

CHAPTER II

LITERATURE REVIEW

2.1 Porous Materials

A porous material or porous medium is a material containing pores, cavities, channels, or interstices. The structural portion of the material is often called the “matrix” or “frame” that is typically a solid and the pores are usually filled with liquid or gas. A porous material is most often classified by its porosity according to IUPAC notation, also divided by other properties, such as diffraction characteristic (e.g., amorphous, sub-crystal, and crystal solids), shape (e.g., cylindrical open, cylindrical blind, and roughness). The porous materials are used in many areas of applied science and engineering since they have high surface area, providing numerous reactive sites.

2.1.1 Mesoporous Materials

Mesoporous materials containing pores with diameters between 2 and 50 nm can be divided into ordered or disordered mesoporous structure according to IUPAC definition. They have many superior properties, such as high surface area and tunable pore structure that allow large molecules to penetrate inside the pores to overcome the limitations of microporous materials. The ordered mesoporous silica M41S series discovered by scientists from Mobil groups can be divided by the different arrays: hexagonal MCM-41, cubic MCM-48, and unstable lamellar MCM-50 mesostructures.

2.1.2 MCM-48

Cubic MCM-48 indexed in the space group of Ia3d is the most attractive material in terms of catalytic activity due to three-dimensional pore structure and interconnected channels, reducing the diffusion limitations and avoiding the pore blocking of coming molecule (Monnier *et al.*, 1993). Moreover, they have also some prominent properties, including narrow pore size distribution, high surface area, long-range order, various structures, wall compositions, and pore

shapes. MCM-48 has been used as an adsorbent, sensor, catalyst, catalyst support, and inorganic template for the synthesis of advanced nanostructure. However, the cubic MCM-48 is an intermediate during the transformation from hexagonal to lamellar phases. Therefore, the synthesis condition has to be carefully controlled.

2.1.3 Synthesis of MCM-48

The synthesis of MCM-48 via sol-gel process consists of 3 steps: formation of supramolecular arrangement of surfactant molecules, templating, and removal of template in order to create the porous material by solvent extraction, calcination, oxygen plasma treatment, or supercritical drying. The size, extent, and shape of micelles and aggregation into liquid crystal relate to the types of mesostructure, depending on the concentration of surfactant and synthetic temperature (Figure 2.1).

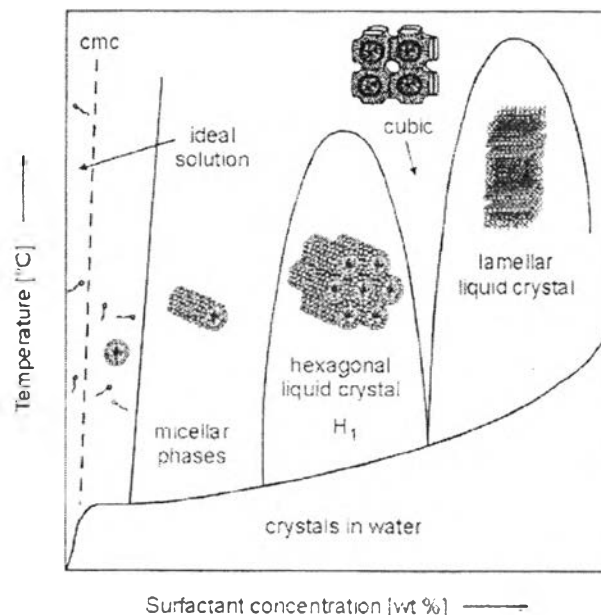


Figure 2.1 Schematic phase diagram for a surfactant in water.

(http://www.uio.no/studier/emner/matnat/kjemi/KJM5100/h06/undervisningsmateriale/16KJM5100_2006_porous_e.pdf).

Moreover, silica sources also affect to the formation of MCM-48 (Xu *et al.*, 1998). Generally, to synthesize MCM-48 via sol-gel process, the most widely used raw materials are tetraethylorthosilicate (TEOS) as a silica source, CTAB as a surfactant, and NaOH as a catalyst. However, TEOS presents significant handling problems due to high toxicity and moisture sensitivity. Longloilert *et al.* introduced another source of silica known as silatrane due to its ease to synthesize from inexpensive and commercially available raw materials, and moisture stability lasting up to several weeks. The optimum synthesis condition of MCM-48 is as follows; SiO₂:0.3CTAB:0.5NaOH:62H₂O at 140 °C for 16 h. The BET surface area of this product is as high as 1,300 m²/g with a narrow pore-size distribution.

