Effect of TiO$_2$ surface properties on the SCR activity of NOx emission abatement catalyst

YE Dai-qi[1], TIAN Liu-qing[1], LIANG Hong[2]

(1.Department of Environmental Science and Engineering, School of Paper Making & Environmental Engineering, South China University of Technology, Guangzhou 510640, China. E-mail: cedqye @ scut. edu. cn; 2. Department of Light Chemical Engineering, Guangzhou University, Guangzhou 510090, China)

Abstract: NOx emission abatement catalysts V$_2$O$_5$ supported on various TiO$_2$ including anatase, rutile and mixture of both were investigated with various physico-chemical measurements such as BET, NH$_3$-TPD, NARP, XRD and so on, and the effect of TiO$_2$ surface properties on the SCR (selective catalytic reduction) activity of V$_2$O$_5$/TiO$_2$ catalysts was studied. It was found that the TiO$_2$ surface properties had strong affect on the SCR activity of V$_2$O$_5$/TiO$_2$ catalysts. The stronger acidic property resulted in the higher exposure of active sites as well as the higher SCR activity.

Keywords: NOx; SCR(selective catalytic reduction); surface acidity; V$_2$O$_5$/TiO$_2$ catalyst

Introduction

The control of NOx emissions in flue gases from thermal power and other industrial facilities as well as automobile is one of the most important applications of catalytic systems for pollution abatement. Up to now, SCR with NH$_3$ technology is recognized as the best available technology for NOx abatement from stationary sources. While, most of industrial catalysts for the SCR(selective catalytic reduction) process are based on TiO$_2$-supported V$_2$O$_5$ oxides due to its efficiency and selectivity in the NOx reduction into nitrogen(Centeno, 2001; Nova, 2000).

From the scientific viewpoint, this V$_2$O$_5$/TiO$_2$ catalytic system is an interesting example of a strong interaction between the support and the active phase. V$_2$O$_5$ supported on TiO$_2$ shows superior spreading to the other kinds of support, such as Al$_2$O$_3$, SiO$_2$, ZrO$_2$, MgO and so on, which leads to an enhancement of its catalytic activity and its SCR activity(Ye, 1993; 1995; Nicolaos, 1999). Although valuable information has been obtained for V$_2$O$_5$/TiO$_2$ catalyst by extensive studies mentioned above, it seems that there is no satisfactory explanation on whether the surface property of TiO$_2$ determines the characteristics of the active phase or not, and how it determines. Obviously, further investigations are necessary in order to clarify questions mentioned above. The aim of the present work is to investigate the selective catalytic reduction activities of various V$_2$O$_5$/TiO$_2$ catalysts in order to reveal the factors determining the interaction between V$_2$O$_5$ active phase and TiO$_2$ support.

1 Experimental

1.1 Preparation

Five kinds of TiO$_2$ listed in Table 1 were used as supports. They were two anatases, two rutiles and a mixture of them denoted by A-1, A-II, R-1, R-II and A + R, respectively. Supported vanadium oxide catalysts were prepared by impregnation of support with an oxalic acid solution of ammonium metavanadate followed by the calcination at 773K in a stream of O$_2$ for 3h. V$_2$O$_5$ content was so determined that the surface concentration of V$_2$O$_5$ on all five TiO$_2$ supports lies in the same range, i.e., 5—100

$\mu mol/m^2$-TiO_2.

1.2　Characterizations

X-ray diffraction diagrams were obtained with Cu-K_α radiation. The BET surface area was determined, in most case, by using a conventional flow-type apparatus with N_2 as an adsorbate. For several samples, the BET surface areas and pore size distribution were determined from the static adsorption of N_2 by using an automated static adsorption apparatus(BELSORP28, Japan Bell Co.).

The acid and basic strength of TiO_2 supports, pretreated in air oven at 773K for 2h, were evaluated from the change of colors of Hammett indicators adsorbed on TiO_2 supports. The acid property also was measured through the temperature programmed desorption (TPD) of adsorbed NH_3 by using a conventional TPD apparatus equipped with a thermal conductivity detector. Experimental procedure was as follows: about 1.0g of sample was evacuated in a quartz cell at 773K for about 1h till the pressure to 0.003 torr. After cooling to room temperature, the sample was exposed to ammonia for 30 min at the equilibrium pressure of 6.65 kPa, and then it was evacuated to 13.3 Pa at room temperature. TPD measurement was done from room temperature to 773 K with a heating rate of 5 K/min. Helium was used as a carrier gas with a flow rate of 60 cm^3/min.

