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A new metal exchanged zeolite for a present environmental problem. An in-situ XAS study.

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Abstract. The medium pore zeolite, TNU-9, is prepared and studied for the selective catalytic reduction (SCR) of NO using C_3H_8 as the reducing agent. The catalytic activity of TNU-9 zeolites for the SCR is comparable to other known highly active zeolites but with the advantage of TNU-9 of having almost the same catalytic performance in the presence of H_2O during reaction. The nature and behaviour of Cu and Co active sites contained in the TNU-9 catalysts have been studied under operation conditions using X-ray Absorption Spectroscopy (XAS) to understand the key parameters controlling the performance of this reaction.[1] It was found that the well dispersed Cu and Co centres need to be in a mixed valence state to obtain good catalytic results for the SCR and that the catalytic performance is related to the topology of the TNU-9 itself.

1. Introduction

The current tendency of modern petrol–fuelled and diesel cars is to run under high oxygen to fuel ratios to maximize fuel efficiency. This operation mode makes impossible the use of the traditional three-way catalysts in future mobile sources which are not able to fulfill the emission regulations of NO_x. An alternative to that is the selective catalytic reduction (SCR) of NO_x with hydrocarbons in the presence of O_2 [1,2]. Some medium and large metal exchanged zeolites have shown to catalyze the reduction of NO_x with hydrocarbons such as propane, propylene and ethylene [1-3]. Nevertheless, the catalytic performance strongly diminishes in the presence of water, SO_2 or after a hydrothermal treatment of the original catalyst, probably due to a modification of the environment of the copper active sites and to the low hydrothermal stability of the material [4].

Our group has found that a new medium pore size zeolite, TNU-9, when exchanged with Cu or Co ions present a high activity towards the reduction of NOx with propane under realistic working conditions. Additionally, the zeolite presents high resistance to water decomposition, especially when exchanged Co is present as balancing cation, which makes the catalyst a potential candidate for on-board applications.

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[1] The full description of this work has been recently accepted for publication in Journal of Catalysis.

To the best of our knowledge, the nature and behaviour of the metallic active sites of Cu and Co containing TNU-9 catalysts have been studied for the first time under operation conditions using X-Ray Absorption Spectroscopy at the Cu and Co K-edges. The catalytic and structure-electronic results of the metal containing TNU-9 are compared with the best reported zeolites for NO_x SCR.

2. Experimental

TNU-9 was synthesized following the procedure described in [5].

The metal exchange was performed in an aqueous solution containing appropriate concentrations of $Cu(CH_3COO)_2$•$4H_2O$ or $Co(CH_3COO)_2$•$4H_2O$ to achieve the desired amount of metal in the zeolite (2-3 wt%) and a degree of interchange above 70%.

The surface area and micropore volume of the catalysts were determined from the adsorption branch of the isotherms by applying the BET equation and the t-plot formalism, respectively. The catalysts retain most of their micropore volume and surface area upon cationic exchange indicating that no pore blocking, or zeolite destruction, takes place during catalyst preparation.

X-ray absorption spectra (XANES and EXAFS) at the Co K-edge (7709 eV) were collected on the Super-XAS beamline at the Swiss Light Source (SLS). XANES spectra at the Cu K-edge (8978 eV) were taken on BM25 (SpLine beamline) at the ESRF. In both cases, a double crystal Si(111) monochromator, detuned by 50% to reject higher energy harmonics, was used to select the X-ray radiation energy. The measurements were performed in transmission mode and ionization chambers recorded the intensity signal of the incident and transmitted X-ray beam. Co or Cu reference foils were measured in parallel for energy calibration. Other Co and Cu reference compounds were also measured by XAS during the experiment; *i.e.* CoO, Co_3O_4, $CoMoO_4$, $CoAl_2O_4$, $Co(CH_3COO)_2$•$4H_2O$, Cu_2O and CuO.

The NOx reduction was carried out in an in-situ cell built as a result of collaboration between the Instituto Químico de Valencia (ITQ; CSIC-UPV) and ALBA Synchrotron Light Facility. All parameters related to the experimental environment of the sample within the cell (temperature, pressure, cooling circuit, gas flows and mixtures, gas evacuation system and safety logic) were controlled by an integrated control unit built by the same groups [6]. The sample was presented as a pressed disk of 13 mm diameter. XAS measurements were carried out at ambient pressure and reproducing the same gas and temperature conditions as in the catalytic measurements. The sample was activated by heating it at 550 ^oC under He. The catalytic reaction was carried out at 450 ^oC with 700 ppm of NO_x and 390 ppm of C_3H_8 balanced in He. Different amounts of O_2 (0-14.5%) were introduced during the reaction. The total flow rate in all experiments was 120 mL•min^{-1}. A 10 min stabilization period was left between changes in gas composition and before collecting the absorption data.

