PRIORITY COMMUNICATION

Improved N₂ Selectivity for Platinum on Alumina Prepared by Sol-Gel Technique in the Reduction of NO_x by Propene

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EXPERIMENTAL

We present results which demonstrate that a 1% Pt/alumina catalyst prepared by a sol-gel technique is superior in its N₂ selectivity in the catalytic reduction of NO_x by propene to similarly loaded Pt/alumina catalysts prepared by the more commonly used impregnation technique. The selectivity of the sol-gel catalyst to N₂ at maximum conversion is 83% as compared to 43% and 60% selectivity observed with Pt catalysts prepared using the impregnation technique. The sol-gel made catalyst does not change its activity and selectivity even in the presence of 2.5% water. © 1998 Academic Press

Key Words: N₂ selectivity; lean burn engines; nitric oxide reduction; platinum/alumina; propene.

INTRODUCTION

Of all the catalysts tested so far alumina-supported Pt has shown the highest activity at the lowest temperatures for selective NO_x reduction from exhaust gas streams (1–7). High activity at low temperatures makes Pt/alumina a desirable catalyst. However, Pt/alumina and Pd/alumina catalysts have very high selectivities for unregulated but highly undesirable nitrous oxide. Based on literature (1,8), Pt on alumina catalysts typically exhibit at least 50% selectivity to N₂O, the remainder being N₂. Thus, it would be very desirable to develop a catalyst with the low temperature activity of Pt but without its high selectivity to N₂O for use in diesel engine vehicles, which have cooler exhaust than gasoline engines.

Recently we have prepared (9) high activity and N_2 selective silver/alumina catalysts for selective NO_x reduction, using a single step sol-gel synthesis. In order to see if we can achieve the same gain that we have seen with silver catalysts with platinum-based catalysts we also prepared single step sol-gel platinum/alumina catalysts. In this study, we report the preliminary results of experiments carried out with some of the 1% Pt/alumina catalysts.

Catalyst Preparation and Activity Tests

In our sol-gel process (10), aluminum tri-sec butoxide, ethanol, excess amount of water, and the necessary amount of hexachloroplatinic acid (as a precursor for Pt loading, to get 1 wt% Pt in the final catalyst) were used to make a gel. The gel was dried at 100°C for 12 h, followed by calcination at 600°C for 24 h. This calcined catalyst was tested and characterized without further pretreatment. In addition to this sol-gel made platinum catalyst (SG-Pt), an impregnation catalyst with 1 wt% Pt loading (IM-Pt) was prepared using Degussa alumina (100 m²/g.) and hexachloroplatinic acid. A second impregnation catalyst (Pt-IMP-Al₂O₃(SG)) was also prepared with alumina produced by the same solgel synthesis technique used in our single step synthesis. Both of the impregnation catalysts were dried at 100°C to remove water and calcined at 500°C for 16 h. These calcined catalysts were reduced with hydrogen prior to activity studies.

The reactant gas mixture was blended by using four independent mass flow controllers to get 750 ppm NO, 750 ppm propene, 6.5% oxygen, 2.5% water (when used) and helium as balance. In addition, all catalysts were ground and sieved to 120–180 mesh size prior to catalytic studies. The total flow rate of reactants and the amount of the catalyst used were 72 ml/min and 0.1 g, respectively.

Catalyst Characterization and Product Analysis

All catalysts were analyzed by using a Rigaku XRD system for the determination of bulk properties and Micromeritics ASAP 2010 for the BET surface area measurement. The effluent gas mixture from the reactor was analyzed by a Thermo Environmental 42CHL NO_x chemiluminescence analyzer and by FTIR with a 10-cm path length gas cell for quantitative determination of CO₂, CO, and N₂O.

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RESULTS AND DISCUSSION

Figure 1 shows the NO_x reduction activities of the three catalysts as a function of temperature. When the combustion of propene is around 95%, as seen in Fig. 2, the maximum in NO_x conversion is observed for all three catalysts. This is a general phenomenon within lean-NO_x catalysis. The temperature at this point is not the same for all the catalysts. For the catalyst made with the impregnation technique using Degussa alumina (IM-Pt), the maximum in NO_x conversion (37%) occurred at 254°C. The impregnation catalyst made with our sol-gel alumina reached a peak conversion of 35% at 255°C and for the single step solgel made catalyst (SG-Pt), a maximum NO_x conversion of 34% was observed at 269°C. Interestingly there is a significant difference in the activity of the three catalysts below their peak conversion temperatures. At 150°C, all have low conversions but at 200°C the impregnation catalysts have conversions of \sim 30% and \sim 25% versus \sim 2% for the single step sol-gel catalyst. Above the peak conversion temperature the shape of the conversion versus temperature is similar for all three. Above 350°C, the single step solgel catalyst has higher conversions. Also, below the peak conversion temperature, NO₂ formation was not observed for all three catalysts. However, above the peak conversion temperature up to 23% (at 350°C) of NO was converted to NO₂ for all the catalysts. This can be explained by a lack of sufficient reductant and platinum catalysts being good oxidizing catalysts under oxygen-rich reaction conditions.

