

CHAPTER VI
LEAN-BURN NO_x REDUCTION BY PROPENE
OVER GOLD SUPPORTED ON ALUMINA CATALYSTS
DERIVED FROM THE SOL-GEL METHOD *

6.1 Abstract

Gold supported on alumina catalysts were investigated for selective NO_x reduction by propene. Two types of alumina, commercial and sol-gel alumina, were employed. The catalytic performance was mainly studied over the impregnated sol-gel alumina catalyst. The catalytic activity was tested under various propene and oxygen concentrations. NO_x conversion and the activity window of the catalysts increased as the propene or oxygen concentration increased. The presence of water also enhanced the NO_x conversion and widened the activity window of the catalysts. The sol-gel alumina supported catalysts gave much higher activity than the commercial alumina supported catalysts.

Keywords: Lean-burn, DeNO_x, HC-SCR, Au/Al₂O₃, Sol-gel, Gold, Propene

6.2 Introduction

Currently, environmental problems are a serious concern, and nitrogen oxide (NO_x) removal has been of worldwide interest. NO_x, mainly consisting of nitric oxide (NO) and nitrogen dioxide (NO₂), comes from the combustion process by the oxidation of nitrogen in air and the nitrogen-containing compounds in fuel. Transportation and industrial plants are the primary emitting sources of these oxides, which lead to a variety of environmental and health problems. The reactions in the atmosphere of NO_x with water and hydrocarbons under sunlight contribute to acid rain, smog, and ground-level ozone, which are the causes of aquatic system

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acidification, visibility reduction, and ecological perturbation [1, 2]. From these reasons, there have been many attempts to develop NO_x -control techniques. One of the potential methods is a technique using a specific reducing agent, so called “selective catalytic reduction” (SCR), as it preferentially reacts with NO_x rather than oxygen. The SCR technique is most successfully developed by using hydrocarbon as a reducing agent due to its non-toxicity, availability, and feasible implementation.

From the point of view of fuel economy and lean-burn engine demands, a catalyst working in “lean”, oxygen-rich conditions, has been extensively improved for the NO_x clean-up in exhaust gas. Zeolite catalysts have been shown to be candidates for this reaction. However, deactivation under high temperatures by water (vapor) has been a critical issue [3, 4]. Supported noble-metal catalysts have also been widely studied [5-8]. Among the precious metals, gold is probably the most interesting material. Many reviews have reported unusual activity and selectivity of gold catalysts for a number of reactions [9-12]. Ueda’s group presented the activity of gold on various supports and compared the reactivity of gold with that of other precious metal catalysts for NO reduction [13-15]. They reported that these supported gold catalysts were active for the reduction of NO with hydrocarbons. There are some studies of these reactions by using titania and ceria as a support [16-18]. However, supported gold catalysts are still less studied for NO_x reduction by hydrocarbons under oxidizing conditions [19-22]. An experiment with higher hydrocarbons as a reducing agent like octane was carried out for gold on alumina and titania as well [23]. Nevertheless, the catalytic activity began above 450 °C. The maximum conversion of NO_x was obtained at 500 °C. In our group, we studied the activity of catalysts prepared by the single-step sol-gel method. In this study, gold catalysts prepared by impregnation over pre-formed sol-gel alumina was mainly studied. The catalytic activity for NO_x reduction with propene as a reducing agent was determined under various conditions. The effects of water and oxygen, as well as the catalytic stability, are presented in this work. In addition, the activity comparisons of the catalysts prepared from different techniques (single-step sol-gel, impregnation, and deposition-precipitation) are demonstrated here.

