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Evolution of active species of nanostructured anatase-supported V–O–Mo catalyst in the course of reduction and oxidation

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Abstract

A nanostructured anatase supported V–O–Mo catalyst with V:Mo:Ti = 1:9:90, obtained by sol–gel method from inorganic substrates, was investigated. The structure of the species formed on the catalyst surface in the course of synthesis was determined and its evolution during oxidation and reduction was studied by the FT Raman spectroscopy. Vanadia-like monolayer islands with some molybdenum atoms substituted for vanadium ones were found to prevail on the surface of the catalyst. Oxidation was revealed to cause monolayer islands to join through monolayer bridges formed by vanadium segregating on the surface. However, reduction of the oxidised catalyst was shown to result in the splitting of the monolayer islands into smaller ones with higher molybdenum content. During the strong reduction irreversible transformation of the vanadia-like surface species into the resembling molybdena ones was observed.
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Keywords: V–O–Mo/anatase; Reduction; Oxidation; Anatase nanocrystallites; Monolayer surface species

1. Introduction

Vanadia supported on anatase is the most frequently used catalyst for selective catalytic reduction (SCR) of NO_x ($x = 1$ or 2) by ammonia to N_2 and H_2O, e.g. [1–6]. Anatase is known as a "structural" support for V_2O_5 catalysts, because of a good crystallographic fit between both phases [7]. This good matching ensures good mechanical strength of the catalyst. Vanadia–tungsta catalysts have been found to be much more active in selective NO reduction than vanadia itself [8–10]. Unfortunately, both vanadia and vanadia–tungsta catalysts undergo poisoning by As_2O_3 [1,8,9]. Molybdena–vanadia catalysts are known to be more active than vanadia but less active than vanadia–tungsta catalysts. However, they are resistant to arsenic poisoning [11]. The very active vanadia-like surface species with some tungsten cations substituted for vanadium ones were recently found on the surface of a rutile supported V–O–W catalyst [12,13]. Analogous species containing molybdenum ions substituted for vanadium ones were expected to be formed on anatase nanocrystallites of V–O–Mo/TiO_2(a) catalyst.

The aim of our research was to determine the structure of surface species of the V–O–Mo/TiO_2(a) catalyst and their evolution during reduction and oxidation. We expected the results will be helpful to anticipate how the catalyst will behave in reaction mixtures with different oxygen concentrations.

2. Experimental

2.1. Synthesis of the anatase supported V–O–Mo catalyst

The precursor of an anatase supported nanostructured V–O–Mo catalyst with V:Mo:Ti = 1:9:90 was prepared by sol–gel method [14] from $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and $VO(NO_3)_2$ substrates. A TiO_2 sol solution (6 wt.%) was instilled into a 12 wt.% mixed salt solution under stirring and

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ammonia was added to accomplish hydrolysis. The obtained gel was dried at 353 K in an evaporator for 1 h and next calcinated in air. The calcination temperature was chosen on the basis of the results of TG/DTA measurements. Weight loss at ca. 770 K became negligible and therefore the temperature of 773 K was chosen for obtaining the catalyst.

Anatase was the only phase detected by XRD and electron diffraction in the catalyst. The average sizes of anatase crystallites were determined from the XRD peaks broadening with the use of Sherrer equation [15] as well as by direct measurements in dark field TEM images. They were equal to 6.7 nm. A detailed physicochemical catalyst characterisation is presented elsewhere [16].

2.2. Oxidation and reduction of the anatase supported V–O–Mo catalyst

Oxidation and reduction of the catalyst were performed in pyrex glass vacuum equipment and in a stainless steel flow reactor.

