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The influence of sulphate on the catalytic properties of V_2O_5–TiO_2 and WO_3–TiO_2 in the reduction of nitric oxide with ammonia

P. Ciambelli [a,*], M.E. Fortuna [a], D. Sannino [a], A. Baldacci [b]

[a] *Dipartimento di Ingegneria Chimica e Alimentare, Università di Salerno, 84084 Fisciano (Sa), Italy*
[b] *ENEL-CRT, Via A. Pisano 120, 56100 Pisa, Italy*

Abstract

The effect of sulphate on the catalytic properties of V_2O_5/TiO_2 and WO_3/TiO_2 in the selective reduction of NO with NH_3 has been investigated. For both catalytic systems, the presence of sulphate results in the enhancement of catalytic activity without reduction of selectivity to nitrogen. The rate of NO reduction depends on the sulphate content, which is affected by the original composition of titania, the method of catalyst preparation and the metal oxide loading.

Keywords: NO reduction; V_2O_5–TiO_2 catalysts; WO_3–TiO_2 catalysts

1. Introduction

The selective catalytic reduction (SCR) of nitric oxide with ammonia is the current commercial process for the treatment of flue gas from power plants. Vanadia/titania is the most commonly used catalyst, but, when sulphur dioxide is present in the flue gas, tungsta/titania type materials are used to limit the activity of catalyst for the oxidation of SO_2 to SO_3 [1]. Moreover, in the formulations of SCR commercial catalysts the presence of sulphate with V_2O_5 and/or WO_3 on TiO_2 is reported [1]. This paper presents some results concerning the effect of sulphate on the catalytic properties of vanadia/titania and tungsta/titania in the SCR reaction.

2. Experimental

Two series of catalysts containing respectively vanadium oxide and tungsten oxide supported on titanium dioxide have been prepared. Different titania have been used: (i) high surface area (120 m^2/g) pure anatase (NP92/1161, Tioxide), (ii) medium surface area (50 m^2/g) rutile/anatase (P25, Degussa), (iii) sulphated (80 m^2/g, 1.2 wt.-% sulphate) anatase (DT-51, Rhone–Poulenc). Metal oxide has been supported by either wet impregnation (60°C) or equilibrium adsorption (25°C) from aqueous solutions of ammonium metavanadate or ammonium paratungstate. The samples have been dried at 120°C and calcined at 400°C for 2 h.

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[*] Corresponding author. Fax. (+39-89) 964057, e-mail ciambelli@vaxsa.csied.unisa.it

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The fraction 180–355 μm particle size has been used for the test of catalytic activity.

The characterization of catalysts has been performed by X-ray diffraction (XRD), X-ray fluorescence (XRF), Fourier transform–infrared (FTIR) spectroscopy, thermal analysis and nitrogen adsorption at 77 K.

Catalytic tests have been carried out with a flow microreactor by feeding a gas mixture containing 700 ppm of NO, 700 ppm of NH_3 and 3.6 vol.-% O_2 in He at 100000 h^{-1} SV. Products analysis has been performed with two on line continuous analysers, for NO (Radas 1G, Hartmann and Braun) and NH_3 (Ultramat 5E, Siemens), respectively and a gas chromatograph (Dani 86.10 HT, equipped with a 2 m length Alltech CTR column) for N_2 and N_2O.

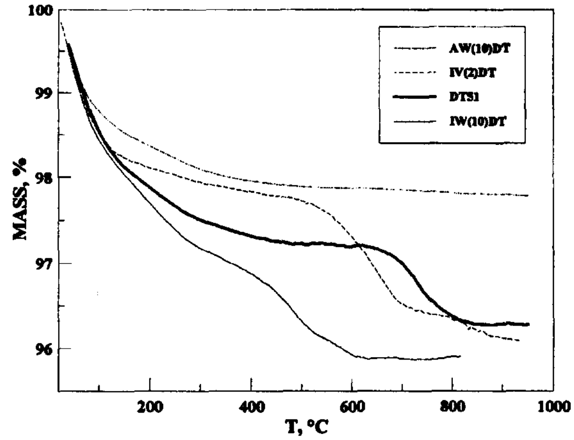

Fig. 1. TG curves of DT51 and DT51-supported catalysts.

