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Journal of Molecular Catalysis A: Chemical 162 (2000) 423–430

JOURNAL OF  
MOLECULAR  
CATALYSIS  
A: CHEMICAL

www.elsevier.com/locate/molcata

# Vanadia–chromia grafted on titania: structural and catalytic properties in the selective catalytic reduction of NO by NH<sub>3</sub>

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Dedicated to H. Knözinger on the occasion of his 65th birthday.

## Abstract

Chromia–vanadia on titania catalysts were prepared by sequential and simultaneous chemical reaction (grafting) of alkoxide and amide precursors of the transition metals with hydroxyl groups of the surface of titania. Their structure and redox properties under mild conditions were investigated by temperature programmed reduction by hydrogen (TPR) and spectroscopic methods, including UV–VIS and EPR. The oxidation state of the grafted transition metals depended strongly on pre-treatment conditions. Catalysts derived by grafting both transition metals (CrO<sub>x</sub>–VO<sub>x</sub>/TiO<sub>2</sub>) as well as corresponding titania-supported single oxide catalysts, VO<sub>x</sub>/TiO<sub>2</sub> and CrO<sub>x</sub>/TiO<sub>2</sub>, were investigated in the selective catalytic reduction of nitric oxide by ammonia. The catalytic properties of CrO<sub>x</sub>–VO<sub>x</sub>/TiO<sub>2</sub> could be explained by the superimposed characteristic behaviours (activity, temperature range, selectivity) of the reference systems VO<sub>x</sub>/TiO<sub>2</sub> and CrO<sub>x</sub>/TiO<sub>2</sub>. Neither catalytic nor spectroscopic investigations indicated any interaction between grafted VO<sub>x</sub> and CrO<sub>x</sub>. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Vanadia–chromia/titania catalysts; Selective catalytic reduction of nitric oxide by ammonia; Grafting

## 1. Introduction

Supported vanadium as well as chromium oxides are known to exhibit interesting, but different catalytic properties for the selective catalytic reduction (SCR) of nitric oxide by ammonia [1–5]. Promoted vanadia systems, which are broadly commercially used since long time, show high activity and selectivity at temperatures above 550 K. Supported chromium oxides are active at still lower temperatures but their selectivity to N<sub>2</sub> is strongly correlated with the na-

ture (oxidation state) of the chromium oxide phase, which is determined by a number of factors such as preparation, pre-treatment, support and dispersion [6,7].

Due to the distinctly different properties of both transition metal oxides in the SCR reaction they represent an interesting system for the study of corresponding mixed catalysts and their mutual influence in catalysis. Novel chemical and catalytic properties could be expected for combined chromium–vanadium oxides on titania, if some catalytic synergy between the transition metals exists. As an example, such a synergy is observed in SCR on titania-supported V<sub>2</sub>O<sub>5</sub>–WO<sub>3</sub> catalysts prepared by grafting [8]. The interaction of the grafted oxide

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components in this system results in higher activity compared to the corresponding titania-supported single oxides. TOF-SIMS investigations revealed the existence of W–O–V connectivities affording a strong interaction between the grafted oxide components.

The objective of this work was to explore whether a similar synergistic effect exists in the  $\text{CrO}_x\text{--VO}_x/\text{TiO}_2$  system. Strong bonding of the transition metals to the surface and high dispersion can be achieved by grafting [9–11]. Consequently catalysts were prepared by sequential (first V and subsequently Cr oxide, or vice versa) and simultaneous grafting (single grafting including both transition metals) of a vanadium alkoxide and a chromium amide, successfully applied in the literature [12,13].  $\text{CrO}_x/\text{VO}_x\text{--TiO}_2$  as well as the corresponding titania-supported single oxide reference catalysts,  $\text{CrO}_x/\text{TiO}_2$  and  $\text{VO}_x/\text{TiO}_2$ , were investigated in the SCR of nitric oxide by ammonia.

## 2. Experimental

### 2.1. Catalyst preparation

Chromium and vanadium were deposited on the titania carrier by a sequential grafting procedure with *tris*-diisopropylamide-chromium(III),  $(\text{Cr}[\text{N}(\text{i-Pr})_2]_3)$ , or vanadium-oxo-triisopropoxide,  $(\text{VO}[\text{O}(\text{i-Pr})]_3)$ , respectively, dissolved in hexane or isopropanol.  $\text{Cr}[\text{N}(\text{i-Pr})_2]_3$  was prepared according to the procedure reported in [14] and  $\text{VO}[\text{O}(\text{i-Pr})]_3$  (> 95% purity) was obtained from Gelest, USA.

