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Supported Ag Catalysts for the Lean Reduction of NO with C_3H_6

K. A. Bethke and H. H. Kung[1]

Ipatieff Laboratory and Department of Chemistry, Northwestern University, Evanston, Illinois 60208

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The activities of 2 and 6 wt% Ag/Al_2O_3 catalysts for lean NO reduction with C_3H_6 were compared. High conversions of NO to N_2 were obtained over 2 wt% Ag/Al_2O_3. In contrast, the NO conversions to N_2 were much lower over 6 wt% Ag/Al_2O_3, and this catalyst formed a substantial amount of N_2O. The difference in the behavior of the two catalysts was attributed to the much higher Ag dispersion for the 2 wt% than the 6 wt% sample, such that the oxidation states of Ag were different under reaction conditions. The 2 wt% Ag/Al_2O_3 was believed to contain silver in the +1 oxidation state under reaction conditions, while the 6 wt% Ag/Al_2O_3 catalyst contained Ag^0 particles, the amount of which decreased at higher temperatures. The presence of Ag^0 resulted in a high rate of C_3H_6 combustion at the expense of NO_x reduction. A synergistic effect was observed over a mixture of Al_2O_3 and 2 or 6 wt% Ag/Al_2O_3 and was attributed to the transfer of a very short-lived intermediate from Al_2O_3 to Ag/Al_2O_3 or vice versa. © 1997 Academic Press

INTRODUCTION

Among various requirements, an effective automotive catalyst for lean NO_x reduction must be able to withstand both high temperatures and high concentrations of H_2O. As γ-Al_2O_3 can be prepared in a hydrothermally stable form, a γ-Al_2O_3-supported metal or metal oxide may be a practical lean NO_x reduction catalyst. Miyadera and Yoshida (1, 2) investigated the reduction of NO with C_3H_6 over 2 wt% Ag/Al_2O_3. The NO to N_2 conversions over this catalyst remained high even in the presence of 10% H_2O and 200 ppm SO_2. High conversions of NO to N_2 have also been obtained over Ag/Al_2O_3 catalysts using oxygenated hydrocarbons, such as ethanol and acetone, as reductants (1, 3).

The effectiveness of the Ag/Al_2O_3 catalyst in the reduction of NO with C_3H_6 was reported by Miyadera (1) to be a strong function of the Ag loading. The NO conversions to N_2 at 723 and 773 increased with loading up to 1 wt% and then showed little change between 1 and 3 wt%. Further increases in loading dramatically decreased the NO conversions. Miyadera attributed the decreased NO conversions over the Ag/Al_2O_3 catalysts with high Ag loading, to an increased rate of C_3H_6 oxidation with O_2 at the expense of its reaction with NO, but the reason for this is not clear. One possibility is that the rate of C_3H_6 oxidation is dependent on Ag particle size with higher rates being associated with larger particles. Precedence for such a dependence exists in the literature where the rate of ethylene epoxidation over Ag/α-Al_2O_3 was reported to be independent of Ag particle sizes between 500 and 1000 Å but more than 20 times slower for particle sizes smaller than 500 Å (4).

The activity of the Ag/Al_2O_3 catalysts may not result solely from Ag, as Al_2O_3 itself may be involved in the reaction mechanism. Hamada and co-workers suggested that Al_2O_3 directly participated in the reduction of NO over both Co/Al_2O_3 (5) and a mixture of Pt/SiO_2 and Al_2O_3 (6). The reduction of NO over Co/Al_2O_3 was proposed to proceed through the oxidation of NO to NO_2 over Co followed by the reduction of NO_2 to N_2 over Al_2O_3. Similar bifunctional mechanisms, in which one component of a catalyst forms NO_2 while the other component reduces NO_2 to N_2, have been proposed by several authors (7–11). The NO conversions over the Pt/SiO_2 and Al_2O_3 mixture were higher than the sum of the conversions over the individual components. It was suggested that this synergistic effect resulted from the spillover or gas phase transfer of a short-lived intermediate, possibly a partially oxidized or activated hydrocarbon species, but not NO_2, from Pt/SiO_2 to Al_2O_3 or vice versa.

The high NO conversions reported over 2 wt% Ag/Al_2O_3 in the presence of 10% H_2O and 200 ppm SO_2 make Ag/Al_2O_3 catalysts worthy of further investigation. The aim of this research is to develop a better understanding of lean NO_x reduction over Ag/Al_2O_3 by investigating the reason why NO conversions decrease as Ag loading is increased beyond 3 wt% and by examining the role of the Al_2O_3 support in the reaction mechanism.

METHODS

γ-Al_2O_3 was prepared from the hydrolysis of aluminum isopropoxide in 2-methylpentane-2,4-diol following the procedure of Maeda *et al.* (12). The obtained white solid was then rinsed once with H_2O and twice with isopropanol

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[1] To whom correspondence should be addressed at Department of Chemical Engineering, 2145 Sheridan Road, Evanston, IL 60208-3120. Fax: 847-467-1018. E-mail: hkung@nwu.edu.

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before being placed overnight in a 373 K oven. Calcination was performed with a 100 mL/min air stream which was saturated with 6% H_2O. The temperature was increased at 1 K/min from 373 to 973 K and then held at 973 K for 2 h. After cooling the Al_2O_3 to room temperature, H_2O was removed from the feed. The temperature was then rapidly increased to 548 K and held at this temperature for 1.5 h. γ-Al_2O_3 prepared by this method had a BET surface area between 200 and 250 m^2/g and an apparent density of 0.5 g/mL.

Ag/γ-Al_2O_3 catalysts with 2 or 6 wt% Ag were prepared by impregnating γ-Al_2O_3 to incipient wetness with $AgNO_3$ (99.9+%, Alfa Products) using 1 mL of solution per gram of solid. The solids were dried overnight in a 373 K oven. They were then heated at 1 K/min from 373 to 973 K and held at 973 K for 2 h in dry air flowing at 100 mL/min. After calcination, the Ag/Al_2O_3 catalysts were white in color.

The 6 wt% Ag/SiO_2 was prepared with Davison 62 SiO_2 (60–80 mesh, surface area 250 m^2/g, apparent density 0.4 g/mL), which had been acid washed with 1 *M* HNO_3 to remove impurities and calcined in a muffle furnace for 17 h at 923 K. The SiO_2 was impregnated to incipient wetness with $AgNO_3$ (99.9+%, Alfa Products), dried overnight in a 373 K oven, and calcined in the same manner as the Ag/Al_2O_3 catalysts. The Ag/SiO_2 catalyst was beige after calcination.

