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Study of nitric oxide reduction over silver/alumina catalysts under lean conditions: Effects of reaction conditions and support

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Abstract

The reduction of NO over silver/alumina catalysts was studied in a flow reactor system at *W*/*F* (catalyst weight/total flow)=0.024–0.012 g/(ml/s). Silver/alumina was shown to catalyze the reduction of NO by propylene or propylene/propane mixture in excess oxygen. The catalytic activity was attributed to the hydrocarbon-oxidation reactivity of a silver catalyst. The activity for NO-reduction increased as the oxygen-content in reaction mixture increased from 1.5% to 10%. This effect of oxygen-content and the temperature range around 500°C for the reduction of NO can be correlated to the activity of hydrocarbon-oxidation. The presence of water and sulfur dioxide had adverse effect on the reduction of NO. The adverse effect could be partially compensated by the enhancement of activity using a proper type of alumina. The type of alumina used had a great effect on the activity of NO-reduction for a silver/alumina catalyst. Preliminary characterization showed that the average pore size and the pore-size distribution of the alumina could be important factors. An active silver/alumina catalyst was prepared with a higher NO-conversion than the best Cu/ZSM5-based catalyst evaluated at Ford under the same reaction conditions in the presence of H_2O and SO_2. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: NO_x reduction; Automotive catalysts; Silver/alumina; Pore-size distribution

1. Introduction

Development of a catalyst that can efficiently catalyze the reduction of NO_x in automotive exhaust with excess oxygen (lean-NO_x reduction) is a prerequisite for the application of lean-burn engine technology to vehicles. Cu/ZSM5 or other zeolite-based materials [1,2] were first shown to have good activities for NO_x reduction by hydrocarbons in excess oxygen. However, the Cu/ZSM5-based catalysts at normal exhaust temperature are vulnerable to deactivation by steam that is present in any automotive exhaust [3–5].

One alternative to the zeolite-based catalysts is to make non-zeolite based catalysts with good activities and durability for lean-NO_x reduction. Alumina is widely used as support in current automotive catalysts and is naturally the first choice as a support. There are reports about the activity of lean-NO_x reduction over alumina-only catalysts [6–8], but the activity tested at Ford under the conditions close to real automobile exhaust was relatively low and this was also reported by Iwamoto and Mizuno [9].

In an earlier report [10], the reactivities of lean-NO_x reduction for Pd-, Cu-, and Au-containing catalysts were correlated to the hydrocarbon-oxidation activities of the catalysts. The observed results can be explained by a proposed reaction scheme in which NO_x is reduced by reacting with intermediates generated from partial oxidation of hydrocarbons used as reductants. If the hydrocarbon-oxidation activity on a

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catalyst is very high, the complete oxidation diminishes the formation of intermediates from partial oxidation and results in low activity of lean-NO_x reduction. If the oxidation activity is too low, the generation of the intermediates is slow and the rate of NO_x-reduction becomes low. The reaction scheme implies that a catalyst with an intermediate activity for hydrocarbon-oxidation may have relatively good activity for lean-NO_x reduction. It was shown that Cu-containing alumina [10] had better efficiency of lean-NO_x reduction than Pd-, or Au-containing catalyst and the hydrocarbon-oxidation activity of the Cu-catalyst was between those of the Pd- and Au-catalysts. One other Cu-catalyst, Cu/ZSM5, has been known to have good activity of lean-NO_x reduction. The hydrocarbon-oxidation activity of a silver-containing catalyst is expected to be between those of Cu- and Au-containing catalysts. A silver catalyst may potentially have a good activity for lean-NO_x reduction. Therefore, alumina-supported silver catalysts were chosen for study.

During the course of this study, silver-containing alumina was first reported by Miyedera [11,12] and then by others [13,14] to catalyze the reduction of NO by C_3H_6, alcohols, and ethers. Some of the reports [11,12] used much lower space velocities than normally encountered in automotive exhaust, while another used a 3-fold higher space velocity [13] than normal. To date, there has been no fundamental explanation for the effectiveness of Ag/alumina, no investigation on the effect of O_2-concentration, and no study of support effect on the activity. The work presented here describes how earlier study at Ford led to the selection of Ag/alumina, and how that study has been extended to show the effect of reaction conditions and properties of the alumina support. A catalyst of Ag/alumina was prepared which has higher NO_x-conversion than the best Cu/ZSM5 catalyst evaluated at Ford under the same reaction conditions.

