负载型 V_2O_5/TiO_2 催化剂表面分散状态和性质对 氨选择性催化还原 NO 性能的影响

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摘要: 采用多种物理化学手段研究了不同负载量 V_2O_5/TiO_2 催化剂的 VO_x 物种分散状态、表面酸性、可还原性及其选择性催化还原 (SCR) NO 性能. 结果表明, V_2O_5 在锐钛矿 TiO_2 表面的实测单层分散容量约为 $1.14 \text{ mmol V}/100 \text{ m}^2 \text{ TiO}_2$, 与“嵌入模型”的估算值相符, 表明分散态的钒离子应键合在 TiO_2 表面的八面体空位上. 随着 V_2O_5 负载量的增加, V_2O_5/TiO_2 催化剂上 NO 转化频率 (TOF) 先急剧增加, 至 $0.70 \text{ mmol V}/100 \text{ m}^2 \text{ TiO}_2$ (略超过分散容量的一半) 时达到极大 (约 $8.3 \times 10^{-3} \text{ s}^{-1}$), 然后又急剧下降; 同时, 孤立 VO_x 物种可能倾向于分散在相邻的八面体空位上, 且通过 V—O—V 化学键相连形成聚合的 VO_x 物种, V—O—V 键所占比例增加而 V—O—Ti 键所占比例减小, 催化剂表面单位钒离子的 Brönsted 酸中心量增加, 故催化剂的 TOF 急剧增加. 随着负载量进一步增加, 虽然催化剂表面单位钒离子的 Brönsted 酸中心量仍缓慢增加, 但 V—O—Ti 键所占比例减少, 导致钒离子的可还原性下降, 另外, 分散容量以上时晶相 V_2O_5 的形成也导致钒离子表面利用率下降, 从而导致催化剂的 TOF 下降. 桥式 Brönsted 酸位 (V—O(H)—V) 也是 SCR 反应活性中心之一, 不同负载量 V_2O_5/TiO_2 催化剂上 SCR 活性与表面 VO_x 物种的分散状态、表面酸性和钒离子可还原性密切相关.

关键词: 钒氧物种; 分散状态; 选择性催化还原; B 酸位; 可还原性; 氮氧化物

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Effect of Dispersion State and Surface Properties of Supported Vanadia on the Activity of V_2O_5/TiO_2 Catalysts for the Selective Catalytic Reduction of NO by NH_3

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Abstract: The effect of the dispersion state and surface properties of supported vanadia on the selective catalytic reduction (SCR) activity of NO over V_2O_5/TiO_2 catalysts was studied by various experimental techniques. The experimental monolayer dispersion capacity of V_2O_5 on anatase ($6.86 \text{ VO}_x/\text{nm}^2$) measured by XRD was almost the same as the concentration of surface vacant sites of anatase estimated by the incorporation model, and it was suggested that isolated vanadia species tend to be dispersed on adjacent octahedral vacant sites. An increase of the NO turnover frequency (TOF) at 300°C to a maximum ($8.3 \times 10^{-3} \text{ s}^{-1}$) at a coverage near half a monolayer was related to the increase of the amount of weak acid sites (Brönsted acid site on each vanadium ion). The TOF decreased rapidly at high VO_x coverages because of a decrease of the reducibility of vanadia species and a decrease of the ratio of exposed vanadia species on the surface. The Brönsted acid sites on bridging V—O(H)—V and terminal V—OH of polymeric vanadia species were all active sites in the SCR reaction. The SCR activity of the V_2O_5/TiO_2 catalysts was related to the dispersion state, acidity, and reducibility of the vanadia species.