The titania support material was conditioned as described previously [13]:  $\text{TiO}_2$  (P25, Degussa; anatase:rutile  $\approx$  3:1) was agglomerated, dried and sieved to particles of 0.3–0.5 mm diameter and finally evacuated ( $< 0.1$  mbar) at 390 K to obtain a mildly dehydrated surface. Before further deposition steps any other sample underwent this conditioning procedure too. Per gram of this sample 0.35 mmol  $\text{Cr}[\text{N}(\text{i-Pr})_2]_3$  or  $\text{VO}[\text{O}(\text{i-Pr})]_3$  were added in 5 ml hexane or isopropanol and the glass reactor was kept at 325 K for 12 h. The solution was then removed and unreacted precursor molecules were washed out three times with fresh solvent. The samples were dried in flowing nitrogen at 360 K for 1 h. For the

sequential grafting, residual organic ligands of the amide or alkoxide precursors were removed from the samples as follows: grafted V-systems underwent calcination at 573 K for 3 h in flowing oxygen with subsequent exposition to moist nitrogen at 425 K, whereas Cr-samples were hydrolysed in a stream of  $\text{H}_2\text{O}$  saturated nitrogen at 425 K for 3 h only. The samples prepared by sequential grafting are denoted as VCr or CrV, depending on the grafting order, and the single component systems are named V, Cr, or 2V and 2Cr for doubly grafted samples, respectively.

For comparison a sample was prepared in a one step grafting procedure using a combination of both precursors (0.3 mmol each) dissolved in hexane (5 ml  $\text{g}^{-1}$  of support). This sample will be denoted as (VCr).

### 2.2. Catalyst characterisation

Surface area (BET) was determined by nitrogen adsorption at 77 K using a micromeritics ASAP2000 equipment. The chromium and vanadium content of the catalysts was determined as follows: ground samples were dissolved in 5 ml aqueous HF (40%, later diluted to a total volume of 50 ml) and the chromium/vanadium content was determined by atomic absorption spectroscopy, AAS.

Temperature programmed reduction in  $\text{H}_2/\text{Ar}$  (5%,  $T$  raised from ambient to 970 K at 10  $\text{K min}^{-1}$ ) was used to characterise the reduction behaviour of samples containing chromium in high oxidation states (Cr(V) and Cr(VI)) after oxidative calcinations ( $\text{O}_2$ , 150  $\text{ml min}^{-1}$ , 573 K, 3 h). The apparatus used has been described in detail in a previous study [15].

Paramagnetic resonance spectra were recorded on a Bruker ESP300(E) system at X-band frequency at temperatures between 77 and 420 K; microwave frequency about 9.4 GHz, microwave power 5 mW, modulation frequency 100 kHz. The  $g$  values were determined with a NMR magnetometer and DPPH as  $g$  marker. The spectra intensity was obtained by numerical double integration of the sample and reference (DPPH) spectra using the ESP300E software.

UV–VIS spectra were recorded on a spectrometer equipped with an integration sphere (Perkin-Elmer, model Lambda 16). The diffuse reflectance spectra were recorded under ambient conditions using  $\text{BaSO}_4$  as a reference. For simulation and presentation the

spectra were transformed to the Kubelka–Munk function.

### 2.3. Catalytic tests

The activity of differently pretreated samples in the SCR of NO by NH<sub>3</sub> was tested. The testing procedure and the apparatus used have been described in detail elsewhere [16]. A feed gas containing 900 ppm of each NO and NH<sub>3</sub> and 1.8% O<sub>2</sub> (Ar balance) was passed over the catalyst bed (0.126 ml). Selectivities to N<sub>2</sub> and N<sub>2</sub>O are defined as

$$S_i = \frac{2F_i}{F_{\text{NO},\text{in}} + F_{\text{NH}_3,\text{in}} - F_{\text{NO},\text{out}} - F_{\text{NH}_3,\text{out}}}$$

where  $F_i$  are the molar flow rates of species  $i$  (N<sub>2</sub> or N<sub>2</sub>O) at the reactor outlet. Both reactants, which were mixed equimolarly in the SCR feed, were taken into account because of the uncertain stoichiometry of the reactions leading to N<sub>2</sub> and N<sub>2</sub>O, respectively [6,17].