2.2 Cerium Oxide

Cerium oxide (CeO₂), also known as ceria, ceric oxide, or cerium dioxide, is an important rare earth oxide and has been widely investigated in automotive exhaust purification and solid oxide fuel cell applications. Cerium oxide has two suitable features for using as catalysts: (1) the redox reaction between Ce³⁺ and Ce⁴⁺ with oxidizing and reducing agents and (2) the exhibition of oxygen storage and release properties. With these remarkable properties, ceria has become very attractive for using as a catalyst in oxidation and reduction, such as CO oxidation and SO₂ reduction (Figure 2.2).

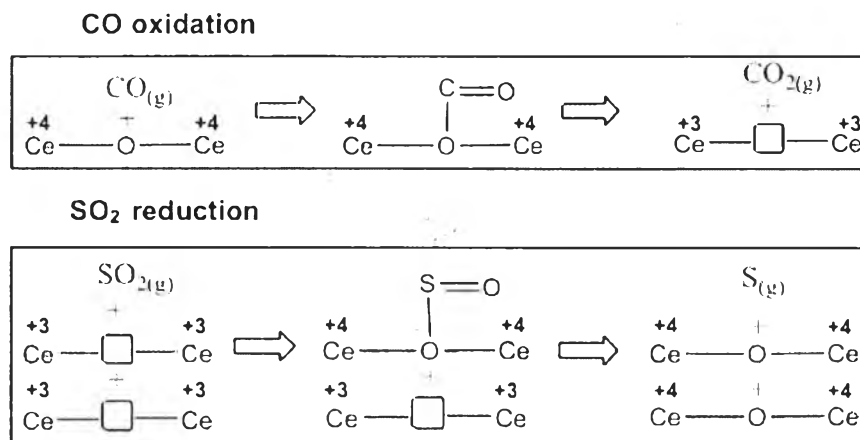


Figure 2.2 The mechanism of CO/SO₂ gas conversion via surface catalysis of CeO₂ (Yu et al., 1995).

2.2.1 Synthesis of Cerium Oxide via Nanocasting Process

Nanocasting process is used for fabricate porous material in nanometer scale by filling the template with desired material (precursor) and removing the template to obtain the replica of the template. Generally, templates in this process can be classified into two kinds; hard and soft templates. The hard templates (i.e. silica, carbon) have more advantages than the soft ones due to the presence of highly crystalline walls, leading to a prevention of the structural collapse during the removal of the template, providing a well-ordered structure of frameworks and high surface area of replica. Moreover, the hard template also provides an ease to control and predict the result of mesostructure. The nanocasting process using a hard template consists of three steps (Figure 2.3). The hard template is first infiltrated with a precursor into the pores, followed by converting the precursor to the desired material inside the pore by thermal treatment. Finally, the hard template is removed by chemical reaction or combustion, depending on the template.

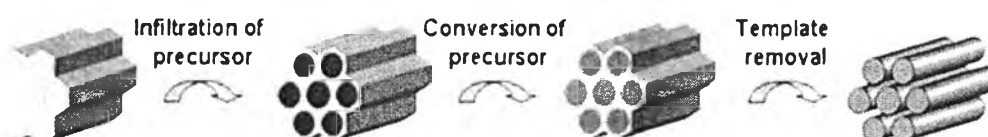


Figure 2.3 Schematic illustration of nanocasting process. (Hui et al., 2010).

Deeprasertkul *et al.*, (2015) synthesized order mesoporous ceria, with high surface area by the nanocasting method using MCM-48 porous material as a hard templete. The optimum conditions were to use 50 wt% of ceria, 30 min stirring time, 100 °C evaporated temperature, and 1 filling cycle. The results showed the removal of the silica template from the ordered mesoporous ceria, exhibiting high surface area (224.7 m²/g) and strong reduction at lower temperature comparing to commercial ceria. Thus, it has attracted particular attention for using as a catalyst support in many applications.