2. Experimental

In this study, alumina-supported silver catalyst was prepared by the wet-incipient technique of impregnating $AgNO_3$ (ACS Grade) solution onto alumina powder. The size of these alumina ranged from 80 to 300 meshes. The particle size had little effect on the activity of the resulted Ag/Al_2O_3 catalysts. The impregnated sample was then dried at 120°C and calcined in air at 550°C for 4 h. The BET surface area and the pore-size distribution of each alumina after calcination at 600°C were determined using a N_2-adsorption technique (Micromeretics ASAP 2400). The effect of the support was investigated using five samples of alumina from different commercial sources. The phases of alumina samples used in this study were determined from XRD. Since 2 wt% loading of Ag resulted in the best activity of lean-NO_x reduction for each Ag/Al_2O_3 catalyst studied, all the activities reported in this paper are for 2 wt% Ag/Al_2O_3. This observed effect of Ag-loading agrees with that reported in [11].

The reduction of NO was studied in a typical flow reactor at $W/F=0.025–0.012$ g/(ml/s). The catalyst powders were packed inside a quartz reactor heated with a furnace. The mixture of reaction gases contained 1.5–10% O_2, 500–1500 ppm C_3H_6 or C3-mixture ($C_3H_6/C_3H_8=2$), 500–1000 ppm NO, and helium or nitrogen as balance. 18 ppm SO_2 and 9% H_2O could be added, if necessary. The concentrations of NO and hydrocarbon in the effluent were monitored using commercial chemiluminescence and flame-ionization analyzers, respectively. A gas chromatograph with TCD could also be used to analyze the concentrations of N_2, CO, CO_2, and C3-mixture with two columns: 5 ft×1/8 in. Haysep T and 6 ft×1/8 in. molecular sieve 5A. The Haysep T column served as a pre-column and the flow was reversed after the light gas molecules evolved. When the gas chromatograph was used, the conversion of NO to N_2 was measured isothermally. If only gas analyzers were used, the disappearance of NO_x ($NO+NO_2$) was measured either isothermally or by ramping at a rate of 10°C/min. The conversion of NO to NO_2 or N_2O was not particularly monitored. The yield of N_2 measured by GC excluded the conversion to NO_2 or N_2O. The conversion of NO to NO_2 was not counted in this report.

3. Results and discussion

3.1. *Effect of reaction conditions*

The conversions of NO_x and C_3H_6 for 2% Ag/Al_2O_3 (Degussa C Al_2O_3, 97 m^2/g surface area) are shown in

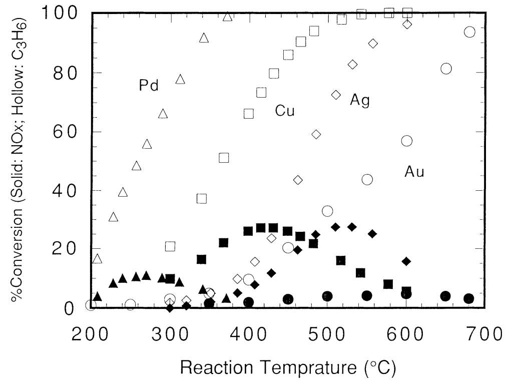

Fig. 1. Conversions of NO_x and C_3H_6 over 5.4% Pd/ZSM-5, 2% Cu/Al_2O_3, 2% Ag/Al_2O_3, and 2% Au/Al_2O_3. 1 g catalyst except 0.6 g Pd/ZSM-5. Feed: 500 ppm NO, 500 ppm C_3H_6, 3% O_2, N_2 balance, 3 l/min total flow.