3. Results and discussion

3.1. Catalyst characterization

The list of catalysts investigated and their supports is reported in Table 1. They are identified by I (impregnation) or A (adsorption), V (vanadium) or W (tungsten), % of metal oxide (V_2O_5 or WO_3), type of titania used. The catalysts have a metal loading up to 4 atoms/nm^2, corresponding to sub-monolayer coverages. With reference to the sulphate content of catalysts supported on DT51, it appears that the equilibrium adsorption method of preparation results in the reduction of this content. TG analyses have also shown that the catalysts prepared by adsorption have lost a fraction of sulphate, whereas the sulphate content is unmodified by the wet impregnation method. This can be due to partial ion-exchange of vanadate or tungstate for surface sulphate during the adsorption.

Sulphate stability at high temperature is affected by the presence of the metal oxide on titania. In Fig. 1, the thermogravimetric (TG) curves of DT51, IV(2)DT, IW(10)DT and AW(10)DT show that the high temperature weight loss step either in vanadia/titania or in tungsta/titania catalysts starts at a temperature lower than in sulphated titania. This weight is reduced in the case of AW(10)DT, as observed above. Catalyst characterization by XRF and FT–IR after treatment at different temperatures

Table 1
List of catalysts and supports investigated and their features

Samples	Metal oxide (wt.-%)	Sulphate (wt.-%)	Surface area (m^2/g)	V or W ($\mu mol/m^2$)
NP92	0	< 0.1	125	0
AW(10)NP	10.9	< 0.1	97	4.5
DT51	0	1.2	81	0
IW(10)DT	10.1	1.1	70	6.2
AW(10)DT	10.1	0.1	71	6.1
IV(2)DT	2.0	1.1	75	3.0
P25	0	< 0.1	51	0
IV(2)P25	2.0	< 0.1	48	4.6

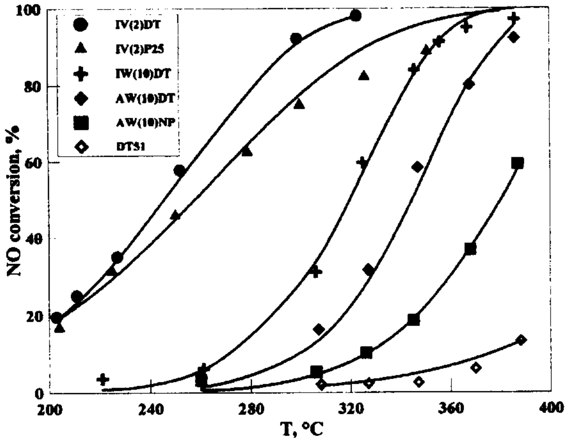

Fig. 2. NO conversions as functions of reaction temperature. Continuous lines have been obtained from the elaboration of integral reactor data.

allows to associate this weight loss step with sulphate decomposition.

The absence in XRD and FTIR spectra of any evidence for the presence of V_2O_5 or WO_3 segregated phases indicates that a metal oxide phase very well dispersed on titania is present in the catalysts. The slight reduction of specific surface area with metal loading supports this conclusion.

3.2. Catalytic activity

The comparison of catalytic activity for the selective reduction of NO with NH_3 is shown in Figs. 2 and 3. Both the sulphate-free titania have negligible activity up to 400°C, whereas the sample DT51 gives 13% conversion at 380°C (Fig. 2). The promoting effect of sulphate on the catalytic activity of titania has been reported by Chen and Yang and attributed to the enhanced chemisorption of ammonia [3].

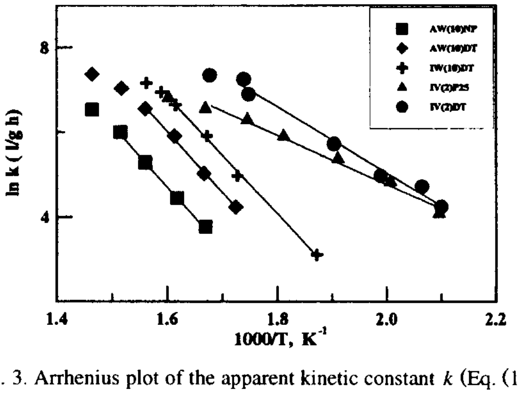

Fig. 3. Arrhenius plot of the apparent kinetic constant k (Eq. (1)).