The SCR activity of V_2O_5 on various supports were determined by using the NO-NH_3 rectangular pulse technique(NARP). The most experiments were carried out under following condition: catalyst weight = 0.02g; flow rate of carrier gas(He) = 150 cm^3/min; concentration of NO = 4.86×10^{-8} mol/cm^3; concentration of NH_3 = 9.25×10^{-7} mol/cm^3; pulse width = 60s; reaction temperature = 550—580K. The catalyst was pre-oxidized in flowing O_2 at 773K for 30 min in advance to the introduction of every rectangular pulse of NO-NH_3 mixture.

$$NO + NH_3 + V = O \longrightarrow N_2 + H_2O + V - OH, \tag{1}$$

$$2V - OH + 2O \text{ (Lattice)} \longrightarrow 2V = O + H_2O. \tag{2}$$
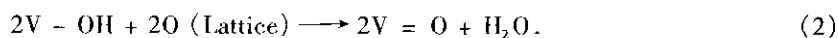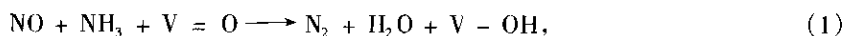
2　Results and discussion

2.1　Surface properties of TiO₂ support

Table 1 shows the properties and preparation methods of TiO_2 supports used in this study. X-ray diffraction of five TiO_2 supports as shown in Fig. 1 confirmed that A-I and A-II are anatase type, R-I and R-II are rutile type, and A + R is the mixture of both. The rutile content was calculated by the following equation:

$$Xr = 2.18/(1 + I_a/I_r).$$

Where I_r and I_a are the intensities of the (110) and the (101) plane reflections of rutile and anatase, respectively. Both of the flow and static adsorption of N_2 indicate that A-I, R-I and A + R have higher BET surface areas than the others, and R-II has only small surface area.

Table 1　List of TiO₂ supports and their textures

Bulk crystalline structure	(A-I)[a] Anatase	(A-II)[b] Anatase	(R-I)[c] Rutile	(R-II)[d] Rutile	(A+R)[e] 36% Anatase 64% Rutile
$S_{BET}/(m^2 \cdot g)$					
Flow method[g]	71.0	15.6	49.5	24.6	50.1
Static method[h]	68.2	13.5	42.8	2.33	39.1
Pore volume, cm^3/g	0.318	0.110	0.361	0.008	0.211

Notes: [a] Prepared by the calcinations of meta-titanic acid at 773—873K; [b] prepared by the calcinations of hydrated titanium oxide at 1073—1123K; [c] prepared by the liquid phase method; [d] prepared by the gas phase reaction of $TiCl_4$ with O_2; [e] prepared by the gas phase reaction of $TiCl_4$ with O_2 and H_2; [g] pretreated at 773K in flowing O_2 for 30 min; [h] evacuated at room temperature for 10—12 h

Table 2 shows the acid-base strength measured through the colours of various indicators adsorbed on the TiO$_2$ surface. In general, the acid sites on anatase type TiO$_2$ are stronger than those on rutile type, and TiO$_2$ supports with large surface area tend to have stronger acid sites than those with small area. However, A + R with large surface area did not exhibit acidic colours of indicators. As for the basic strength, all the samples did not give basic colours of indicators, indicating that the basic strength of all the TiO$_2$ surfaces are almost the same.

Table 2   Acid-base strength of TiO$_2$ measured by titration of Hammett indicators

Indicators	pK_a	A-I	A-II	R-I	R-II	A + R
Anthraquinone	− 8.2	+ / −	−	−	−	−
Benzalacetophenone	− 5.6	+ / −	−	−	−	−
Dicinnamalacetone	− 3.0	+	−	+	−	−
Benzeneazodiphenylamine	1.5	+	+ / −	−	−	−
p-dimethylaminoazobenzene	3.3	+	+ / −	+ / −	−	+ / −
Bromothymol blue	7.2	U	+ / −	+	+ / −	+ / −
Phenolphthalein	9.3	+ / −	−	−	−	−
2,4-dinitroanaline	15.0	−	−	−	−	−
4-chloro-2-nitroaniline	17.2	−	−	−	−	−
4-nitroaniline	18.4	+ / −	−	−	−	−
4-chloroaniline	26.5	−	−	−	−	−

Notes: + : colour changed; − : colour unchanged; + / − : slightly changed and U : unusually changed

