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Detection of reduced W^{n+} sites on WO_3–ZrO_2 and Pt/WO_3–ZrO_2 catalysts by infrared spectroscopy of adsorbed NO

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Adsorption of NO on oxidized WO_3–ZrO_2 catalysts leads to formation of adsorbed N_2O, surface nitrates, NO^+, and $Zr^{4+}(NO_3^-)$–NO species. When NO is adsorbed on a sample reduced at 523 K, W^{5+}–NO (1855 cm^{-1}) and $W^{4+}(NO)_2$ (1785 and 1700 cm^{-1}) species are formed in low concentration. Reduction at 573 K increases the density of W^{4+} sites and this density remains unchanged after reduction up to 673 K. The $W^{4+}(NO)_2$ species are stable towards evacuation and in the presence of oxygen; however, they quickly disappear in the simultaneous presence of NO and O_2 as a result of the oxidation of the W^{4+} cations to W^{6+}. The density of the W^{4+} sites on a Pt/WO_3–ZrO_2 sample is significant even after reduction at 523 K. This is explained by the promotion effect of platinum on the support reduction. The use of NO as a probe molecule for detection of reduced W^{n+} sites on tungstated zirconia is discussed.

KEY WORDS: adsorption; FTIR spectroscopy; nitrogen monoxide; tungstated zirconia; tungsten nitrosyls.

1. Introduction

During the past decade the interest in tungstated zirconia (WZ) and WZ-supported systems, as alternatives to sulfated zirconia (SZ) catalysts for the hydroprocessing of alkanes, has increased [1–5]. Although WZ catalysts are less catalytically active than SZ, they possess superior stability and are more suitable for industrial applications. The catalytic activity of WZ is conventionally attributed to surface $W^{6-n}O_x(nH^+)$ Brønsted acid centers which are formed by the redox mechanism under reaction conditions [1,3,4]. The existence of reduced W^{n+} sites is not yet well documented. The formation of W^{5+} species was detected by *in-situ* ESR spectroscopy [1]; the method, however, failed to unequivocally identify the tungsten ions in lower oxidation states. The development of a technique which is capable of detecting various W^{n+} species is, therefore, of a great interest.

One of the most frequently used techniques for characterization of cationic sites on oxide surfaces is IR spectroscopy of probe molecules [7]. The preferred probe molecule for this purpose is carbon monoxide. We have studied low-temperature CO adsorption on oxidized and partially reduced WZ samples. However, we were unable to confidently identify the formation of W^{n+}–CO species. This is due to the fact that it is practically impossible to discriminate between W^{n+}–CO and Zr^{4+}–CO carbonyl signals as they all absorb in the same spectral region and are of comparable stability. A similar situation has been observed on VO_x/TiO_2 catalysts: the carbonyls of V^{4+} and V^{3+} ions were detected in the same wavenumber region in which Ti^{4+}–CO species also absorb and the stability of all carbonyls was similar [8]. On the other hand, NO was successfully utilized as an IR probe molecule for detection of reduced vanadium sites on vanadia–titania catalysts [9]. NO does not form nitrosyl species with Ti^{4+} and V^{5+} at ambient temperature, whereas $V^{4+}(NO)_2$ and $V^{3+}(NO)_2$ dinitrosyls are stable under these conditions [9]. Thus, NO is thought to be a successful probe molecule for detection of reduced tungsten sites on WZ as well.

NO adsorption on pure zirconia has been studied by several groups [10–14]. No Zr^{4+}–NO species are formed on the surface of pure zirconia. However, NO slowly disproportionates on zirconia, forming surface nitrates which enhance the acidity of adjacent Zr^{4+} cations. As a result, $Zr^{4+}(NO_3^-)$–NO species (1906 cm^{-1}) are formed. Reports on NO adsorption on supported tungsta catalysts are scarce. Ouafi *et al.* [15] studied NO adsorption on a W/Al_2O_3 sample. They observed that the oxidized sample does not adsorb NO. On the reduced sample, however, three bands at 1765, 1852 and 1700 cm^{-1} were observed after NO adsorption. The band at 1852 cm^{-1} was found to disappear after evacuation and was assigned to W^{4+}–NO species. The bands at 1765 and 1700 cm^{-1} characterized irreversible adsorption and were assigned to the antisymmetric ν_{as} and symmetric ν_s stretching modes, respectively, of $W^{4+}(NO)_2$ dinitrosyl complexes. Similar results were published by Yan *et al.* [16], who observed stable $W^{4+}(NO)_2$ species (1780 and 1691 cm^{-1}), whilst W^{5+}–NO nitrosyls (1843 cm^{-1}) were decomposed by evacuation.