Fig. 1. The activities for the Pd-, Cu-, and Au-catalysts from [1] are also compared in Fig. 1. All the activities were measured under the same reaction conditions. The conversion of NO_x or C_3H_6 for the Ag-catalyst occurred at temperatures between those for the Cu- and Au-catalysts. The value of maximum conversion for the Ag-catalyst was close to that for the Cu/Al_2O_3 catalyst. For a given Ag/Al_2O_3 catalyst, the conversion of NO_x increased and shifted toward lower temperature range as the concentration of oxygen in the reaction mixture increased from 1.5% to 7% (Fig. 2(a)). The conversion of C_3H_6 also shifted toward lower temperature range (Fig. 2(b)).

The above reactions were carried out in a flow system with the maximum O_2-concentration at 7% due to the limitation of flow controllers. The conversions of NO_x and C_3H_6 were also measured in a different flow reactor system with an extended range of O_2-concentration. The results for the same Ag/Al_2O_3 catalyst at 3%, 6%, and 10% O_2 are compared in Fig. 3. The %conversion of NO was determined from the yield of N_2 whose amount was measured by GC:

$$(2 \times N_2\text{-concentration})/(NO_x\text{-concentration at inlet}) \times 100\%.$$

Again, the conversion of NO increased with O_2-concentration. In a separate experiment the conversion of NO_x was simultaneously measured using a chemiluminescence NO_x-analyzer and a GC. The result

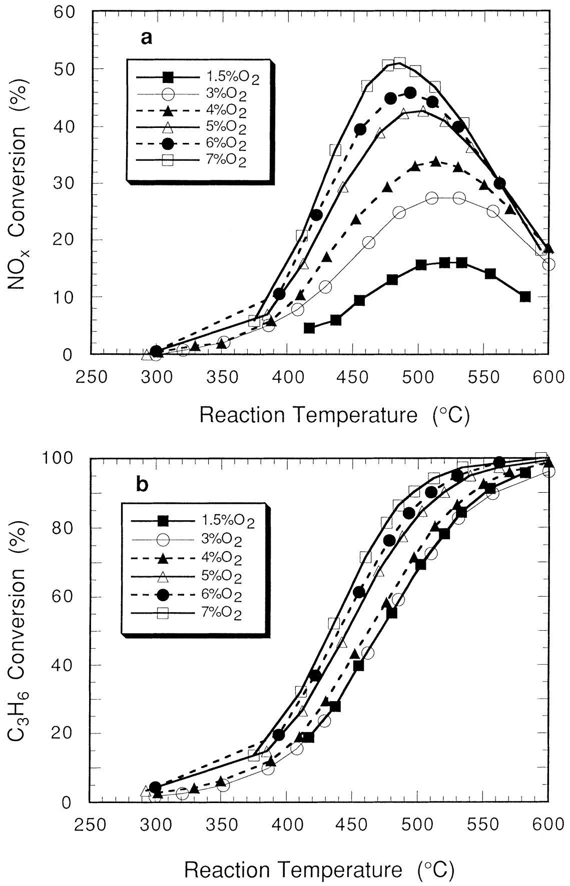

Fig. 2. Effect of $P(O_2)$ on the conversion of (a) NO_x and (b) C_3H_6 over 1 g 2% Ag/Al_2O_3. Feed: 500 ppm No, 500 ppm C_3H_6, N_2 balance, 3 l/min total flow.

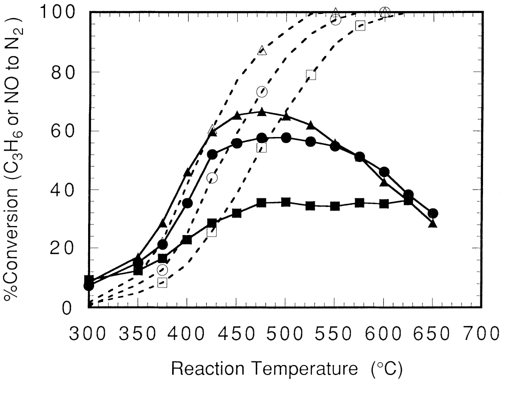

Fig. 3. Effect of $P(O_2)$ on the conversion of NO_x to N_2 (solid line) along with the conversion of C_3H_6 (dotted line) over 0.2 g 2% Ag/Al_2O_3: (■, □) 3% O_2, (●, ○) 6% O_2, (▲, △) 10% O_2. Feed: 1000 ppm NO, 1500 ppm C_3H_6, He balance, 500 ml/min total flow.

showed that majority of NO was converted to N_2 over the Ag/Al_2O_3 catalysts, in agreement with the result by Aoyama et al. [14].