In the first case, three tubes containing the anatase supported V–O–Mo catalyst, that had been stored in laboratory, were sealed in vacuum equipment. The catalyst was first evacuated to 1×10^{-3} Pa at 723 K and next annealed at this temperature in oxygen (2.9×10^4 Pa) for 2 h. After removing the oven from around the catalyst, one of the tubes was detached (but not opened) from the vacuum equipment. The catalyst in the two other tubes was then heated to 773 K in vacuum (1×10^{-3} Pa) at the same temperature for 2 h. After removal from the oven, the second tube was detached. Finally, oxygen under 2.9×10^4 Pa pressure was introduced to the equipment and the catalyst was annealed at 723 K for 2 h. FT Raman spectra of the oxidised and reduced catalysts were taken 3 days later.

In the second case, the first fraction of the catalyst stored in laboratory was annealed in a stainless steel tubular reactor at 613 K in a flow (50 cm^3/min) of He containing 0.08 vol.% NH_3 for 0.5 h. It was next cooled to room temperature in helium and a Raman spectrum was taken after 3 days. The second catalyst fraction was annealed in an 0.08% NH_3/He stream under the same conditions as the first one and then oxidised in an oxygen flow (50 cm^3/min), first at 773 K for 3 h, then at 613 K for 20 h. The catalyst was then cooled to room temperature in an oxygen flow and the FT Raman spectrum was taken after 3 days. The third catalyst fraction was reduced at 613 K in an Ar flow (50 cm^3/min), containing 5% NH_3 for 0.5 h and next oxidised in the same conditions as the second catalyst.

2.3. Investigation of the structure of the surface species

A BIO-RAD FT Raman spectrometer with Spectra Physics Nd Yag Laser with an excitation line 1064 nm was used. The sampling width was 2 cm^{-1}. To follow the evolution of the structure of the catalyst surface, a wavenumber range of 800–1200 cm^{-1} of the Raman spectra, corresponding to the M=O stretching vibrations in V–Mo–O system [17,18] was chosen for detailed analysis.

3. Results and discussion

Fig. 1 presents FT Raman spectra in the M=O stretching vibration range of the catalyst oxidised at 723 K in oxygen (a), of the oxidised catalyst next reduced in vacuum (b), and of the catalyst re-oxidised in oxygen after vacuum reduction (c). Before measurements were taken, the catalysts were stored in Pyrex glass tubes sealed under 2.9×10^4 Pa oxygen or under vacuum. All peaks were normalised on the most intensive anatase peak at 152 cm^{-1}. The common feature of all the spectra is the presence of the intensive peak centred at ca. 1000 cm^{-1} and the weaker one at ca. 1100 cm^{-1}. The first of them is the dominant one in the spectra of oxidised and re-oxidised catalysts. However, in the spectrum of the

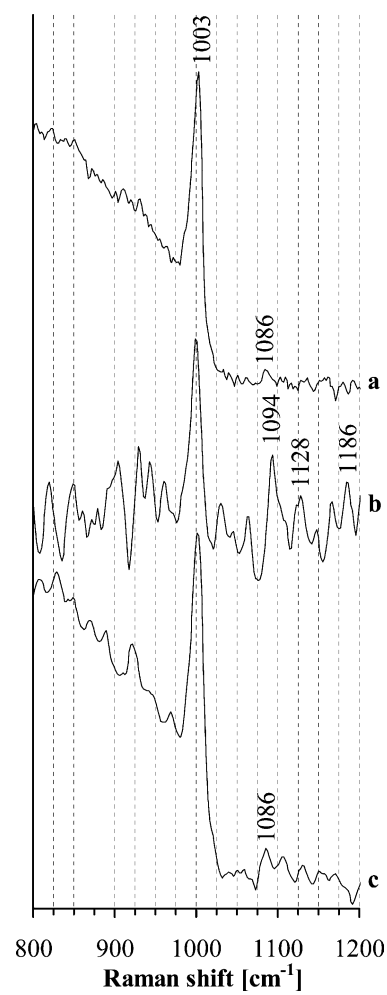

Fig. 1. Raman spectra in Mo=O and V=O double bond stretching vibration range (normalised on anatase peak at 152 cm^{-1}) of anatase supported V–O–Mo catalyst: (a) oxidised at 723 K in oxygen (2.9×10^4 Pa) for 2 h; (b) first oxidised at 723 K in oxygen (2.9×10^4 Pa) for 2 h and next reduced at 723 K in vacuum (1×10^{-3} Pa); (c) reoxidised at 723 K in oxygen (2.9×10^4 Pa) for 2 h.

