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Selective catalytic reduction of NO with NH₃ over Nb₂O₅-promoted V₂O₅/TiO₂ catalysts

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In contrast to previous claims, the addition of niobia to catalysts containing vanadia supported on titania resulted in much enhanced activity for low-temperature SCR of NO with NH₃ only at low vanadia loadings. Niobia promoted catalysts could also be demonstrated to show higher selectivities to N₂, especially at high temperatures and low vanadia loading. This enhancement of the activity cannot be explained only on the basis of the observation that niobia stabilized the surface area of the catalyst: calculations of the activation energy suggest that a different mechanism of the reaction may be at work at low vanadia loadings.

Keywords: Promoter effect; activity; selectivity; activation energy; vanadia [1314-62-1]; niobia [1313-96-8]; titania [13463-67-7]; SCR; DeNO_x

1. Introduction

Supported V₂O₅/TiO₂ is known to be one of the best catalysts for the selective catalytic reduction (SCR) of NO with NH₃ exhibiting practical activity at temperatures usually above 600 K [1,2]. However, the application of this type of catalysts for low-temperature SCR is hampered by the fact that both the activity and the stability of the catalyst are considerably affected by various impurities present in industrial stack gases (like SO₂), and by the presence of water vapour.

It has been reported that the performance of V₂O₅/TiO₂ catalysts in SCR can be modified by the addition of WO₃ [3,4]. In the presence of SO₂, the V₂O₅–WO₃/TiO₂ catalysts show an increased activity as compared to unpromoted V₂O₅/TiO₂. Moreover, the resistance towards deactivation by both alkali metal oxides and arsenous oxide is improved and finally the oxidation of NH₃ (a competitive reaction to SCR occurring at high temperatures) is suppressed. It has been found that WO₃ creates additional (both Brønsted and Lewis) acid sites in V₂O₅–

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WO₃/TiO₂, which are assumed to participate in the SCR reaction mechanism. However, no definite explanation of the role of WO₃ has as yet been presented.

Nb₂O₅ has been reported to be another promising promoter for V₂O₅/TiO₂ catalysts [5]. Addition of Nb₂O₅ considerably increases the activity of the catalyst in SCR of NO particularly at lower temperatures. Also an improved deactivation resistance towards SO₂ was observed. Raman studies of the interaction between V₂O₅ and Nb₂O₅ on TiO₂ surface [6] have revealed that niobia has some influence on the structure of the V₂O₅/TiO₂ system. As a result the surface area loss during calcination of the catalyst at high temperature is considerably reduced by the addition of Nb₂O₅. A reduction in the intensity of the crystalline vanadia Raman band was observed for 8 wt% V₂O₅/TiO₂ when increasing the amount of niobia.

Besides some Japanese patents (cited in ref. [5]) – claiming the benefits of Nb₂O₅ as a promoter for V₂O₅/TiO₂ catalysts – no comprehensive studies of the role of niobia have to our knowledge been reported so far. Selectivity data are missing, which are vital for the industrial applications. Further, the reported promoter effect may indicate important changes in the number of active sites, intrinsic activity and/or mechanism of the reaction. Such a lack of information prompted us to compare in this study the catalytic behaviour of several V₂O₅/TiO₂ and V₂O₅–Nb₂O₅/TiO₂ catalysts.

2. Experimental

V₂O₅–Nb₂O₅/TiO₂ catalysts were prepared with a two-step impregnation procedure in such a way that the sum of the calculated molar amounts of vanadia and niobia was equal to that of vanadia in 6 wt% V₂O₅/TiO₂ (which corresponds to approximate monolayer coverage on TiO₂ [6]). On the first step TiO₂ (Degussa P25) was impregnated with the water solution of ammonium metavanadate (Aldrich) to give V₂O₅/TiO₂ catalysts after drying and calcining in air at 573 K for 16 h. During the second step V₂O₅–Nb₂O₅/TiO₂ catalysts were obtained using the incipient wetness impregnation of V₂O₅/TiO₂ samples by a solution of niobium(V) ethoxide (Aldrich) in absolute ethanol. Due to the moisture sensitivity of Nb(OEt)₅ all operations were carried out under pure Ar. Finally, the V₂O₅/TiO₂ and V₂O₅–Nb₂O₅/TiO₂ catalysts were calcined at 673 K for 16 h in air. The specific surface area, average pore radius and pore volume of the catalysts were measured by the Hg-porosimetry method on Porosimeter 4000 (Carlo Erba) and are presented in table 1.