6.3 Experimental

6.3.1 Catalyst Preparation and Activation

Gold supported on alumina catalysts were prepared using three different methods: single-step sol-gel, impregnation, and deposition-precipitation. For the single-step sol-gel method, a known amount of aluminum isopropoxide was added into hot deionized water at 85 °C. After continuous stirring for 1 h, appropriate amounts of nitric acid and gold acetate in 1,3 butanediol were introduced into the sol solution, respectively. The mixture was further stirred for 1 h at the same temperature, followed by aging overnight at room temperature. Finally, the solvent was removed by a low temperature heating until a gel formed. The resulting gel was dried at 100 °C for 12 h, followed by calcination at 600 °C for 24 h. The impregnation method employed two types of alumina as the catalyst support. The first one was commercial alumina (Aldrich, γ -Al₂O₃), the second one was sol-gel alumina prepared in a manner similar to the single-step sol-gel method, as reported by Seker and Gulari [20]. The alumina supports were impregnated with an appropriate amount of hydrogen tetrachloroaurate dissolved in water to attain the desired 0.8 wt% gold loading. The same drying procedure was applied, followed by calcination at 500 °C for 5 h. The deposition-precipitation catalyst was prepared using the procedure previously reported by Ueda and Haruta [15]. The pH of the aqueous solution of hydrogen tetrachloroaurate was adjusted by adding 0.1 M sodium hydroxide. Then the pre-formed sol-gel alumina was dispersed into the gold solution under a slow agitation for 1 h. The precipitate was washed with deionized water several times to eliminate excess ions. The final precipitate was dried at 100 °C under vacuum for 18 h and calcined at 500 °C for 5 h. After the calcination, all types of catalysts were ground and sieved into 80 to 120 mesh sizes.

The catalysts were activated with a 75 mL/min flow of a gas mixture containing 750 ppm NO_x, 750 ppm C₃H₆, 7% O₂, ~2% H₂O, and He balance. During the activation process, the temperature was increased from 150 °C to 500 °C with a 50 °C step increment. They were held at each temperature for 1 h. Once 500 °C was reached, they were kept at this temperature overnight. Such a heat treatment cycle was employed until the catalysts reached their stable activity levels.

6.3.2 Catalyst Testing

The catalytic activity was studied by using a fixed-bed U-tube microreactor made from a quartz tube with an i.d. of 3.5 mm. The following gas mixtures were used in the tests: 1,000 ppm NO with trace NO₂ (< 20 ppm), 0 to 1,000 ppm C₃H₆, 5 to 14% O₂, and He balance, resulting in an approximate space velocity (SV) of 105,000 cm³ h⁻¹ g⁻¹. Water was introduced into the system by passing the gas mixture through a humidifier at room temperature to obtain a stream containing about 2% water. The reaction was carried out at the temperature range from 150 °C to 500 °C and at the atmospheric pressure. The reaction over the catalyst was held at each temperature for 1 h to reach a steady state, followed by the activity measurement. Experiments were planned such that the effects of propene, oxygen, and water over the gold supported on the impregnated sol-gel alumina catalyst were investigated.

Nitrogen products were measured by a gas chromatograph (GC, SRI 8610C), equipped with a helium ionization detector (HID), a thermal conductivity detector (TCD), and a HayeSep DB column. Nitric oxide and nitrogen dioxide were detected by a chemiluminescence NO_x analyzer (Thermo Environmental 42CHL). Carbon monoxide, carbon dioxide, and nitrous oxide (N₂O) were analyzed by a Fourier-transform infrared (FTIR) spectroscope (Mattson Galaxy 7020A) with a 10 cm path length gas cell. The performance of the catalysts was reported in terms of NO_x conversion and N₂ yield, which were defined as follows:

$$\begin{aligned} \text{NO}_x \text{ conversion (\%)} &= \{[\text{NO}_x]_{\text{in}} - [\text{NO}_x]_{\text{out}}\} / [\text{NO}_x]_{\text{in}} \times 100 \\ \text{N}_2 \text{ yield (\%)} &= 2 \times [\text{N}_2] / [\text{NO}_x]_{\text{in}} \times 100 \end{aligned}$$

where [NO_x]_{in} is the reactor inlet NO_x concentration, [NO_x]_{out} is the reactor outlet NO_x concentration, and [N₂] is the reactor outlet N₂ concentration.

6.3.3 Catalyst Characterization

The crystallite sizes and phases present in the catalysts were determined by the X-ray diffraction (Rigaku powder X-ray diffractometer, operated at 40 kV and 100 mA). The Brunauer–Emmett–Teller (BET) method employed for

determining the surface area and the pore size of the catalysts was performed using a Micromeritics 2010 instrument. Both BET surface area and pore size distribution were calculated from a standard Micromeritics program. In addition, the actual amounts of gold loading on the catalysts were determined by neutron activation analysis.

