

LEAN NO_x REDUCTION OVER Au/ γ -Al₂O₃

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Introduction

The 1990 Clean Air Act Amendment has set a schedule for compliance of new, more stringent standards for automobiles over the next ten years. In the mean time, the strong push to increase fuel economy of vehicles has led to the exploration of the use of lean-burn, gasoline engines. Unlike conventional engines, these engines operate with a large excess of air. The major obstacle in the development of such engines is the lack of a practical exhaust catalyst for the reduction of NO_x emission, since the current three-way catalysts are ineffective for NO_x removal in the oxidizing atmosphere (i.e. under lean conditions) of the exhaust of such engines.

The discovery of Iwamoto (1) and Held (2) et al., showing that Cu-ZSM-5 catalyzes the selective reduction of NO by hydrocarbons in an oxidizing atmosphere, promoted extensive research in this area. Although this catalyst is active and selective, it has hydrothermal stability problems, due to the degradation of the zeolite framework (3). Since zeolites are metastable structures, the problem of hydrothermal stability may be circumvented by the use of metal or metal oxide supported on thermally stable, large surface area oxides, such as γ -Al₂O₃. The use of base metals such as copper are not suitable because they form compounds with alumina at high temperatures. Extensive work on the supported Pt group metal catalysts (4,5) suggests that, although these catalysts may be potential practical catalysts for diesel engines, their optimum range of operation temperatures (200-300 °C) is too low for the lean-burn engines.

A brief report by Haruta et al. (6), showing that a 1 wt. % Au/ γ -Al₂O₃ catalyst, prepared by the precipitation-deposition method, has an NO conversion of 40% in the presence of 1.8% H₂O and 5% O₂ at 300°C, suggests that Au could be a potential component of a practical lean NO_x catalyst. Furthermore, it has been demonstrated by Haruta et al. (7) and Parravano et al. (8) that the Au particle size is strongly dependent on the preparation method, and that the particle size of the Au catalyst has significant influence on both the catalytic and chemical properties of Au. Thus, an investigation of Au/ γ -Al₂O₃ (the dependence of its catalytic properties on the preparative methods and its hydrothermal stability) as potential lean NO_x catalysts may be fruitful.

Experimental Procedures

γ -Al₂O₃ support was prepared by hydrolyzing aluminum isopropoxide (99.99+ % Aldrich) dissolved in 2-methylpentane-2,4-diol (99+ % Aldrich) using the method of Masuda et al. (9). It was dried in air at 100°C and calcined in flowing dry air to 460°C, and then in 2.4% H₂O to 700°C at a ramping speed of 1°C/min. Then the γ -Al₂O₃ was sintered in 7% H₂O for an additional 2 hrs at 700°C. The average surface area of such preparations ranged from 215-240 m²/g.

Co-precipitated Au/ γ -Al₂O₃ was prepared from a solution of HAuCl₄ (99.999% Aldrich) and Al(NO₃)₃ (99.997% Aldrich) using 1 M Na₂CO₃ as the precipitating agent (10). The catalyst was suction filtered, washed and calcined at 350°C for 4 hrs.

Deposition-precipitation of Au/ γ -Al₂O₃ was conducted in a manner similar to that of Haruta et al. (10). This involved the reaction of Au with the support in the presence of Mg citrate. 50 mL of 5.32 mM solution of HAuCl₄ was mixed with 2.5 g of γ -Al₂O₃ powder. The initial pH on mixing γ -Al₂O₃ and HAuCl₄ was 4.01 and the pH 4.4 sample was prepared without adjusting the pH (the value 4.4 being that recorded just before the addition of Mg citrate). For the rest of the samples, the solution was adjusted to the desired pH with Na₂CO₃ or HNO₃. After

the desired pH was achieved, the solution was stirred for half an hour before the addition of Mg citrate. The molar ratio of Mg/Au was 2.5. The reaction was allowed to proceed in the dark with continuous stirring for 2 h after the addition of γ -Al₂O₃ to the Au solution. Then the suspension was suction filtered, redispersed in room temperature doubly distilled H₂O, stirred briefly and suction filtered. This washing procedure was repeated two more times with cold H₂O and once with hot H₂O (about 80°C). The filtered paste was placed in a 100°C drying oven for about 2 h, gently crushed and placed in a 350°C oven for 4 hrs., and finally activated in a reaction mixture of NO, C₃H₆ and O₂ at 450°C. The last procedure was used because sometimes activity increases were observed with time on stream at high temperatures.

The lean NO_x reaction was conducted in a feed of 1000 ppm NO, 1000 ppm C₃H₆, 4.8% O₂ and 1.6% H₂O with the balance He. The weight of the catalyst was 0.5 g and the total flow rate was 104 cc/min. The catalysts were evaluated with respect to three parameters: the maximum NO conversion, the temperature of maximum NO conversion and the NO competitiveness factor at the maximum NO conversion. The NO competitiveness factor is a measure of the efficiency of the catalyst to use NO instead of oxygen in the oxidation of propene and is defined as $\text{NO}_{\text{reacted}} \cdot 100 / (9 \cdot \text{C}_3\text{H}_6_{\text{reacted}})$, where 9 is the number of oxygen atoms needed to convert C₃H₆ completely to CO₂ and H₂O.

The Au and Al contents were determined by ICP. It has been reported (11) that the dissolution of Au required a solution containing a good ligand for Au as well as an oxidizing agent. Thus HCl was added to provide the chloride ligand, and HNO₃ was added as the oxidizing agent. However, γ -Al₂O₃ would only dissolve with the further addition of concentrated HF. Thus all three acids were needed.

