NO adsorption on $ZnAl_2O_4/Al_2O_3$ powder: a NEXAFS study at the nitrogen K edge

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In order to understand the mechanism of the selective catalysis of nitrogen oxide reduction by hydrocarbons on a $ZnAl_2O_4/Al_2O_3$ catalyst, the NO adsorption step has been studied as a function of the surface state of the catalyst by using near-edge X-ray absorption fine structure (NEXAFS) spectroscopy at the nitrogen K edge. The role of oxygen, whose presence is essential for the reaction to occur, is examined. In absence of a preliminary surface oxidation, nitric oxide was found not to be adsorbed on the $ZnAl_2O_4/Al_2O_3$ surface. After this preliminary treatment, we observed that the nitrogen atom of the NO molecule was linked to a surface oxygen with an adsorption mode parallel or slightly tilted with respect to the catalyst surface. Through these experiments we clearly demonstrate the advantages of soft X-ray experiments in catalysis research even in the case of practical application to real materials.

KEY WORDS: nitric oxide; NEXAFS; oxide catalyst; chemisorption; zinc; spinel

1. Introduction

The initial work performed by Held *et al.* [1] on the potentiality of the selective catalysis of nitrogen oxide reduction by hydrocarbons (SCR-HC) has motivated many studies focussed on the adsorption of NO on model surfaces. If the technique most often used to understand this interaction is infrared spectroscopy, several methods of characterisation such as the NEXAFS technique [2] are often used in a complementary fashion. Among them, some authors have studied the adsorption of NO on NiO(100) [3,4] and have shown that the NO is adsorbed by the nitrogen on a Ni site, the molecule being in a tilted geometry with respect to the surface. More recently, Lindsay *et al.* [5] have confirmed by photoelectron diffraction that NO is linked by the N atom to a Ni atom, with a Ni–N bond length of 1.88 Å (the N–O bond is tilted away from the surface normal by 59°). On a CoO(111)/Co(0001) surface covered by hydroxyl groups, NO is bonded to N *via* the oxygen of the hydroxyl and is oriented parallel to the OH surface [6]. Finally, a NEXAFS study at N K edge of the chemisorption of NO on Ru(0001) has led to a determination of the orientation for the various molecular adsorption states of NO on metallic surfaces [7]. Also, an interesting point is the dependence on the surface state for the NO adsorption [8,9].

Thus, our purpose is to specify the interaction between the NO and a real powder catalyst and the influence of the oxygen atom on this interaction. We have undertaken the study of the adsorption of NO on the supported $ZnAl_2O_4/Al_2O_3$ oxide by NEXAFS at the N K edge. The influence of an oxygen treatment upon the adsorption of NO is discussed as well as the nature of the adsorbed NO.

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2. Experimental

2.1. Catalyst preparation

The material selected for this study is a supported catalytic system, $ZnAl_2O_4/\gamma_c$-Al_2O_3 (atomic composition: 2.3% of Zn, 38.1% of Al and 59.6% of O) prepared from $Zn(NO_3)_2{\cdot}6H_2O$ and alumina SB3 from condea by atomization [10]. The compound was then calcined under air at 750 °C for 2 h. Its BET total surface area, determined with nitrogen adsorption at 77 K, is 131 m^2/g.

2.2. NEXAFS spectrometer

The measurements were performed at the SACEMOR beam line (SA72) [11–13] at the Super-ACO storage ring of LURE running at 800 MeV with an average current of 300 mA and a lifetime of 10 h. The SACEMOR beam line is equipped with a high-energy toroidal grating monochromator (experimental resolution of 0.3 eV at the carbon edge).