Key words: vanadia species; dispersion state; selective catalytic reduction; Brønsted acid site; reducibility; nitrogen oxide

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Supported V_2O_5/TiO_2 catalysts have attracted attention because of their unique catalytic properties in the selective catalytic reduction (SCR) of NO_x by NH_3 . They have high activity, thermal stability, and resistance to poisoning by SO_2 , and attention have been paid to both their activity and characterization [1–3]. It has been well established that in the sub-monolayer region, vanadia was present on titania as monomeric and polymeric vanadia species, and that the distribution of these species depends on the VO_x coverage [2–7]. At low VO_x coverage in the sub-monolayer region, the catalytic activity of these catalysts depended on the vanadia loading [7–14]. Baiker et al. [8] carried out kinetic measurements at 150 °C and showed that the NO turnover frequencies (TOF) increased by more than an order of magnitude when the vanadia loading was increased from 1.8 to 3.0 $\mu\text{mol V}^{5+}/\text{m}^2$. When the vanadia loading was increased further, the TOF declined, probably due to an increase in bulk V^{5+} species. Went et al. [7] found that the NO TOF at 227 °C increased substantially with increasing vanadia loading, and reached a maximum in the range of 4%–8% V_2O_5 as the fraction of polymeric vanadia species reached a maximum at 6% (15.2 $\mu\text{mol V}^{5+}/\text{m}^2$). Then the TOF declined as crystallites of V_2O_5 were formed at the expense of the polymeric species, suggesting that the polymeric species were more active than the monomeric species. Lietti et al. [9] found that the TOF measured at 227 °C under steady state conditions over high loading vanadia catalysts was six times higher than that of low loading vanadia catalysts, which was due to their higher amounts of polymeric vanadia species. The increase of NO TOF with increasing VO_x coverage has been attributed to a higher specific activity of the polymeric vanadia species [7] and to the accompanying increase in Brønsted acid sites with VO_x surface coverage [10].

However, Amiridis et al. [15] found that when the SCR reaction was carried out at the high temperatures frequently used for commercial SCR applications and/or at the lower NO concentrations encountered in a typical flue gas, the NO TOF at 350 °C first increased with increasing VO_x surface coverage, reached a maximum at a coverage corresponding to approximately half a monolayer, and then decreased rapidly at higher coverage. They argued that the subsequent decrease of TOF at coverages between half and one

monolayer can be attributed to the loss of the strong acid sites of the TiO_2 support at high VO_x surface coverage. Although there are a number of studies dealing with the SCR activity of V_2O_5/TiO_2 catalysts with different VO_x coverages, there is still a debate about the relationship between surface properties and SCR activity. In this work, the nature of vanadia species supported on anatase with different loadings was explored by X-ray diffraction (XRD), infrared spectroscopy of chemisorbed NH_3 (NH_3 -IR), temperature-programmed desorption of NH_3 (NH_3 -TPD), hydrogen temperature-programmed reduction (H_2 -TPR), and micro-reactor testing of the selective catalytic reduction of NO by NH_3 . The relationship between surface properties (acidity and reducibility of vanadia species) and SCR activity of supported vanadia species is discussed.

1 Experimental

1.1 Catalyst preparation

The anatase support (denoted as TiO_2) with BET surface area of 65.4 m^2/g was obtained by adding under stirring acetic acid into *n*-butanol solution containing the required amount of $Ti(n\text{-C}_4\text{H}_9\text{O})_4$, followed by adding the appropriate amount of water. The yellow gel formed was aged in air for 12 h, dried at 100 °C in air for another 24 h, and calcined at 500 °C in air for 4 h. The V_2O_5/TiO_2 catalysts were prepared by impregnating the TiO_2 support with a solution containing the required amount of NH_4VO_3 dissolved in nitric acid (14 mol/L). The mixture was heated at 80 °C under stirring to remove most of the water and then it was dried at 100 °C in air for 12 h, calcined at 500 °C in air for 4 h.

1.2 Catalytic activity measurement

The catalytic tests for the SCR of NO by NH_3 were carried out in a glass microreactor with catalyst samples of 0.05 g and 250–420 μm in diameter. Prior to the reaction, the sample was pretreated in flowing air at 500 °C for 0.5 h. The catalytic reaction was carried out at 300 °C and 0.1 MPa, with a total flow rate 450 ml/min (ambient conditions) and GHSV = $7.7 \times 10^5 \text{ h}^{-1}$ (based on the total bed volume of

catalyst samples). The inlet concentrations of reactants were 0.075% NO_x , 0.08% NH_3 , 3% O_2 , and N_2 was the remainder. The NO concentrations before and after reaction were determined by an *N*-(1-naphthyl)-ethylenediamine dihydrochloride spectrophotometer method (Saltzman method) [16–17].

