Structural Investigation of the Promotional Effect of Hydrogen during the Selective Catalytic Reduction of NOx with Hydrocarbons over Ag/Al₂O₃ Catalysts

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In situ EXAFS has been used to examine the hydrogen effect on the selective catalytic reduction of NOx over silver/alumina catalysts. For all SCR conditions used, with or without co-reductant (H₂ or CO), the catalyst structure remained the same. Significant changes in the catalyst were only found under reducing conditions. The enhanced activity found in the presence of hydrogen is thought to be due to a chemical effect and not the result of a change in the structure of the active site.

Introduction

The selective catalytic reduction (SCR) of NOx with hydrocarbons has been the focus of much research[1] since Iwamoto et al.[2] and Held et al.[3] first recognized that small quantities of unburnt fuel in lean burn engine exhaust streams could be used to reduce the pollutant NOx to N₂. It is now well established that Ag/Al₂O₃ catalysts are among the most active and selective for the SCR reaction,[1] and recently it has been found that the addition of hydrogen to the feed stream can result in a remarkable improvement in the level of NOx reduction and the range of temperature over which NOx can be selectively reduced.[4] Since then several authors have investigated this "hydrogen" effect using different catalyst formulations and different gas mixes.[5−11] It is clear from this research that hydrogen can promote the reaction when using a variety of alkanes and alkenes and that (to date) this effect is unique to silver and to specific Ag/support combinations, namely, Ag/γ-Al₂O₃ and Ag/MFI. However, the mechanism by which the hydrogen promotes the reaction has not been clearly elucidated and is the subject of some debate. Satokawa and co-workers[4−8] proposed a Ag cluster model and they used UV−vis spectroscopy to show that during the SCR reaction (in the absence of H₂) the silver in a low loading Ag catalyst is predominantly in the form of isolated Ag⁺ ions. However, it was noticed that the addition of small concentrations of hydrogen (<1%) promoted the formation of small clusters of $Ag_n^{\delta+}$ ($2 \leq n \geq 4$). They argue that it is the $Ag_n^{\delta+}$ clusters that are responsible for the high activity of the Ag-based catalysts (Ag/MFI and Ag/γ-Al₂O₃). Richter et al.[10] also invoke the importance of Ag₂O/Ag⁰ nanoclusters in their interpretation of the reaction mechanism. In an earlier publication,[11] we proposed that the enhancing effect of hydrogen was not due to Ag cluster formation. Instead, we proposed that the hydrogen reacts directly either to promote the formation and storage of a reactive species which can then readily reduce NOx or alternatively to remove a species which acts as a poison to the SCR reaction at low temperatures.

In this paper, we use in situ EXAFS to show that the hydrogen effect is not associated with significant structural changes in the Ag/Al₂O₃ catalyst studied.

Experimental Section

Catalyst Preparation and Testing. The catalyst was prepared by the impregnation of Al₂O₃ with a silver nitrate solution followed by drying and calcination to give a sample with a Ag metal loading of 2 wt %.[12] Catalyst testing was performed in a quartz tubular downflow reactor (i.d. 5 mm). A total of 0.083 g of catalyst (with particle sizes ranging from 250 to 850 μm) was held in place between two plugs of quartz wool and a thermocouple was placed in the center of the catalyst bed. The reactant gases, NO, CO₂, H₂, CO, and O₂, and the carrier gas, He, were fed from independent mass flow controllers. Octane and water vapor were introduced to the system by means of two separate saturators placed in ice/water baths. The O₂, CO₂, NO, and He gas mix passed through the water saturator, He from another flow controller and H₂ or CO (when added) passed through the octane saturator. The exit lines from both saturators were connected and passed directly to the catalytic reactor. The same system was used to introduce the gas mix to the in situ EXAFS cell. In these studies, NOx conversion is defined as the reduction of NO and NO₂ to N₂ and N₂O. The NO and total NOx were determined by a Signal 4000 series chemiluminscence detector. The experimental conditions for the SCR reaction were 720 ppm NO, 4.3% O₂, 0.53% H₂O, 7.2% CO₂, 543 ppm C₈H₁₈, balance He. When co-reductant was present either 0.72% H₂ or CO was added. The total flow rate of gases was 100 cm³ min⁻¹.

