



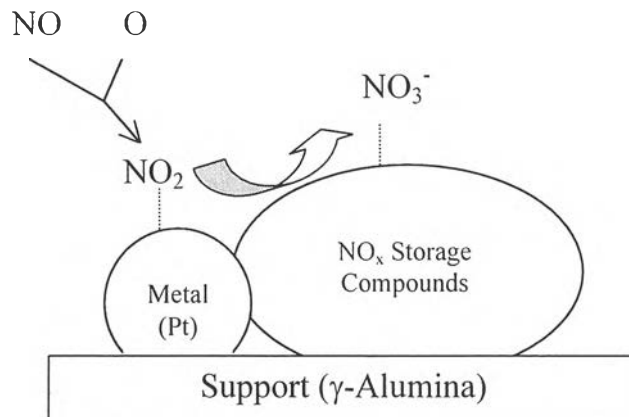
## CHAPTER II LITERATURE SURVEY

### 2.1 NO<sub>x</sub> Storage and Reduction (NSR)

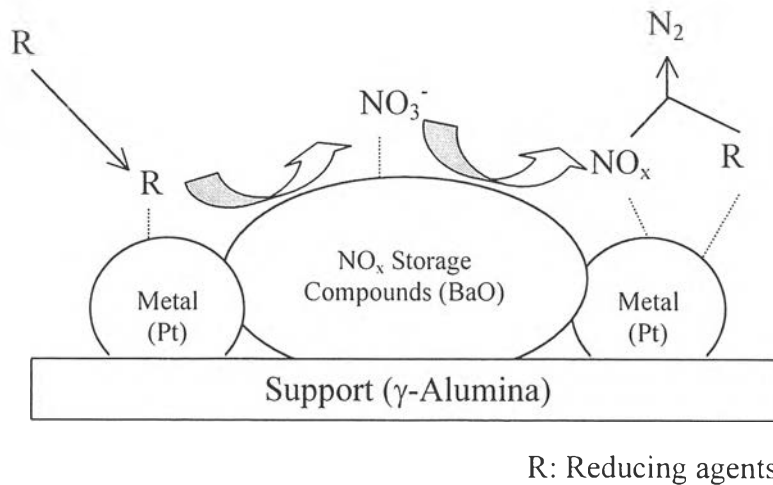
Although selective catalytic reduction method is effective way to remove NO<sub>x</sub>, the catalysts in this approach show very poor thermal durability, losing much of the catalytic activity after aging under real exhaust gas conditions on lean-burn gasoline or diesel engines. In addition, when operated the lean-burn engine, not only lean but also stoichiometric or rich conditions limit the durability of these catalysts. Thus, a NO<sub>x</sub> storage-reduction catalyst has attracted much interest for lean-burn gasoline engines, which are operated at lean and stoichiometric conditions (Bönger *et al.*, 1995).

A model of NO<sub>x</sub> storage-reduction catalyst comprises three essential parts. (i) a high-surface-area substrate material such as  $\gamma$ -alumina, (ii) noble metals that catalyze oxidation and reduction reaction such as platinum, (iii) a NO<sub>x</sub> storage component, which is mainly alkaline earth metal oxides such as barium oxide (Fridell *et al.*, 1999).

Takahashi *et al.* (1996) revealed a summary of NO<sub>x</sub> storage-reduction mechanism. During lean conditions, NO<sub>x</sub> are oxidized on noble metals and combined with neighboring NO<sub>x</sub> storage compounds to form nitrates (Figure 2.1). The nitrates thus formed are decomposed into NO<sub>x</sub> by reducing agents activated on noble metals under stoichiometric and reducing conditions. The emitted NO<sub>x</sub> is reduced to dinitrogen (N<sub>2</sub>) on precious metals by reducing agents (Figure 2.2).