## 3. Results and discussion

### 3.1. Morphology

Table 1 lists morphological properties of the samples. It emerges that each grafting step resulted in the deposition of  $150 \pm 25 \mu\text{mol g}^{-1}$  (metal per gram support), regardless whether Cr or V was deposited

Table 1  
Morphological properties of titania-supported single oxides and mixed CrO<sub>x</sub>/VO<sub>x</sub>-TiO<sub>2</sub> catalysts prepared by grafting

| Sample           | Symbol used in Fig. 3 | AAS: loading ( $\mu\text{mol g}^{-1}$ ) |          | $S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ ) |
|------------------|-----------------------|---|----------|---|
|                  |                       | Cr                                      | V        |   |
| 1Cr <sup>a</sup> | ●                     | 150 ± 10                                | –        | 44.5 ± 0.2                                      |
| 2Cr              | ○                     | 253 ± 26                                | –        |   |
| 1V               | ■                     | –                                       | 137 ± 10 |   |
| 2V               | □                     | –                                       | 263 ± 9  |   |
| CrV              | ◆                     | 149 ± 2                                 | 164 ± 9  | 44.3 ± 0.3                                      |
| VCr              | △                     | 152 ± 11                                | 125 ± 10 |   |
| 2VCr             | ◇                     | 76 ± 3                                  | 242 ± 10 | 44.2 ± 0.3                                      |
| (VCr)            | ▲                     | 144 ± 11                                | 174 ± 9  |   |

<sup>a</sup> Denotation of catalysts is explained in Section 2.

and virtually independent of the order of grafting. The only exception was observed for chromia deposited onto a doubly vanadia grafted sample (2VCr), which lead to a Cr loading of about half the value of that observed in the other cases. After three repeated grafting steps the restricted number of remaining surface OH-groups reduced the amount of transition metal bound to the support. Obviously, the alkoxide and amide precursors prefer to react with surface OH-groups of the titania support and not with the Cr or V surface complexes. Note that the alkoxide and amide ligands were removed by hydrolysis or calcination before each new grafting step.

The specific surface area (BET) did not vary significantly with the catalyst loading, consequently a general value of  $44 \text{ m}^2 \text{ g}^{-1}$  was used for all samples in surface based calculations.

### 3.2. Temperature programmed reduction

Differences in the reducibilities of the titania-supported oxide species were assessed by TPR with hydrogen for in situ calcined samples (O<sub>2</sub>, 570 K, 3 h). The hydrogen consumption profiles were fitted with a minimum number of skewed single Gaussian peaks to describe the relative amounts of H<sub>2</sub> attributed to discernible reduction steps.

The reduction behaviour of ‘single’ V- or Cr-loaded catalysts (1Cr, 2Cr, 1V, 2V) is schematically represented in Fig. 1A. For CrO<sub>x</sub>/TiO<sub>2</sub> the maximum H<sub>2</sub> consumption rate is observed at ca. 590 K and an additional peak appears at 710 K, the latter is attributed to the incorporation of Cr into the TiO<sub>2</sub> lattice (electron paramagnetic resonance (EPR), Fig. 2) [13]. 91% of the total hydrogen consumption were due to the first reduction step. This corresponded to an average lowering of the oxidation state,  $\Delta\text{OS} = 2.8$ , which indicates the predominance of Cr(VI) in the calcined sample (assuming Cr(III) as final oxidation state). For grafted VO<sub>x</sub>/TiO<sub>2</sub> a single maximum was observed at 700–710 K and it was shown by comparison with other V quantification methods (XRF, ICP, NAA) that  $\Delta\text{OS}$  was  $2.0 \pm 0.1$  in TPR [12,18], which indicates a quantitative reduction of V(V) to V(III).