Extended X-ray Absorbance Fine Structure (EXAFS) Spectroscopy. Data were collected at the Synchrotron Radiation Source in Daresbury, U.K., using station 9.3. The transmission detection mode was used with two ionization chambers filled with argon. The spectra were recorded at the Ag K edge using a double crystal Si(220) monochromator. Scans were collected and averaged using EXCALIB which was also used to convert raw data into energy vs absorption data. EXBROOK was used to remove the background. The analysis of the EXAFS was

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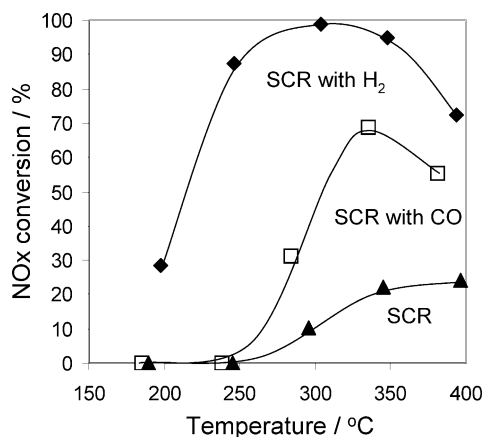
Figure 1. NOx conversion as a function of reaction temperature for the SCR reaction over a 2 wt % Ag/Al$_2$O$_3$ catalyst. Reactant composition: 720 ppm NO, 4.3% O$_2$, 0.53% H$_2$O, 7.2% CO$_2$, 543 ppm C$_8$H$_{18}$, balance He (▲); with 0.72% H$_2$ added (◆); with 0.72% CO added (□).

Figure 2. Comparison of the experimental (solid line) and fitted (dashed line) *pseudo*-radial distribution (lower) functions from 2%Ag/alumina (a) as received, under SCR reaction conditions at 225 °C with (b) no co-reductant (c) 0.72% hydrogen and (d) 0.72% carbon monoxide and (e) at 225 °C in 8% hydrogen/helium (× 0.333).

performed using EXCURV98[13] on the k^3 weighted raw data using the curved wave theory. Phaseshifts were derived from ab initio calculations using Hedin-Lundqvist exchange potentials and von Barth ground states and backscattering amplitudes from experimentally determined data on known standards. The catalyst was pressed into a pellet and supported on a stainless steel holder in a glass in situ EXAFS cell with Kapton windows. The cell was surrounded by a furnace controlled using a Eurotherm PID controller with thermocouples in the furnace and on the sample.

Results and Discussion

Figure 1 clearly shows that the addition of hydrogen has a remarkable effect in promoting the conversion of NOx to N$_2$ and N$_2$O. Substitution of H$_2$ by CO shows that, although there is an enhancement at higher temperatures, at temperatures below ca. 250 °C, the replacement of H$_2$ by CO does not give any enhancement in activity. To investigate the effect of the different feed conditions on the structure of Ag in the catalyst, in situ Ag K edge EXAFS was carried out. The EXAFS data was taken at 225 ± 1 °C; at this temperature, NOx conversion was >60% when H$_2$ was added to the feed, but the catalyst was inactive for the reaction with no co-reductant and also when CO was added.

The EXAFS and related pseudo radial distribution functions (rdf) for the fresh catalyst, and under SCR reaction conditions with and without CO or H$_2$ as the co-reductant, are similar (Figure 2). The main feature in the rdf is associated with a Ag−O distance at ca. 2.2 Å with an additional peak at 2.6−2.8 Å assigned to Ag−Ag (Table 1). Although the uncertainty is high in the coordination numbers as evidenced by the high Debye−Waller factors for each shell, the data indicate that, on exposing the catalyst to SCR reaction conditions, the average Ag−Ag coordination number increases compared with the fresh catalyst. On average over a wide range of conditions and temperatures, the coordination is 2.2. In contrast, for the Ag−O shell, no change is observed on exposing the fresh catalyst to SCR conditions. Under all of the SCR conditions, the EXAFS only showed significant oscillations below $k = 8$ Å^{-1}. However, on switching the atmosphere to a reducing environment, a dramatic change in the EXAFS is observed. In a feed of 8% hydrogen in helium at 225 °C, the rdf indicates no Ag−O coordination, as expected, and a Ag−Ag coordination in the first shell of approximately 4.5. The XANES also shows a
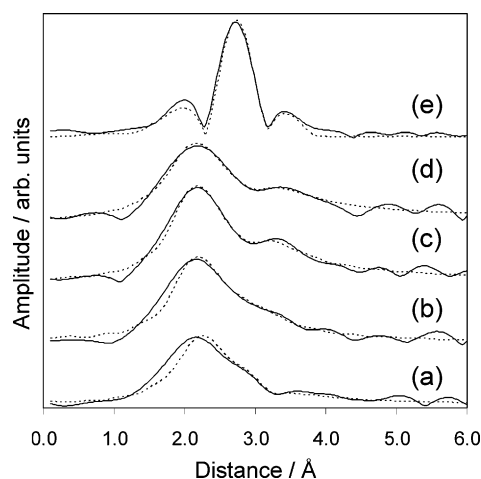
TABLE 1: Structural Parameters from the Fitted EXAFS Spectra for the Catalysts Described in Figure 2a−e[a]