6.4 Results and Discussion

6.4.1 Catalyst Characterization

Table 6.1 summarizes the chemical and physical properties of the prepared catalysts. The actual amounts of gold loading on the catalysts were found to be 0.70, 0.55, 0.75, and 0.75 wt% for the single-step sol-gel (Au-SG), the deposition-precipitation on sol-gel alumina (Au-DP-SG), the impregnated sol-gel alumina (Au-IMP-SG), and the impregnated commercial γ -alumina (Au-IMP-gamma) catalysts, respectively.

The pre-formed sol-gel alumina had a BET surface area of about 300 m²/g and a pore size distribution centered at a diameter of 77 Å. In contrast, the surface area of the commercial γ -alumina was 150 m²/g with a 58 Å pore size. The single-step sol-gel catalyst had a BET surface area of about 300 m²/g, while its pore size centered at a diameter of 98 Å.

The X-ray diffraction (XRD) patterns of the samples showed that all alumina supports in the catalysts were γ -alumina. The crystallite sizes of the gold loaded in the catalysts were calculated from the Debye–Scherrer equation. The average gold crystallite sizes of 24 nm and 34 nm were found for the Au-SG and Au-IMP-SG catalysts, respectively. Since the XRD pattern for the Au-DP-SG catalyst did not reveal any detectable gold species, it could be implied that the gold crystallite sizes in the catalyst were less than 5 nm.

Table 6.1 Chemical and physical properties of gold supported on alumina catalysts

Catalyst	Au loading (wt%)	Surface area (m ² /g)	Pore Size (Å)	Particle size (nm)
Au-SG	0.70	299	98	24
Au-DP-SG	0.55	310	77	< 5
Au-IMP-SG	0.75	310	77	34
Au-IMP-gamma	0.75	150	58	-

6.4.2 Preparation Effect

Catalysts of gold supported on alumina were prepared by various preparation methods. Impregnation is the conventional method that introduces an active metal onto the support by submersion with a metal precursor. Typically, the impregnation method gives lowly dispersing active sites, while the deposition-precipitation method gives a higher dispersion [14]. In this work, the sol-gel method was purposed to obtain a high surface area porous support. All catalysts and supports prepared from the sol-gel method gave a higher surface area than the conventional alumina support (Table 6.1). The activities of the different catalysts are shown in Fig. 6.1. Among these various types of catalysts, the highest activity was obtained with the Au-SG, followed by the Au-IMP-SG, whereas the Au-DP-SG and the Au-IMP-gamma gave a moderate and lowest activity, respectively. This indicates that sol-gel method can greatly contribute to the improvement in the catalytic activity.

The catalyst characterization results also showed that the Au-DP-SG had smaller Au crystallite sizes (less than 5 nm) while the Au-SG and the Au-IMP-SG had a similar range of average Au crystallite size of around 20 nm and 30 nm, respectively. These results were in good agreement with those of Ueda *et al.* [14]. They reported that their deposition-precipitation catalyst had 4.9 nm Au crystallite sizes, while their impregnation catalyst had 32 nm Au crystallite sizes. They addressed the size of gold particles as one of the controlling factors for the catalytic activity. Since Bamwenda *et al.* reported that the initiation of NO SCR on Au/ γ -

Al_2O_3 involved the oxidation of NO to NO_2 at active centers or the interface between Au and Al_2O_3 followed by propagation steps to form N_2 and other products [24, 25], it was suggested that smaller particle size catalysts possess more interfacial active sites for the reaction. So if a comparison between Au-SG and Au-IMP-SG was made in terms of gold particle perimeter, Au-SG would have a higher activity than Au-IMP-SG. This was also verified by our results. However, a moderate activity was observed on Au-DP-SG since its actual gold loading of 0.55 wt% was less than those of the other catalysts (0.70 to 0.75 wt%). During the preparation, some of the gold hydroxide may proceed to the nucleation in a bulk phase and is suspended in the solution, from which it can be readily removed during the washing process. This possibly became a factor responsible for a much lower activity than the other two sol-gel catalysts.

