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Reactivity of V_2O_5–WO_3/TiO_2 catalysts in the selective catalytic reduction of nitric oxide by ammonia

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Abstract

The physico-chemical characteristics and the reactivity of sub-monolayer V_2O_5–WO_3/TiO_2 deNO$_x$ catalysts is investigated in this work by EPR, FT-IR and reactivity tests under transient conditions. EPR indicates that tetravalent vanadium ions both in magnetically isolated form and in clustered, magnetically interacting form are present over the TiO_2 surface. The presence of tungsten oxide stabilizes the surface V^{IV} and modifies the redox properties of V_2O_5/TiO_2 samples. Ammonia adsorbs on the catalysts surface in the form of molecularly coordinated species and of ammonium ions. Upon heating, activation of ammonia via an amide species is apparent. V_2O_5–WO_3/TiO_2 catalysts exhibits higher activity than the binary V_2O_5/TiO_2 and WO_3/TiO_2 reference sample. This is related to both higher redox properties and higher surface acidity of the ternary catalysts. Results suggest that the catalyst redox properties control the reactivity of the samples at low temperatures whereas the surface acidity plays an important role in the adsorption and activation of ammonia at high temperatures.

Keywords: NO reduction; V_2O_5–WO_3/TiO_2 catalysts

1. Introduction

V_2O_5–WO_3/TiO_2 catalysts are widely used in the selective catalytic reduction (SCR) of nitrogen oxides in SO_2-containing power plant stack gases [1]. In spite of their large diffusion in the SCR technology, investigations on the reactivity and physico-chemical characteristics of V_2O_5–WO_3/TiO_2 catalysts are still scarce in the literature [2–6]. The structural, morphological and chemico-physical characteristics of V_2O_5–WO_2/TiO_2 has been recently investigated in our laboratories by means of different techniques including XRD, surface area and pore distribution measurements, EPR, UV–vis. diffuse reflectance, FT–IR and Laser–Raman spectroscopies [6]. Monomeric vanadyls and tungstenyls and polymeric W_xO_y groups have been observed over the catalyst surface by FT–IR and Laser–Raman. Apparently, these surface species are similar to those identified over binary V_2O_5/TiO_2 and WO_3/TiO_2 oxide sys-

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tems. However, over the ternary catalysts the existence of a strong electronic interaction between V and W surface species and the TiO_2 support has also been observed [6], which apparently leads to an higher reducibility of the ternary samples. In the SCR reaction, the ternary catalysts show higher reactivity if compared to the corresponding binary samples: this has been related to the higher reducibility of the catalysts, as suggested by the chemico-physical investigation.

Aim of this work is to provide additional insight on the physico-chemical characteristics and on the reactivity of the surface V and W species present in V_2O_5–WO_3/TiO_2 catalysts. Different experimental techniques have been used for this purpose, including EPR, FT–IR and catalytic activity tests in the SCR reaction under transient conditions.

2. Experimental

V_2O_5–WO_3/TiO_2 samples have been prepared by dry impregnation of WO_3/TiO_2 with a hot water solution of ammonium metavanadate [6]. XRD, FT–IR, EPR, surface area measurements and pore-size distribution have been collected as reported in [6]. Transient experiments (temperature programmed surface reaction, TPSR) were performed in a quartz tubular fixed-bed microreactor. In a typical run, ammonia was adsorbed over the catalyst surface at RT and then desorbed upon temperature programming in flowing He + NO or He + NO + O_2. Further details on experimental conditions and setup can be found elsewhere [7].

3. Results and discussion

3.1. Catalyst characterization

The investigated submonolayer V_2O_5–WO_3/TiO_2 samples with $WO_3 \approx 9\%$ w/w and vanadia loadings ranging from 0 to 1.47% w/w (W + V coverages $\leqslant$ 0.8) present similar textural characteristics. All the samples are monophasic and only the anatase polymorphic form of TiO_2 is detected. Surface areas of the samples slightly decrease from 90 down to 80 m^2/g on increasing the vanadia loading whereas the pore volume and the mean pore radius are almost constant ($V_p = 0.30$–0.33 cm^3/g; $r_p =$ 55–70 Å).