In Fig. 1B the reduction profiles of (VCr) and 2VCr are presented. In both profiles the H<sub>2</sub> consumption shows two maxima at 580–590 and at

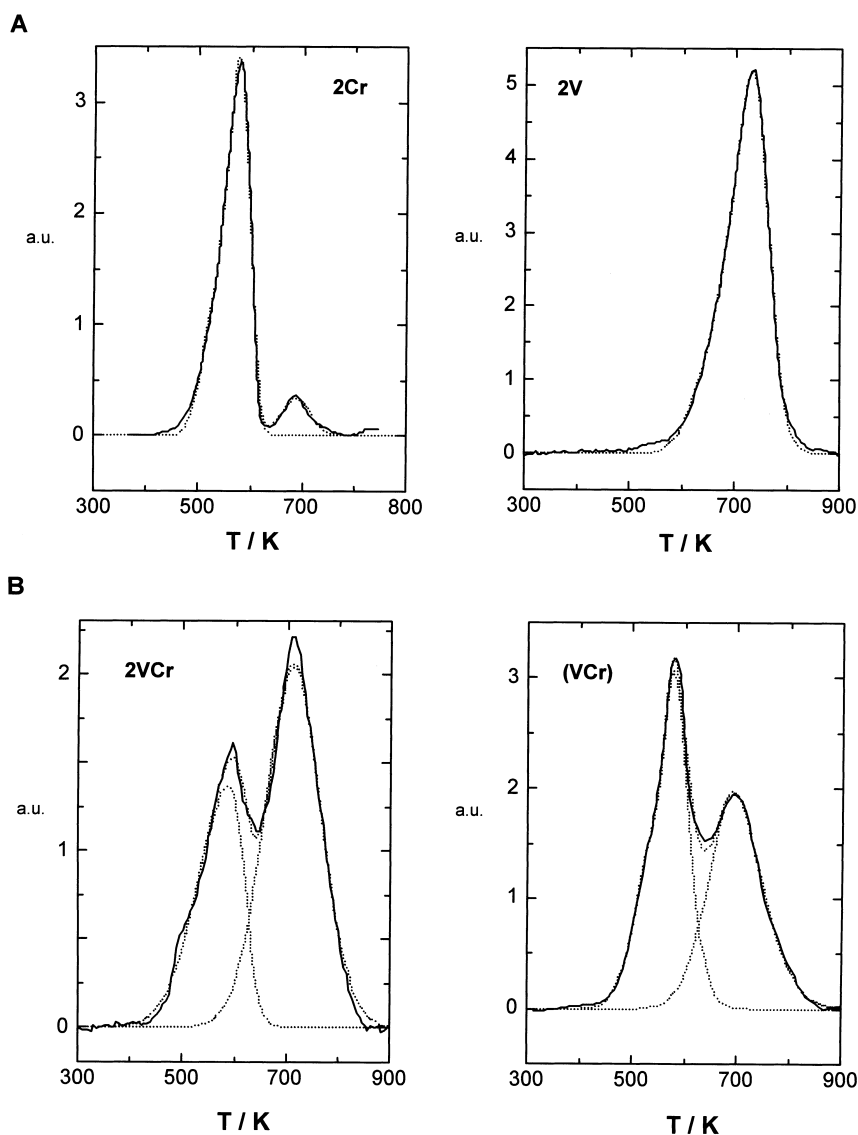


Fig. 1. Temperature programmed reduction (TPR) profiles of the titania-supported single oxide (A: 2Cr, 2V) and  $\text{CrO}_x/\text{VO}_x\text{-TiO}_2$  catalysts (B: 2VCr, (VCr)).

700–710 K. This profiles are consistent with the superimposed profiles of the ‘single’ (V or Cr) grafted catalyst. Further support for such a superposition of  $\text{VO}_x/\text{TiO}_2$  and  $\text{CrO}_x/\text{TiO}_2$  TPR behaviour emerges from the estimation of the relative amounts of hydrogen corresponding to the two peaks (Table 2).

When  $\Delta\text{OS} = 3$  is assumed for Cr species and  $\Delta\text{OS} = 2$  is taken for V, the value of  $3\text{Cr}/(3\text{Cr} + 2\text{V})$

reflects the percentage of hydrogen due to the reduction of Cr(VI) to Cr(III).