1.3 Catalyst characterization

The BET surface areas were obtained by N_2 adsorption using a Micromeritics ASAP 2000 instrument with a computer controlled measurement system. The sample was degassed at 300 °C to a vacuum below 0.4 Pa before measurement. XRD patterns of $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts were obtained with a Philips X'pert pro apparatus employing Ni filtered $\text{Cu K}\alpha$ radiation. The X-ray tube was operated at 40 kV and 40 mA. The amount of V_2O_5 crystallites was determined by XRD quantitative analysis [18]. The intensity ratios of the $\text{V}_2\text{O}_5(001)$ to $\text{CeO}_2(111)$ planes, $I_{\text{V}_2\text{O}_5(001)}/I_{\text{CeO}_2(111)}$, in the $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts with different V_2O_5 loading were measured using crystalline CeO_2 as an internal reference to evaluate the dispersion capacity of V_2O_5 on TiO_2 .

NH_3 -TPD was carried out in a quartz U-tube reactor with a thermal conductivity detector (TCD). The powder catalyst (0.25 g) was oxidized in flowing air (20 ml/min) at 500 °C for 0.5 h and cooled down to 100 °C. The samples were first saturated with pure NH_3 at 100 °C for 0.5 h, and then purged with flowing He (20 ml/min) until the TCD signal was stable. Then, the sample was heated to 600 °C at 5 °C/min in flowing He.

NH_3 -IR adsorbed on the catalysts was performed with a Nicolet 5700 FTIR spectrometer. The samples were pressed to self-supporting pieces with the same catalyst mass and dried in flowing N_2 at 300 °C for 0.5 h. Then a sample was saturated with NH_3 at 100 °C for 0.5 h. After purging with N_2 at 100 °C for 1 h, the sample was heated to 400 °C in flowing N_2 at a rate of 10 °C/min and the NH_3 -IR spectra were recorded at different temperatures.

H_2 -TPR was carried out in a quartz U-tube reactor and 0.10 g sample was used. The 5% H_2 -95%Ar mixture was switched on at a flowing rate of 20 ml/min and the temperature was increased linearly at a rate of 10 °C/min. The consumption of H_2 was detected by TCD. CuO powder was used as reference for the quantitative analysis.

2 Results and discussion

2.1 Catalyst structure

Table 1 shows the composition, BET surface area, VO_x coverage, and SCR activity of the supported $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts. The calculation of VO_x coverage for each sample

Table 1 Composition, BET surface area, VO_x coverage, and SCR activity of the supported $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts

V_2O_5 loading (wt%)	$A_{\text{BET}}/(\text{m}^2/\text{g})$	VO_x coverage (mmol V/100 m^2 TiO_2)	NO conversion (mol%)	TOF* (10^{-3} s^{-1})
0.00	65.4	0.00	3.0	0.0
1.48	56.2	0.29	13.9	3.7
2.29	49.9	0.50	32.3	5.2
2.87	45.3	0.70	68.4	8.3
3.64	51.0	0.78	65.0	5.4
4.29	47.3	1.00	64.0	5.0
6.25	45.0	1.53	61.9	3.0

*Moles of NO converted per mole of V per second.

was based on the BET surface area. Plotted in Fig. 1 are the ratios of the XRD peak intensities of the $\text{V}_2\text{O}_5(001)$ to $\text{CeO}_2(111)$ planes versus loading amount of V_2O_5 , from which the monolayer dispersion capacity of V_2O_5 on anatase was determined by extrapolation to be 1.14 mmol V/100 m^2 TiO_2 (6.86 VO_x/nm^2). This was close to the monolayer surface coverage (7–8 VO_x/nm^2) determined from Raman data [5,19,20]. Above this value, the characteristic peaks attributed to V_2O_5 crystallites appeared in the XRD profiles (sample with V_2O_5 loading of 6.25%). The above experimentally measured monolayer dispersion capacity of V_2O_5 on anatase (1.14 mmol V/100 m^2 TiO_2) was almost the same as the concentration of surface vacant sites on the preferentially exposed (001) plane of anatase [21] (1.16 mmol site/100 m^2 TiO_2) estimated by the incorporation model [22–24]. This suggested that the dispersed vanadium cations were actually located on the octahedral vacant sites on the preferentially exposed (001) plane of anatase TiO_2 , with the accompanying oxygen anions positioned on the top for charge compensation.