Fig. 1 shows TPD spectra of NH$_3$ on TiO$_2$ supports. On A-I, two desorption peaks were observed: the first one at about 370K and the desecond one at about 600K, and the desorption was completed at 700K. On the other hand, A-II gave only the first desorption peak which was completed at about 600K. These results indicate that A-I has stronger acid sites than A-II. R-I gave a similar TPD spectrum to that on A-I, though the second peak appeared at slightly lower temperature. This result indicates that the acid sites of R-I are strong but slightly weaker than that of A-I. In the case of R-II, although only a poor spectrum could be obtained because of very small surface area, the second peak could not be observed, indicating the absence of strong acid sites. These results agree well with the results obtained from the titration of Hammett indicators shown in Table 2. However, the TPD spectrum on A + R is not in agreement with the acid strength obtained from the change in the colour of indicators. The TPD spectrum shows a broader second peak at slightly lower temperature than that on R-I, indicating the presence of strong acid sites, though the indicators did not show the presence of them. It may be concluded from the TPD spectrum of NH$_3$ that A + R has strong acid sites, because it is known that, sometimes, the colours of indicators do not change obviously.

2.2   SCR activity of V$_2$O$_5$/TiO$_2$ catalysts

The active sites of V$_2$O$_5$ catalysts in the selective catalytic reduction of NO were determined by the NARP(NO-NH$_3$ rectangular pulse) technique. When a rectangular pulse of a NO and NH$_3$ mixture is introduced onto the V$_2$O$_5$/TiO$_2$ catalysts, N$_2$ with a concentration profile consisting of initial N$_2$ and tailing N$_2$ is obtained, and the number of the surface V = O species can be determined from the amount of the initial N$_2$ in the same way as reported previously(Ye, 1993; 1995), and the number of the V = O species thus determined is summarized in Table 3.
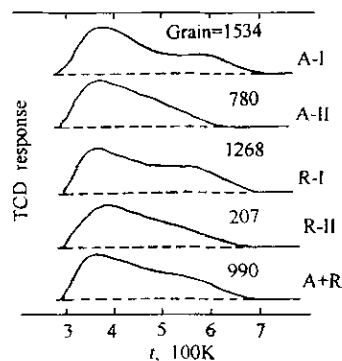

Fig. 1   The NH$_3$-TPD spectra of five TiO$_2$ supports

Table 3   Summarized SCR activity of various V_2O_5/TiO_2 catalysts

Name of V_2O_5/TiO_2	Surface conc. of V_2O_5, $(\mu mol/m^2)/TiO_2$	V_2O_5 content, % mol	S_{BET}, m^2/g	S_{010}, m^2/g	Number of V = O species, $(\mu mol/m^2)/TiO_2$
A- I -0	0	0.0	71.0	0.0	0.0
A- I -1	5	2.8	53.1	25.6	202.6
A- I -2	10	5.4	34.1	29.5	231.3
A- I -3	20	10.2	29.1	22.2	174.4
A- I -5	50	22.1	24.5	19.7	154.5
A- I -10	100	36.2	21.1	14.1	110.5
A- II -0	0	0.0	15.6	0.0	0.0
A- II -1	5	0.6	15.0	6.1	47.5
A- II -2	10	1.2	14.6	10.0	78.3
A- II -3	20	2.4	14.0	8.8	76.7
A- II -4	30	3.6	14.1	8.2	64.0
A- II -5	50	5.9	14.5	8.6	67.7
A- II -10	100	11.1	12.7	6.8	53.5
R- I -0	0	0.0	49.5	0.0	0.0
R-I-1	10	3.8	31.2	24.4	190.9
R-I-2	30	10.6	27.0	25.6	200.7
R-I-3	50	16.5	23.6	21.9	171.3
R-I-4	70	21.7	22.4	17.0	133.0
R-I-5	100	28.3	19.8	15.9	124.5
R-II-0	0	0.0	2.5	0.0	0.0
R-II-1	10	0.2	2.5	1.0	7.7
R-II-2	30	0.6	2.5	1.4	10.7
R-II-3	50	1.0	2.6	1.4	11.3
R-II-4	70	1.4	2.6	1.4	11.4
R-II-5	100	1.9	2.6	1.4	11.2
A + R-0	0	0.0	50.1	0.0	0.0
A + R-0.5	5	2.0	42.1	18.0	140.9
A + R-1	10	3.9	33.6	22.1	173.2
A + R-2	30	10.7	27.9	16.6	129.8
A + R-3	50	16.7	23.1	16.9	132.5
A + R-4	70	21.9	21.6	12.0	94.8
A + R-5	100	28.6	20.6	11.6	90.7

Since V_2O_5 content was so determined that the surface concentration of V_2O_5 lies in the same range for all five types, the active surface areas, S_{010}, were different from type to type of TiO_2 support. According to the crystal structure of V_2O_5, the density of V = O species located on the (010) plane was known as 4.872 nm^{-2}. Thus, the specific area of the (010) plane of V_2O_5, S_{010}, was calculated from the experimentally determined number of the V = O species.