Furthermore, we believe that the nature of the support also influences the reduction of NO. By a comparison, our results show that the sol-gel preparation had a positive effect. The reason for this may be that the high surface area was obtained from the 3-dimensional network, resulting in more exposed active sites available for the reaction. In addition, materials prepared by different methods resulted in different adsorption capacities of NO, water, and so on, leading to different catalytic performances [26]. It was also reported that the surface acidity contributed from the sol-gel improved hydrocarbon activation and NO conversion [27].

Although Au-SG showed the highest activity among other investigated catalysts, the overall performance of catalyst also depended on the desirable N_2 formation. The maximum amount of NO_x converted to N_2 over Au-IMP-SG was as high as ca. 90%, while other catalysts revealed a maximum N_2 yield lower than ca. 50% (data not shown). Therefore, Au-IMP-SG was considered as the best catalyst in terms of overall performance. It was then selected for further investigation in the following sections.

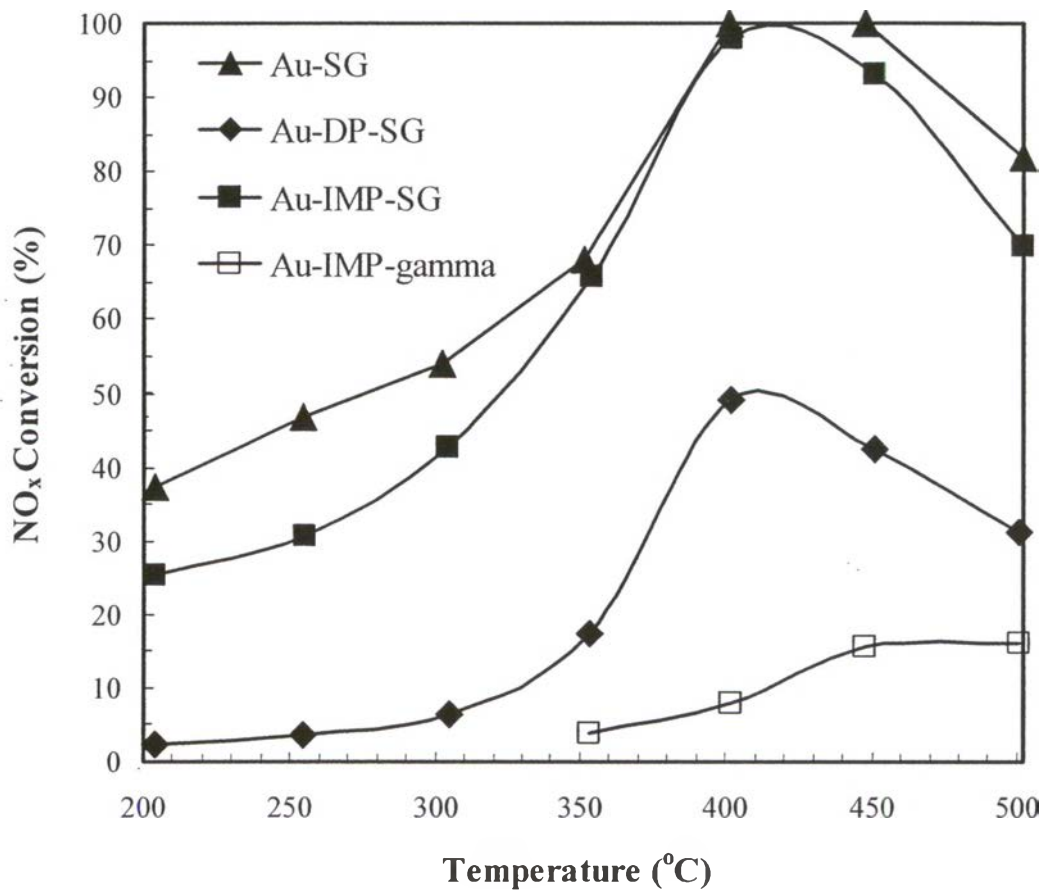


Figure 6.1 Catalytic activity comparison of the Au/Al₂O₃ catalysts from different preparation methods. Reaction conditions: 1,000 ppm NO_x, 1,000 ppm C₃H₆, 14% O₂, 2% H₂O balanced in He, SV = 1x10⁵ cm³ h⁻¹ g⁻¹.