Ag-ZSM5 was prepared by ion exchange of H-ZSM5 with a dilute $AgNO_3$ solution. Twenty grams of H-ZSM5 (donated by UOP, Lot 13923-57C) with a Si to Al ratio of 19 and 1 L of doubly deionized water were placed in a 3-L beaker equipped with a magnetic stir bar. To this mixture, 1 L of 13 m*M* $AgNO_3$ solution ($AgNO_3$: 99.9+%, Alfa Products) was added dropwise at room temperature. The solution was stirred overnight, filtered, and rinsed with water. This ion exchange procedure was repeated two additional times. The solid was dried in a 373 K oven overnight. It was then calcined in air flowing at 100 mL/min at 1 K/min from 373 to 773 K and then at 773 K for 2 h. The entire procedure was conducted with minimal exposure to light. As determined by ICP, the resulting white solid contained 4 wt% Ag (50% exchange). It had an apparent density of 0.5 g/mL.

Reaction studies were conducted in a conventional flow system. For activity measurements, 0.25 g of a catalyst (unless otherwise noted) was placed in a U-tube fused SiO_2 reactor. The 100 mL/min feed stream consisted of 0.1% NO or NO_2, 0.1% C_3H_6, 6% O_2, and, when present, 1.5% H_2O. The effluent from the reactor was analyzed with on-line gas chromatography as described previously (13). The effluent was also analyzed with a Beckman 951 NO/NO_x analyzer when NO_2 was present in the feed stream.

H_2 TPR was performed on samples containing 5.6×10^{-4} mol of Ag in a flow system. Before reduction, the catalyst was cooled in a flow of Ar with a dry ice/acetone slurry. A 60 mL/min feed of 5% H_2/Ar was used for reduction. The reactor temperature was allowed to increase to 223 K without control, before the temperature was ramped at 10 K/min to 973 K.

After H_2 TPR, the 2 and 6 wt% Ag/Al_2O_3 catalysts were transferred without exposure to air to a TPO flow system. Components of the effluent were detected in this system by a Ametek Dycor quadrupole gas analyzer. Before oxidation, the catalyst was cooled in a flow of He with a dry ice/acetone slurry. The 30 mL/min oxidizing feed consisted of 4.75% O_2/He. The reactor was allowed to naturally warm to 223 K at which time a 10 K/min temperature ramp to 973 K was begun.

XRD was performed on a Rigaku powder diffractometer with Cu $K\alpha$ radiation. The tube voltage was 40 kV, and the current was 20 mA. The XRD parameters used for the Ag/Al_2O_3 and Ag/SiO_2 catalysts were a divergence and scattering slit of 1°, a focusing slit of 0.6°, a stepwidth of 0.1°, and a counting time of 4 s. The XRD parameters used for the Ag-ZSM5 were a divergence and scattering slit of 1°, a focusing slit of 0.3°, a stepwidth of 0.02°, and a counting time of 4 s.

UV–Vis diffuse reflectance spectra were recorded in air on a Varian Cary 1 E UV–Vis spectrophotometer. Reference spectra were collected with pressed polytetrafluoroethylene (PTFE) disks. The following parameters were used to collect data: 1.0-nm spectral band width, 0.1-s signal averaging time, and 1.0-nm data interval. The lamps were changed at 310 nm for the 2 wt% Ag/Al_2O_3 catalyst and at 400 nm for the Al_2O_3 and 6 wt% Ag/Al_2O_3 catalysts.

RESULTS

Activity Measurements

Figure 1 compares the lean reduction of NO with C_3H_6 over Al_2O_3 and 2 wt% Ag/Al_2O_3. Oscillations were observed over Al_2O_3 at 793 K. Similar oscillations were reported by Obuchi *et al.* (14). The addition of 2 wt% Ag to Al_2O_3 dramatically increased the NO conversions in the low-temperature region as previously reported by Miyadera (1). Oscillations were not observed over the 2 wt% Ag/Al_2O_3 catalyst. The difference in activity between these two catalysts became more pronounced upon the addition of 1.5% H_2O (Fig. 2); the maximum NO conversion decreased from 81 to 50% over Al_2O_3, while it only decreased from 85 to 80% over 2 wt% Ag/Al_2O_3. The temperature of maximum NO conversion, $T_{\max}$, over these catalysts occurred at the lowest temperature at which almost all of the hydrocarbon was combusted. This indicates that the decrease in NO conversion at high temperatures is due to a shortage of hydrocarbon. This observation is quite typical for lean NO_x reduction catalysts (15–17).

Figure 3 compares the reduction of NO with C_3H_6 over 2 and 6 wt% Ag/Al_2O_3. From the conversions in Fig. 3, specific integral reaction rates were calculated. These rates at 673 and 723 K were, respectively, 0.0070 and 0.014 mmol

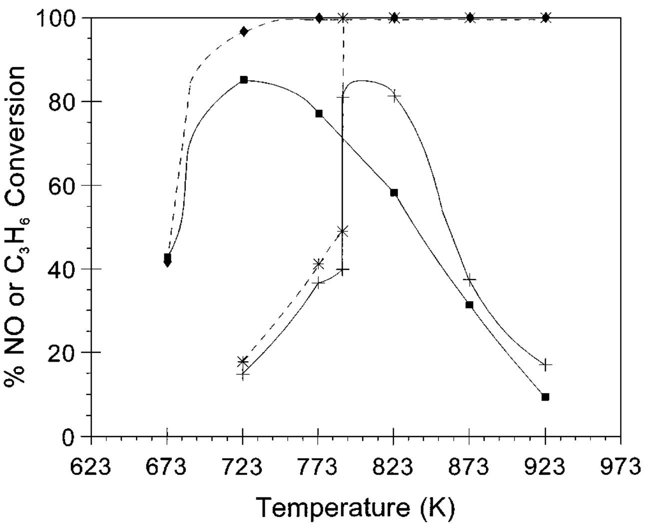

FIG. 1. NO and C_3H_6 conversions vs temperature over Al_2O_3 and 2 wt% Ag/Al_2O_3. (■) NO conversion to N_2; (◆) C_3H_6 conversion over 2 wt% Ag/Al_2O_3. (+) NO conversion to N_2; (✳) C_3H_6 conversion over Al_2O_3. Catalyst weight, 0.25 g. Feed, 0.1% NO, 0.1% C_3H_6, 6% O_2 at 100 mL/min. GHSV = 12,000 h^{-1}.