### 3.3. Structural properties (UV-VIS, EPR)

#### 3.3.1. EPR spectra of samples after hydrolysis at 570 K ( $\text{N}_2$ , water saturated)

The EPR spectra for all samples show broad symmetric lines with  $g = 1.985$  and linewidths  $\Delta B_{\text{pp}}$

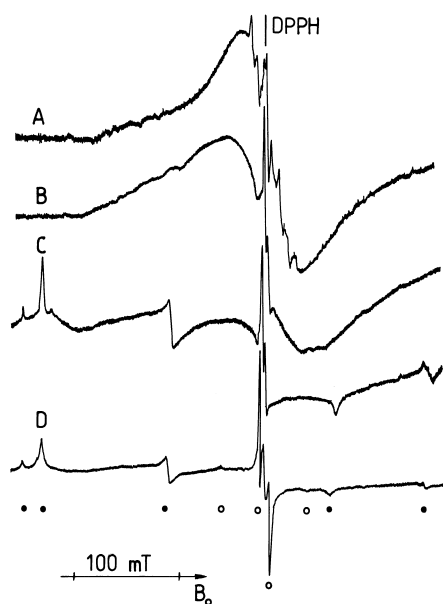


Fig. 2. Electron paramagnetic resonance (EPR) spectra recorded at room temperature in the X-band of mixed  $\text{CrO}_x\text{-VO}_x/\text{TiO}_2$  catalysts (CrV) after hydrolysis in  $\text{N}_2/\text{H}_2\text{O}$  at 573 K (A); after calcination in oxygen (573 K, 3 h) followed by SCR reaction at 623 K (B); after reduction in hydrogen (623 K, 2 h) followed by SCR reaction at 623 K (C) and after temperature programmed reduction in hydrogen up to 873 K (D). Spectrum D represents a superposition of the spectra  $\text{Cr}^{3+}$  incorporated into the lattices of rutile (full circles) and anatase (open circles).

of about 70 mT ( $\beta$ -phase) without remarkable influence ( $\pm 5$  mT) of the chromium concentration (Fig. 2A and [13]). There is no indication of a chromium oxidation state other than +3 by EPR. These signals are assigned to Cr(III)-oxygen clusters ( $\beta$ -phase [19]). Only in this case (after hydrolysis at higher temperatures) the chromium  $\beta$ -signal is superimposed by a vanadium(IV) signal (Fig. 2A). This  $\text{V}^{4+}$  signal ( $3d^1$ ,  $S = 1/2$ ) is characterized by the line octet due to hyperfine interactions between the unpaired vana-

dium electron and the  $^{51}\text{V}$  nucleus ( $I = 7/2$ , natural abundance 100%; only the perpendicular lines are observed due to low intensity of the parallel lines). There is no indication of an interaction between the paramagnetic chromium and vanadium species and only small quantitative differences between samples with different chromium–vanadium ratio were observed.

### 3.3.2. EPR spectra after calcination in oxygen at 570 K for 3 h

In the spectral pattern (not shown) only a signal due to Cr(V) ( $3d^1$ ,  $S = 1/2$ ,  $\gamma$ -signal,  $g_{\perp} = 1.970$  and  $g_{\parallel} = 1.950 \pm 0.002$ ) is observable.

### 3.3.3. EPR spectra after TPR

After TPR (to 700 K) chromium is almost quantitatively incorporated into the rutile and anatase lattices of the support (Fig. 2D, for spectral parameters see [20] and literature cited therein). Note that the titania support used is composed of rutile:anatase  $\approx 3:1$ . The percentage of chromium in rutile is much (about 100 times) larger than in anatase (chromium is known to migrate much easier into rutile than into anatase).

### 3.3.4. EPR spectra of catalysts after SCR reaction ( $T$ up to 600 K, 45 h)

The EPR spectra after SCR depend strongly on the pre-treatment of the catalysts. The samples calcined in oxygen (570 K) after SCR show broad symmetric EPR lines (Fig. 2B) with  $g = 1.98$  ( $\Delta B_{\text{pp}} = 95$  mT at  $T = 293$  K, and  $\Delta B_{\text{pp}} = 120$  mT at 130 K) superimposed by two narrow signals at  $g_{\perp} = 1.974$ ,  $g_{\parallel} = 1.965$  and  $g_{\perp} = 1.989$ ,  $g_{\parallel} = 1.944$ , respectively, which are believed to be due to  $\text{Cr}^{5+}$  and  $\text{Cr}^{1+}$  [21]. Note that after calcination only Cr(V) and