reduced catalyst, many new peaks of different intensities appear beside that at ca. 1000 cm^{-1}. The peak at 1094 cm^{-1} is the most intense among them. Peaks at wavenumbers close to 1000 cm^{-1} could be ascribed to double bond stretching vibrations in the vanadia-like or molybdena-like surface species. However, it should be noted that the wavenumber values of those vibrations reported for V=O perpendicular to the (0 0 1) plane of crystalline vanadia (notification according to Nat. Bur. Stand. Circ. [17]), and for Mo=O perpendicular to the (0 1 0) plane of crystalline molybdena, are a few cm^{-1} lower [18,19]. A peak at 1092 cm^{-1} was observed by Chiker et al. [18] in spectra of anatase supported vanadia catalyst, with loading corresponding to 0.62 and 5.4 vanadia layers. The spectra of both the catalysts were taken at room temperature in air after previous catalyst treatment at 573 K in air.

Thus the peak at 1094 cm^{-1} in spectrum "b" in Fig. 1 can be ascribed to V=O stretching vibration in vanadia-related surface species occurring either as monolayer islands or as crystallites.

The Raman spectra of the samples of microcrystalline unsupported MoO_3–V_2O_5 solid solution, obtained by fusion of molybdena and vanadia [20], provide further insight into a possible origin of that peak. Fig. 2 shows (non-normalised) Raman spectra of the MoO_3–V_2O_5 solid solution containing 7 mol.% V_2O_5, in the V=O and Mo=O double bonds' stretching vibration range. The spectra were taken for the ground samples: (a) annealed at 723 K in vacuum for 40 h, (b) annealed at 723 K in air for 40 h and (c) first annealed at 723 K in vacuum for 40 h and then stored in ambient conditions for a few weeks. Spectra "a" and "b" were taken not later than 0.5 h after cooling the samples. Bands at ca. 1000 and 1100 cm^{-1} are present in all the spectra. However, the bands at ca. 1100 cm^{-1} in the spectra of the samples annealed ("a" and "b") are more intensive than those at ca. 1000 cm^{-1}, whereas in the spectrum of the sample stored in ambient conditions the band at ca. 1000 cm^{-1} is much more intense than that at ca. 1100 cm^{-1}. One can thus think that double bonded oxygen ions, represented by the bands at ca. 1100 cm^{-1}, appear during thermal treatment of the solid solution micro-crystallites and disappear as a result of their room temperature interaction with air. Observed disappearance of the double-bonded oxygen ions in the course of the sample storage in ambient conditions can be explained by the dissociative water adsorption occurring on double-bonded oxygen ions and neighbouring V or Mo ions in the vanadia structure and resulting in the formation of a pair of OH groups. However, formation of the double-bonded oxygen ions during the sample annealing at 723 K can occur as a result of the removal of those groups in the form of water molecules (dehydroxylation process). The results of DFT calculations have shown that the OH groups do not form on the basal vanadia plane at relatively low temperatures [21]. However, according to Anderson [22], those groups form at room temperature on the side faces of vanadia crystallites. It can be thus concluded that the bands observed by Chiker et al. [18] at 1092 cm^{-1} for vanadia catalysts originate from the stretching vibrations of the V=O bonds formed after OH groups have been removed from the side (1 0 0) and (0 1 0) [17] faces of vanadia crystallites or from the edges of the (0 0 1) monolayer islands.

