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Competition between NO reduction and NO decomposition over reduced V–W–O catalysts

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Abstract

The SCR of NO and NO decomposition were investigated over a V–W–O/Ti(Sn)O_2 catalyst on a Cr–Al steel monolith. The conversions of NO and NH_3 over the reduced and oxidised catalysts were determined. The higher conversion of NO than of NH_3 was observed in SCR over the reduced catalyst and very close conversions of both substrates were found over the oxidised one. The increase of the pre-reduction temperature was found to cause an increase in catalyst activity and its stability in direct NO decomposition. The surface tungsten cations substituted for vanadium ones in vanadia-like active species are considered to be responsible for the direct NO decomposition. The results of DFT calculations for the 10-pyramidal clusters: $V_{10}O_{31}H_{12}$ (V–V) and $V_9WO_{31}H_{12}$ (V–W) modelling (0 0 1) surfaces of vanadia and WO_3–V_2O_5 solid solution (s.s.) active species, respectively, show that preferable conditions for NO adsorption exist on W sites of s.s. species and that reduction causes an increase in their ability for electron back donation to the adsorbed molecule. Electron back donation is believed to be responsible for the electron structure reorganisation in the adsorbed NO molecule resulting in its decomposition. The high selectivity of NO decomposition to dinitrogen was considered to be connected with the formation of the tungsten nitrosyl complexes solely via the W–N bond. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: NO reduction; NO decomposition; V–W–O catalysts

1. Introduction

Anatase supported vanadia–tungsta catalysts are commonly applied for NO_x ($x = 1$ or 2) removal from the off-gasses of the stationary sources of emission (power and heat plants, nitric acid factories and stationary diesel engines) [1–3]. Ammonia is used as a selective NO_x reductant in the presence of oxygen. Selective catalytic reduction (SCR) of nitric oxide to dinitrogen occurs according to the formula

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \qquad (1)$$

This process is usually carried out with NH_3:NO = 1. The catalyst reduction is observed in the absence of oxygen and, to a less extent also, in the presence of its stoichiometric amount [4]. The forming dinitrogen molecules were shown [1] to contain one nitrogen atom originating from ammonia and the other from nitric oxide. The formation of the dinitrogen molecules with both the atoms originating from nitric oxide was observed in SCR process over V_2O_4 [5]. It was unambiguously shown that N_2 molecules were formed by NO reaction with V–H species appearing due to ammonia dissociation. N_2 formation via direct NO decomposition was noticed [6] in the course of interaction of NO + O_2 mixture with the unsupported V–W–O catalyst (V:W = 2:9) obtained by vanadia species segregation on the V–W oxide bronze crystallites [7,8] obtained from oxalate precursors [9]. It

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was found that at temperatures 423–563 K nitric oxide undergoes decomposition according to the formula:

$$2NO \rightarrow N_2 + O_2 \qquad (2)$$

with maximum of conversion (ca. 60%) at 443 K and selectivity to N_2 above 95%. Decrease of NO conversion with increase of the temperature from 443 to 573 K was ascribed to gradual changes in the exposed catalyst surface.

Nowadays it is clear that heating of the V–W–O catalyst at temperatures 443–573 K in the presence of oxygen causes oxidation of its surface layers followed by oxidation-induced surface vanadium segregation [10,11]. Thus, the observed gradual decrease of the catalyst activity with the temperature increase from 443 to 573 K may come from both decrease of the surface tungsten concentration and/or increase in the oxidation state of the catalyst surface.

In the present paper effort is undertaken to reveal: (i) if and why the surface tungsten concentration in the V–W–O catalyst influences the rate of NO decomposition, (ii) if and why oxidation state of the V–W–O catalyst surface influences this rate, (iii) which sites in V–W–O catalyst are responsible for NO decomposition, (iv) what is the reason for the exceptionally high selectivity to dinitrogen in the NO decomposition.

2. Experimental

2.1. Synthesis of the monolithic catalyst

The Cr–Al steel monolith was prepared from a steel foil 0.05 mm thick containing 20 wt.% Cr and 5 wt.% Al via the rolling of two sheets, one smooth and the second sinusoidally folded.

To prepare a monolithic catalyst the adhesive alumina layer was formed at the surface of the Cr–Al steel foil [12]. Next the mixture of Al_2O_3 and $Ti(Sn)O_2$ sols was deposited on the foil and the monolith was annealed at 733 K for 3 h. Then $Ti(Sn)O_2$ sol was deposited on the mixed layer and the monolith was again annealed at 733 K for 3 h. The precursor of the monolithic V–W–O/$Ti(Sn)O_2$ catalyst was obtained by deposition of the V_2O_5–WO_3 solid solution hydrate on a $Ti(Sn)O_2$ rutile support similarly as was described earlier [10]. Before the hydrate synthesis tungsten chloride was transformed to tungsten isopropoxide according to the procedure described by Yamaguchi [13]. The dehydration of the deposited solid solution hydrate accompanied by the surface segregation of vanadia-like surface species was performed by annealing at 773 K in air for 3 h [10].