Table 2

Data and interpretation of the TPR experiments for the  $\text{CrO}_x/\text{VO}_x\text{-TiO}_2$  catalysts, compare text

| Sample | Peak at 590 K | Peak at 710 K | AAS: relative Cr content: $\text{Cr}/(\text{Cr} + \text{V})$ | $3\text{Cr}/(3\text{Cr} + 2\text{V})$ |
|--------|---------------|---------------|--|---------------------------------------|
| (V)Cr  | 51%           | 49%           | 0.43   | 0.53                                  |
| 2V)Cr  | 35%           | 65%           | 0.24   | 0.32                                  |

Cr(VI) were observed. The  $\beta$ -signal is assigned to Cr(III)-oxygen clusters. For samples pre-treated in hydrogen at  $T = 573$  K and then exposed to SCR feed, the EPR spectra (Fig. 2C) show that a remarkable amount of chromium is incorporated into the rutile lattice of the support (however, not into anatase modification). The correspondingly reduced chromium surface concentration is assumed to be the reason for the reduced catalytic activity (compare catalytic results).

### 3.3.5. UV–VIS diffuse reflectance spectroscopy

Below 400 nm, all diffuse reflectance spectra were dominated by strong absorptions of the titania carrier. The spectra of the grafted chromium containing samples pretreated by hydrolysis exhibited at least two absorption bands (i) at 480 and (ii) at 660 nm. They are ascribed to the  $A_{2g} \rightarrow T_{1g}$  and  $A_{2g} \rightarrow T_{2g}$  d–d transitions due to Cr(III). Upon calcination in oxygen, the bands due to  $Cr^{3+}$  observed before disappeared. A new pronounced band at 455 nm was assigned to the forbidden  ${}^1A_1 \rightarrow {}^1T_1$  charge-transfer (CT) transition of tetrahedrally coordinated Cr(VI) centres [22]. This band was reduced in intensity for samples, in which vanadium was also present. This is the only difference between pure chromium and mixed chromium–vanadium catalysts in their UV–VIS spectra.

In summary, in line with the TPR results, spectroscopic measurements including EPR and UV–VIS diffuse reflectance spectroscopy, performed on  $CrO_x$ – $VO_x$ /TiO<sub>2</sub> did not indicate the existence of species other than those observed for the corresponding titania-supported single oxides  $VO_x$ /TiO<sub>2</sub> [12,23] and  $CrO_x$ /TiO<sub>2</sub> [13]. Particularly, no indication for the formation of V–O–Cr connectivities could be found in the range of catalyst loadings investigated. This contrasts the structural features observed for titania-supported  $V_2O_5$ – $WO_3$  catalysts of similar loading, for which the existence of V–O–W connectivities was evidenced recently [8]. However, it should be stressed that possible interaction between grafted  $CrO_x$  and  $VO_x$  cannot be ruled out at higher catalyst loading than applied in this study. Higher population density of these species is likely to favour such interactions, but probably also undesired agglomeration of the grafted active species.

## 3.4. Catalytic tests (SCR)

Results of the catalytic tests in the selective reduction of NO by  $NH_3$  are given in Table 3. The calculated turnover frequencies (TOFs) are based on the sum of deposited vanadium and chromium determined by AAS. Values of  $\ln(\text{TOF})$  range from  $-9.7$  to  $-7.2$ , indicating differences in the specific reaction rates of a factor 12.

Striking differences in activity and selectivity were observed depending on the pre-treatment of the catalysts.

### 3.4.1. Catalysts calcined in oxygen

There is little difference between the activity of Cr, V or mixed Cr–V systems calcined in oxygen (values for  $\ln(\text{TOF})$  ranging from  $-7.8$  to  $-7.2$ ). Highest activities were observed for the titania-supported single oxide systems  $VO_x$ /TiO<sub>2</sub> and  $CrO_x$ /TiO<sub>2</sub>. The only exception is the significantly lower activity of singly grafted  $VO_x$ /TiO<sub>2</sub> ( $-9.7$ ), which can be traced to the dependence of the intrinsic

