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Catalytic performance of a novel ceramic-supported vanadium oxide catalyst for NO reduction with NH_3

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Abstract

A novel TiO_2/Al_2O_3/cordierite honeycomb-supported V_2O_5–MoO_3–WO_3 monolithic catalyst was studied for the selective reduction of NO with NH_3. The effects of reaction temperature, space velocity, NH_3/NO ratio and oxygen content on SCR activity were evaluated. Two other V_2O_5–MoO_3–WO_3 monolithic catalysts supported on Al_2O_3/cordierite honeycomb or TiO_2/cordierite honeycomb support, two types of pellet catalysts supported on TiO_2/Al_2O_3 or Al_2O_3, as well as three types of pellet catalysts V_2O_5–MoO_3–WO_3–Al_2O_3 and V_2O_5–MoO_3–WO_3–TiO_2 were tested for comparison. The experiment results show that this catalyst has a higher catalytic activity for SCR with comparison to others. The results of characterization show, the preparation method of this catalyst can give rise to a higher BET surface area and pore volume, which is strongly related with the highly active performance of this catalyst. At the same time, the function of the combined carrier of TiO_2/Al_2O_3 cannot be excluded.

Keywords: SCR; Vanadium oxide; Monolithic catalyst; Cordierite

1. Introduction

The V_2O_5–WO_3–MoO_3–TiO_2 catalyst has been widely used in selective catalytic reduction of NO_x. The catalyst employed for SCR in stationary sources consists primarily of extruded V_2O_5–WO_3–MoO_3–TiO_2 catalyst [1,2], due to its low pressure drop. However, supported catalyst offers a number of potential advantages over their unsupported counterparts, such as increased surface area/volume ratio of the active phase, enhanced mechanical strength, improved heat transfer characteristics and rapid light-off [3]. In addition, a coated catalyst shows the same catalytic activity at temperatures above 573 K with much lower amount of active material necessarily [4].

In this work, we report the catalytic performance of a novel SCR catalyst V_2O_5–WO_3–MoO_3/TiO_2/Al_2O_3/cordierite catalyst for the SCR of NO with ammonia. Two other single-oxide/cordierite honeycomb-supported catalysts and five kinds of non-cordierite honeycomb-supported catalysts were also investigated under the same conditions for the purpose of comparison.

2. Experimental

2.1. Catalysts preparation

Three sorts of catalysts loaded with V_2O_5–WO_3–MoO_3 under the same ratio of $V_2O_5:WO_3:MoO_3 = 1:1:8$ (weight) were prepared (see Table 1).

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Table 1
Composition of the observed catalysts

Catalysts[a]	Composition (mass ratio)
$M/TiO_2/Al_2O_3/CC$	$(V_2O_5–WO_3–MoO_3):TiO_2:Al_2O_3$:cordierite = 2.5:3:13:100
$M/TiO_2/CC$	$(V_2O_5–WO_3–MoO_3):TiO_2$:cordierite = 1:13:100
$M/Al_2O_3/CC$	$(V_2O_5–WO_3–MoO_3):TiO_2$:cordierite = 2.5:13:10
$M/TiO_2/Al_2O_3$	$(V_2O_5–WO_3–MoO_3):TiO_2:Al_2O_3$ = 1:0.2:6
M/Al_2O_3	$(V_2O_5–WO_3–MoO_3):Al_2O_3$ = 1:6
$M–TiO_2–Al_2O_3$	$(V_2O_5–WO_3–MoO_3):TiO_2:Al_2O_3$ = 1:1.4:6
$M–TiO_2$	$(V_2O_5–WO_3–MoO_3):TiO_2$ = 1:6
$M–Al_2O_3$	$(V_2O_5–MoO_3–WO_3):Al_2O_3$ = 1:6

[a] M: $V_2O_5–MoO_3–WO_3$; CC: cordierite honeycomb.

(1) Monolithic catalysts supported on cordierite honeycomb, including $V_2O_5–WO_3–MoO_3/TiO_2/Al_2O_3$/cordierite, $V_2O_5–WO_3–MoO_3/TiO_2$/cordierite and $V_2O_5–WO_3–MoO_3/Al_2O_3$/cordierite. A sol–gel method was followed for preparing the mixed TiO_2/Al_2O_3/cordierite, TiO_2/cordierite and Al_2O_3/cordierite honeycomb supports. The commercial cordierite honeycomb supports, which are 400 cpsi, 30 mm in diameter, 50 mm in height and a BET surface area of 8.0 m^2/g, were impregnated with the sol of $(Al_2O_3{\cdot}nH_2O){\cdot}bH_X{\cdot}cH_2O$, then the sol of $Ti(OH)_4$ to form the mixed oxides support, or merely impregnated with the sol of $(Al_2O_3{\cdot}nH_2O){\cdot}bH_X{\cdot}cH_2O$ or the sol of $Ti(OH)_4$ separately to form the single-oxide supports. After that, they were dried at 393 K for 1 h then calcining at 723 K for 2 h.

Subsequently, the mixed oxides supports were impregnated with aqueous solution of metavanadate, molybdate and tungstate followed by drying at 393 K for 1 h and calcining at 723 K for 2 h.

(2) Pellet catalysts whose supports were prepared by means of sol–gel method, including $V_2O_5–WO_3–MoO_3/TiO_2/Al_2O_3$ and $V_2O_5–WO_3–MoO_3/Al_2O_3$. The Al_2O_3 as the support was obtained by calcining the $(Al_2O_3{\cdot}nH_2O){\cdot}bH_X{\cdot}cH_2O$ collide at 723 K for 2 h then sieving it with screen to obtain particles of 1.0–1.6 mm in diameter. The coating of TiO_2 on Al_2O_3 was also accomplished with sol–gel method. The active components were supported on the supports in the way the same as the preparation of monolithic catalysts.

