CHAPTER II

LITERATURE REVIEWS

2.1 Alumina supports

Alumina (Al_2O_3) exits in many metastable phases before transformation to the stable α-Al_2O_3 (corundum form). The metastable alumina can be divided into two groups: the face-centered cubic (fcc) and the hexagonal close packing (hcp) arrangment of oxygen anions. The distribution of aluminum cations depends on the structure of the polymorphs [29]. The Al_2O_3 structures based on fcc packing of oxygen include γ-, η- (cubic), θ- (monoclinic), and δ- (tetragonal or orthorhombic) phases, where as the Al_2O_3 structures based on hcp packing of oxygen are the α (trigonal), κ (orthorhombic), and χ (hexagonal) phases.

Boehmite is one of the polymorphs of AlO(OH) which often involves in transformation pathway of alumina. The so-called pseudoboehmite is microcrystalline boehmite, which has extra water content due to the surface hydroxyl groups. Pseudoboehmite, one of the most widely used precursors to produce alumina can be decomposed to form transition alumina. Phase transformation , i.e. γ- to δ- to θ- and finally α- phase is then taken placed by heat treatment at various temperatures. It has been generally accepted that the phase transformation is the major cause for the loss of surface area [30].

Normally, transition aluminas start to lose the surface area even at temperature below 800°C due to the elimination of micro-pores. However, drastic loss occurs at temperature higher than 1000°C when the crystallization to the thermodynamically stable α-Al_2O_3 occurs [31]. It has been suggested that the initial stage of sintering at temperature as low as 600°C starts with the elimination of water formed from hydroxy groups of the particles in contacts [32-33].

2.2 Selective catalytic reduction of NO by hydrocarbons

Emissions of nitrogen oxides that are generated primarily from both stationary and mobile sources are important air pollutants. Their effects are reported to contribute to a variety of environmental problems, including acid rain and acidification of aquatic systems, because it is a strong oxidant and soluble in water and can be oxidized within the atmosphere to form nitric acid (HNO_3). Moreover, it is cause of the harmful impact for the respiratory system of human. The formation of NO_x is occurred in combustion process by combining the N_2 and O_2 present in the air at high temperature [34], as the equation 2.1. However, if a compound in combustion process has bound nitrogen, NO_x is readily formed at much lower temperature through an oxidation process.

$$O_2 + N_2 \quad \rightarrow \quad NO_x \quad\quad\quad (2.1)$$

Nitrogen oxides are formed at two stages during combustion:

1. The reaction of oxygen with nitrogen compounds in the fuel - this is termed fuel NO_x;

2. The reaction of nitrogen with oxygen in the combustion air - this is termed thermal NO_x;

The relative contribution of fuel and thermal NO_x depends on the type of fuel being used and the operating conditions.

It is not possible to reduce the nitrogen content of the fuel by physical cleaning as it is combined within the organic matter of the fuel, and at present there are no commercially available methods to reduce organic nitrogen. Hence, the emissions of NO_x generated during the combustion process can be reduced, as with SO_2, by treating the flue gases. For the above reasons, NO_x emissions are regulated in two ways before the flue gases release to environment :

- Preventing the production and release of nitrogen oxides during combustion, i.e. stages combustion and fluidized bed combustion (FBC)

- Removal of nitrogen oxides after combustion, i.e. selective catalytic reduction (SCR), non-selective catalytic reduction (NSCR) and activated carbon process.

However, the major disadvantages of regulations during combustion are the loss of energy consumption to eliminate NO_x at high temperature, and these processes are used with only stationary source. Therefore, the other method such as catalytic technology has been developing in the present time, because it is applied to control the emissions of NO_x both stationary and mobile sources. The SCR of NO_x using NH_3 was first discovered in 1957 [35]. It was discovered that NH_3 can react selectively with NO_x to produce N_2. Nonetheless, applied NH_3 for management of NO_x has some disadvantage including undesirable product, i.e. NO_2, corrosion and fouling [34]. Until the early 1970, the reduction of the emission of NO_x by HC became an important control issue. The other catalysts were investigated for use in SCR and the catalysts are divided into three major groups dependent on catalyst performance as shown in Figure 2.1 [36].
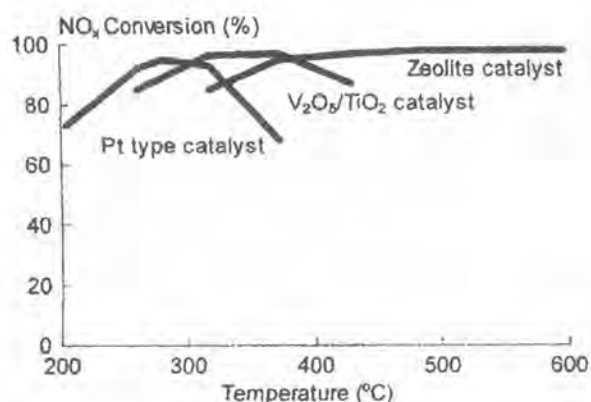
Figure 2.1 Three major families of SCR catalyst [36].

Although the development of catalyst is achieved by promoter to improve the stability with H_2O and sulphur, but the selectivity and activity of this is decreased [37]. Nonetheless, after testing nine different classes of promising catalysts was reported, the other concluded that despite the fact that some nutrient mixture containing catalysts, there is no single phase catalyst capable of satisfying the practical demands for NO_x removal. Although the unsuccessful management to control NO_x removal was reported, but the developments are continually studied to select the suitable catalysts which show both high activity and stability for NO_x removal.

