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An in situ XAS study of Cu/ZrO_2 catalysts under de-NO_x reaction conditions

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Abstract

This paper reports an X-ray absorption spectroscopy investigation of the chemical state of copper in Cu/ZrO_2 catalysts under reaction conditions. The catalysts were subjected to different treatments with hydrocarbons (CH_4, C_3H_8, or C_3H_6) and hydrocarbon/NO and hydrocarbon/NO/O_2 mixtures. The analysis was done for samples heated in situ at temperatures ranging from 298 to 773 K. The first derivative of the X-ray absorption near-edge structure (XANES) spectra of the Cu K edge was analysed by factor analysis (FA). This analysis provided an accurate means of estimating the percentages of Cu^{2+}, Cu^{+}, and Cu^{0} under each reaction condition. Before reaction, the original catalyst consisted mainly of Cu^{2+} species. Heating the catalyst with the hydrocarbon to 573 K led to its partial reduction with formation of a significant amount of Cu^{+}. At the higher temperature, and depending on the hydrocarbon, Cu^{0} species were dominant. When the catalyst was treated at 773 K with mixtures consisting of hydrocarbons plus NO, there was still a significant concentration of Cu^{+} and Cu^{0} species, although the relative concentration of Cu^{2+} generally increased. For these gas mixtures, it was also found that the relative concentration of the three different oxidation states of copper was highly dependent on the type of hydrocarbon. In general, the concentration of reduced species was related to the reactivity of the hydrocarbon ($CH_4 < C_3H_8 < C_3H_6$) and was particularly high with C_3H_6. Finally, the analysis showed that most copper remained as Cu^{2+} when the sample was heated in a hydrocarbon/NO/O_2 mixture at 773 K, although some Cu^{+} can persist under these conditions. Some quantitative discrepancies were observed by comparing the results obtained by XANES/FA and those obtained by fitting analysis of the extended X-ray absorption fine structure spectra. However, the higher concentration of Cu^{+} species detected by XANES/FA analysis under working conditions is congruent with temperature-programmed reduction and X-ray photoelectron spectra experiments on this sample. It is concluded that the combination of these two procedures may yield more reliable information about the physicochemical state of the different Cu^{2+}, Cu^{+} and Cu^{0} species existing in the Cu/ZrO_2 catalyst under de-NO_x reaction conditions.

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1. Introduction

The selective catalytic reduction (SCR) of NO in the presence of oxygen and hydrocarbons has attracted much recent interest because of the significant environmental impact of this process [1,2]. Among the different catalyst and active phase formulations that have been proposed for this reaction, copper with zeolites or other oxide supports have been some of the most widely used options [3–5]. In these systems, a very important point of investigation is analysis of the role of copper in the catalytic reaction and, consequently, the determination of its actual chemical and coordination state under reaction conditions. Various methods, including electron spin resonance (ESR) [6], X-ray photoelectron spectroscopy (XPS) [7], Fourier transform infrared spectroscopy (FTIR) [8], and other techniques [9], have been used for this purpose. However, most of the experimental results have been obtained with after-treated samples, not during reaction conditions. X-ray absorption spectroscopy (XAS) can be applied to investigate catalysts under real working con-

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ditions of temperature and pressure [10]. Several works have been published reporting in situ XAS analysis of Cu-ZSM5 and other related copper-containing catalysts [11–13]. In the present investigation we applied in situ XAS to ascertain the chemical state of copper in a Cu/ZrO_2 catalyst that was previously probed as active for the SCR reaction with different hydrocarbons (methane, propane, and propene) as reductive agents [7,8,14]. The work is focused primarily on the development of a simple and reliable procedure for X-ray near-edge absorption spectra (XANES) that may provide a semiquantitative estimation of the different chemical forms of copper (i.e., Cu^{2+}, Cu^+, and/or Cu^0) under different working conditions (e.g., temperature, reaction mixture) of the catalysts. The procedure developed relies on the factor analysis (FA) technique and the first derivative spectra of the XANES spectra. Using FA to deal with XANES spectra of a Cu–Pd catalyst was proposed by Fernández-Garcia et al. [15]. More recently, other publications have reported the use of this mathematical procedure in both XANES [16] and extended X-ray absorption fine structure (EXAFS) [17]. In the present investigation, we propose using the first derivative of the XANES spectra as a more reliable and simple alternative for applying the FA method. Comparing the results with those obtained from fitting analysis of the EXAFS spectra of copper under the same working conditions allows us to calculate the relative concentration of the different chemical states of copper (i.e., Cu^0, Cu^+, or Cu^{2+}) existing in the catalysts for each reaction mixture and temperature of reaction. The high stability of Cu^+, detected even under oxidizing conditions, has been confirmed by temperature-programmed reduction (TPR) and XPS analysis.