It is well known that the activity of vanadia/titania is much greater than of tungsta/titania catalysts for the SCR reaction [1]. Fig. 2 shows that at 300°C the conversion of NO is between 75% and 90% on vanadia/titania, but only between 5% and 30% on tungsta/titania catalysts. When the activities of IV(2)P25 and IV(2)DT and of AW(10)NP and AW(10)DT are compared, it appears that the presence of sulphate results in a greater conversion of NO. Moreover, comparing the performances of AW(10)DT51 and IW(10)DT51, prepared respectively by adsorption and impregnation, it is evident that there is some effect of the preparation method on their catalytic activity. Taking into account the effect of the preparation method on the sulphate content (Table 1 and Fig. 1), we conclude that the catalysts prepared by equilibrium adsorption are less active, due to the lower sulphate content, as reported before [2]. However, the reduced stability of sulphate (Fig. 1) associated with the presence of the metal oxide surface phase can result in a reduced performance of the catalyst in the treatment of sulphur-free gas at high temperature.

In the range of temperatures from 200 to 350°C, NO and NH_3 are converted with a ratio NO/NH_3 very close to one, with negligible production of N_2O, over all the catalysts investigated, with the only exception of IV(2)P25. On this sample the conversion of NO to N_2O reaches 10% at 350°C and increases by increasing the reaction temperature. However, we assume that the SCR reaction is the unique reaction to be considered responsible for NO conversion. With this assumption the apparent kinetic constant k has been evaluated from the integral reactor data of NO conversion with the first order rate equation:

$$r = kC_{NO} \qquad (1)$$

Table 2
Pre-exponential factor and apparent energy of activation evaluated from Eq. (2)

Samples	k_0 (l/g h)	E_a (kcal/mol)
DT51	8.6×10^8	21.6 ± 2
IW(10)DT	2.9×10^{12}	27.2 ± 3
AW(10)DT	1.3×10^{12}	27.3 ± 3
AW(10)NP	1.1×10^{12}	28.6 ± 3
IV(2)DT	4.1×10^8	14.8 ± 2
IV(2)P25	3.1×10^6	10.1 ± 1

$$k = k_0 \exp\left(-\frac{E_a}{RT}\right) \quad (2)$$

It is generally assumed that the rate of NO reduction with NH_3 is first order with respect to NO and zero order with respect to NH_3, when the concentration of NO in the feed mixture is very low [4,5]. The values of k are reported in the Arrhenius plot of Fig. 3. The pre-exponential factor k_0 and the apparent energy of activation E_a for the SCR reaction have also been evaluated for each catalyst and is reported in Table 2. In the elaboration of NO conversion data we have disregarded the higher values, for which some diffusive effect is evident (Fig. 3). Both the evaluation of the effectiveness factor and the results of catalytic test performed with particle size of about 100 μm indicate that diffusive effects are negligible in the range of temperatures up to 350°C.

For the vanadia/titania catalysts, the values of E_a are smaller than for tungsta/titania catalysts. The pre-exponential factor and the apparent energy of activation evaluated from Eq. (2) are well fitted by the correlation of the compensation effect [6] reported in Ref. [4] for various vanadia-based catalysts.

The values of E_a seem not to be affected by the presence of sulphate for tungsta/titania catalysts.

In the case of IV(2)P25 the value of E_a is lower than expected, but it must be taken into account that on this catalyst the conversion to N_2O is not negligible. The energy of activation evaluated from the data at the three lowest temperatures is 12.1 ± 1 kcal/mol. The NO conversion data calculated from the estimated values of the kinetic parameters are reported as continuous lines in Fig. 2. The agreement with the experimental data is satisfactory in the range of temperatures in which they are unaffected by diffusive effects.

Ramis et al. have reported that tungsta/titania catalysts show strong Brønsted acidity, but also redox properties associated with the reducibility of W^{6+} [7]. The presence of sulphate should result in increased acidity and then increased activity following the mechanism suggested by Topsøe [8] for the SCR reaction.

Acknowledgements

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References

[1] H. Bosch and F. Janssen, Catal. Today, 2 (1988) 369.
[2] P. Ciambelli, M.E. Fortuna, D. Sannino and A. Baldacci, Preprints Second Tokyo Conf. Adv. Catal. Sci. Tech., (1994) 317.
[3] J.P. Chen and R.T. Yang, J. Catal., 139 (1993) 277.
[4] J. Marangozis, Ind. Eng. Chem. Res., 31 (1992) 987.
[5] W.C. Wong and K. Nobe, Ind. Eng. Chem. Prod. Res. Dev., 23 (1984) 564.
[6] G.M. Schwab, J. Catal., 84 (1983) 1.
[7] G. Ramis, G. Busca, C. Cristiani, L. Lietti, P. Forzatti and F. Bregani, Langmuir, 8 (1992) 1744.
[8] N.Y. Topsøe, Science, 265 (1994) 1217.