Selective catalytic reduction of NO with NH_3 over Nb_2O_5-promoted V_2O_5/TiO_2 catalysts

K.A. Vikulov [1], A. Andreini, E.K. Poels and A. Bliek

Department of Chemical Engineering, University of Amsterdam,
Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

Received 11 October 1993; accepted 22 November 1993

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 NH_3 only at low vanadia loadings. Niobia promoted catalysts could also be demonstrated to show higher selectivities to N_2, 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; DeNOx

1. Introduction

Supported V_2O_5/TiO_2 is known to be one of the best catalysts for the selective catalytic reduction (SCR) of NO with NH_3 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 SO_2), and by the presence of water vapour.

It has been reported that the performance of V_2O_5/TiO_2 catalysts in SCR can be modified by the addition of WO_3 [3,4]. In the presence of SO_2, the V_2O_5–WO_3/TiO_2 catalysts show an increased activity as compared to unpromoted V_2O_5/TiO_2. Moreover, the resistance towards deactivation by both alkali metal oxides and arsenous oxide is improved and finally the oxidation of NH_3 (a competitive reaction to SCR occurring at high temperatures) is suppressed. It has been found that WO_3 creates additional (both Brønsted and Lewis) acid sites in V_2O_5–

---

[1] To whom correspondence should be addressed.

WO_3/TiO_2, which are assumed to participate in the SCR reaction mechanism. However, no definite explanation of the role of WO_3 has as yet been presented.

Nb_2O_5 has been reported to be another promising promoter for V_2O_5/TiO_2 catalysts [5]. Addition of Nb_2O_5 considerably increases the activity of the catalyst in SCR of NO particularly at lower temperatures. Also an improved deactivation resistance towards SO_2 was observed. Raman studies of the interaction between V_2O_5 and Nb_2O_5 on TiO_2 surface [6] have revealed that niobia has some influence on the structure of the V_2O_5/TiO_2 system. As a result the surface area loss during calcination of the catalyst at high temperature is considerably reduced by the addition of Nb_2O_5. A reduction in the intensity of the crystalline vanadia Raman band was observed for 8 wt% V_2O_5/TiO_2 when increasing the amount of niobia.

Besides some Japanese patents (cited in ref. [5]) – claiming the benefits of Nb_2O_5 as a promoter for V_2O_5/TiO_2 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 V_2O_5/TiO_2 and V_2O_5–Nb_2O_5/TiO_2 catalysts.

2. Experimental

V_2O_5–Nb_2O_5/TiO_2 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% V_2O_5/TiO_2 (which corresponds to approximate monolayer coverage on TiO_2 [6]). On the first step TiO_2 (Degussa P25) was impregnated with the water solution of ammonium metavanadate (Aldrich) to give V_2O_5/TiO_2 catalysts after drying and calcining in air at 573 K for 16 h. During the second step V_2O_5–Nb_2O_5/TiO_2 catalysts were obtained using the incipient wetness impregnation of V_2O_5/TiO_2 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 V_2O_5/TiO_2 and V_2O_5–Nb_2O_5/TiO_2 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% NH_3/He, O_2 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 – [NO]/

Table 1
Properties of V_2O_5/TiO_2 and V_2O_5–Nb_2O_5/TiO_2 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_2O_5/TiO_2	6V/Ti	21	0.42	40	47
8.8 wt% Nb_2O_5/TiO_2	8.8Nb/Ti	40	0.38	19	19
4.5 wt% V_2O_5/TiO_2	4.5V/Ti	23	0.50	45	48
4.5 wt% V_2O_5/TiO_2 –2.2 wt% Nb_2O_5/TiO_2	4.5V–2.2Nb/Ti	25	0.45	37	48
3 wt% V_2O_5/TiO_2	3V/Ti	23	0.52	47	45
3 wt% V_2O_5/TiO_2 –4.4 wt% Nb_2O_5/TiO_2	3V–4.4Nb/Ti	36	0.43	27	48
1.5 wt% V_2O_5/TiO_2	1.5V/Ti	32	0.55	35	21
1.5 wt% V_2O_5/TiO_2 –6.6 wt% Nb_2O_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 N_2 formation was calculated as $[N_2]/([N_2] + [N_2O])$.