All samples were tested for SCR activity under standard conditions described in table 2. 0.40 vol% NO/He, 0.42 vol% NH₃/He, O₂ and He were supplied by UCAR. Oxygen was dried before use with molecular sieves (5A, Janssen Chimica). The computer operated set-up equipped with a UTI-100 quadrupole mass-spectrometer allowed six samples to be tested simultaneously. The details of the set-up are described elsewhere [7]. NO conversion was calculated as $1 - [\text{NO}]/$

Table 1
Properties of V₂O₅/TiO₂ and V₂O₅-Nb₂O₅/TiO₂ catalysts

Catalyst	Name in the text	Surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore radius (nm)	E _a (kJ mol ⁻¹)
6 wt% V ₂ O ₅ /TiO ₂	6V/Ti	21	0.42	40	47
8.8 wt% Nb ₂ O ₅ /TiO ₂	8.8Nb/Ti	40	0.38	19	19
4.5 wt% V ₂ O ₅ /TiO ₂	4.5V/Ti	23	0.50	45	48
4.5 wt% V ₂ O ₅ /TiO ₂ -2.2 wt% Nb ₂ O ₅ /TiO ₂	4.5V-2.2Nb/Ti	25	0.45	37	48
3 wt% V ₂ O ₅ /TiO ₂	3V/Ti	23	0.52	47	45
3 wt% V ₂ O ₅ /TiO ₂ -4.4 wt% Nb ₂ O ₅ /TiO ₂	3V-4.4Nb/Ti	36	0.43	27	48
1.5 wt% V ₂ O ₅ /TiO ₂	1.5V/Ti	32	0.55	35	21
1.5 wt% V ₂ O ₅ /TiO ₂ -6.6 wt% Nb ₂ O ₅ /TiO ₂	1.5V-6.6Nb/Ti	39	0.47	27	47

[NO]₀ where [NO]₀ stands for the NO inlet concentration. The selectivity to N₂ formation was calculated as [N₂]/([N₂] + [N₂O]).

3. Results and discussion

The conversion of NO and the selectivity towards N₂ formation obtained with V₂O₅/TiO₂ and V₂O₅-Nb₂O₅/TiO₂ catalysts are presented in table 3 as a function of reaction temperature. Pure TiO₂ and γ-Al₂O₃ exhibit a very low activity at high temperatures and the results are not presented. It is noticeable that 8.8Nb/Ti shows an increasing SCR activity above 500 K while the selectivity goes through a minimum between 500 and 600 K due to an increasing N₂O production, apparently as a result of NH₃ oxidation.

Comparison of 6V/Ti, 4.5V/Ti and 3V/Ti with 4.5V-2.2Nb/Ti and 3V-4.4Nb/Ti shows that all catalysts gave a similar NO conversion as a function of

Table 2
Standard experimental conditions for the activity measurements

NO	500 ppm
NH ₃	550 ppm
O ₂	2 vol%
He	balance
temperature	398–723 K
pressure	10 ⁵ Pa
volume hourly space velocity	58.000 h ⁻¹
catalyst amount	13.3 mg mixed with 67 mg of γ-Al ₂ O ₃

Table 3

NO conversion ($X(\text{NO})$) and selectivity to N₂ ($S(\text{N}_2)$) for the SCR reaction over V₂O₅/TiO₂ and V₂O₅-Nb₂O₅/TiO₂ catalysts

T (K)	6V/Ti		8.8Nb/Ti	
	$X(\text{NO})$	$S(\text{N}_2)$	$X(\text{NO})$	$S(\text{N}_2)$
398	0.06	1.00	0.04	1.00
423	0.11	1.00	0.04	0.99
473	0.44	0.99	0.09	0.81
523	0.95	0.98	0.26	0.61
573	1.00	0.95	0.35	0.54
623	1.00	0.86	0.42	0.83
673	0.97	0.69	0.58	0.94
723	0.76	0.47	0.86	0.90
T (K)	4.5V/Ti		4.5V-2.2Nb/Ti	
	$X(\text{NO})$	$S(\text{N}_2)$	$X(\text{NO})$	$S(\text{N}_2)$
398	0.06	1.00	0.06	1.00
423	0.13	1.00	0.12	1.00
473	0.47	1.00	0.44	1.00
523	0.97	0.99	0.93	0.99
573	1.00	0.96	1.00	0.97
623	1.00	0.87	1.00	0.90
673	0.97	0.72	1.00	0.77
723	0.76	0.52	0.85	0.57
T (K)	3V/Ti		3V-4.4Nb/Ti	
	$X(\text{NO})$	$S(\text{N}_2)$	$X(\text{NO})$	$S(\text{N}_2)$
398	0.06	1.00	0.06	1.00
423	0.11	1.00	0.12	1.00
473	0.39	1.00	0.47	1.00
523	0.92	0.99	0.92	0.99
573	1.00	1.00	1.00	0.98
623	1.00	0.94	1.00	0.94
673	1.00	0.84	1.00	0.84
723	0.91	0.64	0.90	0.66
T (K)	1.5V/Ti		1.5V-6.6Nb/Ti	
	$X(\text{NO})$	$S(\text{N}_2)$	$X(\text{NO})$	$S(\text{N}_2)$
398	0.03	1.00	0.05	1.00
423	0.04	1.00	0.10	1.00
473	0.08	0.99	0.38	0.99
523	0.23	0.96	0.78	0.99
573	0.60	0.97	0.93	0.99
623	0.90	0.98	0.97	0.98
673	0.97	0.95	0.97	0.93
723	0.93	0.83	0.93	0.84