2. Experimental and methods

2.1. Catalyst preparation

A Cu/ZrO_2 sample (3% weight of Cu) was prepared by wetting impregnation with a $Cu(NO_3)_2$ solution of a ZrO_2 powder prepared by forced hydrolysis [18]. For the preparation of ZrO_2, a 0.2 M solution of $ZrOCl_2$ placed on a sealed beaker was heated at 363 K for 70 h, then cooled rapidly with cold water. The suspension obtained was dialysed until chlorine ions were eliminated, centrifuged, and rinsed with distilled water several times. The resulting deposit was oven-dried at 323 K for 24 h. The resulting ZrO_2 presented a specific surface area, $S_{BET} = 50\ m^2\,g^{-1}$, after calcination at 673 K. Once impregnated, the solid was oven-dried at 373 K for 5 h, then calcined in a 100 $mL\,min^{-1}$ 3% O_2/He flow at 673 K for 3 h.

2.2. X-Ray absorption spectroscopy

XAS spectra were recorded at the BM29 beam line of the ESRF synchrotron (Grenoble, France). The spectra were acquired in transmission mode using a Specac infrared-transmission cell equipped with Kapton windows that allow in situ treatment of the sample under controlled gas mixtures and temperatures up to 773 K. The sample was placed in a stainless steel holder directly in contact with the gas mixture atmosphere and resistively heated. The samples were pressed as self-supported wafers in a standard 13-mm die, using the optimum weight to maximise the signal-to-noise ratio in the ionisation chambers. For energy calibration, a standard Cu foil introduced after the sample was measured at the same time. Typical EXAFS spectra of Cu K edge were recorded from 8800 to 10,000 eV, with a variable step energy value, with a minimum 0.5-eV step across the NEXAFS region (8970–9010 eV). EXAFS spectra were analysed using a standard package developed by Bonin et al. [19], using the theoretical amplitude and phase shift functions proposed by Rehr et al. (version 7.02 [20]). Data from the XANES region (8970–9010 eV) were normalized and derived analytically using standard algorithms, and treated without further processing.

Reference spectra for Cu^0 and Cu^{2+} oxidation states were recorded using standard reference samples of a metallic foil and CuO powder, respectively. For the Cu^+ oxidation state, no reference was available, but our results were compared with data in the literature [21]. Also, as shown later in this paper, a reference for Cu^+ was obtained from mathematical analysis of the experimental spectra.

For the reaction treatments, NO, hydrocarbons (CH_4, C_3H_8, or C_3H_6) and oxygen were diluted in He (1000 ppm, 2500 ppm, and 3%, respectively). Mass flow controllers were used for dosing the gases to the cell, using a total flow of 100 $mL\,min^{-1}$. The catalysts were placed in contact with the mixture at room temperature, then heated up to the desired temperature using an ascendant heating ramp of 10 $K\,min^{-1}$, followed by a temperature-constant period of 1 h. Then the cell was cooled to room temperature and the spectra were recorded in contact with the reaction mixture.

2.3. Factor analysis

Analysis of the XANES spectra was performed by FA, a multivariate statistical procedure used widely in such areas as ISS, XPS, SIMS, and XAS [22,23]. This mathematical technique enables determination of the minimum number of factors (chemical components in our case) needed to reproduce the data within experimental error. A detailed description of the technique was given previously [24,25]. An important aspect of this technique is that each data point is inherently weighted in proportion to its value. This means that points with higher absolute values (i.e., intensity) will have more importance statistically than those with smaller values. This fact is specially important to take into account in spectral shapes as those found in XAS, where a jump is superimposed on features resulting from, for instance, different oxidation states. Taking the raw spectrum, this feature would mean that those points after the jump (with a higher value) would have statistically more importance than those around the edge, despite the appearance of importance features in that zone. To minimize these effects, we analysed the data of XANES region in a derivative mode, a method proposed by Okamoto et al. [26] for improving the determination of the different oxidation states in Cu K edge spectra. In addition, this method replaces the "background" removal procedure used when analysing data by some other techniques.

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