catalyst	atom	shell distance/ Å	coordination number	Debye−Waller factor/Å^2	fit factor/ %
a	O	2.35	1.6	0.048	42.1
	Ag	2.80	0.8	0.051	
b	O	2.25	1.6	0.039	32.4
	Ag	2.69	2.0	0.062	
c	O	2.25	1.8	0.042	24.7
	Ag	2.68	2.4	0.066	
d	O	2.24	2.0	0.053	29.6
	Ag	2.69	2.6	0.075	
e	Ag	2.81	4.5	0.036	30.4
	Ag	3.52	0.5	0.029	

[a] The data for catalysts a−d were fitted between $k = 3−10$ Å^{-1} and the data for catalyst e were fitted between $k = 3−13$ Å^{-1}.

significant shift and a reduction in the white line intensity as expected from a decrease in the oxidation state of silver. This transformation is reversible. Switching the atmosphere back to the SCR mixture resulted in the original catalyst structure being regenerated.

A number of previous studies have described EXAFS data on ZSM-5, MFI, mordenite, and alumina-supported silver catalysts.[7,14−16] As found in the present study, when supported on alumina, predominantly Ag−O coordination was observed for both the fresh catalysts and those under SCR conditions using propene at 500 °C in the absence of co-reductant. Similarly large Debye−Waller factors were fitted to the data and this was attributed to a high degree of heterogeneity in the silver sites on the catalyst. In contrast, when supported in MFI, predominantly silver clusters were observed in the EXAFS both after reduction at 500 °C and during the SCR reaction with hydrogen as the co-reductant at 300 °C.[7] It is noticeable that, as in the alumina samples reported herein, an increase in the Ag−Ag coordination is observed in MFI supported catalysts on changing from an oxidizing to a reducing environment. Unlike in MFI, mordenite based catalysts showed Ag−O coordination under SCR conditions in the presence of hydrogen. The MFI catalysts showed a strong hydrogen effect on the SCR activity whereas the mordenite-based catalyst showed little activity even in the presence of hydrogen.

Letters

J. Phys. Chem. B, Vol. 109, No. 11, 2005 **4807**

The EXAFS data presented in this study are consistent with the UV−vis data which showed the formation of $Ag_n{}^{\delta+}$ clusters under SCR conditions in the presence of hydrogen. From the coordination numbers, the EXAFS indicates that the cluster size is ca. 3, in agreement with Satokawa and co-workers.[4−8] However, it is clear that the changes in reactivity of the catalyst as a function of the co-reductant cannot be explained by the formation of $Ag_n{}^{\delta+}$ clusters. Although these clusters are formed under SCR conditions, as evidenced by the small increase in the Ag−Ag coordination number compared with the fresh catalyst, removal of co-reductant, or substitution of H_2 by CO, does *not* result in any significant structural changes, yet there is a dramatic loss of catalytic activity. Moreover, under all SCR conditions used between 225 and 330 °C, no change was observed in the EXAFS.

In conclusion, the EXAFS clearly show that, although silver clusters may be formed during the SCR of NOx and could be the active site, other factors, such as a direct chemical effect of the co-reductant with the active site, are more important in determining the activity of the catalyst.

Supporting Information Available: Fitted EXAFS spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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