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The aim of this work is to study NO adsorption on a WZ catalyst and to establish the possibility of detecting reduced tungsten sites. In addition, we studied a Pt/WZ sample to test whether platinum facilitates the reduction of the support as established for a series of catalysts in which an SMSI state could be induced [17,18].

2. Experimental

The WO_3–ZrO_2 sample was prepared by suspending amorphous $Zr(OH)_4 \cdot nH_2O$ (MEL Chemicals) in aqueous solution of ammonium metatungstate ($(NH_4)_6[H_2W_{12}O_{40}]$, 99.999%, Aldrich). The suspension was refluxed for 16 h at 383 K followed by evaporation of water at 383 K. The precipitate was dried for 12 h at 383 K and finally calcined at 923 K for 3 h. The nominal concentration of WO_3 in the sample was 19 wt%. This corresponds to a theoretical monolayer of tungsta on the zirconia surface. The sample thus obtained possessed a BET specific surface area of 120 $m^2\,g^{-1}$.

Pt/WO_3–ZrO_2 (1 wt% Pt) was prepared by impregnation of WO_3–ZrO_2 with an aqueous solution of tetraammineplatinum nitrate ($Pt(NH_3)_4(NO_3)_2$, from Aldrich). The suspension was stirred for 1 h, followed by evaporation of water at 383 K. The residual solid was dried overnight at 398 K and calcined at 823 K for 3 h.

Chemical compositions of synthesized samples were verified by inductively coupled plasma (ICP) spectroscopy.

Nitrogen monoxide (>99.5%), hydrogen (99.999%) and oxygen (99.996%) were supplied by Messer Griesheim.

The IR spectra were recorded on a Bruker IFS-66 spectrometer with a spectral resolution of 2 cm^{-1}. Self-supporting pellets were prepared from the samples and treated directly in the purpose-made IR cell. The latter was designed for low-temperature experiments and connected to a vacuum-adsorption apparatus with a base pressure below 10^{-3} Pa. Prior to the adsorption measurements, the samples were activated by calcination at 773 K for 1 h and evacuation at the same temperature.

3. Results and discussion

3.1. Adsorption of NO on an oxidized WO_3–ZrO_2 catalyst

Analysis of literature data indicates that NO does not form nitrosyl complexes with transition metal cations of groups IV–VI of the Periodic Table in their highest oxidation state [19]. A typical example would be V^{5+}, and we do not expect formation of nitrosyls of W^{6+}, when NO is adsorbed on an oxidized WZ sample. Indeed, it has been reported that NO is not adsorbed as a nitrosyl on oxidized tungsta-containing catalysts [16]. However, in order to discriminate between the species formed on the oxidized and reduced WZ surface, we studied NO adsorption on the oxidized WZ sample first.

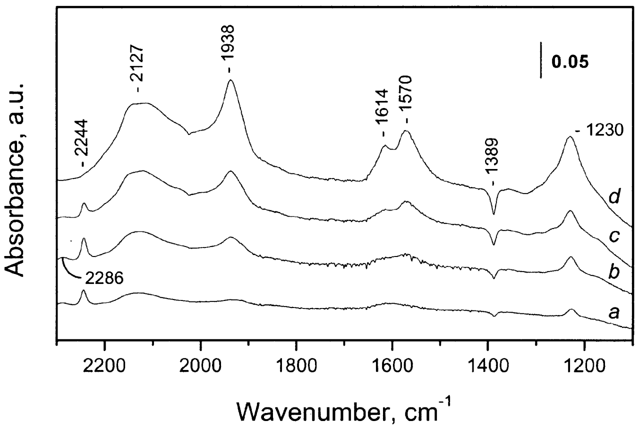

Figure 1. FTIR spectra of NO adsorbed on WO_3–ZrO_2 (equilibrium NO pressure of 500 Pa) (a) and time evolution of the spectra (b–d).