The sample powder was deposited on a tungsten sample holder which was set in a preparation chamber. The gases were introduced into this chamber after three admission–pump cycles until the residual gases were removed in the circuit. The various doses were achieved in the preparation chamber (initial pressure 10^{-10} mbar) isolated from the main analysis chamber (pressure 10^{-10} mbar) in order to minimise further contamination. Uniform coverage was ensured using a micro valve located about 3 cm from the substrate. The NEXAFS spectra were recorded in about 15 min

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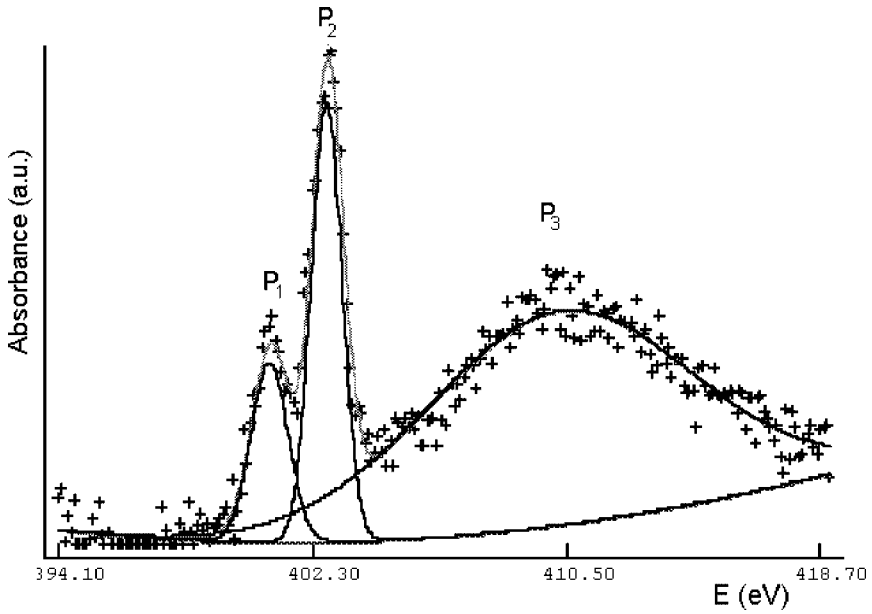

Figure 1. Nitrogen K edge after NO adsorption and its deconvolution.

using two channeltrons collecting the partial secondary electron emission of a clean reference gold grid and that of the sample. The insulating properties of the sample necessitated the use of a flood gun for evacuating the surface charges having an energy below 6 eV. The absorption spectra were calibrated at the carbon K edge ($E = 284.7$ eV).

2.3. Previous experiments on the very same catalyst

In an another paper, we have studied the structure of this catalytic $ZnAl_2O_4/Al_2O_3$ oxide system by TEM, AWAXS and EXAFS [10,14,15]. The majority of zinc atoms are located on the surface of the crystallites of alumina, substituting for the aluminium atoms in the tetrahedral site. This substitution is accompanied by the creation of oxygen vacancies. Moreover, the similarity between the Zn K and the Zn L_{III} edges gives evidence of an overlap between the 3d band and the conduction band (Zn 4s and 4p with O 2p) [16]. Finally, *in situ* EXAFS investigations at the Zn K edge have shown a dependence between the nature of the gas mixture and the evolution of the zinc site.

3. Results

In order to understand the role of oxygen in the NO adsorption mode, the O_2 and NO adsorptions were made at different reaction steps and never simultaneously. Thus no NO_2 formation in gas phase can be retained. The adsorption measurements were carried out on the $ZnAl_2O_4/Al_2O_3$ surface in the following three ways: (i) the sample was exposed to NO gas during 5 min at 10^{-8} bar at room temperature; (ii) the sample was preliminary heated up to 300 °C under vacuum during 15 min. This treatment was carried out to evacuate the adsorbed water on the sample. Once the sample temperature had returned to room temperature, it was exposed to NO during 15 min at 3×10^{-8} bar; (iii) the sample was heated at 400 °C during 60 min, then exposed to O_2 gas during 20 min at 6×10^{-7} bar at 400 °C. When the sample temperature was decreased to room temperature, NO was introduced during 15 min at 3×10^{-8} bar.

No adsorption of NO could be observed in any of the two first cases. In the first case, a signal was obtained at N K edge (figure 1). This signal is decomposed into three peaks, P_1, P_2 and P_3, fitted by a pseudo-Voigt function P_1 and P_2 correspond to the transitions N(1s) $\rightarrow \pi^*$ orbitals and P_3 to N(1s) $\rightarrow \pi^*$ orbital.