6.4.3 Propene Effect

The effect of propene concentration, varied from 0 to 1,000 ppm, was investigated over the impregnated sol-gel alumina catalyst (Au-IMP-SG). Trace NO_2 was present in the reactant stream when NO and O_2 were blended before reaching the reactor inlet; therefore, the activity of the catalysts was measured in terms of NO_x conversion. Negligible N_2O formation (less than 1%) was observed over Au catalysts in all experiments. Fig. 6.2 (a) shows that NO_x conversion was increased with increasing temperature at a given propene concentration as a parabolic curve having a maximum temperature of around 410 °C. An increase in the amount of propene improved the catalytic activity and also enlarged the activity window. The positive effect is clearly observed in the high temperature range between 300 °C and 500 °C. Complete NO_x conversion was achieved with a 1,000 ppm propene concentration at about 410 °C. This shows that propene facilitated the reduction of NO_x . However, in the humid feed stream without propene, it was found that there were 10 to 30% NO_x conversion and no N_2 formation suggesting that NO decomposition did not take place. Our experiment in the dry feed stream (data not shown) revealed that NO was completely converted to NO_2 . However, if water was present in the feed stream, NO_2 could be adsorbed and disproportionated to other species, which possibly further reacted with H_2O to form other products, such as HNO_3 [28].

Fig. 6.2 (b) shows the propene oxidation curves as a function of temperature at different propene concentrations. Complete propene oxidation was observed at about 410 °C, and corresponded to the maximum NO_x conversion. It is apparent that the decrease in the activity coincided with the vanishing of propene by the complete oxidation. Many NO_x reduction mechanisms with hydrocarbons have been proposed in several schemes, e.g. NO could be reduced via a variety of carbonaceous intermediates [1, 3]. Shimizu *et al.* also reported that the consumption of hydrocarbon-derived species and NO_x were closely related [29].