Exposure of the activated WZ sample to NO (500 Pa equilibrium pressure) led to the immediate appearance of two bands at 2286 and 2244 cm^{-1} in the IR spectrum (figure 1, spectrum a). These bands have been observed previously upon adsorption of N_2O on pure zirconia and were assigned to the N–N stretching modes of N_2O located on Zr^{4+} sites [20]. In addition, a weak band at 2140 cm^{-1}, characteristic of NO^+ species [21], and a band at 1936 cm^{-1}, assigned to nitrosyl species [5,13,14], were also visible. Two bands of very low intensity at 1605 and 1220 cm^{-1} were observed in the lower frequency region and were assigned to the ν_3' and ν_3'' modes, respectively, of surface bidentate nitrates [10,19]. The free nitrate ion is characterized by one ν_3 active vibration which is split by symmetry reduction. Part of the absorption at ~1220 cm^{-1} arose also from the N–O modes of adsorbed N_2O. The bands at 2025 and 1389 cm^{-1}, characterizing W–O vibrations, decreased in intensity, indicating interaction of NO with W-containing species.

Allowing the sample to stay in the NO atmosphere (figure 1, spectra b–d) resulted in a strong increase in intensity of all bands except those of N_2O. The higher-frequency component of the nitrate bands was split into two bands at 1614 and 1570 cm^{-1} and a shoulder at 1280 cm^{-1} was visible for the lower-frequency component. The development of the nitrosyl band at 1938 cm^{-1} can be explained by assuming that coordinatively unsaturated Zr^{4+} ions do not form nitrosyls, but that their electrophilicity increases when nitrate ions are coordinated to them. Indeed, an increase of the electrophilicity of cations has been observed after formation of adjacent sulfates [22], carbonates [23,24] and nitrates [25,26].

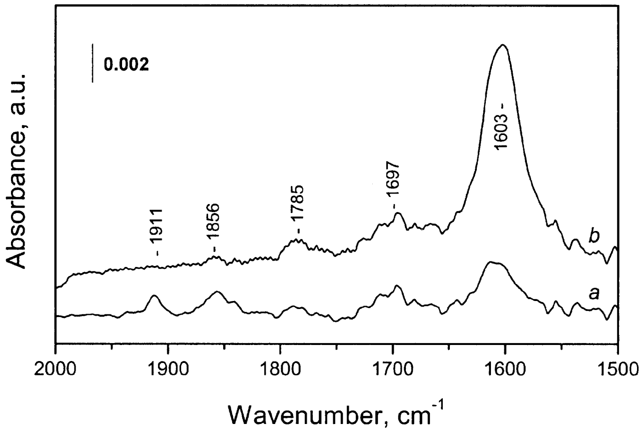

Figure 2. FTIR spectra of NO adsorbed on WO_3–ZrO_2 pre-reduced at 523 K (equilibrium NO pressure of 500 Pa) (a) and after evacuation (b).

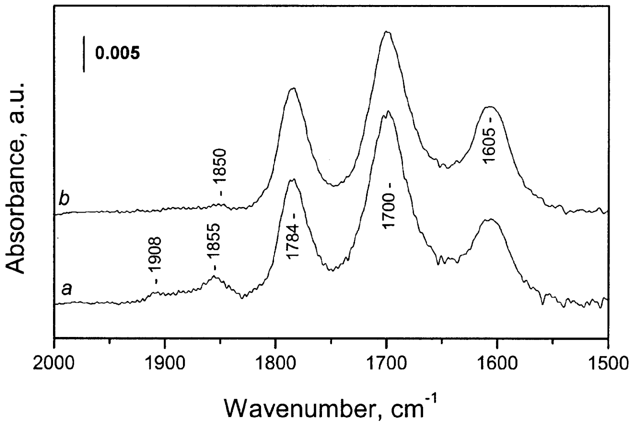

Figure 3. FTIR spectra of NO adsorbed on WO_3–ZrO_2 pre-reduced at 573 K (equilibrium NO pressure of 500 Pa) (a) and after evacuation (b).