2.3   Effect of TiO_2 surface properties

For R-II type of catalysts, S_{010}/S_{BET} is very close to 50%, which indicates the absence of any remarkable interaction between the support and active phase. While for R-I type of catalysts, the maximum S_{010}/S_{BET} is more than 90%. The same situation has been found in anatase type catalysts; the maximum exposure of A-I is close to 90%, but for A-II, it is only less than 70%. It is easily noticed that the TiO_2 supports with large surface area, i.e., A-I, R-I and A + R, gave higher ratio of S_{010}/S_{BET} than those on the other TiO_2 supports. This relationship suggests that the surface activity has an effect on the exposure of the (010) plane, because it is widely accepted that small surface area or, in other words, large crystallites are accompanied with low surface activity.

To this question, Fig.2 shows the ratio of S_{010}/S_{BET} of two anatase type catalysts, A-I and A-II, with the surface concentration of V_2O_5. With the surface increase in V_2O_5 concentration, the ratios of S_{010}/S_{BET}

of both A-I and A-II catalysts are steeply increased at low concentration range, and attained the maximum at the surface concentration of ca. 10×10^{-6} mol/m^2 . With further increase in the surface concentration of V_2O_5, S_{010}/S_{BET} decreased slowly. The catalyst of A-I having a higher S_{BET} always attained higher S_{010}/S_{BET} ratio than that of another catalyst, A-II, having a lower S_{BET} .

As for the rutile type TiO_2, R-1 and R-II, gave results similar to those of A-I and A-II type ratios of S_{010}/S_{BET} initially increased steeply with the increase of V_2O_5 till the ratio attained the maximum at the surface V_2O_5 concentration of about 30×10^{-6}—50×10^{-6} mol/m^2 , then decreased slowly. At the same time, a similar comparison result as A-I and A-II catalysts can be observed here. The catalyst of R-I having a higher S_{BET} always attained higher S_{010}/S_{BET} ratio than that of R-II with lower S_{BET} .
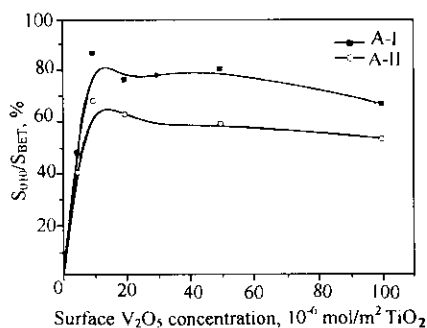

Fig. 2 S_{010}/S_{BET}, the fraction of (010) planes of A-I and A-II type catalysts
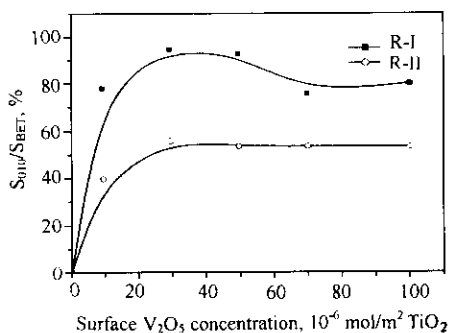

Fig. 3 S_{010}/S_{BET}, the fraction of (010) planes of R-I and R-II type catalysts

As described in Fig. 4, the TiO$_2$ surface is full of various functional groups which act as acid or basic sites.

The acid and base properties of the TiO$_2$ supports were measured through the changes of colours of adsorbed indicators and the TPD or NH$_3$. Although the base property was not different from each other, the acid strength differed from TiO$_2$ support to support. That is,

Fig. 4   Supposed acid sites and basic sites on TiO$_2$ surface

TiO$_2$ with large BET surface areas, i.e., A-I, R-I and A + R, have stronger acid sites than A-II and R-II with small BET surface areas. The small surface area and low acidity of A-II and R-II should be due to the higher calcinations temperature during the preparation of TiO$_2$. As for the anatase supports, for example, A-I was calcined at 773—873K, while A-II was calcined at higher temperatures, i.e., 1073—1123K. The calcinations at higher temperature may result in the sintering of TiO$_2$ particles and the deactivation of the surface, probably due to the desorption of OH group. Thus, the large BET surface area is accompanied with high activity of the surface, especially, strong acid sites on the TiO$_2$ surface. This also may suggest the possibility that the acid property is another factor determining the exposure of the (010) plane, although it is not clear how the acid property of the support determines the exposure.
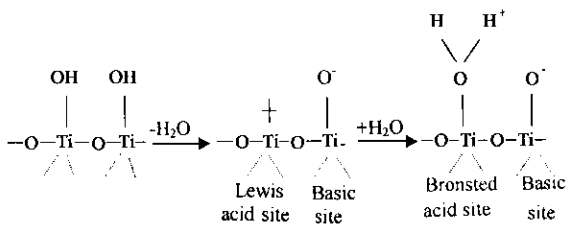
Fig. 5 shows the S_{010}/S_{BET} ratio of all the types of catalysts with the surface V_2O_5 concentration of 10×10^{-6} mol/m^2 . The sequence from left to right of X-axis is A-1, R-I, A + R, A-II and R-II, which is corresponding to the sequence of the acidity amount of TiO$_2$ support from large to small. In general, with the acidity amount of the TiO$_2$ supports decreased, the S_{010}/S_{BET} ratio of the catalyst decreased; TiO$_2$