The temperature range of NO_x conversion and the effect of O_2-concentration on the reactivity for the Ag/Al_2O_3 catalyst can be explained according to the proposed reaction scheme in [1]. The partial oxidation of the hydrocarbon initiates the lean-NO_x reduction and the complete oxidation at high temperatures lowers the concentration of the partially oxidized intermediates and, hence, the rate of the NO_x-reduction. Therefore, the temperature range for lean-NO_x reduction is closely related to that for C_3H_6-oxidation as shown in Fig. 1. Fig. 1 also shows that the Ag- or Cu-catalyst with intermediate temperature range for hydrocarbon-oxidation has relatively better NO_x-conversion than either Pd- or Au-catalyst. This observation agrees with the expectation in Section 1 that the catalyst with an intermediate activity of hydrocarbon-oxidation has a relatively good activity of NO_x-reduction in excess oxygen.

For the Ag/Al_2O_3 catalysts, the activity of lean-NO_x reduction increased as O_2-concentration increased from 1.5% to 10%. In contrast, the NO_x-conversion for 2% Cu/Al_2O_3 at 482°C peaked at 0.25% O_2 [10] and the NO_x-conversion for Cu/ZSM5 at 300°C peaked at 1.5% O_2 [9]. The difference in the effects of O_2-concentration can be attributed to the difference in the activities of hydrocarbon-oxidation. For the Cu-catalyst, only a small amount of O_2 is needed to initiate the partial oxidation of hydrocarbon for the reduction of NO_x. Thus, high levels of O_2 may result in the enhancement of complete oxidation of hydrocarbon, thereby decreasing the concentration of reactive intermediates and the rate of NO_x-reduction. Since the Ag/Al_2O_3 catalyst has lower hydrocarbon-oxidation activity than a Cu-catalyst, increasing the O_2-concentration may promote the rate for partial oxidation of hydrocarbon more than total oxidation. Thus, the catalytic activity of hydrocarbon-oxidation for a given catalyst is reflected in the effect of O_2-concentration on the activity of lean-NO_x reduction.

The conversion of NO_x increased as the concentration of the reductant, C_3H_6, increased (Fig. 4). In addition, the temperature range for lean-NO_x reduction or C_3H_6-oxidation was widened. The result indicates that high concentration of reductant is beneficial to the reduction of NO_x. The reduction of NO_x increased as expected as the total flow rate decreased (Fig. 5). This implies that the lean-NO_x efficiency on a Ag/Al_2O_3 catalyst can be raised by decreasing the space velocity. For all the results in Fig. 4 or Fig. 5, the temperature ranges for lean-NO_x reduction are closely related to those for C_3H_6-oxidation.

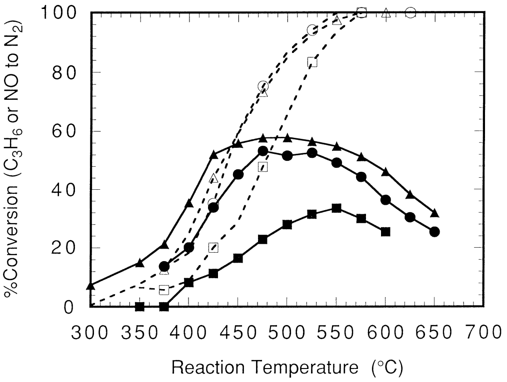

Fig. 4. Effect of $P(C_3H_6)$ on the conversion of NO_x (solid line) and C_3H_6 (dotted line) over 0.2 g 2% Ag/Al_2O_3: (■, □) 500 ppm C_3H_6, (●, ○) 1000 ppm C_3H_6, (▲, △) 1500 ppm C_3H_6. Feed: 1000 ppm NO, 6% O_2, He balance, 500 ml/min total flow.

