

CHAPTER II

BACKGROUND AND LITERATURE SURVEY

2.1 Ceria-Zirconia Mixed Oxide Catalyst

The catalytic oxidation of carbon monoxide is an important technology for reducing pollutant emissions. Catalysts used in automotive system promote the complete oxidation of pollutant gases. In oxidation reaction, carbon monoxide reacted with oxygen, as shown in reaction (2.1)



Carbon monoxide oxidation was not a new technology, there were many researchers studying on this reaction. Böttcher *et al.*, (1997) studied carbon monoxide oxidation over oxygen-rich Ru(001) surfaces. They found that high reaction rate requires the accumulation of an appreciable amount of oxygen atom under surface. Then, Bondzie *et al.*, (in press) examined carbon monoxide oxidation by adsorbed oxygen on well-defined gold particles on TiO₂(110). Recently, there was the study of catalytic low-temperature carbon monoxide oxidation over cobalt oxide and related transition metal oxides by Jansson (2002). He investigated carbon monoxide over metal oxides, for instance, MnO₂, Fe₂O₃, Co₃O₄, NiO, CuO, ZnO, and CeO₂.

CeO₂ is mostly used as automotive catalysts because of its redox properties and high oxygen storage capacity. It has been reported that CeO₂ has potential uses for the removal of post-combustion pollutants, for the removal of organics from waste water (catalytic wet oxidation), and in fuel cell technology. (Trovarelli *et al.*, 1993). However, pure CeO₂ has poor thermal stability. The way to achieve more thermally stable catalytic materials is to modify them by doping with other oxides, such as La₂O₃, Ga₂O₃ and ZrO₂. ZrO₂ was found to be the most effective dopant. Hori *et al.*, (1999) prepared solid solutions of cubic Ce_xZr_yO₂ having Zr up to 50 mol% by two methods: precipitation of Ce and Zr hydroxides, and firing acetate mixtures by using cerium (IV) ammonium nitrate, cerium acetate, and zirconium nitrate as starting materials. They discovered that at higher Zr concentrations, tetragonal Ce-Zr solid solutions were formed. For both preparation methods, the best Zr concentration among those tested was 25 mol% Zr. For example, aged at 1000°C,

the oxygen storage performance of the solid solution was quite sensitive to Zr loading between 25 and 50 mol %.

The addition of ZrO₂ to ceria leads to the improvements of ceria's oxygen storage capacity, redox property, thermal resistance and better catalytic activity at lower temperatures. These effects were resulted from the partial substitution of Ce⁴⁺ with Zr⁴⁺ in the lattice of ceria, which caused a solid solution formation. Many preparation methods for CeO₂-ZrO₂ mixed oxide catalysts were employed, such as high-temperature firing or high-energy milling of a mixture of the oxides, conventional precipitation and sol-gel technique. Sol-gel techniques were found to be very useful, because they produce products with high purity, homogeneity, well-controlled properties, and low temperature processing. Thammachart *et al.*, (2001) prepared CeO₂-ZrO₂ mixed oxide catalysts via sol-gel technique using cerium nitrate and zirconium oxychloride as starting materials. The studies were focused on the oxidation of carbon monoxide over the mixed oxide catalysts in a packed bed quartz U-tube reactor. Comparisons of activity were made in terms of "light-off" temperature. It was found that the activity decreased with decreasing Ce/Zr ratio. Because of high reducibility, the Ce_{0.75}Zr_{0.25}O₂ solid solution was reported to have the highest activity among others. It might be due to the presence of ceria-zirconia solid solution in cubic phase, which was suitable for carbon monoxide oxidation, while the tetragonal phase reduced the yield of catalytic reaction.

Furthermore, there were many work dealing with the application of ceria-zirconia mixed oxide catalyst, for instance, Pt/ Ce_{0.75}Zr_{0.25}O₂ on carbon monoxide oxidation to study the oxygen release reaction (Hori *et al.*, 1999). Pd/ceria and Pd/ceria-zirconia supports were also studied for characterization of modeled automotive exhaust catalysts (Jen *et al.*, 1999).

It was acknowledged that the properties of catalysts and support catalysts mostly depended on their preparation method, for instance, the dispersion, size distribution of metal crystallites and the homogeneity of components in a multi-component catalyst (Schwarz *et al.*, 1995).

The remarkable application as inorganic metal oxides for catalyst results in the development of novel metal oxides. However, those metal alkoxides have some disadvantages, which are highly relative cost and high sensitivity to water.