3.2. Adsorption of NO on a reduced WO_3–ZrO_2 catalyst

The WZ sample was reduced in flowing H_2 at different temperatures and then tested by NO adsorption.

Upon adsorption of NO (500 Pa equilibrium pressure) on a sample reduced at 523 K five bands of very low intensity at 1911, 1856, 1785, 1697 and 1603 cm^{-1} (figure 2, spectrum a) were detected. Evacuation led to the disappearance of the 1911 and 1856 cm^{-1} bands, but a weak component at 1856 cm^{-1} remained visible. The bands at 1785 and 1697 cm^{-1} were not affected, whereas the intensity of the band at 1603 cm^{-1} increased (figure 2, spectrum b). The band at 1603 cm^{-1} was assigned to surface nitrates that were also observed in higher concentration on the oxidized sample. The band at 1911 cm^{-1} was assigned to nitrosyl species on Zr^{4+} sites affected by nitrates. In agreement with the results reported by Ouafi *et al.* [15] and Yan *et al.* [16] we assigned the pair of bands at 1785 and 1697 cm^{-1} to the ν_{as} and ν_s modes, respectively, of $W^{4+}(NO)_2$ species. The band at 1856 cm^{-1} was attributed to linear nitrosyls of the W^{5+}–NO type [15,16].

Following this experiment, the sample was reduced at 573 K. Subsequent NO adsorption (500 Pa equilibrium pressure) resulted in the appearance of the same bands as observed after reduction at 523 K. However, in this case the intensity of the $W^{4+}(NO)_2$ bands (detected at 1784 and 1700 cm^{-1}) was strongly enhanced (figure 3, spectrum a). The weak band at 1908 cm^{-1} (due to zirconium nitrosyls) disappeared after evacuation, while the intensity of the W^{5+}–NO band at 1855 cm^{-1} strongly decreased (figure 3, spectrum b). These nitrosyl bands of similar intensity were also detected when the sample was reduced at 623 and 673 K (figures 4 and 5, spectra a).

Some experiments were carried out to test the stability of different tungsten nitrosyls in an oxidative atmosphere. After adsorption of NO on the sample which was reduced at 623 K, the system was evacuated (figure 4, spectrum b) and oxygen added (figure 4, spectrum c). As a result, the weak residual band at 1853 cm^{-1} disappeared and the nitrate band at 1606 cm^{-1} gained intensity. These results suggest that NO which has been adsorbed on the W^{5+} sites was converted to nitrates. This is, however, not evidence for the oxidation of the W^{5+} sites as, possibly, the process has occurred after desorption of NO. The $W^{4+}(NO)_2$ species are hardly affected, which indicates that they are stable in an oxygen atmosphere. A careful inspection of the spectra shows that after evacuation of NO and after subsequent addition of O_2 the intensity ratio between the 1788 and 1700 cm^{-1} bands increases. This observation can be rationalized assuming the existence of W^{4+}–NO species absorbing around 1788 cm^{-1}: evacuation leads to a partial conversion of the dinitrosyls into mononitrosyls. Partial oxidation of the dinitrosyls probably occurs in the presence of oxygen. We infer that $W^{4+}(NO)(O_2)$

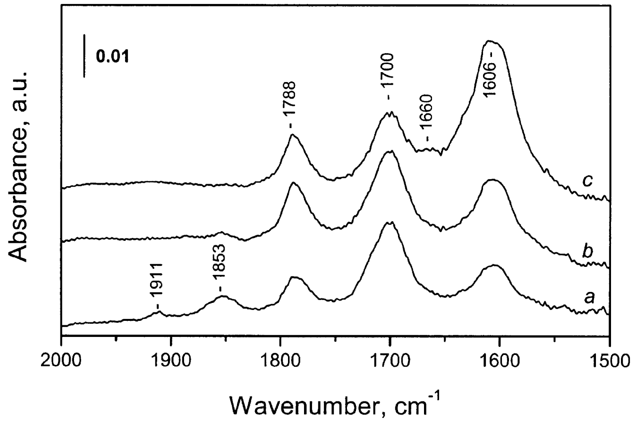

Figure 4. FTIR spectra of NO adsorbed on WO_3–ZrO_2 pre-reduced at 623 K (equilibrium NO pressure of 500 Pa) (a), after evacuation (b) and after subsequent addition of oxygen (1 kPa pressure) (c).