Fig. 1. XRD quantitative analysis of the $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts.

2.2 SCR activity

The NO conversion and NO TOF (expressed in units of moles of NO converted per mole of V per second) were measured at 300 °C under steady state conditions. The results are listed in Table 1 and plotted in Fig. 2. The NO TOF

Fig. 2. Effect of VO_x coverage on NO conversion and NO TOF for $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts at 300 °C.

initially increased with VO_x surface coverage and reached a maximum value of $8.3 \times 10^{-3} \text{ s}^{-1}$ at coverage corresponded to slightly more than half a monolayer (2.87% V_2O_5 , 0.70 mmol V/100 m^2 TiO_2). The TOF then decreased rapidly at higher coverages. The decline of TOF with increase of VO_x coverage from 1.00 to 1.53 mmol V/100 m^2 TiO_2 can be understood by that the existence of V_2O_5 crystallites reduced the ratio of exposed vanadia species on the surface, as indicated by the XRD quantitative analysis results (see Fig. 1) over VO_x monolayer dispersion capacity. Previous studies of the activity of $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts have also shown an increase in the rate of SCR reaction with VO_x surface coverage in the sub-monolayer region [7,10]. This increase has been attributed to a higher specific activity of the polymeric vanadia species [7], and to the accompanying increase of Brönsted acid sites with VO_x surface coverage [10]. The subsequent decrease of TOF at coverages between half and one monolayer has been attributed to the loss of the strong acid sites of the TiO_2 support at high VO_x surface coverages [15]. The relationship between the TOF and VO_x surface coverage observed in this work was similar to those given by Amiridis et al. [15], Mutin et al. [25], and Giakoumelou et al. [26]. The reason for the effect of VO_x surface coverage on the SCR activity needs to be further clarified.

2.3 Surface acidity

To discuss the effect of VO_x surface coverage in the sub-monolayer region on the SCR activity, the surface acidity should be taken into consideration. Figure 3 shows the NH_3 -IR spectra of the $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst with 0.70 mmol V/100 m^2 TiO_2 and the maximum NO TOF (see Fig. 2). There were four absorption bands. The absorption bands at 1430 and 1680 cm^{-1} can be assigned to the N–H bending vibration of NH_3 chemisorbed on Brönsted acid sites (V–OH), while the bands at 1200 and 1552 cm^{-1} can be assigned to the N–H vibration of NH_3 chemisorbed on

Fig. 3. FT-IR spectra of NH_3 adsorbed on $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst with 0.70 mmol V/100 m^2 TiO_2 .

Lewis acid sites (V=O) [10,27,28]. These data indicated that the dispersed vanadia species in the sub-monolayer region have both Brönsted and Lewis acid sites. With increasing desorption temperature from 100 to 375 °C, the band intensities of the Brönsted acid sites decreased, while those of the Lewis acid sites only changed slightly, suggesting that the Brönsted acid sites of dispersed vanadia species have weaker acidic strength than the Lewis acid sites.

Figure 4 presents the NH_3 -TPD profiles of the $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst with different VO_x coverages. Only a broad peak around 270 °C was observed in the profile of the anatase TiO_2 support (Fig. 4(1)). For the supported $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts, the desorption peak shifted to 180 °C and a new desorption peak appeared at 450 °C (Fig. 4(2)). This indicated

Fig. 4. NH_3 -TPD profiles of $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts with different VO_x coverages. (1) TiO_2 ; (2–7) $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts (mmol V/100 m^2 TiO_2): (2) 0.29; (3) 0.54; (4) 0.70; (5) 0.78; (6) 1.00; (7) 1.53.

that the dispersed vanadia species have two kinds of acid sites, weak and strong acid sites. Combining these results with the NH₃-IR results, one can conclude that the Brönsted acid sites of dispersed vanadia species were the weak acid sites, while the Lewis acid sites of dispersed vanadia species were the strong acid sites.