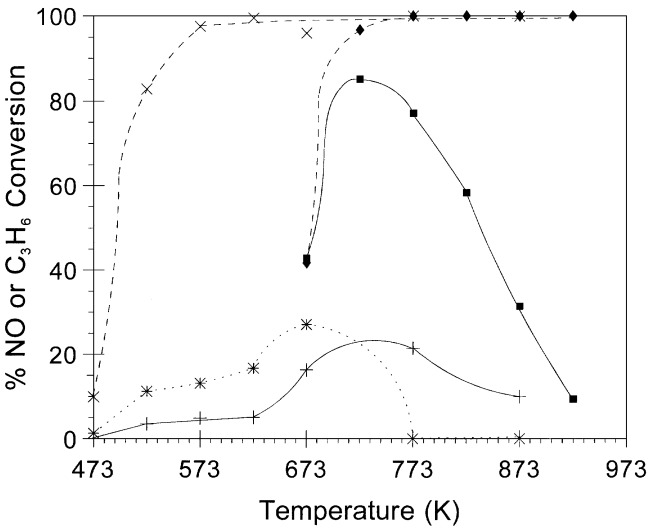

FIG. 3. NO and C_3H_6 conversions vs temperature over 2 and 6 wt% Ag/Al_2O_3. (■) NO conversion to N_2; (◆) C_3H_6 conversion over 2 wt% Ag/Al_2O_3. (+) NO conversion to N_2; (✳) NO conversion to N_2O; (×) C_3H_6 conversion over 6 wt% Ag/Al_2O_3. Catalyst weight, 0.25 g. Feed, 0.1% NO, 0.1% C_3H_6, 6% O_2 at 100 mL/min. GHSV = 12,000 h^{-1}.

of NO converted to N_2/min-g cat. for 2 wt% Ag/Al_2O_3 and 0.0027 and 0.0038 mmol of NO converted to N_2/min-g cat. for 6 wt% Ag/Al_2O_3. Thus, in agreement with the report of Miyadera (1), rates of N_2 formation were much higher over the lower loading sample. Besides being less active for N_2 formation than 2 wt% Ag/Al_2O_3, 6 wt% Ag/Al_2O_3 formed a substantial amount of N_2O and was exceedingly active for C_3H_6 combustion. When the amounts of Ag/Al_2O_3 catalysts were varied such that they each contained 4.64×10^{-5} mol of Ag, complete C_3H_6 combustion was achieved at 573 K over 6 wt% Ag/Al_2O_3 but not until 723 K over 2 wt% Ag/Al_2O_3. The NO conversions over 6 wt% Ag/Al_2O_3 were not strongly inhibited by the addition of 1.5% H_2O, similar to the case of 2 wt% Ag/Al_2O_3. The NO conversion at $T_{\max}$ over 6 wt% Ag/Al_2O_3 was 43% (16% to N_2, 27% to N_2O) in the absence of H_2O and 34% (19% to N_2, 15% to N_2O) in its presence.

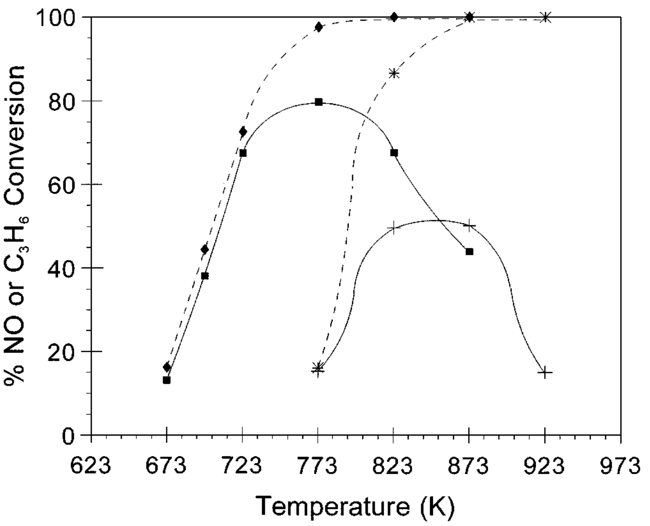

FIG. 2. NO and C_3H_6 conversions vs temperature over Al_2O_3 and 2 wt% Ag/Al_2O_3 in the presence of H_2O. (■) NO conversion to N_2; (◆) C_3H_6 conversion over 2 wt% Ag/Al_2O_3. (+) NO conversion to N_2; (✳) C_3H_6 conversion over Al_2O_3. Catalyst weight, 0.25 g. Feed, 0.1% NO, 0.1% C_3H_6, 6% O_2, 1.5% H_2O at 100 mL/min. GHSV = 12,000 h^{-1}.

Unlike Al_2O_3 and 2 wt% Ag/Al_2O_3, the position of the $T_{\max}$ for 6 wt% Ag/Al_2O_3 occurred at a temperature 100 K higher than the lowest temperature at which the C_3H_6 was completely combusted. This phenomenon could result from a change in the reaction mechanism or the catalyst at high temperatures. In order to check if a shift in the mechanism from NO reduction to NO decomposition was responsible for this observation, 0.1% NO and 6% O_2 were flowed over the catalyst. No NO decomposition occurred in the temperature range of 573 to 873 K.

The 2 and 6 wt% Ag/Al_2O_3 catalysts differed not only in their lean NO reduction behavior but also in their colors after reaction. After reaction at 523 K, 6 wt% Ag/Al_2O_3 was dark gray while 2 wt% Ag/Al_2O_3 was white. It was unlikely that the dark gray color of 6 wt% Ag/Al_2O_3 was due to a carbonaceous deposit because this catalyst was more active for hydrocarbon combustion than 2 wt% Ag/Al_2O_3, and the C balance remained close to 100% throughout the reaction.

Catalyst Characterization

A possible explanation for the color change of 6 wt% Ag/Al_2O_3 is that there was a change in Ag oxidation state. To determine if this indeed was the case, the oxidation

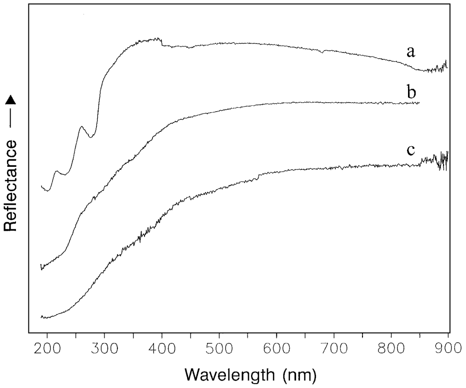

FIG. 4. UV–Vis diffuse reflectance spectra of (a) Al_2O_3, (b) 2 wt% Ag/Al_2O_3, and (c) 6 wt% Ag/Al_2O_3 after calcination.

states of the 2 and 6 wt% Ag/Al_2O_3 catalysts after calcination and after reaction were investigated. In addition, the redox properties of these catalysts were probed by H_2 TPR and TPO.

After calcination, XRD of the Ag/Al_2O_3 catalysts revealed neither the presence of silver oxide nor metallic silver. Moreover, neither catalyst exhibited an EPR signal which indicated the absence of Ag^{2+} or any small paramagnetic Ag^0 particles. Figure 4 presents the UV–Vis diffuse reflectance spectra of the Al_2O_3 and Ag/Al_2O_3 samples after calcination. The Ag/Al_2O_3 catalysts showed an absorbance peak between 200 and 230 nm. While the contribution of the Al_2O_3 support to this peak cannot be determined, it may be indicative of Ag^+ as isolated Ag^+ ions have an absorption band near 220 nm from the $4d^{10}$ to $4d^95s^1$ electronic transition (18, 19). Noticeably absent from the UV–Vis diffuse reflectance spectra of the Ag/Al_2O_3 catalysts were peaks between 270 and 290 nm and 370 and 390 nm which have been attributed to $Ag_n^{\delta+}$, a peak at 315 nm attributed to metallic Ag film and a peak between 420 and 460 nm attributed to metallic Ag clusters and aggregates. It should be noted that large Ag_2O particles are not detected by UV–Vis diffuse reflectance (20, 21). The lack of Ag^0 absorption peaks indicate that the Ag/Al_2O_3 catalysts contain small Ag_2O particles and/or isolated Ag^+ atoms after calcination. This is intriguing as bulk Ag_2O decomposes to metallic Ag rapidly at a temperature of 523 K in air (22).