The O_2-concentration is about 10% in the exhaust of a typical internal combustion engine operating at $A/F=26$ which may be a reasonable value for a future lean-burn engine. Thus, the high conversion of NO_x at 10% O_2 for the Ag/Al_2O_3 catalyst enhances the possibility of Ag/Al_2O_3 being a practical lean-NO_x catalyst. However, the NO_x-conversion of this parti-

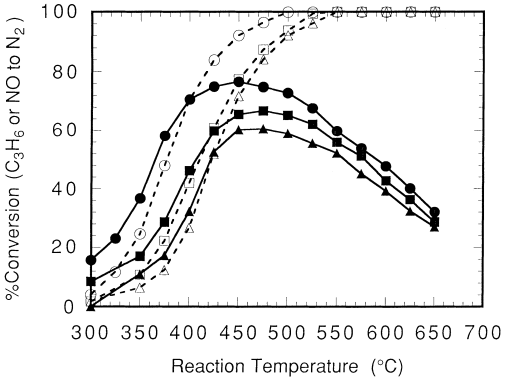

Fig. 5. Effect of total flow on the conversion of NO_x (solid line) and C_3H_6 (dotted line) over 0.2 g 2% Ag/Al_2O_3: (●, ○) 250 ml/min flow, C_3H_6, (■, □) 500 ml/min flow, (▲, △) 1000 ml/min flow. Feed: 1000 ppm NO, 1500 ppm C_3H_6, 10% O_2, He balance.

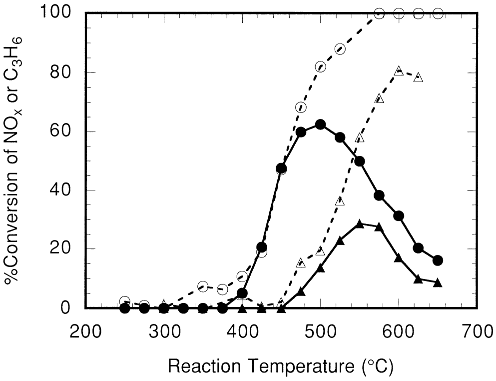

Fig. 6. Effect of H_2O and SO_2 on the conversion of NO_x (solid line) and C3-mixture (dotted line) over 0.2 g 2% Ag/Al_2O_3; (●, ○) 0% H_2O+0 ppm SO_2, (▲, △) 9% H_2O+18 ppm SO_2. Feed: 1000 ppm NO, 950 ppm C_3H_6, 520 ppm C_3H_8, 10% O_2, He balance, 500 ml/min total flow.

cular Ag/Al_2O_3 catalyst was severely decreased from 62% to 28% by the addition of 9% H_2O and 18 ppm SO_2 (Fig. 6). In addition, the conversion curves for both NO_x and hydrocarbon shifted to higher temperature range. Because H_2O is always present in automobile exhaust and the gasoline in North America still contains significant amount of sulfur, the Ag/Al_2O_3 catalyst will always be exposed to H_2O and SO_2 in the exhaust. The effect of these two inhibitors may be compensated by improving the overall activity of a Ag-catalyst, and enhancement in activity resulting from modifications to the alumina support is described below.

3.2. *Effect of support*

The XRD patterns for the five samples of alumina after 600°C-calcination in air showed that Al_2O_3-1 to -4 were γ-Al_2O_3 and Al_2O_3-5 was mainly δ-Al_2O_3. Al_2O_3-3 has broader XRD-lines than the other γ-Al_2O_3, indicating smaller particle size or less crystalline structure. The XRD data agree with the result of surface area measurement (Table 1) in which Al_2O_3-3 has the largest surface area among all the five samples of Al_2O_3. Nominally, the support is Al_2O_3 except that Al_2O_3-4 contains 4 wt% La. The pore-size distributions of the supports are shown in Fig. 7. The value for "% of pore in most populated 50 Å range" in Table 1 was the percentage of pore volumes in a range of 50 Å centered at the pore size corresponding to the maximum in the dV/d log(D) plot of Fig. 7. The larger the value, the narrower the distribution.

