Selective catalytic reduction (SCR) of NO by NH₃ over TiO₂-supported V₂O₅–WO₃ and V₂O₅–MoO₃ catalysts

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A comparison between commercial and model WO₃–V₂O₅/TiO₂ and MoO₃–V₂O₅/TiO₂ SCR catalysts is considered in this study. The data indicate that WO₃ and MoO₃ behave as “structural” and “chemical” promoters for the catalysts. MoO₃-based catalysts are more active but less selective than WO₃–V₂O₅/TiO₂ catalysts in the SCR reaction, although in the presence of water the catalytic performances of the investigated samples are comparable.

Keywords: selective catalytic reduction, V₂O₅–WO₃/TiO₂ catalysts, V₂O₅–MoO₃/TiO₂ catalysts, DeNOx-SCR

1. Introduction

NOₓ emission from both mobile and stationary sources is a problem of great concern nowadays, and several methods were proposed in order to meet the current NOₓ legislation emission limits [1–3]. In the case of stationary sources, the selective catalytic reduction (SCR) of NOₓ by NH₃ is to date considered the best available technology, being able to reduce NOₓ emission at ppm levels. In this process [2,3], NO contained in the flue gas is catalytically converted into water and nitrogen by NH₃ injected in the feed stream:

\[
4\text{NO} + 4\text{NH}_3 + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \tag{1}
\]

NO₂, which is also contained in the flue gases in much lower amounts if compared to NO (NOₓ are constituted by ~95% of NO and 5% of NO₂), is reduced as well.

Commercial SCR catalysts, which are employed in the shape of honeycomb monoliths or plates, are made up by an anatase TiO₂ carrier that supports the active components, i.e., vanadium pentoxide and tungsten- or molybdenum-trioxide. Vanadia is active in the reduction of NOₓ but also in the undesired oxidation of SO₂ to SO₃; accordingly the V₂O₅ content is kept low, being usually below 1% w/w. WO₃ or MoO₃ are employed in much larger amounts (nearby 10 and 6% w/w, respectively); it has been reported that they act both as “chemical” and “structural” promoters since they increase the reactivity of V₂O₅/TiO₂ catalysts and improve the mechanical, structural and morphological properties of the catalysts [3–5].

In spite of the fact that several studies are reported in the literature on both the V₂O₅–WO₃/TiO₂ [5–11] and V₂O₅–MoO₃/TiO₂ catalytic systems [12–17], still some aspects concerning the effect of the WO₃ and MoO₃ promoters on the catalyst activity and selectivity in the SCR reaction need to be clarified. Accordingly, in our work we have focused the attention on a direct comparison of the role of MoO₃ and WO₃ promoters on the catalyst structural and morphological characteristics and on the reactivity in the SCR reaction. Model V₂O₅/TiO₂ samples having different vanadia contents (in the range 0–2.5% w/w, i.e., of interest for SCR applications) and promoted with equal amounts (on a molar basis) of MoO₃ or WO₃ were prepared and characterized, and their reactivity in the SCR reaction was investigated. Finally, the reactivity in the SCR of commercial V₂O₅–WO₃/TiO₂ and V₂O₅–MoO₃/TiO₂ catalyst samples has also been investigated, in order to make a more detailed comparison of the role of MoO₃ or WO₃ promoters.

2. Experimental

2.1. Catalyst preparation

TiO₂-supported V₂O₅–MeO₃ catalysts (Me = Mo, W) with different vanadia contents (in the range 0–2.5% w/w) and promoted with 4 × 10⁻² mol/gcat WO₃ or MoO₃ (~9 and 6% w/w, respectively) were prepared by the incipient wetness method starting from a home-made titania anatase support (prepared by neutralization at pH ≈ 7 of Ti tetra-chloride (TiCl₄) with a NH₄OH solution) calcined for 4 h at 823 K. In a typical preparation, MoO₃ or WO₃ were added to the TiO₂ support by impregnation with an aqueous solution of ammonium heptamolybdate or paratungstate (Carlo Erba RPE) complexated with citric acid (J.T. Baker). The resulting precursors were dried at 383 K overnight and calcined at 823 K for 3 h. Vanadium was then added to the MoO₃/TiO₂ binary systems by impregnation with an aqueous solution of ammonium heptamolybdate or paratungstate (Carlo Erba RPE) complexated with citric acid (J.T. Baker). The resulting precursors were dried at 383 K overnight and calcined at 823 K for 3 h. Vanadium was then added to the MeO₃/TiO₂ binary systems by impregnation starting from a water solution of ammonium metavanadate and oxalic acid, followed by drying and calcination at 823 K for 2 h.