Table 3

Results of selective catalytic reduction of NO by  $NH_3$  over of titania-supported single oxides and mixed  $CrO_x$ /VO<sub>x</sub>–TiO<sub>2</sub> catalysts<sup>a</sup>

| Sample           | Pre-treatment                  | $\ln(\text{TOF})^b / s^{-1}$<br>(473 K) | $S_{N_2O}^c$<br>(473 K) |
|------------------|--------------------------------|---|-------------------------|
| 1Cr <sup>d</sup> | H <sub>2</sub> /Ar; 720 K; 2 h | $-7.8$                                  | 0.07                    |
| 1Cr              | O <sub>2</sub> /Ar; 570 K; 2 h | $-7.2$                                  | 0.41                    |
| 2Cr              | O <sub>2</sub> /Ar; 570 K; 2 h | $-7.3$                                  | 0.43                    |
| 1V               | O <sub>2</sub> /Ar; 570 K; 2 h | $-9.7$                                  | 0.01                    |
| 2V               | O <sub>2</sub> /Ar; 570 K; 2 h | $-7.3$                                  | 0.01                    |
| CrV              | H <sub>2</sub> /Ar; 720 K; 2 h | $-7.7$                                  | 0.04                    |
| CrV              | O <sub>2</sub> /Ar; 570 K; 2 h | $-7.7$                                  | 0.07                    |
| VCr              | H <sub>2</sub> /Ar; 720 K; 2 h | $-8.0$                                  | 0.08                    |
| VCr              | O <sub>2</sub> /Ar; 570 K; 2 h | $-7.6$                                  | 0.13                    |
| 2VCr             | H <sub>2</sub> /Ar; 720 K; 2 h | $-8.0$                                  | 0.02                    |
| 2VCr             | O <sub>2</sub> /Ar; 570 K; 2 h | $-7.7$                                  | 0.03                    |
| (VCr)            | H <sub>2</sub> /Ar; 720 K; 2 h | $-7.6$                                  | 0.04                    |
| (VCr)            | O <sub>2</sub> /Ar; 570 K; 2 h | $-7.8$                                  | 0.08                    |

<sup>a</sup> Conditions are quoted in Section 2.

<sup>b</sup> As a measure of the catalytic activity turnover frequencies (TOF) per Cr/V atom are given. It represents the specific NO reaction rate per total amount of Cr + V in the catalyst determined by AAS, cf. Table 1.

<sup>c</sup> Determined at constant GHSV = 24000 h<sup>-1</sup>.

<sup>d</sup> Denotation of catalysts is explained in Section 2.

sic activity on the V loading reported before [24]. For combined Cr–V systems the sequence of deposition had no effect on the activity of the catalysts (CrV, VCr, 2VCr, (VCr):  $\ln(\text{TOF}) = 7.7 \pm 0.1$ ).

### 3.4.2. Reductive pre-treatment

Pre-treatment of the catalysts in  $\text{H}_2$  at 720 K resulted mostly in a significant decrease of the intrinsic SCR activity. For chromia on titania systems this behaviour was attributed to the partial incorporation of  $\text{Cr}^{3+}$  into the lattice of the titania support [13]. In fact,  $\text{Cr}^{3+}$ -incorporation was confirmed by EPR measurements also of the mixed Cr–V systems (Fig. 2C).

Interestingly, the effect of the reductive pre-treatment on the product distribution was beneficial. Compared to the catalysts calcined in oxygen, the formation of undesired  $\text{N}_2\text{O}$  was reduced in all cases. In Fig. 3 the dependence of the selectivity to  $\text{N}_2\text{O}$  on both the pre-treatment and the relative composition of the catalysts is shown. The beneficial effect of the reductive pre-treatment in  $\text{H}_2$  (Fig. 3B) is pronounced at 473 K, whereas exposition to higher reaction temperatures (re)enhances the formation of nitrous oxide. The selectivities observed for the combined V–Cr systems lie between those determined for the titania-supported single oxides,  $\text{VO}_x/\text{TiO}_2$  and  $\text{CrO}_x/\text{TiO}_2$ , irrespective of catalyst pre-treatment and composition.

The strong influence of pre-treatment and reaction temperature on the selectivity to  $\text{N}_2\text{O}$  (Fig. 3) correlates well with the literature results for the SCR reaction catalysed by supported chromium oxide catalysts [7,13]. It is known that higher chromium oxidation states (in particular  $\text{Cr}^{4+}/\text{CrO}_2$ ) are responsible for the production of  $\text{N}_2\text{O}$  (originating from ammonia oxidation [25]). Higher oxidation states arise from oxidative pre-treatment as well as exposure of the catalysts to SCR conditions at higher temperature (oxidation by oxygen (1.8%) in SCR feed gas mixture).