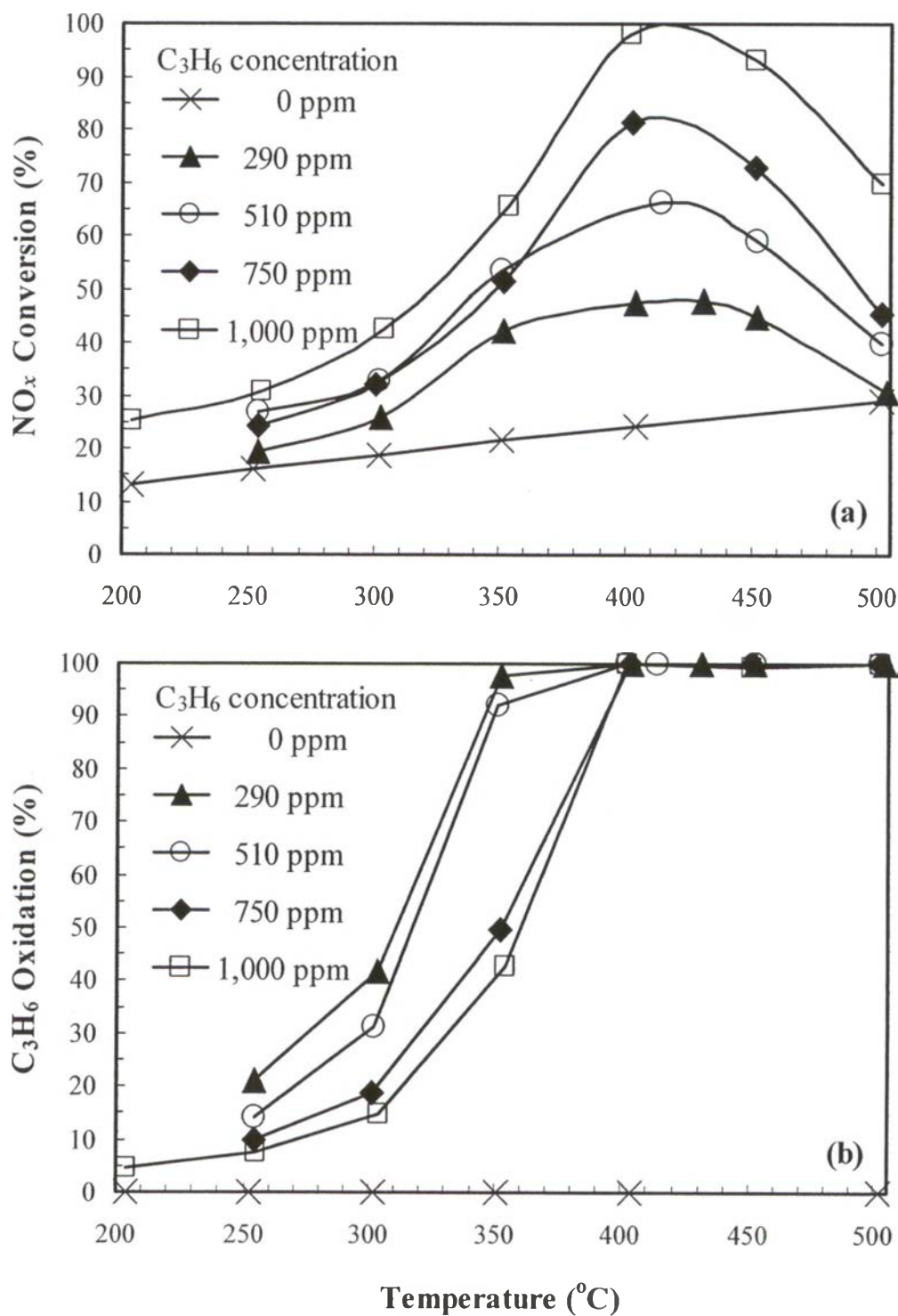


Figure 6.2 Propene concentration effect on the activity of the Au-IMP-SG catalyst as a function of temperature. Reaction conditions: 1,000 ppm NO_x, 0 to 1,000 ppm C₃H₆, 14% O₂, 2% H₂O balanced in He, SV = 1 × 10⁵ cm³ h⁻¹ g⁻¹.

6.4.4 Oxygen Effect

A positive effect of oxygen was found over the Au-IMP-SG catalyst as well. Fig. 6.3 shows that the reduction of NO_x could occur even in the large excess oxygen amount of 14%, instead of activity inhibition. When a higher oxygen concentration was used, the maximum NO_x conversion shifted towards a lower temperature. A larger activity window was observed with a slight improvement in the activity. The oxidation of propene corresponded to the reduction of NO_x for both oxygen concentrations, suggesting that the hydrocarbon was activated via a partial oxidation to form several oxygenated forms ($\text{C}_x\text{H}_y\text{O}_z$), such as formate and acetate, before subsequently participating in the reduction of NO_x [30, 31]. The results from this present work also showed that propene was more easily converted, and its complete conversion shifted to lower temperatures in a stream containing a larger amount of oxygen. In addition to hydrocarbon activation, oxygen could activate NO to surface-bound nitrates, as well as oxidize NO to the more reactive NO_2 . These activated species were further transformed through several routes to form the N_2 product [5, 26].

6.4.5 Water Effect

The catalytic behavior of the Au-IMP-SG catalyst in dry and humid conditions is shown in Fig. 6.4 (a) and Fig. 6.4 (b), respectively. Water remarkably enhanced the NO_x conversion. The maximum conversion of 60% in a dry stream was raised up to 98% in the presence of water. The obtained NO_x reduction curves also correspond to the propene conversion profiles in both conditions. In humid conditions, the NO_x reduction is more favorable at a lower temperature, which enlarged the catalytic activity window. NO_x was completely converted to N_2 in dry conditions, while the selectivity to N_2 was decreased in the presence of water. This is possibly due to other by-products formation, such as HNO_3 [20, 28]. In addition, the propene oxidation was actually close to the formation of N_2 , but not to the NO_x conversion. This shows that the activated hydrocarbon was actually used in the production of N_2 .