4. Discussion

4.1. N(1s) $\rightarrow \pi^*$(N) transition study

Depending on which NO_x species is adsorbed on the catalyst surface, the N(1s) toward π^*(N) transitions can be observed at different positions and intensities. Indeed, for the N_2O molecule (even if there is no possibility to form N_2O in this system as pointed by one referee, we want to evaluate each possibility here), there are two transitions N(1s) $\rightarrow \pi^*(N_t)$ and N(1s) $\rightarrow \pi^*(N_c)$, respectively, associated to terminal and central nitrogen atoms. They differ by the initial state of the two non-equivalent nitrogen atoms. The energy corresponding to these transitions has been established, respectively, as 401.1 and 404.7 eV [17] for the gaseous state and 400.4 and 404.3 eV for the solid state [18]. These authors also give for these transitions the integrated intensities ratio $RN_c/N_t = 1.44$.

ISEELS studies [19] on gaseous NO_2 lead to two N(1s) $\rightarrow \pi^*$ transitions due this time to a degeneracy lifting of the final state (N(1s) $\rightarrow 6a_1$ and N(1s) $\rightarrow 2b_1$). The correspondent energies were given as 401.04 and 403.28 eV.

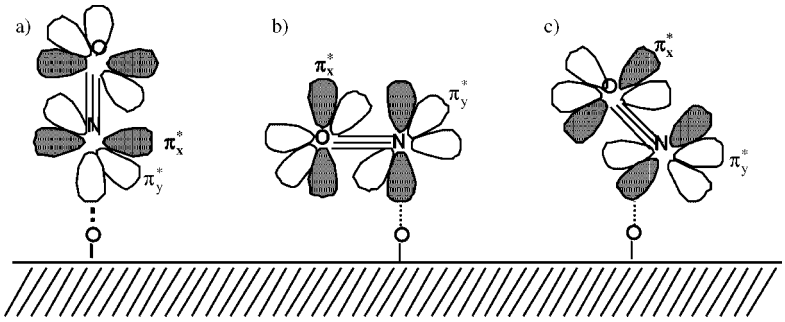

Figure 2. Adsorption modes for NO on the catalyst surface: (a) perpendicular adsorption by the free nitrogen doublet, (b) parallel adsorption by the π^* orbitals and (c) tilting adsorption by one nitrogen π^* orbital.

Table 1
Results of the deconvolution of the three peaks in figure 2.

No. peak	Intensity	Position (eV)	FWHM (eV)	Distance to P_3 (eV)
P_1	0.01	400.9	1.4	−9.3
P_2	0.025	402.7	1.2	−7.5
P_3	0.11	410.2	10.2	0

An energy difference of 2.4 eV has likewise been found in gaseous NO_2 by Schwarz [20].

On gaseous NO, only one transition N(1s) $\rightarrow$ π^* can be observed because the two antibonding molecular orbitals (π_x^*, π_y^*) are degenerate. The energies were found to be equal to 399.7 [21] and 399.5 eV [19]. For adsorbed NO, several geometries could be proposed (figure 2, table 1). At first (figure 2(a)), the NO adsorption occurs *via* the free doublet of the nitrogen, in analogy with the carbon terminal adsorption in CO/Pt [22,23]. This mode will give only one degenerate transition N(1s) $\rightarrow$ π^* with a possible energy shift depending on the nature of the support atom (401 eV for NO/Ru(0001) [7], 408 eV for NO/NiO(111)/Ni(111) [4]). Secondly (figure 2(b)), the NO fixation by π^* orbitals takes place with an adsorption mode parallel to the surface, where it should have a degeneracy lifting for the antibonding nitrogen and oxygen orbitals ($2\pi_x^*$ and $2\pi_y^*$). This phenomenon is observed with the acetonitrile adsorbed on Pt (111) or Ni(111) [24] as analysed by grazing and normal incidence NEXAFS techniques. Thirdly (figure 2(c)), the adsorption occurs *via* the π^* orbital of the nitrogen atom with NO tilting on the surface [4]. The degeneracy lifting occurs as before, but only on the nitrogen orbitals. In this case, an interaction between the surface and the nitrogen free doublet should be possible.

