

Selective Catalytic Reduction of NO_x with Hydrocarbon Fuels as Reductants

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Introduction

The reduction of nitric oxide to dinitrogen typically involves two main steps: the oxidation of NO to NO₂ and the reduction of NO₂ to N₂. Single catalysts, such as Cu-ZSM-5 or Pt/Al₂O₃, have the ability to perform these two tasks sequentially [1,2]. Researchers have also approached this set of reactions with bifunctional catalysts. In this type of materials an active component is optimized for the oxidation of NO while a second component is reserved for the final reduction of NO₂. That is the case for two metals co-impregnated on a support, zeolites co-exchanged with two metals, or even, physical mixtures of catalysts. When the two reactions are suitably overlapped, an enhancement in activity not observed in the individual components can be produced.

Cerium oxide is known to promote oxidation reactions, including the oxidation of NO to NO₂. Bifunctional catalysts have been produced by adding cerium to zeolites known to catalyze NO_x reduction. Different approaches have been used to accomplish this bifunctionality. Some include cerium ions co-exchanged in Cu-ZSM-5 for NO decomposition and in Ag-ZSM-5 for CH₄-SCR [3,4]. In other cases, composites of ceria and In-ZSM-5 have been prepared via physical mixtures or precipitation of cerium hydroxide onto the surface of the zeolite for CH₄ and C₃H₈-SCR [5]. The results vary with the type of reaction. In some cases the temperature of maximum activity is lowered by about 50 °C relative to the unmodified catalyst, while in others the activity at high temperature is enhanced. Longer stability towards hydrothermal zeolite degradation has also been reported.

Our group has recently reported a novel approach for the preparation of this type of bifunctional catalysts [6]. By impregnating a metal-exchanged zeolite with a metal oxide colloidal sol, a fine coating of oxide is produced on the zeolite surface. The method produces not only a unique topology and physical structure of the catalyst at the submicron level but also maximizes the benefits already observed in other materials with similar active component combinations. In particular, CeO₂/Cu-ZSM-5 prepared this way shows a temperature drop for its activity maximum of 150 °C under wet C₃H₆-SCR conditions relative to the native Cu-exchanged zeolite. As in other combinations of Cu-ZSM-5 and cerium, the coated catalyst also shows better stability than Cu-ZSM-5 towards hydrothermal zeolite degradation. In addition, the deNO_x activity displayed by the coated catalyst is enhanced in the presence of water, which is a unique property among modified Cu-ZSM-5 catalysts.

In this work the interaction of the active components in the coated system is studied by in situ X-ray absorption near edge spectroscopy (XANES). Coupled to other standard analytical techniques such as temperature programmed reactions (TPR) and thermogravimetric analysis (TGA), the means by which this catalytic system displays the observed benefits are established.

Methods and Materials

In situ X-ray absorption spectroscopy (XAS) studies were performed at the Materials Research Collaborative Access Team (MR-CAT) beamline (10-ID) at the Advanced Photon Source (APS). Cu-K and Ce-L3 edge XAS spectra were collected in transmission mode, with the X-ray beam passing through ionization chambers filled with N₂ before and after the sample cell. The energy was selected with a cryogenic double-crystal Si(111) monochromator; an uncoated glass mirror reduced higher order harmonics. Approximately, 20mg of up to four samples were loaded as self-supporting wafers into a 0.50 in. multi-sample metal holder with four individual 0.16 in. diameter holes. The holder was placed into a quartz sample tube (3/4 in. o.d.), centered in a clam shell furnace, described by Neylon et al. [7]. The sample temperature was measured by a thermocouple positioned near the sample holder inside the quartz tube. Before moving the sample cell onto the beamline, the samples were treated off-line in air (TPR) or H₂ (4%) in He (TPO) up to 500 °C for at least an hour. Once on-line, the four samples were scanned sequentially using a precision motion stage. The samples in the cell were heated up to 600 °C with a temperature ramp of 2 °C/min under a 30 sccm flow of H₂ (4%) in He (TPR) or dry air (TPO). Scans of all samples were recorded every 2–3 min during the reaction with 40–60 spectra per sample collected during each run. In addition, a Cu foil reference spectrum was collected for energy calibration using a third ionization chamber.