The nature of the V surface species have been investigated by EPR. All the ternary V_2O_5–WO_3/TiO_2 samples exhibit, after calcination in air, a quite intense and complex EPR powder spectrum whose intensity further grows upon outgassing at increasing temperatures up to 470 K. The spectrum is due to the presence of surface tetravalent vanadium ions both in magnetically isolated form (displaying the well known hyperfine structure of V^{IV} in axial symmetry) and in clustered, magnetically interacting form (responsible of the wide unstructured signal appreciable in terms of non-linearity of the base line). The spin-hamiltonian parameters of the magnetically isolated species unambiguously indicate that the V^{IV} centers are in the form of vanadylic VO^{2+} ions. They are grafted on the matrix of titanium dioxide as demonstrated by the fact that the same vanadylic species are observed on binary vanadia/titania reference samples upon outgassing at moderate temperatures (420–470 K). On the starting binary samples, differently from the case of the ternary ones, no V^{IV} EPR spectrum is observed. This fact indicates that the presence of tungsten oxide increases the propensity of the vanadia phase to be stabilized in the partially reduced V^{IV} form. Preliminary quantitative measurements indicates that the V^{IV} fraction of the total vanadium (namely the V^{IV}/V_{total} ratio) depends on several parameters including the preparation procedure of the samples. This ratio, however, is maximum after the thermovacuum treatment at 420 K for all the samples and ranges, in these conditions, between 4% and 15% increasing with decreasing the vanadia loading of the system. The vanadia/titania binary reference samples and the ternary V_2O_5–WO_3/TiO_2 samples exhibit a different behavior upon outgassing at 823 K. Indeed after this treatment, the tuning of the spectrometer was practically impossible in the case of the V_2O_5–WO_3/TiO_2 sample because the concentration of quasi-free electrons in the sample exceeds a limiting value. As opposite, the EPR spectrum could be monitored in the case of the vanadia/titania samples. It is concluded that the ternary V_2O_5–WO_3/TiO_2 catalysts show an higher reducibility than the binary vanadia/titania samples and have a higher propensity to stabilize V^{IV} ions.

3.2. FT–IR study of ammonia adsorption and reaction with NO

The interaction of NH_3 with the catalyst surface has been investigated by FT–IR. Fig. 1 shows the FT–IR spectra obtained upon adsorption of ammonia at RT over a V_2O_5–WO_3/TiO_2 sample and upon evacuation at increasing temperatures.

In the spectrum recorded at RT, the sharp band at 1605 cm^{-1} is due to the asymmetric deformation of ammonia coordinatively held over Lewis acid sites. The corresponding symmetric deformation mode is complex showing a band with maximum at 1225 cm^{-1} and shoulders at higher frequencies; this band shifts progressively at higher frequencies and splits in two components upon heating. The bands observed at 1680 and 1430 cm^{-1} are characteristic of ammonium ions produced by ammonia protonation over WOH Brønsted acid sites. A comparison of these results with those obtained in the case of the binary reference V_2O_5/TiO_2 and WO_3/TiO_2 catalysts [8] indicates that both tungstenyls and vanadyls centers act as adsorption sites for molecularly adsorbed ammonia.

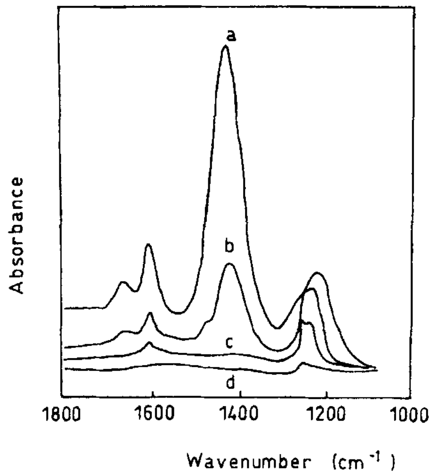

Fig. 1. FT–IR spectra of the adsorbed species arising from adsorption of ammonia over a V_2O_5–WO_3/TiO_2 sample (WO_3 = 9% w/w and V_2O_5 = 1.47% w/w) and subsequent outgassing at RT (a), 400 K (b), 523 K (c), and 623 K (d). The spectra of the activated catalyst has been subtracted.