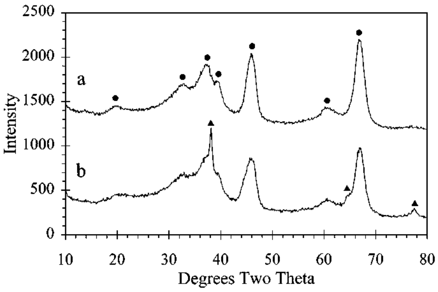

FIG. 5. XRD of (a) 2 wt% Ag/Al_2O_3 and (b) 6 wt% Ag/Al_2O_3 after reaction at 523 K. (▲) Ag^0; (●) γ-Al_2O_3. Feed, 0.1% NO, 0.1% C_3H_6, 6% O_2 at 100 mL/min. Catalyst weights, 0.25 g (GHSV = 12,000 h^{-1}) 6 wt% Ag/Al_2O_3 and 0.75 g (GHSV = 4000 h^{-1}) 2 wt% Ag/Al_2O_3.

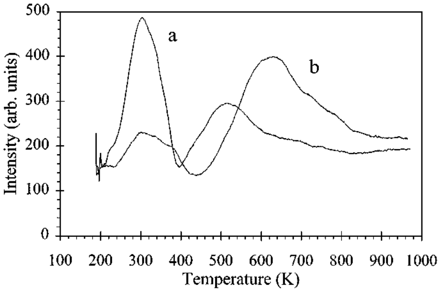

FIG. 6. H_2 TPR of (a) 6 wt% Ag/Al_2O_3 and (b) 2 wt% Ag/Al_2O_3. Catalyst amount, 5.6×10^{-4} mol Ag. Feed, 5% H_2/Ar at 60 mL/min. Ramp rate, 10 K/min.

Figure 5 shows the XRD patterns of the Ag/Al_2O_3 catalysts after reaction. To ensure that an uniform sample was analyzed, the reactions were carried out under conditions where the propene conversion was less than 100%. After 5 h of reaction at 523 K, the catalysts were quenched cooled in He. The 6 wt% Ag/Al_2O_3 catalyst was dark gray in color (0.25 g, 83% C_3H_6 conversion) while the 2 wt% Ag/Al_2O_3 catalyst was white (0.75 g, 2% C_3H_6 conversion). XRD revealed the presence of metallic Ag on 6 wt% Ag/Al_2O_3, but no Ag metal or oxide peaks were observed on 2 wt% Ag/Al_2O_3. After reaction at 673 K, 6 wt% Ag/Al_2O_3 contained a mixture of dark gray and white particles (0.02 g, 72% C_3H_6 conversion) while 2 wt% Ag/Al_2O_3 was white (0.25 g, 42% C_3H_6 conversion). No Ag XRD peaks were observed on either catalyst.

H_2 TPR of the catalysts after treatment in O_2 for 1 h at 773 K (Fig. 6, Table 1) revealed that the amount of H_2 taken up by the Ag/Al_2O_3 catalysts corresponded within error to complete reduction of Ag_2O to Ag^0. The H_2 TPR profiles of the two catalysts were very different, and Ag^+ was found to be much more stable over 2 wt% Ag/Al_2O_3 than 6 wt% Ag/Al_2O_3. After H_2 reduction, both catalysts were rust in color and contained Ag^0 particles large enough to be observed by XRD. UV–Vis diffuse reflectance spectra of the reduced catalysts (Fig. 7) were quite different from the spectra of the catalysts after calcination (Fig. 4) confirming that

TABLE 1

H_2 TPR Data of Supported Ag Catalysts[a]

Catalyst	Temperature of reduction in K (% Ag reduced)
6% Ag/SiO_2	302 (45 ± 7), 398–973 (17 ± 3)
6% Ag/Al_2O_3	302 (34 ± 5), 513 (50 ± 8)
2% Ag/Al_2O_3	299 (16 ± 2), 630 (80 ± 12)
4% Ag-ZSM5	402 (43 ± 6), 548 (13 ± 2), 921 (48 ± 7)

[a] 5.6×10^{-4} mol of Ag. Feed, 5% H_2/Ar at 60 mL/min. Ramp rate, 10 K/min.

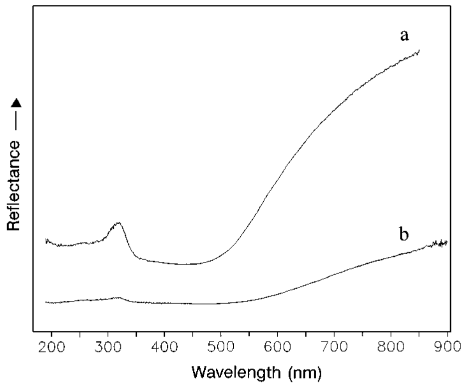

FIG. 7. UV–Vis diffuse reflectance spectra of reduced (a) 2 wt% Ag/Al_2O_3 and (b) 6 wt% Ag/Al_2O_3.

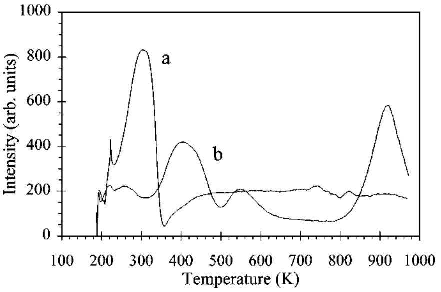

FIG. 9. H_2 TPR of (a) 6 wt% Ag/SiO_2 and (b) 4 wt% Ag-ZSM5. Catalyst amount: 5.6×10^{-4} mol Ag. Feed, 5% H_2/Ar at 60 mL/min. Ramp rate, 10 K/min.

the Ag/Al_2O_3 catalysts were oxidized after calcination. The strong absorption observed in the reduced catalysts in the vicinity of 400 nm is attributed to the metallic plasma resonance absorption band.

The TPO profiles of the reduced catalysts were similar for both 2 and 6 wt% Ag/Al_2O_3 (Fig. 8). The TPO profile of 6 wt% Ag/Al_2O_3 had an O_2 consumption peak at 634 K while 2 wt% Ag/Al_2O_3 exhibited a similar peak at 647 K. A second TPR after TPO revealed that the Ag had been completely reoxidized over both catalysts during TPO. The TPR profiles obtained after TPO were similar to those taken before TPO.