temperature, the higher selectivity to N₂, however, was observed for niobia containing catalysts at high temperatures. Much more dramatic differences could be observed with 1.5V/Ti and 1.5V–6.6Nb/Ti (fig. 1). First of all, the activity of 1.5V/Ti was considerably lower than that of 3–6V/Ti catalysts. When Nb₂O₅ was introduced into 1.5V/Ti the conversion of NO increased 2–4 times at low temperatures. Thus, the activity of 1.5V–6.6Nb/Ti appeared to be almost equal to that of 6V/Ti. It is also noticeable that the selectivity in the case of 1.5V–6.6Nb/Ti remained close to 1 up to 623 K while in the case of 6V/Ti it started falling off as from 523 K. Thus, one can conclude that niobia has considerable promoting effect on low-vanadia/titania catalysts at low reaction temperature.

These results disagree to some extent with the data presented in ref. [5] where the addition of small amount of Nb₂O₅ (2.7 wt%) is shown to result in dramatically enhanced NO conversions also for a 5 wt% V₂O₅/TiO₂, as compared with 7.5 wt% V₂O₅/TiO₂.

The promoting effect of niobia on V₂O₅/TiO₂ may be associated with the stabilisation of the surface area of the catalyst [6]. Data presented in table 1 indicate that the surface area of 1.5V–6.6Nb/Ti was almost twice as high as that of 3–6V/Ti (39 and 21–23 m²/g respectively). However, the surface area of 1.5V/Ti (32 m²/g) and that of 1.5V–6.6Nb/Ti were rather alike, while their catalytic properties differed considerably.

Reaction orders of 1 (for NO) and 0 (for NH₃) have been reported for the SCR reaction over V₂O₅ catalysts, the apparent activation energy (*E*_a) being about 48 kJ/mol [1]. In order to check these values for the V₂O₅/TiO₂ and V₂O₅–Nb₂O₅/TiO₂ catalysts additional studies were performed with NO/NH₃ concen-

Fig. 1. NO conversion and selectivity to N₂ for the SCR reaction over 1.5% V₂O₅/TiO₂ and 1.5% V₂O₅–6.6% Nb₂O₅/TiO₂ catalysts. (+) Conversion over 1.5% V₂O₅/TiO₂; (Δ) selectivity over 1.5% V₂O₅/TiO₂; (○) conversion over 1.5% V₂O₅–6.6% Nb₂O₅/TiO₂; (▼) selectivity over 1.5% V₂O₅–6.6% Nb₂O₅/TiO₂.

trations increased to 750/775 and 1000/1100 ppm respectively. All other parameters listed in table 2 remained unchanged. The results showed that for all the catalysts the NO conversion at given temperature was approximately independent of the concentration of the reactants. This is in agreement with the above mentioned reaction orders found for vanadia catalysts.

Assuming that the reaction orders for NO and NH₃ are 1 and 0 respectively one can estimate the apparent activation energies (E_a) from the kinetic data ($X(\text{NO}) < 0.5$) presented in table 3. E_a values for different V₂O₅/TiO₂ and V₂O₅-Nb₂O₅/TiO₂ catalysts are presented in the last column of table 1. These data show that E_a for the 1.5V-6.6Nb/Ti catalyst (47 kJ/mol) was distinctly different from that for 1.5V/Ti (21 kJ/mol) and was close to the values of E_a for 3-6V/Ti and other V-Nb/Ti catalysts (45-48 kJ/mol, table 1). Consequently, one can assume that the rate-determining step in the SCR reaction may be the same for 6V/Ti and 1.5V-6.6Nb/Ti, while it appeared to be different for the 1.5V/Ti. The origin of the effect may be associated with the structure of V₂O₅-Nb₂O₅/TiO₂ catalysts that has not been studied thoroughly so far.

In conclusion, the results of this study reveal that addition of niobia promoted low-V₂O₅/TiO₂ catalysts for SCR of NO with NH₃. This is also demonstrated by Tanabe [5], but his data suggest a promoting effect at high vanadia loadings. In contrast, our results demonstrate a promoting effect to exist only at low loadings. The effect is the most prominent at reaction temperatures below 500 K where the conversion of NO could be increased 2-4 times. For a comparable activity, the addition of niobia to vanadia/titania resulted in significantly enhanced selectivities at temperatures above 500 K.

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