As shown in Table 1, the NO_x efficiency for Ag/Al_2O_3 varies significantly with the type of Al_2O_3 support used. Al_2O_3-1 and Al_2O_3-2 have the largest fractions of pores in the 15–100 Å range as well as the largest fractions in the most populated 50 Å range. 2% Ag/Al_2O_3-1 and 2% Ag/Al_2O_3-2 also had better NO_x-efficiency than the other Ag/Al_2O_3 catalysts. For Al_2O_3-1 to -4, there is apparently a correlation between the NO_x-efficiency and the pore-size distribution or the range of pore size. The greater the fraction of pore volumes in the range 15–100 Å or the narrower the pore-size distribution, the larger the NO_x-conversion for the 2% Ag/Al_2O_3 catalyst. Comparison of the results for Al_2O_3-3 and Al_2O_3-5 reveals that the higher percentage of pores in the range between 15 and 100 Å results in significantly larger NO_x-conversion at similar pore-size distribution. The comparison for Al_2O_3-4 and Al_2O_3-5 indicates that the narrowness of pore-size distribution probably has a larger effect on NO_x-efficiency than the fraction of pores in the 15–100 Å range. Al_2O_3-3 has the largest surface area but not the best NO_x-efficiency. Surface

Table 1
Properties of alumina used and No_x-conversion of Ag/Al_2O_3

	Al_2O_3-1	Al_2O_3-2	Al_2O_3-3	Al_2O_3-4	Al_2O_3-5
XRD pattern	γ-Al_2O_3	γ-Al_2O_3	γ-Al_2O_3	γ-Al_2O_3 (4 wt% La)	δ-Al_2O_3
S (m^2/g)	226	182	275	192	92
AV. pore size (Å)	64	71	55	133	219
% of pore in 15–100 Å range	98%	97%	67%	15%	3%
% of pore in most populated 50 Å range	95%	88%	59%	42%	63%
%NO_x-Conv.[a]	85%	85%	68%	42%	59%

[a] 0.2 g 2% Ag/Al_2O_3; Feed: 500 ml/min, 10% O_2, 550 ppm NO, 1100 ppm C3, 10% H_2O, 18 ppm SO_2, He balance.