As large metal oxide clusters are typically easier to reduce than small metal oxide clusters or ions, and as bulk Ag_2O is known to reduce readily (22), the low-temperature peaks observed in the H_2 TPR of 2 and 6 wt% Ag/Al_2O_3 near 300 K were assigned to the reduction of large Ag_2O clusters, while the higher temperature reduction peaks were assigned to well-dispersed metal oxide clusters or ions.

In order to verify that well-dispersed Ag_2O particles or Ag^+ ions are more difficult to reduce than large Ag_2O particles, TPR was performed on 6 wt% Ag/SiO_2 and 4 wt% Ag-ZSM5 after treatment in O_2 for 1 h at 773 K (Fig. 9, Table 1). As SiO_2 does not typically interact strongly with transition metal oxides, large Ag_2O clusters are expected to be present on this catalyst. In contrast, isolated transition metal ions are typically well stabilized on ZSM5. The Ag/SiO_2 catalyst was beige after calcination, and metallic Ag was observed by XRD (Fig. 10b). In contrast, Ag-ZSM5 was white after calcination and contained neither Ag^0 nor Ag_2O particles large enough to be observed by XRD.

In agreement with the XRD data which showed the presence of Ag^0, the amount of H_2 consumed by Ag/SiO_2 during TPR corresponded to only $62\pm10\%$ of Ag_2O to Ag^0 (Table 1). The reduction occurred readily at a low temperature of 302 K. In contrast, a substantial fraction of the Ag in Ag-ZSM5 was reduced at the very high temperature of 921 K. This reduction peak is attributed to isolated Ag^+ ions. The presence of other reduction peaks on Ag-ZSM5 at 402 and 548 K may result from the presence of Ag_2O clusters inside or on the external surface of the zeolite.

Relationship between Ag^+ Stability and NO Reduction

It would be interesting to compare the lean NO reduction behaviors of Ag-ZSM5 and Ag/SiO_2 with those of Ag/Al_2O_3 to see if there is a correlation between the reducibility of a catalyst and its NO reduction ability. Although the activity of Ag-ZSM5 could not be compared to the other catalysts due to rapid coking, Ag/SiO_2 was investigated. This catalyst showed no NO reduction to N_2 at 673 K and only 8% NO reduction to N_2O. In addition, the C_3H_6 conversion decreased with time on stream; it was 96%

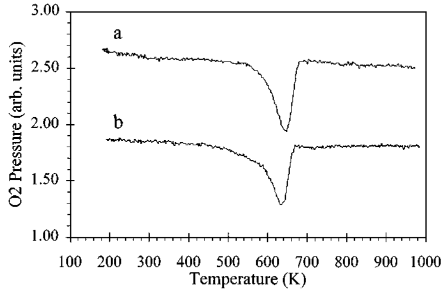

FIG. 8. TPO of (a) 2 wt% Ag/Al_2O_3 and (b) 6 wt% Ag/Al_2O_3 after H_2 TPR. Catalyst amount, 5.6×10^{-4} mol Ag. Feed, 4.75% O_2/He at 30 mL/min. Ramp rate, 10 K/min.

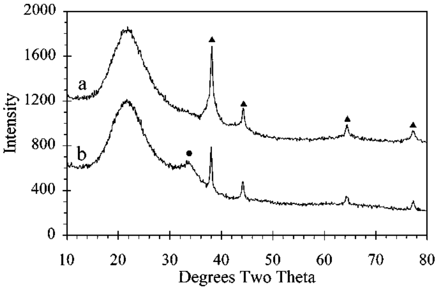

FIG. 10. XRD of 6 wt% Ag/SiO_2 (a) after reaction and (b) after calcination. (▲) Ag^0; (●) Ag_2O. Reaction conditions, 0.25 g; 0.1% NO, 0.1% C_3H_6, 6% O_2 at 100 mL/min. GHSV = 9600 h^{-1}.

after 0.27 h and 65% after 6.7 h. As the C balance remained close to 100%, it is believed that this decrease was due to a change in the catalyst rather than as a result of coking. XRD of this sample after reaction revealed the presence of metallic Ag (Fig. 10a). Since the ratio of the intensities of a Ag peak to that of the amorphous SiO_2 was higher after reaction at 673 K than after calcination, some of the Ag_2O particles remaining after calcination were converted to Ag^0 under reaction conditions.

As the order of NO conversions to N_2, 6 wt% $Ag/SiO_2 <$ 6 wt% $Ag/Al_2O_3 <$ 2 wt% Ag/Al_2O_3, was in the same order as the stability of Ag^+, it seems possible that the activities of the catalysts are related to their abilities to stabilize Ag^+ under reaction conditions. In order to compare NO reduction to N_2 over Ag^0 and Ag^+, the NO reduction activities of 2 and 6 wt% Ag/Al_2O_3 at 673 K were compared before and after H_2 TPR. Conversions over the reduced and oxidized forms of the catalysts were identical even after only 10 min on stream. This indicates that the oxidation state of Ag under reaction conditions was rapidly achieved. However, if the 2 wt% Ag/Al_2O_3 was pretreated by H_2 TPR followed by an additional 5 h in the H_2/Ar feed at 973 K, its NO reduction activity at 673 K resembled that of 6 wt% Ag/SiO_2. It had an exceedingly low NO conversion to N_2 (<4%), and as the time on stream increased from 0.17 to 7.7 h, its C_3H_6 conversion decreased from 95 to 71%, and its NO conversion to N_2O increased from 9 to 22%.

Effect of NO_2

Figure 11 compares the reduction of NO with that of NO_2 over the Al_2O_3 and Ag/Al_2O_3 catalysts. Replacing NO with NO_2 over Al_2O_3 resulted in a dramatic increase in N_2 formation as has been previously reported (23, 24). NO_2 also enhanced the N_2 formation rate but not the N_2O