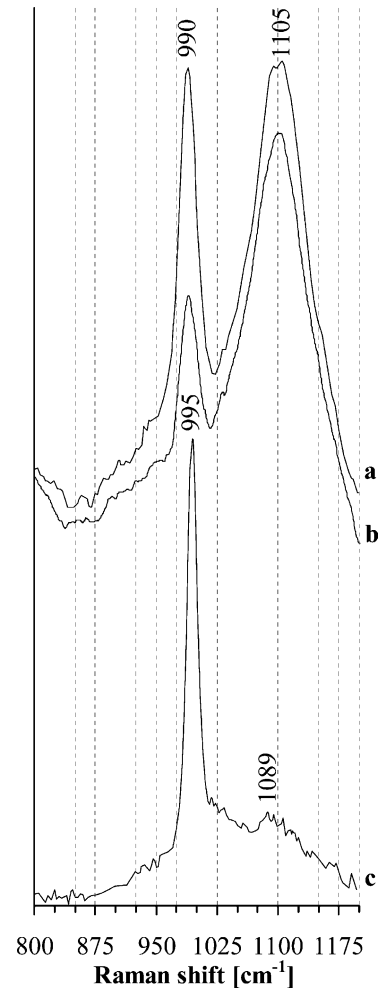

Fig. 2. Raman spectra (non-normalised) in Mo=O and V=O double bond stretching vibration range of: microcrystalline MoO_3–V_2O_5 solid solution (7 mol.% MoO_3): (a) annealed at 723 K in vacuum for 40 h; (b) annealed at 723 K in air for 40 h; (c) first annealed in vacuum at 723 K for 40 h and next stored in ambient conditions for a few weeks.

The very low intensities of the bands at ca. 1100 cm^{-1} in the spectra of the oxidised and re-oxidised catalysts (Fig. 1a and c) and significant intensity of that band in the spectrum of the evacuated catalyst (Fig. 1b) can thus be explained by vanadia-like monolayer formation in oxygen and its partition into numerous islands, with a long line of edges, in vacuum. The monolayer can be formed as a result of oxidation-induced surface vanadium segregation. Contrary to this, partitioning of the monolayer results from reduction-induced vanadium diffusion from vanadia-like monolayer into anatase crystallites. The XPS results [16] confirm an increase of the surface vanadium concentration in the course of the catalyst oxidation and a distinct decrease

during catalyst reduction. The decrease of the intensity of the band at ca. 1100 cm^{-1} during catalyst annealing in oxygen could also be attributed to ionic radical O^- formation on the edges of monolayer islands. However, the absence of oxygen radicals in the EPR spectrum of the oxidised catalyst [16] allows this possibility to be rejected.

The peaks at ca. 1130 and 1180 cm^{-1} were observed by Belokopytov et al. [23] in spectra of molybdenum trioxide obtained from ammonium paramolybdate as well as from molybdic acid. Therefore the weak bands at 1128 and 1186 cm^{-1} in the spectrum of the evacuated catalyst can be ascribed to stretching vibrations of Mo=O on island edges. The presence of molybdenum on island edges suggests substitution of molybdenum atoms for vanadium ones in the surface vanadia-like monolayer. Formation of the bulk MoO_3–V_2O_5 solid solution, containing up to 30 mol.% MoO_3, was reported earlier [20].