The NH₃-TPD peak areas of the V₂O₅/TiO₂ catalysts with different VO_x coverages were integrated after peak fitting and deconvolution. As discussed above, the dispersion capacity of vanadium oxide on anatase (complete monolayer) was 1.14 mmol V/100 m² TiO₂ (see Fig. 1). For the V₂O₅/TiO₂ catalysts with different VO_x coverages, the contribution of the bare anatase TiO₂ support to the NH₃-TPD peak area of the catalysts was estimated to give the VO_x coverages based on the NH₃-TPD peak areas as

$$A_{\text{bare TiO}_2 \text{ contribution}} = \left(1 - \frac{C_V}{C_{V_m}}\right) \times A_{\text{TiO}_2}$$

where A_{TiO_2} was the NH₃-TPD peak area contributed by the pure TiO₂ support, C_V was the VO_x coverage volume (mmol V/100 m² TiO₂), and C_{V_m} was the monolayer dispersion capacity of vanadium oxide on anatase (1.14 mmol V/100 m² TiO₂). The results are shown in Table 2 and Fig. 5. It can be seen that while the acid amount contributed by the support TiO₂ decreased (Fig. 5(2)) and the relative acid amount of strong acid sites also decreased slightly (Fig. 5(3)), the acid amount of weak acid sites increased gradually with increasing VO_x coverage (Fig. 5(4)). This trend was similar to the increase of the total amount of acid sites of the V₂O₅/TiO₂ catalysts (Fig. 5(1)), indicating that the increase of the total amount of acid sites was due to the increase in the weak acid sites of the vanadia species.

By subtracting the contribution of the bare anatase TiO₂ support to the NH₃-TPD peak area, the NH₃-TPD peak area due to dispersed vanadia species can be calculated by the formula below, which gives the amount of acid sites due to vanadia species. The result is shown in Fig. 5(5).

$$A_{\text{vanadium oxide contribution}} = \frac{A_{\text{V}_2\text{O}_5/\text{TiO}_2} - \left(1 - \frac{C_V}{C_{V_m}}\right) \times A_{\text{TiO}_2}}{n_V}$$

Fig. 5. Effect of VO_x coverage on the NH₃-TPD peak area of the V₂O₅/TiO₂ catalysts. (1) Total NH₃ desorption peak area; (2) Contribution from TiO₂; (3) Strong acid site; (4) Weak acid site; (5) Average NH₃ desorption peak area per V ion of the vanadia species.

where A_{TiO_2} was the NH₃-TPD peak area due to the pure TiO₂ support, $A_{\text{V}_2\text{O}_5/\text{TiO}_2}$ was the NH₃-TPD peak area due to the V₂O₅/TiO₂ catalyst, and n_V was the number of vanadium ions of the V₂O₅/TiO₂ catalyst. It can be seen from Fig. 5(5) that the relative amount of acid sites contributed by each vanadium ion increased with VO_x coverage in sub-monolayer region. This means that the relative amount of weak acid sites associated with each vanadium ion also increased with increasing VO_x coverage in the sub-monolayer region. As suggested by Topsøe et al. [10,29], the surface Brönsted acid sites of the V₂O₅/TiO₂ catalysts are the active sites for the SCR reaction. In our cases, the increase of NO TOF below a VO_x coverage of 0.70 mmol V/100 m² TiO₂ was correlated with the increase

Table 2 NH₃-TPD peak areas of V₂O₅/TiO₂ catalysts with different VO_x coverages

V ₂ O ₅ loading (wt%)	VO _x coverage (mmol V/100 m ² TiO ₂)	NH ₃ -TPD peak area (a.u.)					
		Acid amount			Contributed by		
		Weak	Strong	Total	TiO ₂	Vanadia	Each V ion of vanadia (10 ⁵ /mol _V)
0.00	0.00	—	—	—	130	—	—
1.48	0.29	58.5	45.9	104.4	95.5	8.9	2.19
2.29	0.50	71.4	40.7	112.1	66.8	45.3	6.87
2.87	0.70	71.4	45.1	116.5	48.7	67.8	8.59
3.64	0.78	83.5	45.7	129.2	39.6	89.6	8.96
4.29	1.00	93.7	35.3	129.0	15.3	113.7	9.64
6.25	1.53	107.9	33.8	141.7	0	141.7	7.48

of the relative amount of weak acid sites, i.e., Brønsted acid sites of the vanadium ions.