Outgassing at progressively higher temperatures causes the disappearance first of the bands characteristic of the protonated ammonia species and later on of those corresponding to the molecularly adsorbed NH_3. This clearly indicates that protonated NH_4^+ species are thermally less stable than molecularly coordinated species. It is also worth noticing that a shoulder is observed at 1500 cm^{-1} upon heating on the high-frequency side of the NH_4^+ ammonium ion band at 1430 cm^{-1}. A possible assignment for this band is the NH_2 scissoring mode of an inorganic amide species, which is similar but not identical to that already observed at 1485 cm^{-1} in the case of WO_3/TiO_2 samples and at 1550 cm^{-1} for V_2O_5/TiO_2 catalysts [8]. One may speculate that on the ternary catalysts the activation of ammonia occurs through the amide species, even if is not clear whether it involves the vanadyl and/or the wolframyl centers.

When the same experiment is carried out in the presence of NO instead of vacuum, the bands corresponding to the molecularly adsorbed species disappear faster than those of the protonated species. Moreover, the bands of water appear in the spectrum. This has been interpreted by considering that a reaction has been occurred between adsorbed ammonia and NO producing water and N_2 which however is not detectable by FT–IR. The reaction appears to involve the coordinated ammonia species which is possibly activated via the amide species, even if the participation of the protonated species cannot be excluded.

3.3. Temperature programmed surface reaction (TPSR) of NH_3 with NO

TPSR experiments were performed in order to investigate the reactivity of adsorbed ammonia with gaseous NO. Fig. 2 shows the NO consumption profiles measured when NO is fed over the NH_3 pre-dosed surface in the absence (Fig. 2 left) and in the presence of oxygen (Fig. 2 right). In the absence of oxygen, over the WO_3/TiO_2 sample ($WO_3 = 9\%$ w/w, trace c) NO is consumed starting from 520 K. A parallel evolution of N_2 and water (not shown in the figure) was also monitored, thus indicating the occurrence of the SCR reaction. The NO consumption trace shows a maximum near 700 K due to the depletion of adsorbed ammonia surface species. Similar results have been obtained over the V_2O_5/TiO_2 ($V_2O_5 = 1.47\%$ w/w) and the V_2O_5–WO_3/TiO_2 ($V_2O_5 = 1.47\%$ w/w; $WO_3 = 9\%$ w/w) samples. However, in these cases NO consumption is monitored at lower temperatures, starting from 400–450 K and below 400 K in the case of the V_2O_5/TiO_2 and the V_2O_5–WO_3/TiO_2 samples, respectively. This possibly indicates that the reactivity of the catalysts increases in the order V_2O_5–$WO_3/TiO_2 > V_2O_5/TiO_2 > WO_3/TiO_2$. As discussed into details elsewhere [7], it is likely that at low temperatures the occurrence of the SCR reaction requires the participation of the catalysts lattice oxygen, thus, resulting in catalyst reduction. Accordingly, the temperature threshold for the occurrence of the SCR reaction is likely related to the availability of the catalyst lattice oxygen atoms, that is to catalyst reduction. As pointed out by on-line mass spectrometer analysis, our gas stream contained traces amounts of oxygen. These oxygen impurities were consumed during the TPSR run starting from the temperature indicated with the arrows in the left part of Fig. 2. In agreement with the catalyst reduction process previously suggested, it is concluded that the catalyst is partially re-oxidized by gas-phase oxygen impurities. As apparent in the left part of Fig. 2, the temperature threshold for oxygen consumption, which is indicative of a catalyst reoxidation process, increases in the order $WO_3/TiO_2 > V_2O_5/TiO_2 > V_2O_5$–$WO_3/TiO_2$. Considering that both catalyst reduction and catalyst reoxidation are observed at lower temperatures over the ternary V_2O_5–WO_3/TiO_2 catalyst, it is concluded that this sample shows superior redox properties if compared to the corresponding binary reference samples.