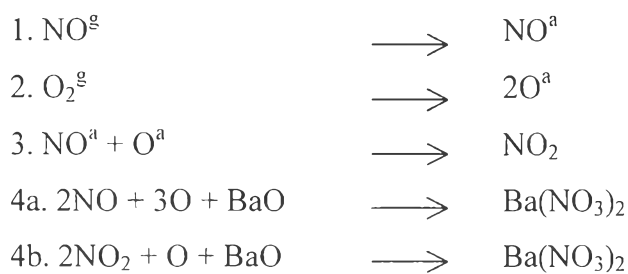
**Figure 2.1** NO<sub>x</sub> storage period of NSR catalyst



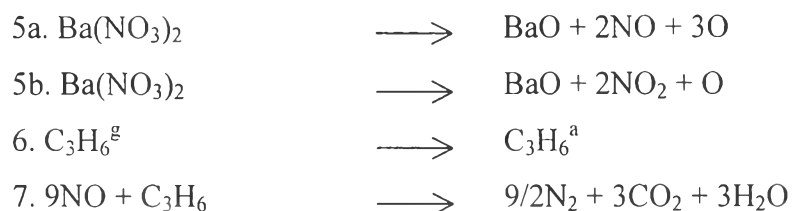
**Figure 2.2** NO<sub>x</sub> reduction period of NSR catalyst

Another similar mechanism was reported by Fridell *et al.* (1999). For one lean NO<sub>x</sub> storage–reduction, cycle can be assumed to comprise of the following steps:

For lean conditions:



For rich conditions:



where

a = adsorbed species

g = gas species

The essential functions of the  $\text{NO}_x$  storage–reduction catalyst are (i) oxidation of hydrocarbons and NO on noble metal site, (ii) storage of  $\text{NO}_x$  as nitrate form, (iii) release and reduction of storage  $\text{NO}_x$  under rich conditions (Fridell *et al.*, 2000).

Mahzoul *et al.* (1999) studied in Pt/Ba/ $\text{Al}_2\text{O}_3$  catalysts at  $300^\circ\text{C}$ . They found that amount of platinum loading in the range of 0.50-1.47 wt % showed a moderate effect on the amount of NO adsorbed while the amount of barium in level of low, standard and high show a significant effect on amount of NO stored. A very interesting result was that, even in the absence of platinum within the standard barium containing catalyst, a significant amount of NO stored was observed.

Takahashi *et al.* (1996) investigated the effect of oxygen to  $\text{NO}_x$  storage in Pt/Ba/ $\text{Al}_2\text{O}_3$  catalyst. They revealed that the  $\text{NO}_x$  storage amount was very low without oxygen, and rapidly increased with increasing the concentration of oxygen and finally reached a constant value at above 1%  $\text{O}_2$ .

Another study was done by Mahzoul *et al.* (1999). They developed Pt/Ba/ $\text{Al}_2\text{O}_3$  added with La and Rh catalysts. It was demonstrated that the time required for the catalyst to be saturated with  $\text{NO}_x$  decreased over the 0-15% range of increasing oxygen concentrations.

Further study confirmed that increasing 0-10% range of oxygen in the gas mixture inhibited the release of  $\text{NO}_x$  from the noble metal/BaO-type catalyst. The thermodynamic equilibrium calculations indicated the barium nitrate was stabilized by the presence of oxygen, shifting the decomposition temperature of barium nitrate

towards higher values. This means that more NO<sub>x</sub> storage occur when increasing oxygen concentration (Amberntsson *et al.*, 2001).

Amberntsson *et al.* (2001) also studied an effect of water in a commercial monolith catalyst containing noble metals and BaO (wash coat loading). They reported that in the presence of humidity in feed gases seemed to make slightly decreasing of NO<sub>x</sub> stored amount. This can be examined by the calculations of thermodynamic terms and the inspection of the calculated decomposition curves of barium nitrate in the presence of 0% and 5 % H<sub>2</sub>O. The results showed that the stability of barium nitrate in dry surrounding was higher than in humid condition.