To follow the surface species evolution in the conditions of the stronger reduction, the catalysts were subjected to interaction with solutions of ammonia in noble gases, 0.08 vol.% NH_3/He or 5 vol.% NH_3/Ar, at 613 K. Fig. 3 presents spectra of: (a) the catalyst stored in ambient conditions; (b) the catalyst maintained at 613 K in a He stream (50 cm^3/min) containing 0.08 vol.% NH_3; (c) the catalyst additionally oxidised in an oxygen stream (50 cm^3/min), first at 773 K and next at 613 K; (d) the catalyst heated at 613 K in an Ar stream containing 5% NH_3 (50 cm^3/min) and next oxidised in the same conditions as catalyst "c". The bands at ca. 1000 cm^{-1} are missing in the spectra of all the catalysts. However, the bands at ca. 970 cm^{-1} are observed instead. The intensity of that band decreases as a result of the catalyst reduction with 0.08 vol.% NH_3/He (b) increases as a result of the next catalyst oxidation (c). Thus they seem to originate from vanadium containing oxidic species. The reduction of the catalyst during interaction with ammonia and its oxidation in the course of the thermal treatment in oxygen were confirmed by XPS measurements [16]. As reported by Chiker et al. [18], water adsorption weakens the Mo=O double bonds in molybdena-like surface species and causes the peak to shift to 966 cm^{-1}. Water adsorption can also be expected to weaken the M=O (M=V and Mo) bonds in the vanadia-like monolayer species on the surface of the V–O–Mo catalyst stored in ambient conditions. Experimental confirmation of this expectation is shown in Fig. 4, which presents spectrum of the anatase-supported V–O–Mo catalyst annealed at 723 K in air (a) and spectrum of that catalyst next stored in ambient conditions for 20 days (b). Spectrum "a" was taken 0.5 h after the catalyst was removed from the hot oven. The presence of the band at ca. 1100 cm^{-1} in the spectra of both catalysts and the band centred at 993 cm^{-1} in the spectrum of the annealed catalyst shows the presence of vanadia-like monolayer islands with high V concentration. The shift of the band from 993 to 970 cm^{-1} as a result of catalyst storage in ambient conditions clearly confirms weakening of the M=O bonds in vanadia-like monolayer species by water adsorption.

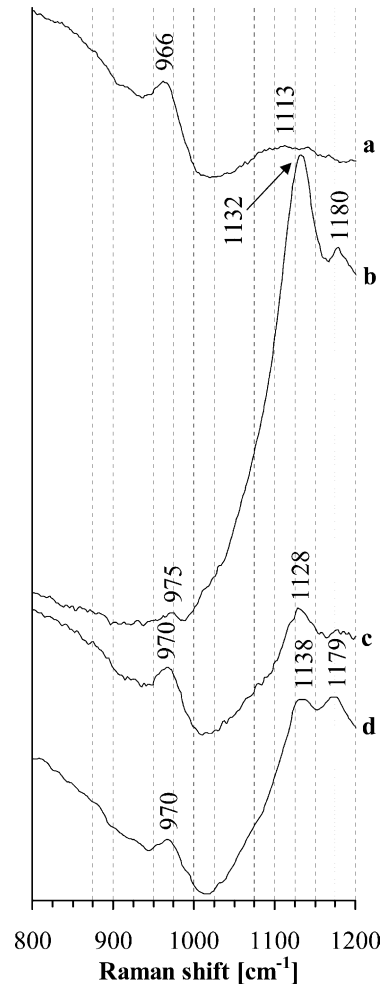

Fig. 3. Raman spectra in the Mo=O and V=O double bond stretching vibration range (normalised on the anatase peak at 152 cm^{-1}) of anatase-supported V–O–Mo catalyst: (a) stored in ambient conditions for several weeks; (b) reduced at 613 K in a He flow containing 0.08 vol.% NH_3 for 0.5 h; (c) first reduced at 613 K in 0.08% NH_3/He flow for 0.5 h, next oxidised in oxygen flow at 773 K for 3 h and at 613 K for 20 h; (d) first reduced in 5% NH_3/He flow for 0.5 h next oxidised in oxygen flow at 773 K for 3 h and at 613 K for 20 h.

Thus it can be concluded that thermal treatment of the catalyst in an ammonia-containing atmosphere causes vanadia-like monolayer species to partition into parts of the smaller total surface. The large band centred at 1113 cm^{-1} in the spectrum of the stored catalyst (a) is composed of the peaks at ca. 1100 and 1130 cm^{-1}. It shows that the vanadia-like monolayer islands with some molybdenum atoms substituted for vanadium ones are present at the catalyst surface. The disappearance of the band at ca. 1100 cm^{-1}, the increase of the intensity of the band at ca. 1132 cm^{-1}, and the appearance of the band at ca. 1180 cm^{-1} in the spectrum of the catalyst subjected to interaction with ammonia (b) show reduction-induced diffusion of vanadium into anatase nanocrystallites. This occurrence has also been detected by XPS [16]. However, partial reappearance of the band at ca. 1100 cm^{-1} and a decrease in

