyst pellets being placed at the reactor to under reaction simultaneously. After reaction, coke amount was determined by TGA while catalyst composition was determined by decoding thermal barcode using DSC. 15 kinds of catalyst samples tagged with 15 kinds of thermal barcode have been tested and decoded successfully. Factors influencing coke formation (temperature, reaction time, catalyst species and concentration, reactant species, and support species) were studied to know how these factors work. Fe and Co catalysts have good coke deposition ability comparing to Ce and Bi, due to the high carbon dissolving and precipitating rates. 10 wt.% is the optimal percentage for the Fe catalyst undergoing catalytic reaction. Kaolin has almost no coke deposition thus can be used as binder. The order of coke deposition ability of supports was SiO$_2$>Al$_2$O$_3$>TiO$_2$. The interaction between catalyst and support determines the size of catalyst nanoparticles and degree of
coke formation. Compared to saturated hydrocarbons like ethanol, aromatic hydrocarbon such as cyclohexane cause heavier coke deposition because the straight hydrocarbon is easier to decompose and to produce small molecule items. No coke formed below 500 °C. Coke deposition increased rapidly as temperate increased from 500 °C to 600 °C. However, coke amount decreased as temperature increased from 600 °C to 700 °C. Thus, 600 °C is the optimal temperature for coke formation on Fe/SiO₂. Coke amount increased rapidly to arrive steady state for the initial 60 mins, then increased slowly due to the saturated deposition.

Coke dispersion along radial direction of cylinder pellet was studied. Scraping the coked catalyst pellet layer by layer, the color changed from black on surface to brown in center. The coke deposition of each layer thus was measured using TGA, which decreasing from 15 wt.% on surface to 3 wt.% in center. Based on the steady state mass balance of carbon species, coke amount as a function of radius was described as \( C_A = 0.0185r^2 + 0.00343 \), which consisted with the experiment results. Finally, Characterizations like SEM, TEM and FTIR have also been applied to further analyze the carbon species structure. The growth of carbon nanotubes depending on temperature was captured using SEM. TEM study showed that nanotubes formed were multiwall. FTIR results showed that an interaction existed for iron nanoparticles and carbon nanotubes.

The feasibility of building a high-throughput screening method based on thermal barcode was studied. Size-dependent melting behavior of PCM nanoparticles was studied first. Bismuth nanoparticles with size of 400 nm, 100 nm and 20 nm were synthesized and had their melting points tested as 270.0 °C, 265.5 °C, and 245.5 °C. Gibbs-Thomson equation was used to calculated the melting point change of bismuth nanoparticles. The
obtained curve was consisted with the experiment results. The melting behavior of PCM particles influenced by particles dispersion was studied as well to select particles with reasonable size. Bismuth nanoparticles with size of 100 nm, 2 µm and 20 µm were mixed homogeneously with binder to measure their thermal signals. DSC melting peak became wider as the particles size increasing. Heat transfer equation was applied to study this phenomenon. When the radius of bismuth particles increased from 0.05µm, 1µm, 10µm to 250 µm, the melting time calculated increased from 1.465×10⁻⁸ s, 5.805×10⁻⁶ s, 5.823×10⁻⁴ s to 4.582×10⁻² s. Thus nanoparticles with a size around 100 nm – 200 nm were selected as increasing particles size resulting in increasing melting time and wider melting peak.

The difference of gas diffusion in powder and in pellet samples was studied. Gas diffusion rate in pellet was 30% of that in powder while encapsulation of PCM only decreased 5% of diffusion rate. Catalytic ability of PCM was studied using TGA-DSC. For samples Bi₂Se₃, Ge, Bi₂S₃ and Ge₂Sb₂Te₅, the weight loss percentages due to coke deposition were 0.8wt.% , 0.8wt.%, 1.1wt.% and 1.0wt.%, respectively. Meanwhile, there were few materials losing due to the formation of carbide (Bi₂Se₃: 0.2 wt.%, Ge: 0.1wt.%, Bi₂S₃: 0.5wt.% and Ge₂Sb₂Te₅: 0.8wt.%). Multi-cycle experiment was done to test the stability of thermal signal. Interaction among PCM nanoparticles and catalyst nanoparticles was studied using XRD. After forming pellets, the crystalline sizes of both PCM and catalyst were increased with no change in strain, which is very likely stemming from Ostwald ripening. Thus, the silica shell round PCM nanoparticles works well to prevent the interaction among catalyst and PCM nanoparticles.
6.0 Recommendations

I. To minimize uneven distribution of coke in catalyst pellet, the size of catalyst pellet was reduced to micrometer level. The pellet was designed to have three-layer structure with catalyst layer on the top, silica-insulated layer in the middle and thermal barcode layer at the bottom (Figure 49A). The three-layer structure created via spin coating has a thickness no more than 100 µm (Figure 49B, C). The thin film was cut into small patterns with a side no more than 500 µm (Figure 49C) prior to totally dry. Robust patterns could be obtained after drying and calcination, and scraped with blade. The micro pellet can be applied into micro reactor. To achieve high-throughput screening of coke resistant catalyst with these micro pellets, a lot work need to be done.

![Figure 49](image)

**Figure 49.** Three-layer structure of catalyst pellet (A), spin coating structure (B), and micro pellets generated by using laser cutting (C).

II. To study the interaction between PCM and catalyst, the changes of crystalline size and strain were studied by using XRD. It assumes that the formation of ternary compound is the reason for increasing crystallite size. In this case the formation of ternary compound is suggested to be detected using X-ray photoelectron spectroscopy (XPS) by detecting the valence change of Fe and Bi species. XPS is a surface-sensitive quantitative spectroscopic technique that measures the elements composition at the parts per thousand.
range, empirical formula, chemical state and electronic state of elements that exist within materials. If there is valence change of Fe and Bi species, the ternary compound may exist; otherwise, no ternary compound exist.

III. In the paper, the idea of high-throughput screening has been demonstrated preliminary by using four kinds of PCM nanoparticles. We have searched ten kinds of PCM to use as thermal barcodes for coke deposition reaction. Therefore, high labeling capacity of \(2^{10^3}\) (1023) and high-throughput screening can be achieved. However, some of the materials selected may not work for the coke deposition reaction, or may not have significant thermal signal during coke deposition reaction. Other materials thus should be explored and studied. Ternary alloys such as GeSbTe series are suggested to use as thermal barcode as well due to their high melting points, thermal stability and variability.
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