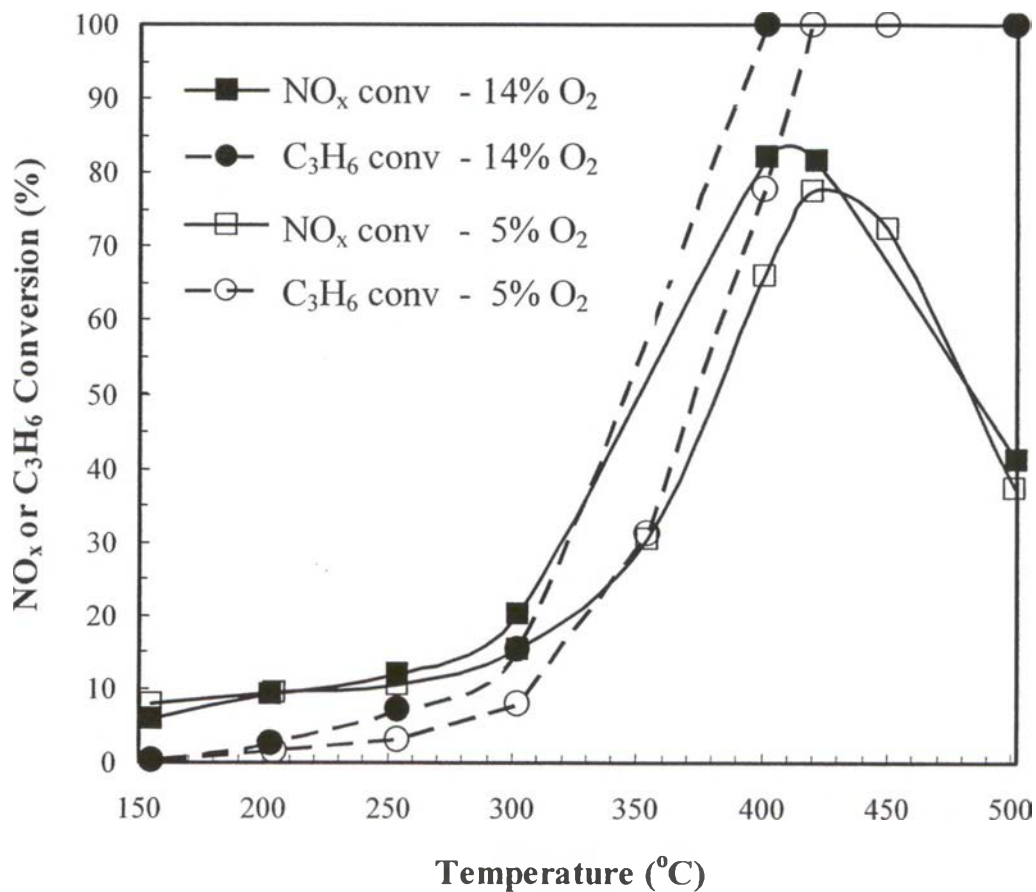


Figure 6.3 Oxygen concentration effect on the activity of the Au-IMP-SG catalyst as a function of temperature. Reaction conditions: 700 ppm NO_x, 700 ppm C₃H₆, 5% and 14% O₂, 2% H₂O balanced in He, SV = 1×10^5 cm³ h⁻¹ g⁻¹.