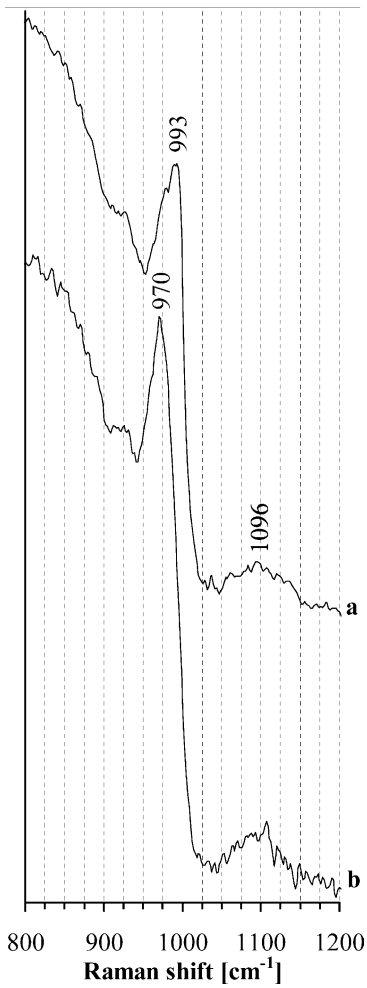

Fig. 4. Raman spectra in the Mo=O and V=O double bond stretching vibration range (normalised on anatase peak at 152 cm^{-1}) of anatase-supported V–O–Mo catalyst: (a) annealed at 723 K in air for 3 h and (b) first annealed at 723 K in air for 3 h and next stored in ambient conditions for 20 days.

the intensity of the bands at ca. 1132 and 1180 cm^{-1} in the spectra of the catalysts additionally annealed in oxygen (c and d) revealed oxidation-induced surface vanadium diffusion also detected by XPS [16]. The oxidation results only in partial recovering of the initial species on the catalysts' surface (c and d). Recovery is more advanced in the case of the catalyst reduced by less-concentrated ammonia (c). The observed difficulties in recovering the initial species, increasing with a degree of reduction (compare "c" and "d") show deep changes in the surface species' structure. It could be concluded that strong reduction-induced enrichment of vanadia-like species in molybdenum causes their transformation into molybdena-like ones. Recovery of the V–O–V vanadia-like species by the next surface vanadium diffusion accompanying oxidation is not possible because of vanadium poor solubility in molybdena [24]. Thus oxidation of the strongly reduced catalyst results mostly in the formation of V–O vanadia-like monolayer species and the oxidation of molybdena-like ones.

4. Conclusions

A nanostructured V–O–Mo–O–Ti catalyst with V:Mo:Ti = 1:9:90 was obtained by sol–gel method from $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, $VO(NO_3)_2$ and 6 wt.% TiO_2 sol solution. The structure of the species formed on the catalyst surface in the course of its synthesis was determined and its evolution during catalyst oxidation and reduction was investigated.

It was found that: (i) vanadia-like monolayer islands with some molybdenum atoms substituted for vanadium ones are formed on the catalyst surface in the course of the synthesis, (ii) mild vacuum catalyst reduction causes monolayer islands to partition into smaller ones as a result of inward vanadium diffusion, (iii) surface catalyst oxidation results in an almost complete recovery of the vanadia-like V–O–Mo species, (iv) catalyst reduction with ammonia leads to irreversible changes in the surface species structure. The molybdena-like monolayer islands appear and a great number of them stay at the surface during the next oxidation. Thus instead of initial V–O–Mo vanadia-like monolayer islands, separated V–O vanadia-like and Mo–O molybdena-like monolayer islands are formed.

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