2.2. Catalyst reduction

The reduction of the catalyst was performed at 516 and 613 K in a helium stream containing 800 ppm NH_3 for 0.5 h.

2.3. NO SCR by ammonia

SCR of NO by ammonia was investigated at temperatures 300–573 K. An on-line Hewlett-Packard 5890 GC with a 5971 MS as a chromatographic detector was used for analysis of the gases passing through an HP-1 (cross-linked methyl silicone gum) column. The chromatograms for selected ions ($15NH_3$, 30NO, $32O_2$, $44N_2O$ and $46NO_2$) were registered and integrated. The feed introduced to the reactor contained 350 ppm nitric oxide, 350 ppm NH_3 and 8.5% of oxygen in helium. The total GHSV measured by an Omega mass flowmeter was equal to $6100\,h^{-1}$. The measurements were performed for the catalyst reduced at 573 K directly before measurements and for the catalyst previously used in NO SCR at 300–573 K.

2.4. NO decomposition

The direct NO decomposition was investigated at 427 and 407 K for $GHSV = 2500\,h^{-1}$ over the catalysts reduced at 613 K as well as at 427 K over the catalyst reduced at 516 K.

2.5. Quantum chemical modelling

All calculations were carried out using the Gaussian 98 program set [15]. The B3LYP hybrid functional [16], i.e., the combination of the Becke's 1988 exchange functional [17] with Hartree–Fock exchange and the correlation functional of Lee et al. [18,19] was used in Kohn–Sham scheme. The Lan2DZ basis set, namely, D95 basis set [20] for oxygen and hydrogen atoms, and Los Alamos [21–23] effective core potential plus double zeta for metal atoms was employed. On the base of FT Raman spectra of the V–W–O unsupported [11] and supported [10] catalysts it was found that vanadia-like species with some tungsten atoms substituted for vanadium ones are formed as a result of vanadium segregation at the catalyst surface. These species are also thought to be responsible for catalyst activity in NO decomposition. To model the structure of such species the 10-octahedral cluster $V_9WO_{31}H_{12}$ representing the basal (0 0 1) surface of the vanadia structure containing one tungsten atom was built. As it was earlier found the (0 0 1) surface of vanadium pentoxide is well represented by the $V_{10}O_{31}H_{12}$ cluster model [24].

3. Results and discussion

In Fig. 1 the conversions of NO (shaded column) and ammonia (white column) at 423 (a), 473 (b) and 573 K (c) over the reduced catalyst as well as at 423 (d) and 473 K (e) over the one used are presented. The selectivity to nitrogen over both catalysts was above 95%. As seen, the ammonia conversion at 423 K over the reduced catalyst is 34% lower than that of NO. The difference between both the conversions at 473 K over this catalyst is only 4% and both conversions are close to 100% at 573 K. Conversely, over the used catalyst already at 423 K both conversions are the same. It strongly suggests that NO decomposition occurs beside NO SCR over the reduced catalyst but it does not occur over the used one. As it was shown in [10] the use of the catalyst in NO SCR with an excess of oxygen causes oxidation of the active species followed by surface vanadium segregation. It can be thus concluded that the loss of the catalyst activity is caused by diminishing in the amount of the exposed tungsten atoms.

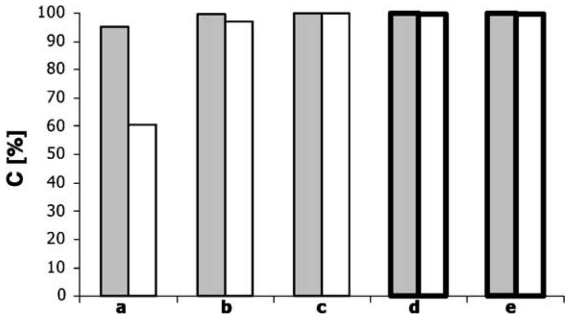


Fig. 1. The NO (shaded column) and NH_3 (white column) conversions in SCR conditions (350 ppm NO, 350 ppm NH_3, 0.4% O_2, 6100 h^{-1}) at 423 (a), 473 (b) and 573 K (c) over the catalyst reduced (He + 800 ppm NH_3) at 613 K for 0.5 h as well as at 423 (d) and 473 K (e) over the catalyst previously used in NO SCR in the temperature range of 300–573 K.