## 2.2 Properties of Gold

Gold, Au, atomic number 79, is a third row transition metal on Group 11 (IB) of the Periodic Table. It occurs in the nature as a high pure metal, and it is treasured because of its color, its extraordinary ductility, and its resistance to corrosion. The electronic configuration of gold is [Xe] 4f<sup>14</sup> 5d<sup>10</sup> 6s<sup>1</sup>. Common oxidation states are 0, 1, and 3. Gold is characterized by high density, high electrical and thermal conductivities and high ductility.

Gold reacts with various oxidizing agents at ambient temperatures, yielding a good ligand present in lower the redox potential below that of water. Thus, gold is not attacked by most acids under ordinary conditions, and is stable in basic media. Gold can, however, dissolve readily in 3:1 hydrochloric-nitric acid (*aqua regia*).

Gold is very corrosive and tarnish resistant, and imparts corrosion resistance to most of the commonly used gold alloys, especially to those containing 50 or more atom % of gold (Grant, 1994).

## 2.3 Heterogeneous Catalyst Using Gold

Gold was once thought to be poorly active as a heterogeneous catalyst. Gold and TiO<sub>2</sub> are individually poorly active by themselves for CO oxidation. While it is deposited in the form of small particles on a metal oxide support, TiO<sub>2</sub>, a very active CO oxidation catalyst is created (Kozlov *et al.*, 1999).

Many research works in a number of laboratories have shown that if care is taken in the preparation of well defined supported gold systems, then, these systems can be unusually active and/or selective for a number of reactions of commercial importance (Thompson, 1998).

The catalytic performance of gold markedly depends on dispersion, supports and preparation methods. When gold is deposited on selected metal oxides as hemispherical ultrafine particles, it exhibits surprisingly high activities and/or selectivity in the combustion of carbon monoxide and saturated hydrocarbons, the oxidation/decomposition of amines and organic halogen compounds, the partial oxidation of hydrocarbons, the hydrogenation of carbon oxides, unsaturated carbonyl compounds, and the reduction of nitrogen oxides (Haruta, 1997<sup>a</sup>).

There are two constraints in gold catalyst preparation by impregnation method. The first one is size distribution, which is not narrow even under low metal loadings, ranging from small clusters to relatively large particles. The second one is chloride, which poisons catalysts for many reactions and remains on the catalyst surfaces when a metal oxide support is impregnated with  $\text{HAuCl}_4$  and calcined in air at temperature below 873 K (Okumura, 1999).

Haruta (1997<sup>b</sup>) showed that the method of catalyst preparation in carbon monoxide oxidation was very important and that if a co-precipitation procedure was used, high activity catalysts were obtained. He has found that this method resulted in a very uniform dispersion of small metallic gold particles on the support. The best results were obtained when these particles were 5 nm or less in diameter.

For a number of supported gold catalysts in the hydrogenation for carbon dioxide reaction, Sakurai (1995) found that the activity per unit surface area increased with decreasing particle diameter of gold.

Effect of moisture on the catalytic activity of  $\text{Au/TiO}_2$  for CO oxidation was investigated by Date (1999). He observed that a maximum reaction rate occurred at 200 ppm of water. It is interesting that moisture at ppm level does not deactivate the catalyst, but even promote the catalytic reaction, which indicates the advantage of gold catalysts in the practical use.

## 2.4 Nitric Oxide Reduction (Selective Catalytic Reduction, SCR) with Hydrocarbons over Gold Catalysts

The requirement for moisture resistance has motivated us to investigate the catalytic behavior of gold supported on metal oxides for NO reduction.

Gold supported on several metal oxides (MgO, TiO<sub>2</sub>, ZnO, Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>) were studied. It was found that 0.82 wt% gold on Al<sub>2</sub>O<sub>3</sub> could provide the highest conversion to N<sub>2</sub> at 700 K.