Reference V₂O₅/TiO₂ samples were also prepared for comparison purposes by impregnation of the bare TiO₂ support followed by drying and calcination at 823 K for 2 h.

In the following, catalysts are denoted as V₂O₅(x)–MeO₃(y)/TiO₂, with x and y representing the % w/w metal oxide loading.
Commercial V2O5–WO3/TiO2 and V2O5–MoO3/TiO2 samples have also been considered in this study. The WO3-containing sample contains ~0.8% w/w V2O5 and ~9% WO3, whereas the V2O5–MoO3/TiO2 catalyst contains ~0.65% w/w V2O5 and ~6% MoO3.

2.2. Catalysts characterization

Surface areas were determined by N2 adsorption at 77 K with the BET method using a Carlo Erba Sorptomatic 1900 Series instrument. Pore size distribution measurements were obtained by N2 adsorption–desorption at 77 K with the same apparatus used for surface area measurements and by the mercury penetration method using a Carlo Erba Porosimeter 2000 Series instrument.

Powder X-ray diffraction analyses were performed with a Philips vertical goniometer PW 1050/70 and Ni-filtered Cu Kα radiation. XRD spectra were used to estimate the mean crystal size of the TiO2 crystallites (dcryst) by using the Scherrer equation.

The FT-IR spectra were recorded with Nicolet Magna 750 and S7DX Fourier transform spectrometers at RT (4 cm\(^{-1}\) resolution). The powders were pressed into self-supporting disks and activated by outgassing at 623 K before adsorption experiments. The skeletal spectra in the region 2000–400 cm\(^{-1}\) were recorded with KBr-pressed disks.

FT Raman spectra were recorded using a Brucker RFS100 (Nd:YAG laser) instrument.

2.3. Reactivity measurements

Catalytic activity measurements were performed in a quartz tubular fixed-bed microreactor (i.d. = 7 mm) operating at atmospheric pressure and inserted into an electric furnace. The temperature of the catalyst was measured and controlled by means of a K-type thermocouple (o.d. = 0.5 mm) directly immersed in the catalyst bed. In a typical run, 160 mg of catalyst (100–150 mesh) were used and a stream containing NH3 (800 ppm) and Ar (1500 ppm, internal standard) in He (total flow rate = 120 cm\(^3\)/min (STP)) was fed to the reactor kept at 313 K. When the mass spectrometer signals had stabilized (typically within 30 min), the catalyst was heated up to 773 K at 15 K/min by maintaining the flow rate constant while monitoring the concentration of the various species.

3. Results

3.1. XRD and morphology

The effect of the vanadia loading on the catalysts structural and morphological properties was investigated at first. For all the samples, the only detected phase by XRD is the anatase polymorphic form of TiO2. The mean crystallite dimension of the anatase support (estimated by the Scherrer equation) is similar and is in the range 140–165 Å: no significant differences are observed in the crystallite dimensions of anatase on increasing the V2O5 content. No diffraction lines attributable to crystalline V2O5, MoO3 or WO3 were detected: the absence of these bulk phases in the XRD patterns implies that for these samples the Mo, V and W oxides are present in either a non-crystalline state or as small crystallites.

Figure 1 shows the BET surface areas of the WO3- and MoO3-containing catalysts as a function of the vanadia content. The BET surface areas of the unpromoted V2O5/TiO2 catalysts are also reported for comparison. Although the same scatter is apparent in the data, the figure clearly shows that vanadia addition to both the pure TiO2 support and to MoO3/TiO2 and WO3/TiO2 leads to a progressive decrease of the surface area values. The unpromoted V2O5/TiO2 catalysts experience an even greater decrease of the specific surface area, thus clearly indicating that the presence of the MoO3 and WO3 dopants preserves the sintering of the TiO2 matrix upon addition of vanadia. This effect is particularly evident for the WO3-doped samples, for which only a limited decrease in the surface area values is observed upon increasing the V2O5 loading.

The other morphological characteristics samples are very similar and are only slightly modified upon V2O5 addition in the investigated range: the pore volume and the mean pore radius are not significantly affected by vanadia addition and are in the range 0.27–0.31 cm\(^3\)/g and 70–100 Å, respectively.

From the surface area values and from the nominal metal oxide loading the V, Mo and W coverages can be esti-