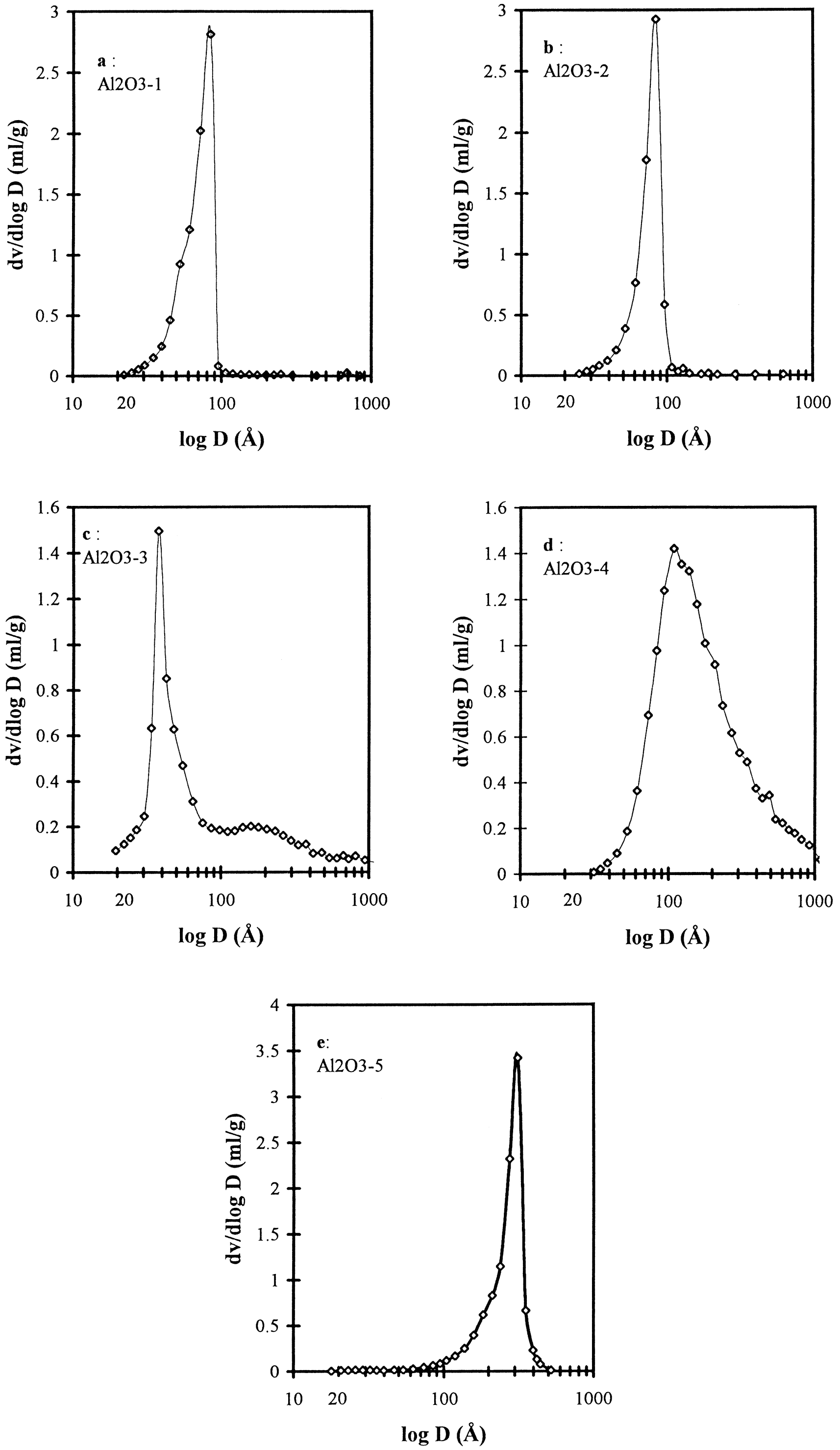

Fig. 7. Pore-distribution, dV/d log D, measured from the desorption of N_2 at liquid nitrogen temperature for five samples of Al_2O_3 from different commercial sources. V=pore volumes in ml/g, D=pore size in Å.

area appears not to be as important as narrowness of pore-size distribution.

Al_2O_3-4 contains 4 wt% La and is a type of stabilized Al_2O_3 support commonly used in automotive catalysts. The presence of 4 wt% La may affect the activity for 2% Ag/Al_2O_3-4 in addition to the distribution or the size of pores discussed above. Whether La has any effect on the NO_x-efficiency is not known at present and needs further study. Al_2O_3-5 contains mostly δ Al_2O_3 which may exert different effect from γ-Al_2O_3 on the reactivity of Ag/Al_2O_3. It has been proposed that the size and the valence state of Ag-species have great effect on the lean-NO_x activity of Ag/Al_2O_3 [14,15]. The influence of various Al_2O_3-samples on the nature of the Ag-species may have important role in determining the activity.

However, it is not clear that the size and the valence state of Ag can be much different from one another for 2% Ag/Al_2O_3-1 to -4 based on the values of surface area and the result of XRD. The only apparent correlation in Table 1 indicates that narrower distribution and smaller size of the pores result in better NO_x-efficiency for 2% Ag/(γ-Al_2O_3). Additional work is needed to further characterize the pore-size effect on lean-NO_x activity. One possible explanation is that some important steps of NO_x-reduction occur on or near the surface of Al_2O_3. The small pore and the uniformity of the size facilitate these steps by confining the reaction intermediates inside the pore and close to the surface of Al_2O_3. Lean-NO_x reduction was observed at Ford in an empty tube and on Al_2O_3 powders depending on temperature and residence time. Others also reported the reaction over Al_2O_3 [6–9]. A recent paper [15] showed that the activity of NO_x-reduction was enhanced by placing Al_2O_3 powders above or below Ag/Al_2O_3 powders, or by mixing the Al_2O_3 and the Ag/Al_2O_3 powders. The mixing generated a greater enhancement. Those authors propose that the increase in the boundary between the two powders increases the overall activity. This observation indicates that the cross-boundary process of some intermediates to the vicinity of Al_2O_3 surface can enhance the NO_x-reduction. In a uniform pore with a small diameter containing 2% Ag, the same process is confined in a small space and may proceed efficiently. The nature of pores may be one important factor for the Al_2O_3 support on the lean-NO_x reduction over Ag/Al_2O_3 in addition to the influence on the nature of Ag-species. Based on the correlation established above, it appears that the best Ag/Al_2O_3 catalyst for lean-NO_x reduction may come from a zeolite-like Al_2O_3 containing one type of small pores.