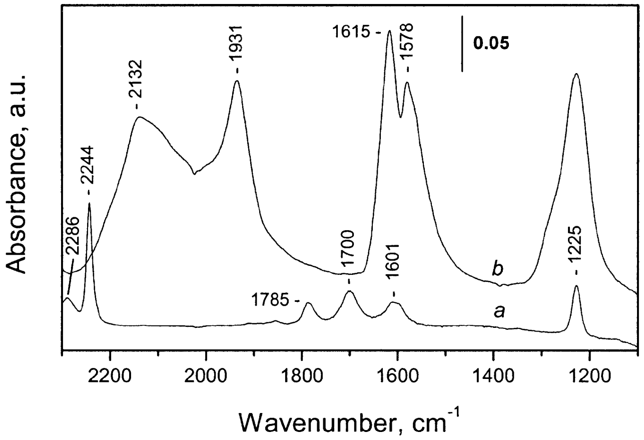

Figure 5. FTIR spectra of NO adsorbed on WO_3–ZrO_2 pre-reduced at 673 K (equilibrium NO pressure of 500 Pa) (a) and after evacuation of oxygen (1 kPa initial pressure) (b).

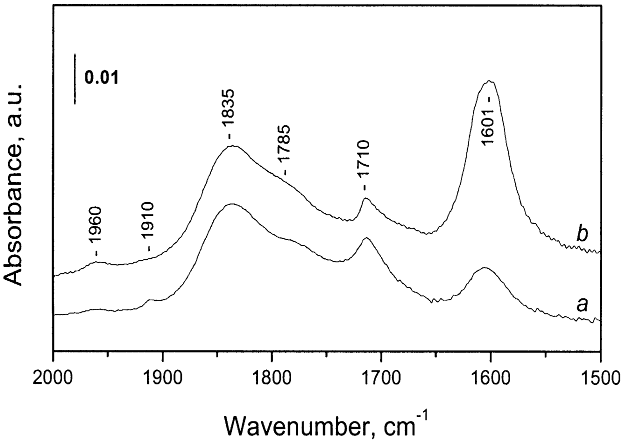

Figure 6. FTIR spectra of NO adsorbed on Pt/WO_3–ZrO_2 pre-reduced at 523 K (equilibrium NO pressure of 500 Pa) (a) and after evacuation (b).

species might also be formed which are characterized by the very weak broad band at ~1660 cm^{-1} (figure 4, spectrum c).

It is known that NO + O_2 mixtures have a higher oxidation potential than oxygen. To verify the stability of the nitrosyls of reduced tungsten ions in a NO + O_2 atmosphere, firstly NO (500 Pa equilibrium pressure) was adsorbed on a sample reduced at 673 K (figure 5, spectrum a), followed by introduction of oxygen (1 kPa) (figure 5, spectrum b). The bands at 1785 and 1700 cm^{-1}, characterizing $W^{4+}(NO)_2$ species, immediately disappeared and bands observed after NO adsorption and NO + O_2 coadsorption on an oxidized sample appeared instead. This indicates oxidation of the reduced tungsten sites in the NO + O_2 atmosphere.