Factor analysis was used to analyze the data from the TPR and TPO runs in the XANES region of the Cu and Ce edges [7]. The energy of the Cu-edge spectra was calibrated using the reference Cu foil transmission spectrum to better than ±0.05 eV relative offset. The spectra were normalized and cubic splines were used to convert each spectrum to a constant energy grid at 0.5 eV increments. The normalized discrete data was collected in a matrix, and singular value decomposition was used to find the associated eigenvalues and eigenvectors. Iterative key set factor analysis (IKSFA) [8] was used to determine which of the initial XANES data sets were most fundamental, and the other data in the set were fitted using a least squares

Results

H₂-TPR, is shown in Fig. 1. The different oxidation states of copper have unique features in the XANES region (Fig. 1c) [7]. Cu²⁺ shows a single peak just in the post-edge region with a very weak pre-edge feature at 8785 eV. A strong pre-edge feature dominates the Cu¹⁺ XANES spectra at 8983 eV and Cu⁰ shows a doublet after the edge and some weak features. Visual inspection of these XANES traces easily shows the transformation of Cu²⁺ → Cu¹⁺ → Cu⁰ at expected temperatures for Cu-ZSM-5. A comparison between the waterfall plots indicates that, in the case of CeO₂/Cu-ZSM-5, both Cu redox transitions (Cu²⁺ → Cu¹⁺ → Cu⁰) occur at least at 50 °C lower temperatures. Similar XANES experiments monitoring the Ce-L3 edge of CeO₂/H-ZSM-5 and CeO₂/Cu-ZSM-5 are shown in

Fig. 2. Ce^{4+} shows a strong doublet in the post-edge region while Ce^{3+} is comprised of only a single peak (Fig. 2c).

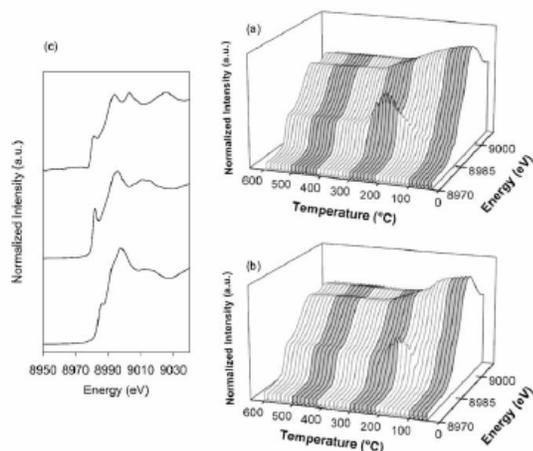


Figure 1. TPR of (a) Cu-ZSM-5 and (b) $CeO_2/Cu-ZSM-5$ as detected by the Cu-K edge in XANES. The peak at 8983 eV corresponds to Cu^{1+} . Insert (c) displays the XANES profile from top to bottom of Cu foil, Cu_2O and CuO.