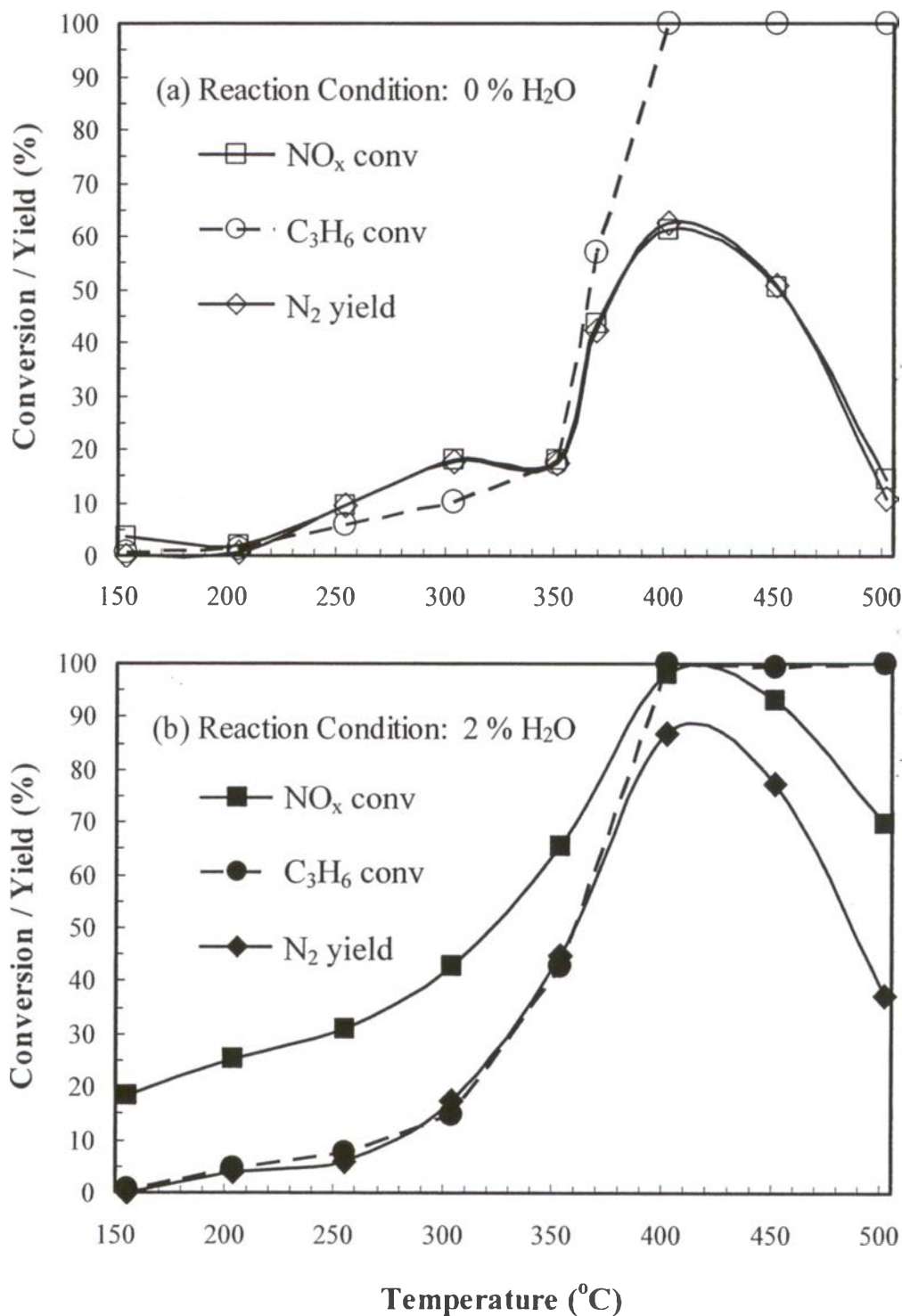


Figure 6.4 Activity of the Au-IMP-SG catalyst in dry and humid feed streams. Reaction conditions: 1,000 ppm NO_x, 1,000 ppm C₃H₆, 14% O₂, 0 and 2% H₂O balanced in He, SV = 1×10⁵ cm³ h⁻¹ g⁻¹.

6.4.6 Catalyst Stability

The stability of the Au-IMP-SG catalyst was investigated to see whether it would be stable for the prolonged period under normal operating conditions. The catalyst was exposed to a 2% water-containing reactant gas mixture at a low temperature of 150 °C for 56 h. Then, the catalyst was treated in a flow of helium at a high temperature of 500 °C overnight. Then the activity of the treated catalyst was re-investigated over the same temperature range between 200 °C and 500 °C in both the dry and the humid conditions (data not shown). After a few tests, the catalytic activities resumed to its initial for both conditions without any changes in N₂ selectivity. This implies that the catalyst was tolerant to the testing conditions.

6.5 Conclusions

Gold catalysts prepared from sol-gel derived techniques showed higher activity than the catalysts supported on commercial γ -alumina. The single-step sol-gel catalyst showed the highest activity, followed by the impregnated sol-gel alumina catalyst. The deposition-precipitation on the sol-gel alumina catalyst showed moderate activity while the impregnated commercial alumina catalyst yielded the lowest activity. However, the impregnated sol-gel alumina catalyst gave the highest N₂ yield among the investigated catalysts. Water considerably enhanced the catalytic activity. The activity was also influenced by oxygen and propene, higher amounts of which resulted in increasing activity and activity window enlargement. This work also demonstrated the catalyst stability in the humid and oxygen-rich conditions. The catalyst could perform well under the lean-burn conditions, various propene concentrations, and it had a good long-term performance.

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6.7 References

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