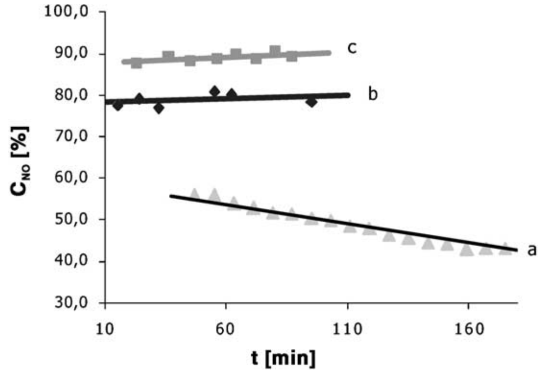


Fig. 2. The NO conversion in the reaction of the direct NO decomposition (in the absence of ammonia in the feed) at 427 K over the catalyst reduced (He + 800 ppm NH_3, for 0.5 h) at 516 K (a), at 407 K over the catalyst reduced in the same conditions at 613 K (b), at 427 K over the catalyst reduced at 613 K (c).

In Fig. 2 the results of the investigation of the direct NO decomposition (feed without ammonia) are presented as the conversion at 427 K over the catalysts reduced at 516 (a) and 613 K (c), as well as at 407 K over the catalyst reduced at 613 K (b). The increase of the conversion with the increase of the decomposition temperature from 407 to 427 K over the catalyst reduced at 613 K confirms the results obtained for the unsupported catalyst showing the maximum activity at 443 K [6]. The conversions at both temperatures do not change for 100 min. On the other hand, a distinct decrease in NO conversion with time is observed over the catalyst reduced at 516 K. This can be explained by the instability of the active species formed during catalyst reduction at 516 K. As it was shown earlier [7,8,11] polymeric and crystalline vanadia-like species containing some tungsten atoms substituted for vanadium ones are formed as a result of the surface vanadium segregation which occurs during the catalyst annealing at 773 K in air. The reduction-induced cation segregation in these species [8,11], similarly as in earlier investigated [25] molybdenum containing species, causes inward vanadium diffusion. The increase of the surface activity at 427 K with the increase of the reduction temperature suggests that the number of the tungsten atoms exposed at the catalyst surface is higher in the catalyst reduced at a higher temperature. The gradual decrease in surface tungsten concentration as a result of the gradual oxidation of both the cation concentrations is thought to be responsible for the decrease of NO conversion at 427 K in the course of experiment. The stable NO conversions at 407 and 427 K over the catalyst reduced at 613 K show the stability of the active species. This suggests that reduction-induced strong enrichment of the catalyst surface in tungsten results in the appearance of the vanadia–tungsta intermediate phase (IP) more resistant to oxidation than the WO_3–V_2O_5 solid solution. None such phase is known for the V–W–O system but the IP with formula V_2MoO_8 [26] does exist in the related V–Mo–O system. It is formed on MoO_3–V_2O_5 solid solution crystallites as a result of the surface molybdenum segregation following their reduction [27]. The comparison of the Raman spectra of the V–W–O [8,10,11] and V–Mo–O catalysts [28] confirms the presence of IP V–W–O structurally related to V_2MoO_8.

To discuss the possible influence of tungsten atoms and the degree of the reduction of vanadia-like species on their activity in NO decomposition, quantum mechanical calculations were performed for the 10-pyramidal cluster representing vanadia structure with some tungsten atoms substituted for vanadium ones. The cluster modelling WO_3–V_2O_5 solid solution with a cross-section along $y = 0$ plane is presented in Fig. 3. The hydrogen atoms are introduced to achieve cluster embedding. The saturation of missing bonds at the cluster periphery also minimises the electronic parameter dependence on cluster size. In the model, all structurally different oxygen atoms are well described, namely vanadyl O(1) coordinated to one vanadium atom; bridging oxygen O(2) coordinated to two vanadium atoms; O(3) coordinated to three vanadium atoms. The substitution of the central vanadium atom by one of tungsten in the vanadia-like structure mimics the WO_3–V_2O_5 solid solution. Such an exchange results in simultaneous reduction of the nearest vanadium atom from V^{5+} to V^{4+}. The $V_9WO_{31}H_{12}$ cluster can be considered as a natural extension of the previously employed small VWO_9H_8 model [11,14].