3.3. *Adsorption of NO on a reduced Pt/WO_3–ZrO_2 catalyst*

A Pt/WZ sample was reduced at 523 K and NO (500 Pa equilibrium pressure) was adsorbed. As a result, bands or shoulders at 1960, 1910, 1835, 1780, 1710 and 1601 cm^{-1} appeared in the spectrum (figure 6). After short evacuation the band at 1960 cm^{-1} gained intensity and the band at 1601 cm^{-1} strongly increased (figure 6, spectrum b). The band at 1835 cm^{-1} was not affected, while the band at 1910 cm^{-1} almost disappeared and the 1710 cm^{-1} band decreased in intensity. In agreement with literature data, the band at 1960 cm^{-1} can be assigned to Pt^{n+}–NO species [27], whereas the band at 1835 cm^{-1} is attributed to linear NO nitrosyls on reduced platinum sites [27,28]. The 1601 cm^{-1} band was already assigned to nitrates. However, a possible origin of this band from twofold bridged NO species on metallic Pt [28] or bent nitrosyls is not excluded [29]. The band at 1710 cm^{-1} could also characterize platinum nitrosyls, namely of the Pt^0–NO type that have been observed at 1740 cm^{-1} [28]. However, we infer that this band is due to the ν_s modes of $W^{4+}(NO)_2$ species, the respective ν_{as} vibrations being observed as a shoulder of the 1835 cm^{-1} band around 1785 cm^{-1}. Note that the $W^{4+}(NO)_2$ bands are of considerably higher intensity than the same bands observed on the WZ sample reduced at the same temperature (figure 2). Thus, the presented results suggest that platinum decreases the reduction temperature at which W^{4+} cations are formed on tungstated zirconia. Unfortunately, we cannot draw any conclusions about the concentration of W^{5+} sites, since the strong band of Pt^0–NO species masks the eventual W^{5+}–NO band.

3.4. *Relevance of observed reduced W^{n+} sites for the catalytic performance*

The presented results help us to elucidate the catalytic behavior of WZ and Pt/WZ systems. The redox mechanism of formation of Brønsted acid sites is in part supported by the adsorption experiments on the reduced WZ catalysts which clearly demonstrate that partial reduction of the WO_x layer takes place at temperatures close to reaction temperature. As expected, the presence of platinum facilitates the reduction of WO_x and increases the number of Brønsted acid sites on the surface. At the same time, platinum also promotes a deeper reduction of the tungsten layer forming a significant amount of W^{4+}-containing sites. The acid strength of $W^{4+}O_x(2H^+)$ sites is lower than one of $W^{5+}O_x(H^+)$ due to a higher electronegativity of the central tungsten ion. Thus, they are expected to be less active in promoting a carbocationic reaction mechanism. Our supposition is qualitatively supported by the experimental studies of pretreated Pd/WO_x systems, which indicate that the acid strength of a reduced tungsten oxide support decreases in the order $W^{6+}O_x > W^{5+}O_x > W^{4+}O_x$ [30]. Deep reduction of a tungsten layer should, therefore, cause a long-term decrease in activity, the effect being more pronounced at higher temperatures, which was indeed observed experimentally [31, 32].

4. Conclusions

1. Reduced tungsten sites can be detected on tungstated zirconia by using NO as an IR probe molecule. With NO, W^{5+} sites form linear W^{5+}–NO nitrosyl species that are characterized by an IR band at $1855\,cm^{-1}$ and are removed by evacuation. The W^{4+} sites form stable $W^{4+}(NO)_2$ dinitrosyls characterized by symmetric and antisymmetric stretching modes at $\sim$1785 and $1700\,cm^{-1}$, respectively.
2. The reductive pretreatment of the unpromoted WZ catalyst at all temperatures studied leads to the formation of W^{5+}- and W^{4+}-containing Brønsted acid sites. The easy reduction of the WO_x layer, observed by IR, strengthens in part the general assumption which states that active reaction centers, namely Brønsted acid sites, are generated *in situ* by the redox mechanism [1,3,4].
3. Platinum considerably promotes the reduction of tungstated zirconia and generates larger amounts of active reaction centers on the surface. On the other hand, a deep reduction of a WO_x layer creates weaker Brønsted acids which is believed to lead to a long-term decline of catalytic activity.
4. An IR spectroscopic study of adsorbed NO is a powerful tool for characterizing WZ-based systems, as it is able to detect different reduced tungsten sites. Application of this approach in combination with catalytic measurements should give a better insight into the reaction mechanism and predict the long-term stability of the catalysts.

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