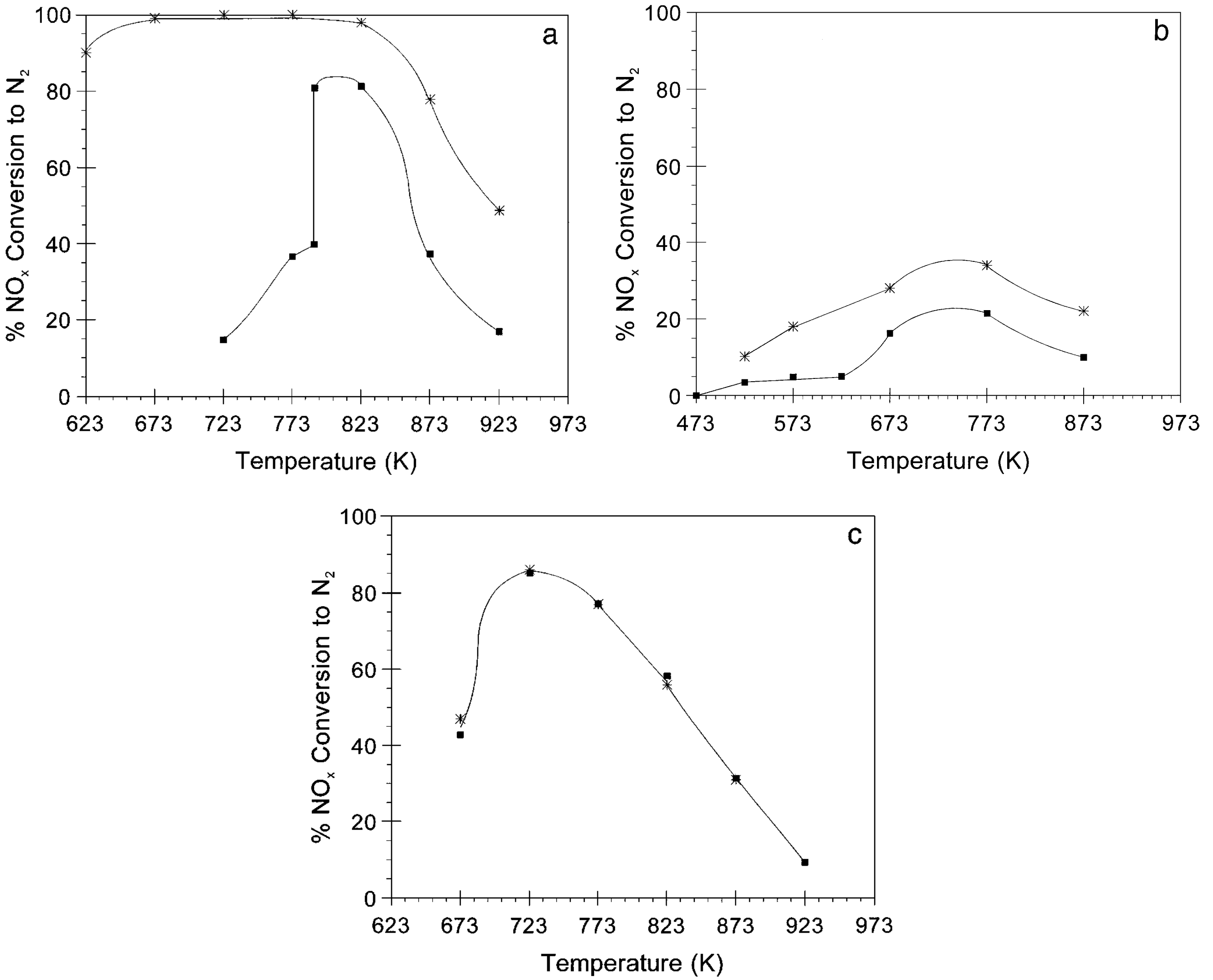

FIG. 11. Comparison of NO_2 and NO reduction to N_2 as a function of temperature over (a) Al_2O_3, (b) 6 wt% Ag/Al_2O_3, and (c) 2 wt% Ag/Al_2O_3. (■) NO and (✳) NO_2 conversion to N_2. Catalyst weight, 0.25 g. Feed, 0.1% NO or NO_2, 0.1% C_3H_6, 6% O_2 at 100 mL/min. GHSV = 12,000 h^{-1}.

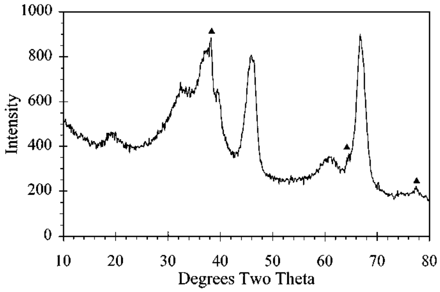

FIG. 12. XRD of 6 wt% Ag/Al_2O_3 after reaction in a NO_2-containing feed at 523 K. (▲) Ag^0. Catalyst weight, 0.25 g. Feed, 0.1% NO_2, 0.1% C_3H_6, 6% O_2 at 100 mL/min. GHSV = 12,000 h^{-1}.

formation rate over 6 wt% Ag/Al_2O_3. The NO_2 conversions were higher over Al_2O_3 than over 6 wt% Ag/Al_2O_3. This suggests that the active sites for NO_2 reduction on Al_2O_3 may be blocked by the presence of Ag or that Ag rapidly destroys a necessary reaction intermediate. A similar observation has been made by Hamada *et al.* (5) for Al_2O_3 and Co/Al_2O_3.

While the replacement of NO with NO_2 enhanced the NO_x conversions over 6 wt% Ag/Al_2O_3 at all temperatures investigated, the C_3H_6 conversion at 523 K decreased from 85 to 50%. This was unexpected since NO_2 is more oxidizing than NO. As previously mentioned, 6 wt% Ag/Al_2O_3 was dark gray after reaction with the NO-containing feed at 523 K, and XRD revealed the presence of Ag^0. In contrast, the majority of the sample remained white and only a small portion turned dark gray after reaction at 523 K with the NO_2-containing feed, and XRD revealed less Ag^0 relative to the Al_2O_3 peak intensities (Fig. 12) than observed after reaction with the NO-containing feed (Fig. 5).

Analysis of the effluent from NO_2 reduction over 6 wt% Ag/Al_2O_3 indicated that NO_2 was rapidly reduced to NO (Table 2). At 573 K the NO_2 to NO conversion was 57%, a value larger than the 16% NO_2 to NO conversion predicted from thermodynamic equilibrium (25). The rapid conversion of NO_2 to NO beyond equilibrium has been previously observed for several catalysts (26, 27). At 673 K and above, almost all of the emitted NO_x in the effluent was NO.

TABLE 2

Percentages of NO_2 Converted to N_2, N_2O, and NO and the Percentage of NO_2 Left Unreacted[a]

Temp. (K)	Al_2O_3			6 wt% Ag/Al_2O_3				2 wt% Ag/Al_2O_3		
	N_2	NO	NO_2	N_2	N_2O	NO	NO_2	N_2	NO	NO_2
523	—	—	—	10	7	74	9	—	—	—
573	—	—	—	18	16	57	7	—	—	—
623	90	4	7	—	—	—	—	—	—	—
673	99	2	0	28	26	37	2	47	31	13
723	100	1	0	—	—	—	—	86	8	4
773	100	2	0	34	0	55	2	77	10	11
823	98	4	1	—	—	—	—	56	25	16
873	78	18	8	22	0	72	4	31	55	12
923	49	51	6	—	—	—	—	—	—	—

[a] Catalyst weight, 0.25 g. Feed, 0.1% NO_2, 0.1% C_3H_6, 6% O_2 at 100 mL/min. GHSV = 12,000 h^{-1}.

Unlike over Al_2O_3 and 6 wt% Ag/Al_2O_3, the rate of N_2 formation over 2 wt% Ag/Al_2O_3 was identical for the NO- and NO_2-containing feeds. NO_2 was converted less effectively to NO over 2 wt% Ag/Al_2O_3 than over 6 wt% Ag/Al_2O_3 as can be seen by the significant fraction of NO_2 remaining in the 2 wt% Ag/Al_2O_3 effluent at temperatures as high as 873 K.