It can also be seen from the NH_3 -TPD results that the relative amount of the surface acid sites due to the vanadium ions increased from 0.70 mmol V/100 m^2 TiO_2 and to one monolayer of VO_x . This cannot explain the subsequent decline of NO TOF beyond half monolayer of VO_x . Some other factor of the $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst at higher V_2O_5 loading and its effect on the NO-TOF activity should be taken into consideration. The NH_3 -TPD results also showed that the relative amount of surface acid sites contributed by each vanadium ion decreased beyond one monolayer. This was because the existence of V_2O_5 crystallites reduced the ratio of exposed vanadia species on the surface.

2.4 Reducibility of the $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts

It has been established that the oxidative dehydrogenation of adsorbed ammonia species by vanadia species is a key step in the SCR of NO by NH_3 [27,30–32]. To investigate the reducibility of vanadium ions with different VO_x coverages in the sub-monolayer region, the H_2 -TPR results of a series of samples are shown in Fig. 6. More information can be obtained from the H_2 consumption of each vanadium ion shown in Fig. 7. As shown in Fig. 6(1), pure TiO_2 has a small reduction peak at 660 $^\circ\text{C}$, corresponding to the reduction of $\text{Ti}^{4+} \rightarrow \text{Ti}^{3+}$. In contrast, profile of pure V_2O_5 (Fig. 6(2)) has three reduction peaks located at 700, 726, and 808 $^\circ\text{C}$, corresponding to the following stepwise reduction of the vanadium oxide [33]: $\text{V}_2\text{O}_5 \rightarrow \text{V}_6\text{O}_{13} \rightarrow \text{VO}_2 \rightarrow \text{V}_2\text{O}_3$. In comparison with pure V_2O_5 ,

Fig. 6. H_2 -TPR profiles of $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts with different VO_x coverage. (1) TiO_2 ; (2) V_2O_5 ; (3–8) $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts (mmol V/100 m^2 TiO_2): (3) 0.29; (4) 0.54; (5) 0.70; (6) 1.00; (7) 1.43; (8) 2.37.

Fig. 7. Effect of VO_x coverage on the average H_2 consumption per vanadium ion.

the main feature of the TPR profiles of the $\text{V}_2\text{O}_5/\text{TiO}_2$ samples was the clear shift of their reduction peaks to lower temperatures, as shown in Fig. 6(3). This revealed that the interaction between V ions and Ti ions have changed the process of the reduction of V ions, and supported vanadia species on anatase were easier to reduce. However, the reduction peaks (Fig. 6(3)–(8)) shifted gradually to higher temperature and the H_2 consumption of each vanadium ion (Fig. 7) decreased rapidly with the increase of VO_x coverage. These results implied that the vanadium ion reducibility of the $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts decreased with the increase of VO_x coverage beyond the VO_x coverage of 0.70 mmol V/100 m^2 TiO_2 , and this resulted in a drastic decline of NO TOF with increased VO_x coverage. This may be the reason for the subsequent decline of NO TOF at coverage between half and one monolayer, even when the relative amount of weak acid sites contributed by each vanadium ion increased.

2.5 Discussion

The existence of isolated vanadia species, polymeric vanadia species, and V_2O_5 crystallites on $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts has been shown in the literature [2–7,9,12,20,26,34–36]. Our work suggested that the isolated vanadia species located on the octahedral vacant sites on the surface of anatase TiO_2 were the dominant species at VO_x coverages far below the monolayer, and there was an interaction through bridging V–O–Ti bonds between vanadia species and anatase TiO_2 (see Scheme 1(A)). As the VO_x coverage increased, isolated vanadia species tend to get dispersed on adjacent octahedral vacant sites, and interacted with their nearest neighbors (either isolated or polymeric vanadia species) through bridging V–O–V bonds to form polymeric vanadia species at the expenses of V–O–Ti bonds below the VO_x monolayer coverage, even if there were still some vacant sites not occupied on the TiO_2 surface at this time. This

Scheme 1. Proposed structure for isolated (A), dimeric (B), and polymeric (C) of vanadyl species and schemes of the generation of the Brønsted acid sites for polymeric vanadia species on the surface of anatase TiO_2 .