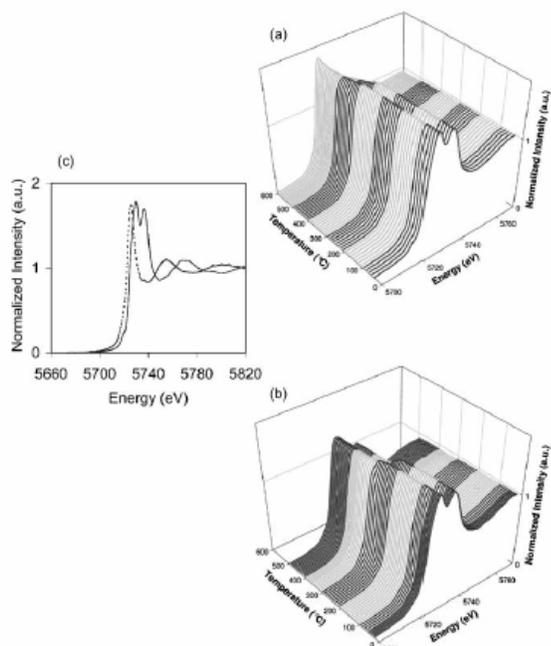


Figure 2. TPR of (a) $CeO_2/H-ZSM-5$ and (b) $CeO_2/Cu-ZSM-5$ as detected by the Ce-L3 edge in XANES. The insert (c) shows the XANES absorption profile for CeO_2 (solid line) and $Ce(NO_3)_3$ (dotted line).

As with the Cu XANES, the transformation from Ce^{4+} to a mixed oxidation state is apparent for both samples. For the $CeO_2/H-ZSM-5$ sample, this reduction starts near 400 °C, in agreement with the previous H_2 -TPR runs. For the bifunctional sample, the reduction appears to start near 275–300 °C and is completed by 350 °C.

Discussion

Results obtained by TPR and XAS definitely show an interaction between copper and cerium atoms. H_2 -TPR experiments reveal a new hydrogen absorption event at low temperatures (150 °C) not displayed by the individual phases of the catalyst or by $CeO_2/H-ZSM-5$. This low temperature peak

resembles those observed in the H_2 -TPR of doped ceria [9]. In particular, doping of ceria with CuO has been found to increase the reducibility of ceria significantly [10].

In situ XANES analysis allows the direct observation of the state of both metals during a similar temperature programmed reduction with H_2 . The results shown in Figs. 1 and 2 confirm the proposed Ce–Cu interaction. Not only is the cerium reducibility drastically affected when in contact with Cu-ZSM-5 (partial reduction of ceria occurs at 100–125 °C lower temperature than in $CeO_2/H-ZSM-5$) but also the copper redox transitions take place at lower temperatures in the bifunctional catalyst relative to Cu-ZSM-5. The fact that, in the case of cerium, only a partial reduction is observed is in agreement with a model of two different types of cerium atoms: those on the interface actually interacting with the zeolite and those on the external ceria crystals of the coating. Thus, the reducibility of a significant fraction of both metals (Cu and Ce) appeared to have been modified during the coating procedure. It is unclear if the higher reducibility of Cu comes from the same Ce–Cu interaction that lowers the redox potential of Ce. Still, the ability to be reduced at lower temperatures is a relevant catalyst benefit since the oxidative activation of NO and the hydrocarbon can take place at lower temperatures and thus shift the overall HC-SCR activity.

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References

1. M. Guyon, V. LeChanu, P. Gilot, H. Kessler, G. Prado, Appl. Catal. B: Environ. 8 (1996) 183.
2. R. Burch, T.C. Watling, Appl. Catal. B: Environ. 11 (1997) 207.
3. Y.P. Zhang, M. Flytzani-Stephanopoulos, in: J.N. Armor (Ed.), Environmental Catalysis, American Chemical Society, Washington, DC, 1994, p. 7.
4. Z.J. Li, M. Flytzani-Stephanopoulos, Appl. Catal. A: General 165 (1997) 15.
5. H. Berndt, F.W. Schutze, M. Richter, T. Sowade, W. Grunert, Appl. Catal. B: Environ. 40 (2003) 51.
6. M.K. Neylon, M.J. Castagnola, N.B. Castagnola, C.L. Marshall, Catal. Today 96 (2004) 53.
7. M.K. Neylon, C.L. Marshall, A.J. Kropf, J. Am. Chem. Soc. 124 (2002) 5457.
8. E.R. Malinowski, Factor Analysis in Chemistry, Wiley, New York, 1991.
9. M.F. Luo, Y.J. Zhong, X.X. Yuan, X.M. Zheng, Appl. Catal. A: General 162 (1997) 121.
10. P. Bera, K.R. Priolkar, P.R. Sarode, M.S. Hegde, S. Emura, R. Kumashiro, N.P. Lalla, Chem. Mater. 14 (2002) 3591.

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