The oxidation of NO to NO_2 in a feed containing 0.1% NO and 6% O_2 was also measured over the Ag/Al_2O_3 and Al_2O_3 catalysts. The Ag/Al_2O_3 catalysts displayed a very low activity for this reaction which was barely higher than that observed over pure Al_2O_3. At 673 K the NO to NO_2 conversions were 7% over 2 wt% Ag/Al_2O_3, 8% over 6 wt% Ag/Al_2O_3, and 5% over Al_2O_3.

Role of Al_2O_3

In order to determine if the Al_2O_3 support plays any role in the reaction, 0.022 g of 6 wt% Ag/Al_2O_3 was placed directly on top of 0.23 g of Al_2O_3 (Table 3). The NO conversion at 673 K over this two-layer catalyst was 45% (36% to N_2, 9% to N_2O). This was significantly higher than the 32% NO conversion (16% to N_2, 16% to N_2O)

TABLE 3

Summary of Reaction Data at 673 K[a]

Catalyst	% NO_x to N_2	% NO_x to N_2O	% C_3H_6 conversion
0.25 g Al_2O_3	11	0	8
0.23 g SiO_2	0	0	0.6
0.25 g 2 wt% Ag/Al_2O_3	43	0	42
0.25 g 6 wt% Ag/Al_2O_3	16	27	100
0.022 g 6 wt% Ag/Al_2O_3	7	15	72
0.067 g 2 wt% Ag/Al_2O_3	9	0	11
Separated Al_2O_3 (first) and 6 wt% Ag/Al_2O_3[b,c,d]	15	14	80
Separated 6 wt% Ag/Al_2O_3 (first) and Al_2O_3[b,c,e]	16	16	82
6 wt% Ag/Al_2O_3 directly on Al_2O_3[b]	36	9	74
Al_2O_3 directly on 6 wt% Ag/Al_2O_3[b]	37	9	65
6 wt% Ag/Al_2O_3 mixed with Al_2O_3[b]	42	12	77
6 wt% Ag/Al_2O_3 mixed with SiO_2[b]	7	15	68
Separated 2 wt% Ag/Al_2O_3 (first) and Al_2O_3[c,e,f]	22	0	18
2 wt% Ag/Al_2O_3 directly on Al_2O_3[f]	26	0	18
2 wt% Ag/Al_2O_3 mixed with Al_2O_3[f]	31	0	19

[a] Feed, 0.1% NO, 0.1% C_3H_6, 6% O_2 at 100 mL/min.
[b] Catalyst weight, 0.022 g of 6 wt% Ag/Al_2O_3; 0.23 g of Al_2O_3 or SiO_2.
[c] Catalysts are separated by quartz wool and quartz chips.
[d] Gas flow reaches Al_2O_3 before Ag/Al_2O_3.
[e] Gas flow reaches Ag/Al_2O_3 before Al_2O_3.
[f] Catalyst weight, 0.066 g of 2 wt% Ag/Al_2O_3; 0.18 g of Al_2O_3.

TABLE 4

Reaction Data at 673 K of a Mixture of 60–80 Mesh Al_2O_3 and 170+ Mesh 6 wt% Ag/Al_2O_3 and of the 60–80 Mesh Portion Obtained after Sieving[a]

Catalyst	% NO_x to N_2	% NO_x to N_2O	% C_3H_6 conversion
6 wt% Ag/Al_2O_3 mixed with Al_2O_3[b]	54	9	82
0.11g 60–80 mesh obtained after sieving	8	0	7
0.11 g Al_2O_3 (60–80 mesh)	9	0	10

[a] Feed, 0.1% NO, 0.1% C_3H_6, 6% O_2 at 100 mL/min.

[b] Catalyst weight, 0.022 g of 6 wt% Ag/Al_2O_3; 0.23 g of Al_2O_3.

obtained when the two catalysts were separated by quartz chips and quartz wool. The NO conversion over the separated catalysts was virtually identical to the sum of the NO conversions over the individual catalysts. Intriguingly, the same NO conversions were obtained whether the 6 wt% Ag/Al_2O_3 was placed on top of or beneath the Al_2O_3. As the NO conversion could be decreased by separating the 6 wt% Ag/Al_2O_3 from the Al_2O_3, it could also be enhanced by mixing them together. The mixture of 6 wt% Ag/Al_2O_3 and Al_2O_3 showed a NO conversion which was reproducibly 8% or more higher than when the 6 wt% Ag/Al_2O_3 was placed on top of or beneath the Al_2O_3. Al_2O_3 was found to be important for the enhanced NO conversions as the NO conversion over a mixture of 6 wt% Ag/Al_2O_3 and SiO_2 showed no enhancement effect.

To further investigate the interaction between 6 wt% Ag/Al_2O_3 and Al_2O_3, Al_2O_3 with particles of 60–80 mesh was mixed with 6 wt% Ag/Al_2O_3 with particles of 170+ mesh. After reaction over this mixture, the different size particles were separated by sieving. The 60–80 mesh portion of Al_2O_3 after sieving showed identical conversions of NO and C_3H_6 to those observed over the same amount of Al_2O_3 (Table 4). Separate experiments revealed that the conversions over 6 wt% Ag/Al_2O_3 also remained unchanged.

A similar although smaller cooperative effect was also observed when 2 wt% Ag/Al_2O_3 was placed directly on top of or mixed with Al_2O_3 (Table 3).

DISCUSSION

While XRD revealed the presence of metallic Ag on the 6 wt% Ag/Al_2O_3 catalyst after reaction at 523 K, no metallic Ag was observed on the 2 wt% Ag/Al_2O_3 catalyst after reaction at this temperature. Moreover, no Ag XRD peaks were observed over either catalyst after reaction at 673 K. When these results are taken together with the TPR results which show that 6 wt% Ag/Al_2O_3 is easier to reduce than 2 wt% Ag/Al_2O_3 and the TPO results which show that the reduced forms of both catalysts can be reoxidized at 647 K in a feed of 4.75% O_2, it seems reasonable to assume that the 6 wt% Ag/Al_2O_3 contains a significant fraction of reduced Ag at low temperatures and less at high temperatures. In contrast, the 2 wt% Ag/Al_2O_3 is believed to be in the oxidized form at all reaction temperatures.

As the order of NO reduction activity, 6 wt% $Ag/SiO_2 <$ 6 wt% $Ag/Al_2O_3 <$ 2 wt% Ag/Al_2O_3, was in the same order of Ag^+ stability in these catalysts, the high oxidation rate of C_3H_6, the formation of N_2O, and the low NO conversions to N_2 obtained over 6 wt% Ag/Al_2O_3 are attributed to the presence of metallic Ag, while the high conversion of NO to N_2 and the relatively low C_3H_6 combustion rate over 2 wt% Ag/Al_2O_3 are attributed to Ag^+.