Therefore, these are problems in processing inorganic oxides from metal oxides by sol-gel techniques. Many researchers have tried to develop new alternatives, for the synthesis. The zirconium and cerium glycolate complexes, that can be used as alkoxide precursors, have been prepared by the Oxide One Pot Synthesis (OOPS) method. Both corresponding products are less sensitive to water, and the OOPS method can debottleneck the catalyst preparation via sol-gel technique (Ksapabutr *et al.*, 2000).

2.2 Combinatorial Approach

Combinatorial approach is an approach to the discovery and study of new materials in which it combines high-speed chemical synthesis, high-throughput screening and high-capacity information processing to create, analyze and interpret large numbers of new, and diverse material composition (McFarland and Weinberg, 1999).

Holzwarth *et al.* (2001) stated that this combinatorial approach might be viewed as two complementary methodologies: primary and secondary screening.

Primary screening involves in the discovery of new materials via the systematic exploration of combination of elements for the preparation of multi-component materials. A throughput of 10,000 catalyst formulations per month has been reported on primary screening techniques (Holzwarth *et al.*, 2001). Typical screening techniques for primary screening are scanning mass spectroscopy and infrared thermography.

Secondary screening deals with the optimization of already-existing formulations or selected formulations from primary screening. The main characteristic of this screening is the association of high throughput preparation with evaluation of materials under the conditions as realistic as possible. This screening can be achieved by employing continuous flow parallel microreactor with additional identification of reaction product.

2.3 High Throughput Screening

The use of high throughput methods for screening catalyst formulations has become more and more common. The development of the reaction system is needed to allow testing a large number of catalyst formulations at the same time. High-throughput screening has created a revolution in pharmaceutical development, and has been extended to optimization of materials (Xiang *et al.*, 1995). Many types of reactors and screening techniques could be designed for high-throughput screening. The next sections will discuss about the frequently-used screening approaches in catalysis: microreactor and IR-technique.

2.3.1 Microreactor

Parez-Ramirez *et al.* (2000) studied the six-flow parallel reactor technology significantly enhancing the number of catalysts simultaneously tested and reducing the time for kinetic studies. The operation principle of the system was similar to that of a single-flow reactor system. The reactor system consisted of three sections: gas mixing, reactor, and analysis sections. The set-up contained six small fixed-bed reactors running in parallel. The flow rate, the composition of the catalyst bed, and reactor pressure can be selected independently, whereas the feed composition and the temperature were the same in all reactors. The number of six parallel reactors was not fixed, so more or less number of reactors can be installed in parallel, depending on the demands. They also reviewed the related issues, such as assumption of ideal plug flow behavior, pressure drop, mass and heat transport limitations, and catalytic bed dilution. Product analysis was performed by a mass spectrometer.

Claus *et al.* (2001) focused on miniaturized screening systems. In this work, they developed a monolithic reactor and a microreactor system. For the monolithic reactor, ceramic reactor module was developed, as shown in Figure 2.1. Arranging in 16 columns and 16 rows, each channel of monolith having dimension of 2.2mm. x 2.2 mm. and 150 mm. long and, represented a single fixed-bed reactor and contained a different catalyst materials. Microreaction system can be named as microchannel reactors. These reactors consisted of a very large number of parallel microchannels having a cross section of, for instance, 500µm x 500µm. The key elements for success of this approach were a suitable reactor module and the analysis

cases, scanning mass spectrometry technique was successfully applied for quantitative product analysis within 60 seconds per catalyst.

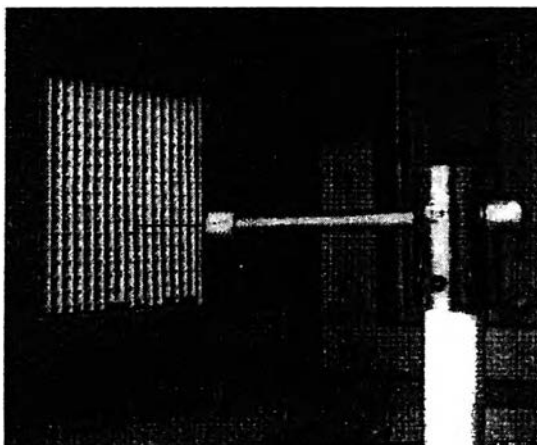


Figure 2.1 The monolithic reactor consisting of 256 narrow holes (Claus *et al.*, 2001).