The Cl⁻ concentration was determined using Quantab titrators (Fisher Scientific). The accuracy of the titrators were verified using different concentrations of NaCl solutions.

Results and Discussion

The deposition-precipitation method is a multistep process, it involves (a) hydrolysis of AuCl₄⁻ anion to a mixture of [AuCl₃(OH)]⁻, [AuCl₂(OH)₂]⁻ and [AuCl(OH)₃]⁻, (b) adsorption of the negatively charged [AuCl_{4-x}(OH)_x]⁻ species onto the positively charged sites on the oxide surface, and subsequent formation of Al-O-Au bond by the condensation of the OH groups on the γ -Al₂O₃ and OH ligand of the Au complex, (c) polymerization of the surface Au complex through further reaction of the OH groups of the adsorbed Au complex with other Au species in solution, and (d) addition of Mg citrate to physically block the adsorbed Au polymeric clusters from coagulating. Each of these steps could affect the final Au particle size through their influence on the relative rates of condensation and polymerization. Of all the preparation variables, the pH of the solution appears to be of primary importance as it controls both the number of adsorption sites on the γ -Al₂O₃, and the distribution of the various Au complexes in solution.

The isoelectric point (IEPS) of γ -Al₂O₃ ranged from 6.5 to 9.4 (12). As the pH of the solution deviates from the IEPS towards the more acidic regime, the positive charge density on the alumina surface increases. This translates to more condensation sites for the anionic Au complexes, and thus higher uptake of Au.

The nature of [AuCl_{4-x}(OH)]⁻ in solution as a function of pH was determined by measuring the Cl⁻ concentration in solution. Surprisingly, the hydrolysis of the AuCl₄⁻ complex was very rapid in the range of pH 4-8, resulting in an average replacement of 2.6 Cl⁻ ligands by OH⁻ ligands per Au complex within half an hour of reaction. Longer reaction time did not increase the Cl⁻ concentration in solution. Thus it appears that the effect of pH is primarily in the determination of the number of condensation sites for Au on γ -Al₂O₃. Since the lower pH preparations have more nucleation sites, it is possible that the average Au particle sizes are smaller on such preparations.

Table I shows the % Au deposited on γ - Al_2O_3 as a function of the pH of preparation solution (if all of the Au in solution was deposited onto the γ - Al_2O_3 , a Au loading of 2.5% was expected). The pH 4.4 sample (one with no adjustment of pH) had the highest Au loading and the Au loading decreased with increasing pH. This is in accordance with the fact that the density of positively charged sites on the support surface decreases with increasing pH. The pH 4.0 sample, for which the pH was maintained by continuous addition of HNO_3 , had a lower Au loading, possibly because of the competitive adsorption of the anionic NO_3^- ions and the dissolution of alumina.

Table I: Effect of pH during Au Precipitation on NO Reduction Activity

pH	4.0	4.4	5.5	7.0	8.2
Au loading, wt. %	1.3	1.8	1.7	1.4	1.0
Temp. °C at max NO conv.	385	385	365	365	365
Max. NO conv. %	33.3	42.4	45.1	33.5	28
NO competitiveness factor, %	3.8	5.1	4.4	3.6	2.8

The temperature of maximum NO conversion is usually a reflection of how active a lean NO_x catalyst is. At this temperature, the hydrocarbon conversion is close to or at 100%. The Au samples with the highest Au loading (pH 4.4) had the highest temperature of maximum NO conversion. Assuming that this sample also had the smallest particle size, then the activity of the catalyst is probably dependent on the particle size of Au. Interestingly, the NO competitiveness factor of the various samples also decreased with increasing pH of the preparation solution. This suggested that the effectiveness of the catalyst in the reduction of NO_x might be related to the particle size of Au also.

These samples, prepared by deposition-preparation method, were compared with a sample prepared by co-precipitation. The Au content of the co-precipitated sample was 0.33%, although it was prepared with a solution which would result in a 2% Au loading if complete precipitation of Au was achieved. This sample reduced NO exclusively to N_2O ; showing a 24% conversion of NO to N_2O and 70% conversion of C_3H_6 at 375°C. Although the Au loading of this catalyst is low, a 0.21% Au sample prepared by the deposition-precipitation method converted NO exclusively to N_2 . Thus, different preparation method resulted in catalysts with different lean NO_x behavior. Besides the possible structural difference that may contribute to this difference in catalytic behavior, the presence of Na^+ may also be a factor. The co-precipitated catalysts has substantially more Na^+ left over left in the sample after washing.

An essential property of a practical lean NO_x catalyst is high hydrothermal stability. The stability of a 1 g sample of a 1.0% Au/ γ - Al_2O_3 prepared by the deposition-precipitation method was tested in a lean NO_x reaction mixture with 1.5% H_2O for 22 h between 400 and 500°C, and then at 500°C for 7 more hours with the water in the feed increased to 6%. No deactivation was observed. However, in a more stringent test using only 0.5 g of the 1% Au sample and 9% water in the feed, a 19% decrease in activity was observed after 8 h of reaction at 500°C, and another 20% decrease after another 8 h.

Conclusions

The activity and selectivity of supported Au catalysts varies with the pH of the solution during preparation in the deposition-precipitation method. These catalysts are superior to that prepared by the co-precipitation method. The Au/ γ - Al_2O_3 catalysts showed unexpectedly high stability

under reaction conditions at high temperatures and high water concentrations. Thus, Au supported on γ - Al_2O_3 has the potential of being an important component of a practical lean NO_x catalyst.

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