The widths of the NO_x conversion curves for the catalysts are also significantly different. The IM-Pt catalyst has



FIG. 1. Steady state catalytic activity of the three catalysts.



FIG. 2. Propene combustion for IM-Pt catalyst and SG-Pt catalysts as measured by CO_2 concentration in the reactor effluent.

a broad conversion curve showing detectable activity from 150°C to 350°C with a full width at half peak of almost 150°. The Pt-IMP-Al₂O₃(SG) catalyst conversion curve has a full width at half maximum of almost 130°C. These widths can be compared to a maximum width of 100°C observed by Burch and co-workers (2) with their Pt catalysts. In comparison the shape of the SG-Pt conversion curve is similar to those observed by Burch and co-workers (2). It is sharply peaked and has a full width at half peak conversion of \sim 75°C. We speculate that the unusual widths of the activity curves of the impregnation catalysts are most likely due to broader particle size distribution of these catalysts compared to the single step sol-gel catalyst, but as of now we do not have any conclusive evidence. Figure 2 shows that the combustion of propene is slower on the SG-Pt catalyst and there is a difference of $\sim 50^{\circ}$ C between the two catalysts. The combustion rate increases almost linearly between 150°C and 240°C for the two impregnation catalysts, whereas the rate increase seen with the SG-Pt catalyst is more exponential in nature, indicative of a higher activation energy combustion. The difference in combustion catalysis is obviously the reason for the broader activity peaks of the impregnation catalysts.

The selectivities of the three catalysts are shown in Fig. 3. With platinum catalysts using hydrocarbons as reductants there are two main products of NO reduction: N_2O and N_2 . N_2 is the desired product as N_2O will eventually decompose to produce NO in the atmosphere. Based on literature reports (1,2), at least 50% of NO is reduced to nitrous oxide by alumina-supported platinum catalysts. This was also seen with our IM-Pt catalyst as shown in the Fig. 3.



FIG. 3. Comparison of conversions of the three catalysts to N_2 and N_2O . Note that conversion here is defined as the percentage of the original NO_x reduced to N_2 or N_2O . The total conversion is the sum of the two conversions.

The N₂ selectivity of the Pt-IMP-Al₂O₃(SG) is better than about 60% at peak conversion. However, our SG-Pt catalyst with the same metal loading is better than either of the impregnation catalysts and shows ~83% N₂ selectivity at peak conversion. Note that the percentage of selectivity, in the reduction of NO_x (NO + ~3% NO₂ present in the NO as an impurity), is defined as 100 × the amount of N₂/(amount of N₂ + amount of N₂O). We also tested the effect of water on total conversion and selectivity of our sol-gel-made catalyst and did not observe any changes in the total conversion or the selectivity to nitrogen.

In order to explain the difference in the selectivites and activities observed between the two catalysts we measured the particle sizes of the IM-Pt and SG-Pt catalysts by XRD. XRD results indicated that we had metallic platinum in both catalysts and that the average crystallite size was \sim 11 nm for the impregnation catalyst and 17 nm for the sol-gel catalyst. BET measurements revealed that the Degussa alumina we used had a surface area of 100 m^2/g and the sol gel catalysts both had surface areas of 250 m^2/g with a narrow pore size distribution sharply peaked at \sim 2.7 nm. Thus, based on the limited information provided by XRD and BET, it is not possible to explain the reasons for the large difference in selectivity. One possible speculative explanation is that since the SG-Pt catalyst had Pt incorporated into the alumina gel before the gel was dried and calcined, some of the Pt may be atomically dispersed and/or covered by a thin layer of alumina perhaps similar to what is observed with titania-supported platinum after high temperature reduction. These strong interactions with alumina may change the oxidation state of some of the Pt atoms on the surface and lead to the formation of more N₂, either by only dissociatively adsorbing NO, or by changing the surface recombination rates between N and NO molecules. We also carried out some preliminary FTIR investigation of surface species seen on impregnation and sol-gel single step catalysts. FTIR in situ reaction studies show that organic nitro and organic nitrite species appear to be present under reaction conditions on the SG-Pt catalyst surface. In comparison, on impregnation made Pt catalysts, isocyanate species were also present (11,12). So far the results obtained with all the catalysts appear to be very reproducible within experimental error $(\pm 2\%)$ over a period of several months. The reproducibility error in selectivity at low conversions (<10%) is higher because of the very low concentrations of N₂O measured. We have also successfully synthesized several different batches of the SG-Pt catalyst which show the same enhanced selectivity with respect to N_2 in NO_x reduction by hydrocarbons.

CONCLUSIONS

We have shown that it is possible to make a highly selective alumina-supported Pt catalyst for the reduction of NO_x by propene under oxidizing conditions by changing the preparation procedure. This new procedure narrows the temperature window on the low temperature side while increasing the selectivity dramatically. Preliminary studies show that addition of water widens the temperature window on the high temperature side without negatively affecting the conversion or selectivity. We are continuing our studies of N₂ selectivity enhancement for Pt catalysts prepared by the sol-gel method. We are also in the process of using other surface science techniques such as XPS and electron microscopy to further understand the differences between the catalysts and will report on our other findings in the near future.

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