Concluding, we can state that neither the results of the spectroscopic investigations nor the catalytic tests do indicate a strong interaction of the active components,  $\text{VO}_x$  and  $\text{CrO}_x$ , in the  $\text{CrO}_x\text{--VO}_x/\text{TiO}_2$  system. The structural and catalytic properties of these catalysts in SCR of NO are reflecting the

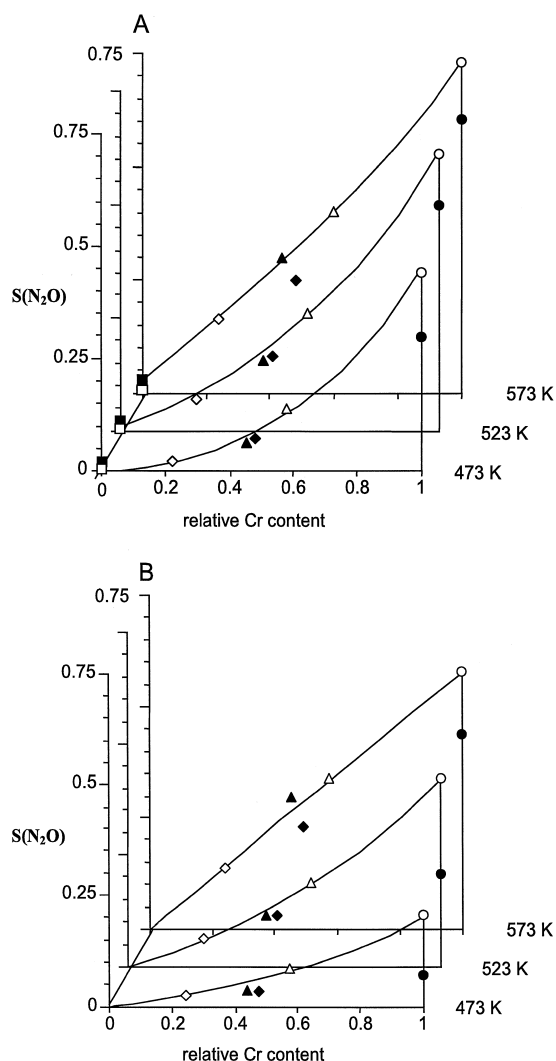


Fig. 3. Schematic representation of the selectivity of the  $\text{CrO}_x/\text{VO}_x/\text{TiO}_2$  catalysts in dependence of the relative content of chromium and vanadium (relative chromium content =  $n_{\text{Cr}}/(n_{\text{Cr}} + n_{\text{V}})$ ) for oxidative (A:  $\text{O}_2/\text{Ar}$ , 7.2%, 573 K, 2h) and reductive (B:  $\text{H}_2/\text{Ar}$ , 5%, 723 K, 2h) pre-treatment for different temperatures of the catalytic reaction (473, 523 and 573 K). For the notation/symbols compare Table 1. Note that catalysts  $\circ$  (2Cr) and  $\bullet$  (1Cr) differ in Cr loading.

properties of the corresponding titania-supported single oxide catalysts. This observation stands in contrast to the recently investigated  $\text{V}_2\text{O}_5\text{--WO}_3/\text{TiO}_2$  catalysts prepared by grafting, for which higher SCR activity compared to the corresponding titania-supported single oxides was observed [8].

#### 4. Conclusions

Titania-supported chromium–vanadium oxide catalysts were prepared by sequential and simultaneous grafting of corresponding alkoxide and amide precursors. In the single grafting steps chromium and vanadium species were bound to the surface and isolated from each other. Up to the third grafting step about similar amounts of transition metals were immobilized. In multiple graftings the alkoxide and amide precursors were found to react preferentially with surface OH-groups of the titania support and not with the previously immobilised Cr or V surface complexes.

The physico-chemical characteristics of the chromia–vanadia/titania catalysts, as well as their catalytic behaviour in the selective reduction of NO by NH<sub>3</sub>, fully reflect the properties of the corresponding titania-supported ‘single oxides’ VO<sub>x</sub>/TiO<sub>2</sub> and CrO<sub>x</sub>/TiO<sub>2</sub>. Thus, no indication was found for a synergistic effect caused by interaction of the two grafted active transition metal oxides.

#### Acknowledgements

Financial support by the Swiss National Science Foundation is kindly acknowledged. K.K. thanks the Fonds der Chemischen Industrie in Germany for financial support.

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