EXAFS data analysis followed standard procedures using the software package Viper v. 10.1 for Windows [7].

3. Results and Discussion

In order to understand why certain medium pore zeolites, when exchanged with Cu or Co, are active towards the Selective Catalytic Reduction (SCR) of NOx with propane in the presence of O_2, is important to discern the electronic and structural changes occurring in the course of the activation and reaction on these catalysts. This in-situ approach allows correlating the catalytic performance with the structuro-electronic changes under the optimal reaction conditions.

For the case of the Cu exchange zeolites, in-situ XANES measurements at the Cu K-edge were performed. Inspection of the XANES spectrum of Cu-TNU-9 taken at RT in He (Figure 1) showed that on average the Cu centers in this zeolite are present as Cu(II). The absence of any pre-peak in the spectrum suggested that the local average structure is very symmetric around Cu, similar to the monomeric copper acetate structure in aqueous solution.

Following the experimental procedure for NO SCR catalytic testing of the Cu-catalysts, the Cu-TNU-9 sample was activated at 550^{o}C in He prior to XAS measurement. It was observed that, after heating at 550ºC, the Cu(II) sites were completely reduced to Cu(I) as shown by the characteristic red shift in Figure 2. Subsequently, the Cu-TNU-9 sample was brought to the reaction temperature (450ºC), with no change in the XANES region (Figure 2). The fact that the Cu-catalysts studied herein are not active under reaction conditions in the absence of O_2 (see Figure 3) suggests that the active sites in Cu-TNU-9 are not solely Cu(I) species. At the maximum conversion rate, when 0.33 % O_2 was added into the reaction feed, partial oxidation of the Cu(I) sites was observed, demonstrating that a mixed –or intermediate- oxidation state is necessary to attain high catalytic performance. XANES spectra of Cu-TNU-9 under reaction conditions (450 ºC, 700 ppm of NO_x and 390 ppm of C_3H_8) and different contents of O_2 are shown in Figure 4.

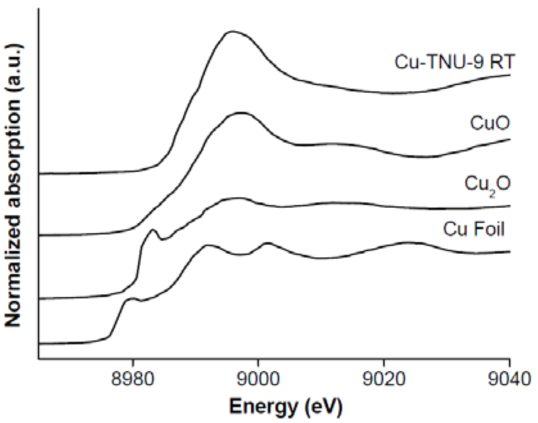

Figure 1. Cu K-edge XANES spectra of reference compounds (Cu foil, Cu_2O and CuO) and Cu-TNU-9 at RT.

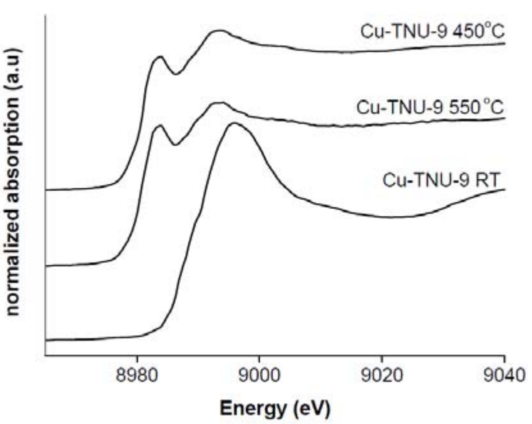

Figure 2. Cu K-edge XANES spectra of Cu-TNU-9 in He at different temperatures of catalyst treatment: RT, 550ºC and 450ºC.