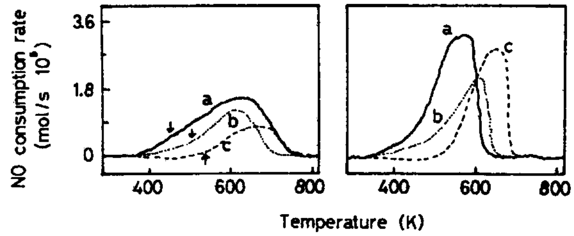

Fig. 2. TPSR of ammonia in He + NO (left) and in He + NO + O_2 (right) over V_2O_5–WO_3/TiO_2 ($V_2O_5 = 1.47\%$ w/w; $WO_3 = 9\%$ w/w, trace a), V_2O_5/TiO_2 ($V_2O_5 = 1.47\%$ w/w, trace b) and WO_3/TiO_2 ($WO_3 = 9\%$ w/w, trace c) samples. The arrows indicate the temperature threshold for the impurity oxygen consumption.

The SCR reaction is no longer monitored for temperatures above 700 K in the vanadia/titania catalyst, due to the depletion of adsorbed ammonia species. On the other hand, in the case of the tungsten oxide/titania sample, NO consumption is evident at temperatures as high as 780 K. This is possibly related to both the lower activity and the higher acidity of the WO_3/TiO_2 sample. In the case of the ternary catalyst the SCR reaction is effective already at low temperatures and is observed up to high temperatures, thus, suggesting the high activity and the high acidity of the sample. It is concluded that under TPSR conditions the catalyst redox properties likely determines the temperature threshold for the occurrence of the SCR reaction, whereas surface acidity plays a role in the high-temperature region in the adsorption and activation of ammonia.

When the reaction is carried out in the presence of 1% v/v of oxygen (Fig. 2 right), a significant increase in NO conversion is observed for all the samples. The temperature threshold for the occurrence of the SCR reaction is apparently unaffected by the presence of gas-phase oxygen, but above a temperature roughly corresponding to the consumption of impurity oxygen in the TPSR run in He + NO, the NO consumption is greatly increased. The reaction is completed at lower temperatures due to the faster depletion of adsorbed ammonia surface species, thus, resulting in a shift towards lower temperatures of the maximum of the NO consumption peak. The results confirm the order of reactivity pointed out in the case of the TPSR experiments in He + NO and indicate that the presence of gaseous oxygen enhances the rate of NO removal. In line with the role of oxygen in a redox mechanism, gaseous oxygen does accelerate the reaction above the temperature corresponding to O_2 consumption during TPSR experiments in He + NO, that is associated with catalyst reoxidation.

The results of steady-state activity runs reported elsewhere [6] confirm the higher activity of the V_2O_5–WO_3/TiO_2 catalysts if compared to the corresponding binary samples. Calculations showed that the reactivity of V and/or W over the ternary samples is greater than that measured in the corresponding binary systems, thus, suggesting the existence of a specific synergism in the SCR reaction between V and W in the ternary catalysts. This synergism can be related to the strong electronic interactions that exist between V and W surface species and the TiO_2 support, which lead to a higher catalyst reducibility. The present study also indicates that the V_2O_5–WO_3/TiO_2 catalysts are more easily reoxidized than the corresponding binary references catalysts, thus pointing out the superior redox properties of the ternary samples with respect to the binary V_2O_5/TiO_2 and WO_3/TiO_2 samples.

4. Conclusions

The main conclusions of the present investigation on the physico-chemical characteristics and reactivity of sub-monolayer V_2O_5–WO_3/TiO_2 catalysts can be summarized as follows:

(1) the V surface species present over sub-monolayer V_2O_5–WO_3/TiO_2 samples identified by EPR are tetravalent vanadium ions both in magnetically isolated form and in clustered, magnetically interacting form grafted on the matrix of titanium dioxide. The presence of tungsten oxide stabilizes the surface V^{IV} and apparently modifies the collective properties of V_2O_5/TiO_2 samples in that the ternary samples show an higher reducibility than the corresponding vanadia/titania samples;

(2) ammonia adsorbs over the ternary catalysts in the form of molecularly coordinated species and of ammonium ions, this latter species showing lower thermal stability. Upon heating, activation of ammonia via an amide species is also suggested;

(3) V_2O_5–WO_3/TiO_2 catalysts exhibits higher activity in the SCR reaction than the corresponding binary vanadia/titania and tungsten oxide/titania reference samples; this has been related to both the higher redox properties and the higher surface acidity of the ternary catalysts;

(4) The catalyst redox properties appears to control the reactivity of the samples at low temperatures whereas the surface acidity plays an important role in the adsorption and activation of ammonia at high temperatures.

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