Support that the oxidation of C_3H_6 occurs at a higher rate over Ag^0 than Ag^+ was obtained from the comparison of the reduction of NO_2 and NO over 6 wt% Ag/Al_2O_3 at 523 K. Changing from a NO- to a NO_2-containing feed caused about 75% of the catalyst to change from dark gray to white and decreased the amount of Ag^0 as determined from the ratio of Ag^0 to Al_2O_3 XRD peak intensities. This indicates that the catalyst is more oxidized in the NO_2- than in the NO-containing feed. At the same time, a higher C_3H_6 conversion was observed in the NO- compared to the NO_2-containing feed (85 vs 50%). This supports the idea that metallic Ag is much more effective at C_3H_6 oxidation than Ag^+.

In agreement with this idea, Pestryakov *et al.* (28–30) reported that Ag catalysts which increase the charge on Ag^+ and which stabilize the oxidized state of Ag show a high selectivity in the oxidation of methanol to formaldehyde. In contrast, Ag catalysts in which the Ag^+ charge is decreased show high activities for the complete oxidation of methanol and of pentane.

If 6 wt% Ag/Al_2O_3 contains large Ag_2O clusters that are readily reduced, then the formation of similar Ag_2O clusters on 2 wt% Ag/Al_2O_3 by sintering should cause it to behave like the 6 wt% sample. In agreement with this, the C_3H_6 and NO to N_2O conversions were high and the NO to N_2 conversions were low over the 2 wt% Ag/Al_2O_3 which was pretreated by H_2 TPR followed by an additional 5 h in 5% H_2/Ar at 973 K.

The sintering of the 2 wt% Ag/Al_2O_3 catalyst by reduction appears to disagree with the recent results of Aoyama *et al.* (31) who reported that particles on oxidized 5 wt% Ag/Al_2O_3 were larger than those on the reduced form of the catalyst. The variations in Ag weight loading and in the oxidation and reduction procedures used in the two studies may be responsible for this difference. Despite this, however, Aoyama *et al.* observed both higher N_2 formation rates and higher selectivities to N_2 over the oxidized form of the catalyst, in agreement with the proposed beneficial role of Ag^+.

The model that Ag^+ is better at N_2 formation than Ag^0 can explain the different effects of NO_2 on 2 and 6 wt%

Ag/Al_2O_3. The NO_2-containing feed increases N_2 formation over 6 wt% Ag/Al_2O_3 by increasing the amount of Ag^+ which favors N_2 formation. However, no increase in N_2 formation occurs for 2 wt% Ag/Al_2O_3 because this catalyst is already oxidized.

The model can further explain the observation that the T_{max} for the 6 wt% Ag/Al_2O_3 is higher than the lowest temperature of complete propene combustion. As the temperature increases, the amount of the Ag^+ also increases, which improves the effectiveness of the catalyst to reduce NO to N_2. In contrast, as the Ag in the 2 wt% Ag/Al_2O_3 is oxidized at all reaction temperatures, the T_{max} occurs at the lowest temperature of complete hydrocarbon combustion as is typically observed.

While Ag^+ appears to be important for effective N_2 formation, Al_2O_3 may also play a role in the reaction mechanism as indicated by the higher conversion of NO obtained when Ag/Al_2O_3 was in direct contact with Al_2O_3 compared to when these two catalysts were separated by quartz wool and quartz chips. Since no enhancement in NO conversion was observed when the catalysts were separated, a long-lived intermediate, such as NO_2, cannot be responsible for the increase in NO conversion. The fact that the NO conversion was similar whether 6 wt% Ag/Al_2O_3 was placed directly on top of or below Al_2O_3 eliminated all but two explanations for the enhanced NO conversions. The first possibility was that the enhanced NO conversions were due to a reaction occurring at the 6 wt% Ag/Al_2O_3 and Al_2O_3 interface or to migration of a reaction intermediate across the interface, since the area of this interface would be similar regardless of whether 6 wt% Ag/Al_2O_3 was placed on top of or beneath the Al_2O_3. Moreover, although the 0.022 g layer of 6 wt% Ag/Al_2O_3 placed on top of the Al_2O_3 was very thin (ca. 0.6 mm average) and, therefore, already in good contact with the Al_2O_3, a mixture of 6 wt% Ag/Al_2O_3 and Al_2O_3 should have a slightly higher interparticle contact area, and, therefore, a slightly higher NO conversion than 6 wt% Ag/Al_2O_3 placed on top of or below Al_2O_3. This is in agreement with the data. This suggestion is similar to that proposed by Inaba *et al.* (6) to explain the higher NO conversions obtained for a mixture of Pt/SiO_2 and Al_2O_3.

The other possible explanation for the enhanced NO conversion was that some of the Ag migrated from the 6 wt% Ag/Al_2O_3 to the Al_2O_3 resulting in a catalyst of lower Ag loading and higher activity for N_2 formation. Data of Table 4 in which catalysts of different mesh sizes were used do not support this explanation. After separating the Al_2O_3 particles from the Ag/Al_2O_3 particles, the activity of the Al_2O_3 particles remained identical to that of Al_2O_3 which had not been in contact with Ag/Al_2O_3. Moreover, the activity of the 6 wt% Ag/Al_2O_3 also remained unchanged. Thus, there was no migration of Ag onto Al_2O_3.

Enhanced NO conversions at the interface of 6 wt% Ag/Al_2O_3 and Al_2O_3 imply that there is a difference between the reactivity of the unmodified Al_2O_3 and the Al_2O_3 supporting Ag. Such a difference may result if the Ag blocks the active Al_2O_3 sites. This explanation seems reasonable as the reduction of NO_2 to N_2 with C_3H_6 in the presence of O_2 occurred to a much greater extent over Al_2O_3 than over the Ag/Al_2O_3 catalysts.

CONCLUSIONS

The 2 wt% Ag/Al_2O_3 catalyst is much more effective at lean NO_x reduction than 6 wt% Ag/Al_2O_3. This difference is attributed to the Ag in the catalysts having different oxidation states under reaction conditions. The 2 wt% Ag/Al_2O_3 catalyst is in the oxidized form under all reaction conditions, while the 6 wt% Ag/Al_2O_3 catalyst contains a large number of Ag^0 particles at lower temperatures and less at higher temperatures. The presence of Ag^0 leads to a high rate of C_3H_6 combustion at the expense of N_2 formation. The promotional effect of NO_2 on 6 wt% Ag/Al_2O_3 is attributed to the oxidation of Ag^0 to Ag^+ by NO_2. Such a promotion is not seen on 2 wt% Ag/Al_2O_3 as this catalyst is already completely oxidized. A synergistic effect was observed when Al_2O_3 was mixed with either 2 or 6 wt% Ag/Al_2O_3. This promotional effect results from surface migration of a reaction intermediate from Ag/Al_2O_3 to Al_2O_3 or vice versa.

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