supports with larger acidity amount tend to obtain higher S_{010}/S_{BET} ratio than those with smaller acidity amount.

All of these V$_2$O$_5$/TiO$_2$ catalysts are prepared by impregnation from aqueous vanadium complex solutions, and the surface of TiO$_2$ support present a certain amount of acid sites, so that the adsorption of vanadium complex anion takes place on acid sites. The Lewis acid sites on TiO$_2$ surface are favorable to share the electron pair offered by adsorbing vanadium complex anion as demonstrated in Fig.6.

The Bronsted acid site on TiO$_2$ surface can also share its proton with the adsorbing vanadium complex anion. So vanadium complex anion can either be adsorbed on Lewis or Bronsted acid sites. Obviously, The adsorption depends on the strength of the acid sites. The experimental results mentioned above clearly showed that the stronger acid sites lead to the stronger interaction between the support and the active phase and then the
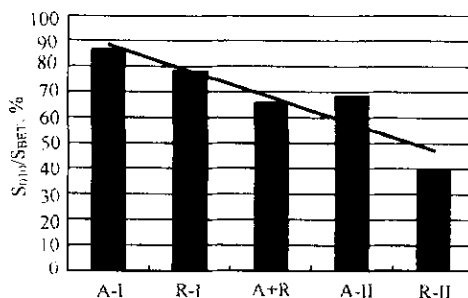

Fig.5 S_{010}/S_{BET}, the fraction of (010) planes of all five types catalyst under surface concentrations of V$_2$O$_5$ with 10
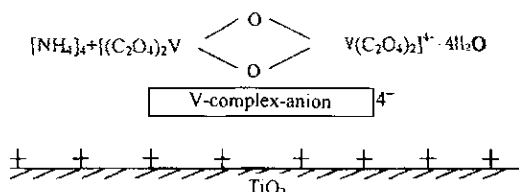

Fig.6   Mechanism of supposed interaction of TiO$_2$ surface acid site with vanadium complex anion

higher exposure of V = O active sites. As mentioned above, TiO$_2$ supports with larger surface area tend to have stronger acid sites than those with small area. In another word, TiO$_2$ supports with larger S_{BET} tend to have stronger interaction with vanadium oxides.

3   Conclusion

The TiO$_2$ surface properties had strong effect on the SCR activity of V$_2$O$_5$/TiO$_2$ catalysts. The surface activity such as the acid strength determined the extent of maximum exposure of the V = O active sites. SCR activity of V$_2$O$_5$/TiO$_2$ catalysts is much higher on the TiO$_2$ supports with larger BET surface area than those with small surface areas. The stronger the acid sites of TiO$_2$ surface, the stronger the interaction of TiO$_2$ support and V$_2$O$_5$ active phase.

References:

Centeno M A, Carrizosa I, Odriozola J A, 2001. NO-NH$_3$ coadsorption on vanadia/titania catalysts[J]. Applied Catalysis B: Environmental, 29:307—314.

Nicolaos V E, Donovan A et al., 1999. Comparison of TiO$_2$-based oxide catalysts for the selective catalytic reduction of NO[J]. Applied Catalysis B: Environmental, 23: 123—134.

Nova I, Lietti L, Tronconi E et al., 2000. Dynamics of SCR reaction over a TiO$_2$-supported vanadia commercial catalyst[J]. Catalysis Today, 60:73—82.

Ye D Q, Satsuma A, Hattori T et al., 1995. Factors determining the selective exposure of (010) plane of V$_2$O$_5$ catalyst supported on various TiO$_2$[J]. Res Chem Intermed, 21(2): 95—114.

Ye D Q, Liang H, Huang Z T, 1993. Study on the interation between the active phase and support on V$_2$O$_5$/TiO$_2$ catalyst[J]. Acta Physico-Chimica Sinica, 9(4): 501—508.