2.3 Copper Loaded Mesoporous Ceria

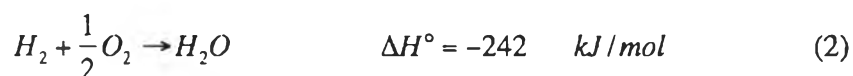
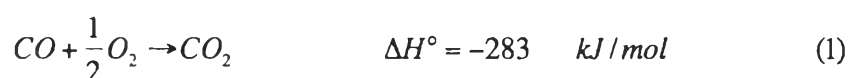
Cerium oxide (CeO₂) plays an important role in many applications in catalyst fields. However, it is known that the pure CeO₂ has a poor thermal stability and high operation temperature. The loading transition metal oxide to CeO₂ lattice could improve the activity, selectivity, and stability of the ceria surface at high temperature due to increasing vacancy sites in the anion sublattice that results in better redox properties. Copper doped CeO₂ materials are gaining popularity as they are very active and selective catalysts for CO-PROX reaction. However, the catalytic activity of a metal loaded CeO₂ is strongly related to the preparation method, affecting a great difference in particle size, dispersion, and interaction with the support. The favorite methods for doping metal on support are impregnation and deposition-precipitation methods. The impregnation method is less preferable because it tends to produce aggregation, resulting in large particle sizes (Lee *et al.*, 2002). The most commonly used method is the deposition-precipitation (DP) method because it producing of small particle size with well distribution (Haruta *et al.*, 1993) and a closed interaction between the metal particles and the support (Bond *et al.*, 1999).

Cu-modified or doped CeO₂ materials were proposed as candidates for the PROX reaction since they exhibited high activity and selectivity in CO oxidation (Liu *et al.*, 1995) and were active at significantly lower temperatures than Pt-based catalysts. Many researchers investigated on CuO-ceria catalyst preparation carried out to achieve catalyst with intimate CuO-ceria interface, responsible for their high

ability for oxidation reactions (Wang *et al.*, 2002). Ayastuy *et al.*, (2010) investigated the preparation of copper-ceria catalyst with three different Cu loadings (1, 7, and 15 wt%) by IWI, dried at 120 °C, and calcined in air at 500 °C. The results showed a high dispersion of copper for catalysts with 1 and 7 wt% Cu, and bulk CuO formation when using 15 wt% Cu loading. Moreover, the catalyst with 7 wt% of copper indicated very high activity (100% in a wide temperature) and selectivity (higher than 80%) due to its highest interaction of CuO and the support, which makes it attractive for its use in purification of hydrogen for fuel cell applications. Moreover, the CuO/CeO₂ with 7 wt% Cu exhibited the best performance in the presence of CO₂ and H₂O in all reaction temperature ranges.

2.4 Activity Measurement for PROX Reaction

An alternative to produce energy is the use of hydrogen as fuel via polymer electrolyte membrane (PEM) fuel cell since it is very clean, highly efficient, and environmentally friendly fuel that has attracted much attention for using as energy carrier, automotive and residential applications (St-Pierre *et al.*, 2001). The PEM fuel cells convert the chemical energy between H₂ and O₂ directly into electricity without combustion. However, the major problem in the utilization of PEM fuel cell is the supply of high-purity H₂ since small amount of CO can react with Pt-based anode catalyst. The PROX reaction has been widely used in purification process of H₂ due to its low cost and ability to reduce the CO content to less than 10 ppm without excess hydrogen consumption. Moreover, this reaction is suitable for using in case of non-stationary applications (Echigo *et al.*, 2003). The CO-PROX reaction consists of 2 chemical reactions. The first reaction is the conversion of CO to CO₂ using oxygen and the second one is the reaction of oxygen with H₂ (H₂ consumption) to give water (equations 1 and 2, respectively).



An efficient catalyst for the PROX reaction must be active and selective in order to prefer CO oxidation (equation 1) and to avoid parallel H₂ oxidation (equation 2). CO conversion or the activity of catalyst and the selectivity towards CO₂ are calculated using equations 3, and 4, respectively, using the volume flows of CO and O₂ at inlet and outlet of the reactor.

$$X_{CO} (\%) = 100 \times \frac{[F_{CO,in} - F_{CO,out}]}{F_{CO,in}} \quad (3)$$

$$S_{CO} (\%) = \frac{100}{2} \times \frac{[F_{CO,in} - F_{CO,out}]}{[F_{O_2,in} - F_{O_2,out}]} \quad (4)$$