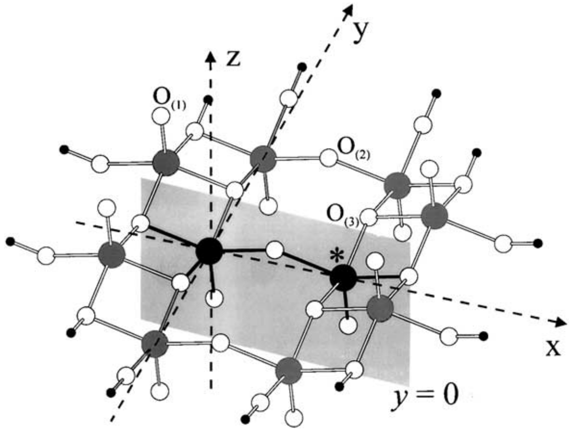
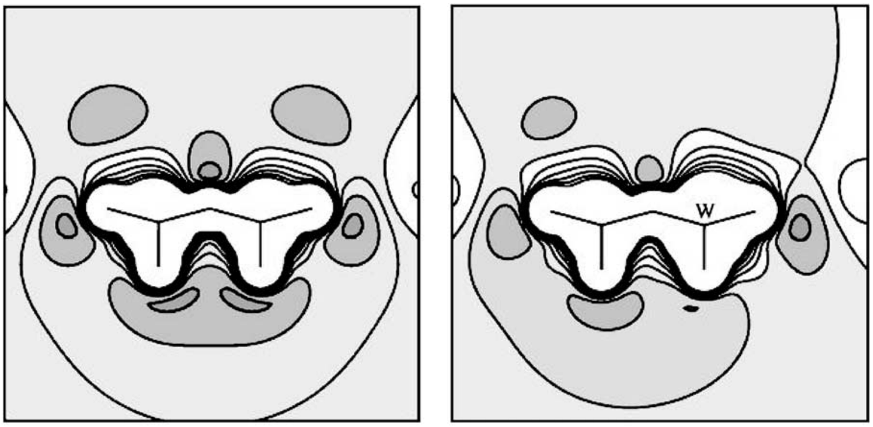


Fig. 3. The 10-pyramidal cluster representing the structure of (0 0 1) layer of WO_3–V_2O_5 solid solution. The V (O) atoms are shown as shaded (white) balls while small black balls correspond to hydrogen atoms used to saturate oxygen atoms, artificially cut from the (0 0 1) surface layer. The star indicates the point at which V to W exchange takes place. Electrostatic potential discussed in the paper is illustrated in $y = 0$ plane.

In Fig. 4 the electrostatic potential in $y = 0$ plane (see Fig. 3) is plotted for the $V_{10}O_{31}H_{12}$ cluster modelling (0 0 1) V_2O_5 (a) and for the $V_9WO_{31}H_{12}$ cluster representing (0 0 1) layer of WO_3–V_2O_5 solid solution (b). The negative basins above and below the active sites containing two metal ions joined by double bridging oxygen are due to the lone electron pairs located on oxygen atoms. Although both patterns of electrostatic potential are qualitatively similar, it is seen distinctly that the W-adsorption site is less screened by valence electrons than the V-active site. It is also reflected by Mulliken population data [29]. The charge on W atom (close to 2.1) is greater than on V one (close to 1.2). Thus, the W for V replacement may facilitate nucleofilic attack of the NO molecule on the less screened W-adsorption site. This situation was also observed for the two-pyramid cluster model [14], where the binding energies favoured the water adsorption on W site instead of the neighbouring V one.

It has been recently shown, by DC conductivity measurements [4], that NO adsorbs on the surface of slightly reduced V–W–O catalysts in the form of negatively charged ions. The results of DFT calculations indicate that electron chemical potentials for the reduced $V_9WO_{31}H_{12}$ clusters are distinctly higher than for $V_{10}O_{31}H_{12}$ ones [29]. It may be the reason of the easier electron transfer from catalyst to antibonding NO orbital on reduced solid solution species than on



(a) (b)

Fig. 4. Contour plots of the electrostatic potential at $y = 0$ plane (see Fig. 3). Parts (a) and (b) correspond to $V_{10}O_3H_{12}$ and $V_9WO_{31}H_{12}$ clusters, respectively.

reduced V_2O_5 ones. It could be expected that the electron donation to the NO molecule results in its inverse polarisation leading to dissociation.

On the other hand, nitric oxide is known to form nitrosyl complexes with tungsten ions in which NO molecules are bonded with W only by nitrogen atoms [30]. Interaction of neighbouring nitrosyl ligands is believed to result in the formation of N_2 and O_2 molecules.

4. Conclusions

The investigations of the NO SCR and the direct NO decomposition over the V–W–O/Ti(Sn)O_2 catalyst on the Cr–Al steel monolith previously reduced or oxidised were performed. The results showed that

(i) NO decomposition competes with NO reduction under SCR conditions over the reduced catalyst, while only NO reduction takes place under the same conditions over the oxidised catalyst;
(ii) in the absence of ammonia in the feed, direct NO decomposition occurs over the reduced catalysts;
(iii) the results of quantum mechanical calculations (DFT) for the 10-pyramidal clusters representing vanadia and V_2O_5–WO_3 solid solution structures were used in the discussion of the reduced catalyst activity in NO decomposition.

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