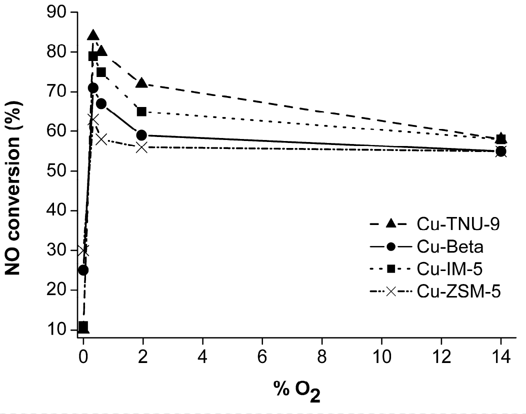

Figure 3. Influence of oxygen concentration on the SCR of NO with propane. (▲) Cu-TNU-9; (●) Cu-Beta; (■) Cu-IM-5; ( ) Cu-ZSM-5. Experimental conditions: 700 ppm NO, 390 ppm C_3H_8, N_2 as carrier, T= 450 ºC, total flow: 900 $ml.min^{-1}$, 0.6 gr. of catalyst.

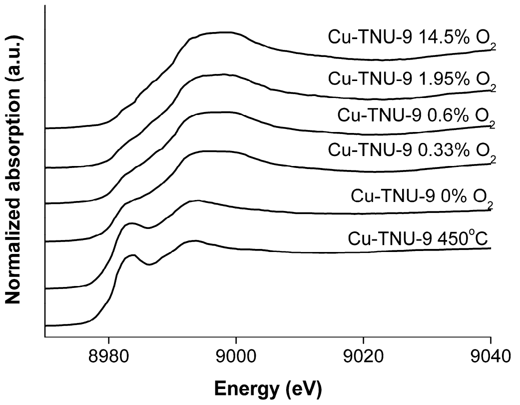

Figure 4. Cu K-edge XANES spectra of Cu-TNU-9 obtained under catalytic conditions (T= 450 ºC; 700 ppm NO and 390 ppm C_3H_8 balanced in He) and at different O_2 concentrations (0-14.5 %).

Figure 5 shows the Co K-edge XANES spectra of reference compounds with different oxidation states (Co^0, Co^{2+} and $Co^{2+/3+}$) and of the Co-TNU-9 at RT and after activation at 450ºC. The energy threshold and the XANES features show that at RT the Co-TNU-9 contains mostly Co(II) sites and that the average environment around Co is octahedral. After activation the threshold shift towards lower energies indicates that the Co sites are present in a reduced Co^{2-x} form. No Co metal particles were observed. The presence of a pre-edge peak suggests that at 450ºC the Co atoms occupy a 4-fold site, probably in a distorted tetrahedral environment.

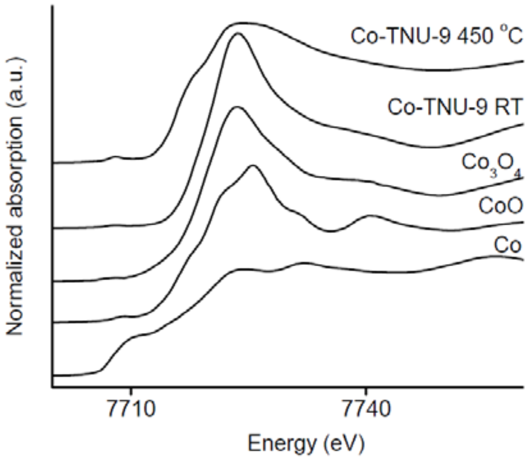

Figure 5. Co K-edge XANES spectra of reference samples (Co, CoO and Co_3O_4); and Co-TNU-9 at RT and at 450 °C in He.

When the zeolite was submitted to operation conditions under the required gas atmospheres of NO and propane, and different amounts of O_2 (0-14.5%) were flown, no apparent changes with respect to the sample at 450ºC were observed. Additional EXAFS spectra were acquired to see if there were perceptible changes at a structural level. The analysis of the EXAFS spectra obtained under working conditions were in agreement with the XANES observations, but no structural change was distinguished during the reaction. This analysis also showed that the zeolite contained isolated, or *quasi*-isolated, Co sites, highly dispersed across the channels of the zeolites, with no extraframework phase present.

4. Conclusions

In-situ XAS measurements of Cu and Co exchanged TNU-9 catalyst under real catalytic conditions were performed to understand the electronic and structural behavior of metal sites and to identify which are the key parameters on the catalyst activity for the SCR of NOx.

From these studies we could conclude that:

(a) the metal ions are well dispersed in the pores of the TNU-9 zeolite structure and are present as isolated or *quasi*-isolated small particles; as deduced from both XAS and XRD studies.

(b) during activation at 550°C in He the Cu and Co sites get reduced completely to Cu(I) and mostly to a reduced Co^{2-x} form, respectively. However, it is necessary the presence of metal centers having mixed valence state to obtain good catalytic results in this reaction.

(c) the catalytic reaction rate per unit of surface area is related to the topology of the TNU-9 itself.

Acknowledgements

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