resulted in an increase of the ratio of V–O–V bonds and a decrease of the ratio of V–O–Ti bonds of the vanadia species (shown in Scheme 1(B) and (C)). According to Miyata et al. [37], the Lewis acid sites can be converted to Brønsted sites upon the introduction of water. The model of the generation of Brønsted acid sites from surface vanadia species suggested by Busca et al. [30] showed that two Brønsted acid site structures of –OH and –O(H)– exist on surface vanadyl centers. Thus from our experimental results, we supposed that there was also a Brønsted acid site on bridging V–O(H)–V besides the terminal V–OH on the polymeric vanadia species (shown in Scheme 1).

As discussed above, in our work, the vanadium ion reducibility decreased with increased VO_x coverage, and the increase of NO TOF was correlated to the increase of the relative Brønsted acid sites per vanadium ion. By combining these with previous results that the bridging V–O–V sites are active sites for the SCR reaction [3,7,25–26,38–39], it can be suggested that the Brønsted acid sites on bridging V–O(H)–V were also active sites in the SCR reaction, in addition to the terminal V–OH of polymeric vanadia species. The increase of the ratio of V–O–V bonds led to the increase of the relative amount of weak acid sites (Brønsted acid sites per vanadium ion) with increasing VO_x coverage, which resulted in the sharp increase of NO TOF below a VO_x coverage of 0.70 mmol V/100 m^2 TiO_2 . As the VO_x coverage increased further, the decrease of the ratio of V–O–Ti bonds of the vanadia species implied that the interaction between V_2O_5 and TiO_2 becomes weaker and led to the decrease of vanadium ion reducibility of the vanadia species. This resulted in a drastic decline of NO TOF between half and one monolayer of VO_x coverage, although the relative amount of weak acid sites still increased. The decline of NO TOF beyond the monolayer can be understood by that the existence of V_2O_5 crystallites reduced the ratio of exposed vanadia species on the surface and reduced vanadium ion reducibility, which was caused by that it was

then more difficult for vanadia species to interact with the TiO_2 support. Thus, it can be concluded that the acid properties of dispersed vanadia species are the key factors controlling the SCR activity of $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts at low VO_x coverage, while the reducibility of dispersed vanadia species play a role at high VO_x coverages.

3 Conclusions

On $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts, the NO TOF of SCR at 300 °C initially increased with increasing VO_x coverage, reached a maximum ($8.3 \times 10^{-3} \text{ s}^{-1}$ at a coverage corresponding to slightly higher than half a monolayer (0.70 mmol V/100 m^2 TiO_2), and then decreased rapidly at higher coverages. For V_2O_5 dispersed on anatase TiO_2 , the experimentally measured (from XRD) monolayer dispersion capacity of V_2O_5 on anatase (1.14 mmol V/100 m^2 TiO_2) was almost the same as the concentration of surface octahedral vacant sites of anatase estimated by the incorporation model. Isolated vanadia species were dispersed on adjacent octahedral vacant sites, which then formed polymeric vanadia species through bridging V–O–V bonds at the expense of V–O–Ti bonds. The Brønsted acid sites on bridging V–O(H)–V and the terminal V–OH of polymeric vanadia species are active sites in the SCR reaction. With increasing VO_x coverage, the relative amount of weak acid sites (Brønsted acid sites per vanadium ion) of vanadia species increased due to an increase in the ratio of the V–O–V bonds of vanadia species. This led to the sharp increase of NO TOF below VO_x coverage of 0.70 mmol V/100 m^2 TiO_2 . With further increase in the VO_x coverage, the vanadium ion reducibility of the vanadia species decreased due to a decrease of the ratio of V–O–Ti bonds of the vanadia species, and this resulted in a decline of NO TOF between half and one monolayer of VO_x coverage. The decline of NO TOF beyond a monolayer can be understood by that the existence of V_2O_5 crystallites reduced the ratio of exposed vanadia species and reduced

vanadium ion reducibility because there was less interaction of vanadia species with the TiO_2 support. The SCR activity of $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts was related to the dispersion state, acidity and reducibility of the vanadia species.

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