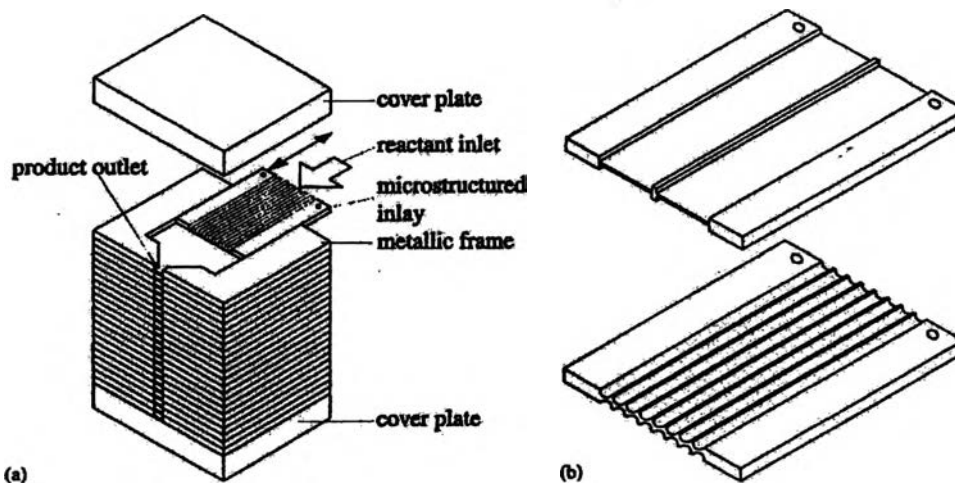


Figure 2.2 Array Microreactors: (a) Reactor module consisting of 35 stacked metallic frames, and (b) Microstructure catalyst inlays (Claus *et al.*, 2001).

In Figure 2.2, metallic frames are stacked together, and several parallel and independent microreactors were constructed.

Furthermore, a study of 15-tube reactor module that allowed catalytic testing up to 15 samples at the same time was accomplished. Rodemerck *et al.* (2001) also studied the multi-channel reactor module, in which each array contained

20 channels (1 mm x 1 mm) each with a cylindrical well (4 mm diameter by 1 mm high). Thus, it was possible to test up to 80 catalytic materials simultaneously.

2.3.2 Infrared (IR) Technique

The advance in IR imaging developed for military purposes have resulted in the creation of thermal monitoring systems capable of imaging temperatures with the accuracy of ± 0.01 K and approximately 100,000 points per second. With this ability, it is possible to screen for catalyst activity based the heat of reaction. Also, the reaction kinetics can be determined from the time dependence of the heat generation (Taylor and Morken, 1998)

In IR thermography, radiation energy is emitted from surfaces according to the modified Stefan-Boltzmann law.

$$q = e\sigma T^4 \quad (2.2)$$

Where T is absolute temperature,

e is temperature and composition dependent emissivity of the surface and

σ is Stefan-Boltzmann constant.

From equation, energy radiation is extremely sensitive to surface temperature, allowing the detection of very small differences in temperature by the IR technique. However, although IR thermography is an extremely fast and nonintrusive screening technique, it does not clearly provide information on the chemical identity of the products formed in reaction (Senken, 2001).

As many chemical reactions are exothermic, the most active catalyst is the one giving the highest amount of heat generation and, therefore, it gives the highest conversion. An IR imaging camera can be used to simultaneously measure the temperature of all the samples involving in the catalyzed reactions, so the active catalysts can be identified. Based on the same principle, IR thermometer could replace an IR camera for catalytic screening in educational research institutions due to its much less expensive price. The main disadvantage of IR thermography is that it is not suitable to determine the selectivity of catalysts (Pescarmona *et al.*, 1999).

However, the technique can be well applied for a one-reaction system due to its 100% selectivity nature.

IR thermography was applied to monitor the kinetics of the well-known oxidation of hydrogen over supported metal catalysts. Moates *et al.* (1996) used an aluminum reactor equipped with an IR-transparent sapphire window, electrical heating elements and an IR imaging to record 60 frames per second. Hydrogen and oxygen were introduced into the chamber, and reactor temperature gradually increased while the surface temperature of library elements was monitored by IR thermography. IR thermography can be used to screen the activity and lifetime.

In this work, the new alkoxide precursor, sodium tris (glycozirconate), was used as a starting material to prepare the gel of zirconium through the sol-gel process. The gel was then mixed with an appropriate amount of cerium nitrate hexahydrate solution to prepare a mixed $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_y$ oxide support. Subsequently, one and/or two metals, such as Ni, La, Fe, and Li were loaded on the support with totally 5% by weight of the catalysts. The single and dual metal loaded $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_y$ mixed oxide catalysts were tested for their activity on carbon monoxide oxidation by IR-thermometer. Finally, the lead formulations selected from primary screening were conventionally tested for more accurate activity in order to compare the performance among the lead formulation themselves.