In recent year, silver (Ag) is a promising catalyst for HC-SCR of NO_x, because the silver-based formulation is an effective catalyst for NO_x removal from exhaust gases under lean-burn conditions. It shows a good activity and selectivity for the SCR of NO by various hydrocarbons. Several organic compounds such as methane [38-40], methanol [37,41], ethane [39-40], hexane [39], butane [39], propene [41-51], methane, ethane, propane, ethanol [43,52-55], decane [56], propane [39-40,51,57-60], octane [39,61] were used as the reductant. Moreover, the other advantageous performance is a broad temperature window and a lower selective harmful product. Also, several studies investigated the activity, selectivity and stability of the silver-based material. At the present time, although many authors have reported to advantages of the silver-based catalyst in the HC-SCR of NO under excess oxygen, the reaction mechanism and active intermediate species are rather complicated and have not been fully elucidated. Typically, application of in situ Fourier transform infrared spectroscopy has been only used to predict the reaction mechanism and identify the intermediates [62-71]. The possible simultaneous occurrence of at least two reaction pathways results in complication of the analysis and therefore other procedures have to be made in order to obtain more information.

2.3 Oxidation of Carbon monoxide

A large amount of the emissions from cars is released during the first minutes after a "coldstart," before the catalyst becomes hot enough to convert the harmful emissions [72, 73]. Also, new and fuel-efficient engines generate colder exhaust gases than current engines, resulting in slower heating of the catalyst. This places new demands on the low temperature activity for the catalytic converters used in future emission abatement systems.

A series of papers have been published concerning low temperature oxidation of carbon monoxide and hydrocarbons over various transition metal oxides [74-76], but very few of these materials seem to work under realistic conditions, i.e., in the presence of H_2O, SO_2, etc. However, by gaining a fundamental understanding of the catalytic properties of such materials, it might be possible to indicate how commercial catalytic converters should be modified to improve their low-temperature activity.

In a previous paper [77], where the low-temperature activity of cobalt oxide and ceria-promoted Pt and Pd catalysts was studied, the cobalt-containing catalysts seemed to be the most active ones even in the absence of noble metals. They showed light-off temperatures of 167–197 °C for carbon monoxide and propene, while the unpromoted Pt and Pd catalysts had their light-off at 247–307 °C. It is therefore of interest to find out why cobalt-containing catalysts are so active.

The selective oxidation of CO in a H_2-rich atmosphere (PROX [78]) has long been of considerable technical interest for purification of hydrogen feed gas, e.g., for H_2 supply in ammonia synthesis. Over the last years, the PROX process has attracted new interest due to its use in fuel cell technology. To avoid the issue of hydrogen distribution and storage for H_2-PEM fuel cells (polymer electrolyte membrane), in particular in vehicle applications, H_2 can be produced locally (on-board) by steam reformation of methanol [79]. The resulting gas mixture (reformer gas) of ~75% H_2 in ~25% CO_2 is, however, contaminated with 1–2% CO [78, 80, 81].

Unfortunately, trace amounts of CO in the H_2-PEMFC affect a devastating deterioration of the energy conversion efficiency of the fuel cell via CO-induced poisoning of the anode catalyst and, therefore, the maximum acceptable CO concentration for state of the art Pt–Ru electrodes is ≤ 100 ppm [82].

Considering the problems associated with other methods for CO removal (methanation and membrane-based processes [78, 83, 84]), the selective oxidation of CO seems to be the most straightforward method to reduce the CO contamination in the reformate down to the ppm-level. The crucial requirements for the PROX reaction are high CO oxidation rate and, equally important, high selectivity, S. The latter is defined as the ratio of oxygen consumption for the CO oxidation reaction (to CO_2) over the total oxygen consumption, which includes the oxygen loss due to H_2 oxidation (to H_2O):

$$S = \frac{\Delta O_2^{(CO)}}{\Delta O_2^{(CO)} + \Delta O_2^{(H_2)}} \qquad (2.2)$$

The formation of water reduces the amount of hydrogen which can be fed into the fuel cell, so that the selectivity must be large enough to not reduce the fuel efficiency of the overall system. For example, a selectivity of 50% implies that equal amounts of CO_2 (desired reaction) and H_2O (side reaction) are being produced, equating to a loss of approximately 2.7% in fuel efficiency for typically 2%vol CO in the reformate. Similar losses of hydrogen can also be caused by other side reactions, the methanation of both CO and CO_2.

Catalysts proposed for the selective CO oxidation are alumina-supported platinum, ruthenium, and rhodium, operating at temperatures between 120 and 160°C. In a mixture of ~1% CO in H_2-rich gas, CO was found to be completely oxidized by addition of an approximately fourfold stoichiometric amount of oxygen, corresponding to an overall process selectivity of ~25% [85-87]. The dependence of the CO conversion rate and selectivity as a function of temperature, and contact time was examined in detail for alumina-supported platinum metals [83, 88–90] and for Pt supported on zeolite [91]. Oh and Sinkevitch [88] observed a selectivity of ~40% for Pt/γ-Al_2O_3 and a much higher selectivity and reactivity of ~80% for the Ru/γ-Al_2O_3 and Rh/γ-Al_2O_3 catalysts at close to

100% CO conversion in an integral flow reactor under non-steady state conditions in H_2-rich gas (0.85% H_2, 900 ppm CO). Studies using more realistic H_2 concentrations arrived at a smaller overall selectivity of ~25% on Ru/γ-Al_2O_3 and Rh/γ-Al_2O_3 [85], or 40–50% for close to 100% CO conversion on Pt/A-zeolite and Pt/γ-Al_2O_3 [91].