Comparison of the effect of moisture on Au/Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> catalysts was also studied. Although the conversion of NO to N<sub>2</sub> over Al<sub>2</sub>O<sub>3</sub> markedly decreases with increasing concentration of water in the range of 0-9.8 vol%, in case of (0.17wt%) Au/Al<sub>2</sub>O<sub>3</sub>, an increase in water concentration gives rise to small increase in the conversion to nitrogen. The catalysts which contain the oxides of base transition metals such as Cu, Ag and Co, as catalytically active species were appreciably deactivated by moisture. Thus, this enhancing effect of moisture provides gold catalysts with a significant advantage in applications for combustion of exhaust gases.

Effect of oxygen over gold supported alumina catalysts was further observed. On (0.17wt%) Au/Al<sub>2</sub>O<sub>3</sub> at 723 K, in the absence of oxygen, the NO conversion to N<sub>2</sub> was very low while the addition of oxygen in the reactant stream enhances the conversion of NO. The conversion remained almost constant in the oxygen concentration range of 6-20 vol%. In the same trend for (0.82 wt%) Au/Al<sub>2</sub>O<sub>3</sub>, the NO conversion to N<sub>2</sub> in the absence of oxygen was lower than in the presence of (5 vol%) oxygen. These results showed that oxygen is indispensable for reduction of NO by propene over gold catalysts (Ueda *et al.*, 1996-1999).

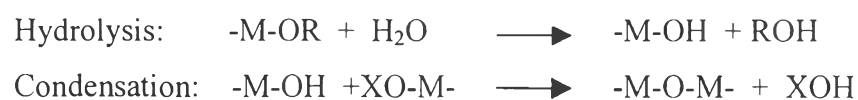
## 2.5 Catalyst Preparation

### 2.5.1 Sol-Gel Method

It has long been recognized that the properties of catalysts and catalyst supports, for example, the dispersion, size distribution of metal crystallites and the homogeneity of components in a multi-component catalyst often depend on

their preparation method. A sol-gel method is a promising technique for catalyst preparation. The single most important characteristic of sol-gel preparation of catalytic materials is its ease of control that refers to the following advantages: (i) the ability to maintain high purity because of purity of starting materials; (ii) the ability to change physical characteristics such as pore size distribution and pore volume; (iii) the ability to vary compositional homogeneity at a molecular level; (iv) the ability to prepare samples at low temperature; (v) the ability to introduce several components in a single step; and (vi) the ability to produce samples in different physical forms (Ko, 1994).

The sol-gel process involves first formation of a sol followed by that a gel. The hydrolysis and partial condensation of a precursor can obtain a sol, which is a liquid suspension of solid particles ranging in size from 1 nm to 1 micron. The further condensation of sol particles into a three-dimensional network produces a gel. Sol-gel chemistry with metal alkoxides can be described in term of two classes of reactions:



where

M = metal corresponding to the alkoxide

X = H or R (an alkyl group)

(Ko, 1994)

The relative rates of hydrolysis and condensation determine the extent of branching of the inorganic polymer and colloidal aggregation in the gelation mixture. These relative rates are functions of many parameters, such as temperature, pH and concentration of the metal ion precursors. In addition, drying and calcination conditions also affect the extent of branching and cross-linking, and the properties of the final oxide (Kung and Ko, 1996).

Seker *et al.* (1999) studied the NO conversion to N<sub>2</sub> in NO reduction by propene of silver supported on alumina catalyst comparing between sol-gel and co-precipitation method. They found that Ag/Al<sub>2</sub>O<sub>3</sub> catalyst by sol-gel method showed good activity and reached a maximum in conversion of 78% at 500<sup>0</sup>C while

the catalyst prepared by co-precipitation technique gave poor conversion where its maximum conversion reached only 30% at the same temperature.

#### 2.5.2 Incipient Wetness Impregnation Method

This procedure requires that the support is contacted with a certain amount of solution of metal precursor, then it is dried and calcined. The volume of the solution containing the precursor does not exceed the pore volume of the support. In the simplest way, the impregnation solution is sprayed on the support, which is maintained under stirring and has been previously evacuated. In principle this method appears to be simple, economical (especially when using solutions of costly active components) and able to give a reproducible metal loading which is however limited by the solubility of the metal precursor (Pinna, 1998).