3. Results and discussion

The conversion of NO and the selectivity towards N_2 formation obtained with V_2O_5/TiO_2 and V_2O_5–Nb_2O_5/TiO_2 catalysts are presented in table 3 as a function of reaction temperature. Pure TiO_2 and γ-Al_2O_3 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 N_2O production, apparently as a result of NH_3 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_2O_3

Table 3

NO conversion ($X(\mathrm{NO})$) and selectivity to $\mathrm{N_2}$ ($S(\mathrm{N_2})$) for the SCR reaction over V_2O_5/TiO_2 and V_2O_5–Nb_2O_5/TiO_2 catalysts

T (K)	6V/Ti		8.8Nb/Ti	
	$X(\mathrm{NO})$	$S(\mathrm{N_2})$	$X(\mathrm{NO})$	$S(\mathrm{N_2})$
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	
	$X(\mathrm{NO})$	$S(\mathrm{N_2})$	$X(\mathrm{NO})$	$S(N_2)$
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	
	$X(\mathrm{NO})$	$S(\mathrm{N_2})$	$X(\mathrm{NO})$	$S(\mathrm{N_2})$
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	
	$X(\mathrm{NO})$	$S(\mathrm{N_2})$	$X(\mathrm{NO})$	$S(\mathrm{N_2})$
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 N_2, 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 Nb_2O_5 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 Nb_2O_5 (2.7 wt%) is shown to result in dramatically enhanced NO conversions also for a 5 wt% V_2O_5/TiO_2, as compared with 7.5 wt% V_2O_5/TiO_2.

The promoting effect of niobia on V_2O_5/TiO_2 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 m^2/g respectively). However, the surface area of 1.5V/Ti (32 m^2/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 NH_3) have been reported for the SCR reaction over V_2O_5 catalysts, the apparent activation energy (E_a) being about 48 kJ/mol [1]. In order to check these values for the V_2O_5/TiO_2 and V_2O_5–Nb_2O_5/TiO_2 catalysts additional studies were performed with NO/NH_3 concen-

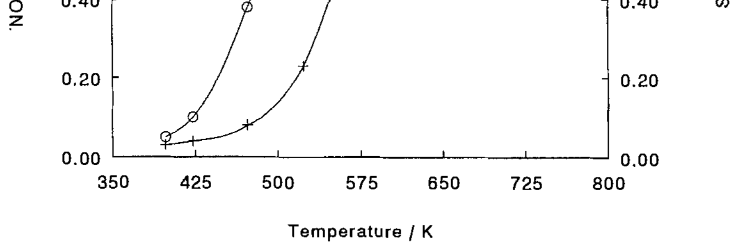

Fig. 1. NO conversion and selectivity to N_2 for the SCR reaction over 1.5% V_2O_5/TiO_2 and 1.5% V_2O_5–6.6% Nb_2O_5/TiO_2 catalysts. (+) Conversion over 1.5% V_2O_5/TiO_2; (△) selectivity over 1.5% V_2O_5/TiO_2; (○) conversion over 1.5% V_2O_5–6.6% Nb_2O_5/TiO_2; (▼) selectivity over 1.5% V_2O_5–6.6% Nb_2O_5/TiO_2.

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 NH_3 are 1 and 0 respectively one can estimate the apparent activation energies (E_a) from the kinetic data ($X(NO) < 0.5$) presented in table 3. E_a values for different V_2O_5/TiO_2 and V_2O_5–Nb_2O_5/TiO_2 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 V_2O_5–Nb_2O_5/TiO_2 catalysts that has not been studied thoroughly so far.

In conclusion, the results of this study reveal that addition of niobia promoted low-V_2O_5/TiO_2 catalysts for SCR of NO with NH_3. 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.

Acknowledgement

The authors thank Mrs. M. Mittelmeijer-Hazeleger for performing the porosimetry measurements.

References

[1] H. Bosch and F. Janssen, Catal. Today 2 (1988) 369.
[2] G.C. Bond and S.F. Tahir, Appl. Catal. A 71 (1991) 1.
[3] J.P. Chen and R.T. Yang, Appl. Catal. A 80 (1992) 135.
[4] G. Ramis, G. Busca and P. Forzatti, Appl. Catal. B 1 (1991) L9.
[5] K. Tanabe, Catal. Today 8 (1990) 1.
[6] I.E. Wachs, J.-M. Jehng and F.D. Hardcastle, Solid State Ionics 32/33 (1989) 904.
[7] L. Singoredjo, M. Slagt, J. Van Wees, F. Kapteijn and J.A. Moulijn, Catal. Today 7 (1990) 157.