In our case, the hypothesis N_2O was rejected because of the energies for the π^* transitions. For NO, only two cases are possible: these are the modes in figure 2 (b) and (c) due to the presence of the two transitions N(1s) $\rightarrow$ π^*. That hypothesis is confirmed by the intensity ratio P_2/P_1 of about 2 because the lower energy antibonding orbital has one electron while the higher none. NO_2 adsorption can also be considered as regards the π^* transition energy and their intensity ratio [19]. In consequence, it seems that the NO adsorption does not occur on a metallic site (Zn or Al), but rather on a surface oxygen by the nitrogen atom.

4.2. N(1s) $\rightarrow$ σ^* (N) transition study

With regard to this transition, some authors [25,26] have shown for some non-linear molecules that the difference δ (eV) between the ionisation energy and the σ^* orbital energy is directly proportional to the interatomic distance of two atoms with a total atomic weight Z. Basing on the same principle, Esch *et al.* [7] have calculated an interatomic distance for NO. They have used a relation ($\Delta R = m\Delta E$ with $1/m = 30 \pm 5$ eV) given by Stöhr for NO [27] based on the difference between the π^* energy orbital and that for σ^*.

Using the first method ($\delta = -2.3$ eV and $Z = 15$), we obtain a distance for N–O equal to 1.3 Å. Using the second, ($\Delta E_{\pi^*-\sigma^*} = 14.8$ eV for 1.15 Å [27] for gaseous NO and $\Delta E_{\pi^*-\sigma^*} = 9.3$ eV in our case), we obtain a distance for N–O equal to 1.39 Å. Although these calculations are approximate, this distance is exceptionally long for a N–O distance (NO ($d_{\mathrm{N–O}} = 1.15$ Å), NO_2 ($d_{\mathrm{N–O}} = 1.197$ Å), N_2O ($d_{\mathrm{N–O}} = 1.186$ Å)) [28]. We think that the N(1s) $\rightarrow$ σ^* transition observed here is not a transition associated with the intramolecular N–O bond, but a transition linked to the distance between the nitrogen atom and the substrate [24]. Then, the formed species could be written as $O{=}N{-}O_{ads}$, with a double bond in ON and a single bond $N{-}O_{ads}$.

5. Conclusion

Up to now, the NEXAFS technique has been widely used to characterise the interaction between a molecule and a well-defined metallic surface. This study shows clearly that this technique can bring major information on the interaction between the NO and a real powder catalyst.

Among the different key results obtained, a first conclusion is that the adsorption of NO molecules on the oxide supported catalyst $ZnAl_2O_4/Al_2O_3$ needs a preliminary treatment by oxygen performed at 400 °C. The study at the nitrogen K edge shows several transitions: two narrow peaks assigned to two non-degenerate transitions N(1s) $\rightarrow$ π^* and one transition N(1s) $\rightarrow$ σ^* linked to an exceptionally long distance N–O (1.35 Å).

Based on these observations, we suggest the following mechanism for the NO adsorption (figure 3). The first step which consists of an oxygen treatment leads to an oxidation

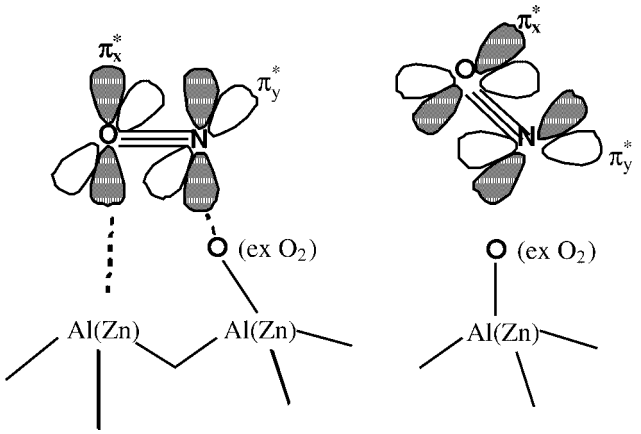

Figure 3. NO adsorption modes on the $ZnAl_2O_4/Al_2O_3$ oxidized catalyst surface.

or to a surface reconstruction. Then, NO adsorption can occur on an oxygen of the catalyst by the N atom. Moreover, the NO adsorption mode is parallel or slightly tilted on the surface.

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