3.3. *Ag/alumina vs.* Cu/ZSM5

No previous studies were found directly comparing the NO_x-conversion for a Ag/Al_2O_3 catalyst to that for a Cu/ZSM5 catalyst under same reaction conditions. In this study, the activity for the best Ag/Al_2O_3 catalyst was compared to that for the best Cu/ZSM5-based catalyst evaluated at Ford. To minimize packing difference between the two catalyst powders, each catalyst was pelletized into thin wafers of 0.05 g per wafer. The thin wafers were then broken into pieces to be loaded into a U-shaped quartz reactor. The NO_x-conversion for 0.1 g of each catalyst was measured at a total flow of 500 ml/min, equivalent to 50 000 h^{-1} space velocity for a typical monolith catalyst on a car. Fig. 8 shows 63% NO_x-conversion at 525°C for 2% Ag/Al_2O_3-1 in 10% O_2 vs. 42% (in 5% O_2) for a LaCu/ZSM-5 catalyst prepared in this laboratory [16]. The NO_x-conversion for the zeolite catalyst would be expected to be even lower if 10% O_2 was used. The Ag/Al_2O_3 catalyst had higher NO_x-conversion between 480°C and 600°C than the LaCu/ZSM-5 catalyst, but had a narrower range of operating temperature (Fig. 8). In addition, the NO_x-reduction occurred at higher temperature for the Ag/Al_2O_3

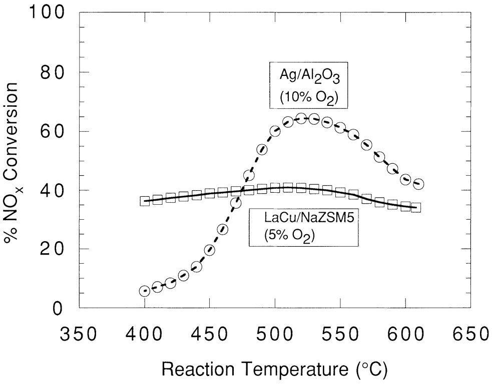

Fig. 8. NO_x-conversion over 0.1 g of (○) 2% Ag/Al2O3-1 in 10% O_2, (□) $La_{0.14}Cu_{2.68}Na_{0.68}Al_{4.02}Si_{91.98}O_{192}$ in 5% O_2. Feed: 500 ppm NO, 1200 C3-mixture (C_3H_6/C_3H_8=2), 9% H_2O, 18 ppm SO_2, He balance, 500 ml/min total flow.

catalyst. For practical purpose, the operating window for Ag/Al_2O_3 needs to be widened to lower temperature range to produce an attractive catalyst for lean-burn vehicles.

4. Conclusions

1. Under simulated exhaust conditions, Ag/Al_2O_3 showed a good activity for lean-NO_x reduction. The activity increased as the O_2-concentration increased from 1.5% to 10%. The reactivity of the Ag-catalyst for the NO_x-reduction was closely related to the activity for hydrocarbon-oxidation.
2. The activity of a Ag/Al_2O_3 catalyst increased as the concentration of hydrocarbon increased and the space velocity of the gas mixture decreased. H_2O and SO_2 poisoned the activity of a Ag/Al_2O_3 catalyst for lean-NO_x reduction.
3. The type of alumina had great effect on the activity of lean-NO_x reduction for Ag/Al_2O_3 catalysts. γ-Al_2O_3 with narrower pore-size distribution and smaller pore size resulted in better activity for lean-NO_x reduction.
4. A catalyst of 2 wt%Ag/γ-Al_2O_3 has higher NO_x-conversion than the best Cu/ZSM5-based catalyst evaluated at Ford under the same reaction conditions (except O_2-concentration). The Ag-catalyst had a narrower and higher window of operating temperatures for lean-NO_x reduction.

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