(3) Pellet catalysts were made by the co-precipitation method. This sort of catalyst includes $V_2O_5–MoO_3–WO_3–TiO_2–Al_2O_3$, $V_2O_5–MoO_3–WO_3–TiO_2$ and $V_2O_5–MoO_3–WO_3–Al_2O_3$. The aqueous solution of metavanadate, molybdate and tungstate was mixed with TiO_2, or $(Al_2O_3{\cdot}nH_2O){\cdot}bH_X{\cdot}cH_2O$, or both of them, followed by drying at 473 K till the water was completely evaporated. Subsequently, the dry material was calcined in air at 723 K for 2 h, ground and sieved to 1.0–1.6 mm.

2.2. *Catalytic testing*

The catalytic performances were examined by the continuous flow reaction of the selective reduction of NO with ammonia. The tests were carried out in a fixed-bed quarts reactor of 33 mm inner diameter. Four gas streams, 1000 ppm NO, 1000 ppm NH_3, 5% O_2 and N_2 in balance, were used to simulate flue gas. Four anticorrosive mass flow controllers were used to control the gas streams. The inlet gases were mixed in a chamber filled with glass wool before entering the reactor. The concentrations of NO and O_2 both at the inlet and the outlet of the reactor were simultaneously monitored by an on-line FSI (China) Flue Gas Analyzer equipped with NO and O_2 sensors.

2.3. *Supports and catalysts characterization*

The catalysts were analyzed and characterized by means of BET, Flourier transform-infrared spectroscopy (FT-IR), and X-ray photoelectron spectroscopy (XPS) as described in following sections.

2.3.1. *The BET surface area and pore size measurement*

The BET surface area was calculated from the nitrogen adsorption isotherms at 77 K with a Micromeritics ASAP 2010 accelerated surface area and porisimetry system (Micromeritics Instrument, Norcross, GA). Prior to the measurements, the samples were evacuated at 343 K for 1 h and then at 423 K for at least 3 h. Pore volume and pore size were determined by the BJH method.

2.3.2. *FT-IR*

The FT-IR spectra were recorded by using an FT-IR spectrometer (Bruker Vector33, 0.3 cm^{-1} resolution) at room temperature. Self-supported wafers (15 mm diameter, 15 ± 1 mg) were formed by pressing the catalyst powder scratched from the catalysts with cordierite support. Thirty-two scans were recorded each time.

2.3.3. *XPS*

The XPS analyses of the catalyst samples were carried out in a PHI (USA) Quatum2000 electron spectrometer equipment using non-monochromatic Al Kα radiation ($h\nu = 1486.6\,\mathrm{eV}$) to excite photo-electrons. Vacuum in the test chamber during the collection of spectra was typically less than 5×10^{-7} Pa. To compensate for the steady state charging effects, the binding energies (BE) were normalized with respect to the position of the C 1s signal (284.6 eV) resulting from adsorbed hydrocarbon fragment. Gaussian and/or Lorentzian peaks were deconvoluted using a non-linear least-squares algorithm. The atomic compositions were estimated based on comparisons of the integrated peak area normalized by the atomic sensitivity factors [5].

3. Results

Both performance and characterization of this novel cordierite honeycomb-supported monolithic catalyst have been investigated with various methods. In order to compare it with general catalysts, catalysts supported on other supports or catalysts prepared with different methods also have been investigated under the same condition. For this set of experiments we kept the composition of active component (V_2O_5–WO_3–MoO_3) constant in order to isolate the effect of the supports and preparing method.

3.1. *Catalytic performances*

3.1.1. *Performance of V_2O_5–WO_3–MoO_3–TiO_2/Al_2O_3/cordierite honeycomb monolithic catalyst*

The catalytic performance of this binary oxides/cordierite supported catalysts has been tested in detail. The correlations between inlet oxygen rate, NH_3/NO ratio, space velocity and the temperature of reaction with the conversion of NO are shown in Figs. 1–4, respectively. From the test results, this catalyst performed a satisfying activity similar to that of commercial V_2O_5–MoO_3–WO_3/TiO_2 monolithic extruded catalysts reported in literature.

3.1.1.1. Effect of the oxygen content. Fig. 1 shows the effect of oxygen content of inlet on the conversion of NO at various temperatures with SV of 6000 h^{-1} and NH_3/NO of 1.0, indicating that inlet oxygen content only slightly influenced the conversion of the NO. A high conversion of NO can be obtained when the oxygen content was in the range of 5–7%, similar to the emission of industrial flue gas.

3.1.1.2. Effect of NH_3/NO ratio. Fig. 2 shows the correlation between NH_3/NO ratio of inlet with the conversion of NO at various temperature with SV of 6000 h^{-1} and inlet oxygen rate of 5%. As can be seen, NH_3/NO ratio also did not have great effect on NO conversion, and higher conversion could be found when NH_3/NO was in the range of 1.2–1.6, while the NH_3/NO ratio of 1.2 was high enough for getting reasonable NO conversion.

3.1.1.3. Effect of reaction temperature. As shown in Fig. 3, a peak of NO conversion could be observed in the temperature range of 673–723 K, indicating that the best operation temperature of the catalyst is near 673 K. At SV 6000 h^{-1} and temperature 673 K, the NO conversion was higher to 92%. In general, the higher conversion is more liable to be obtained at lower SV. Furthermore, the optimal reaction temperature also differed with the space velocity. The lower the SV, the lower the optimal temperature.

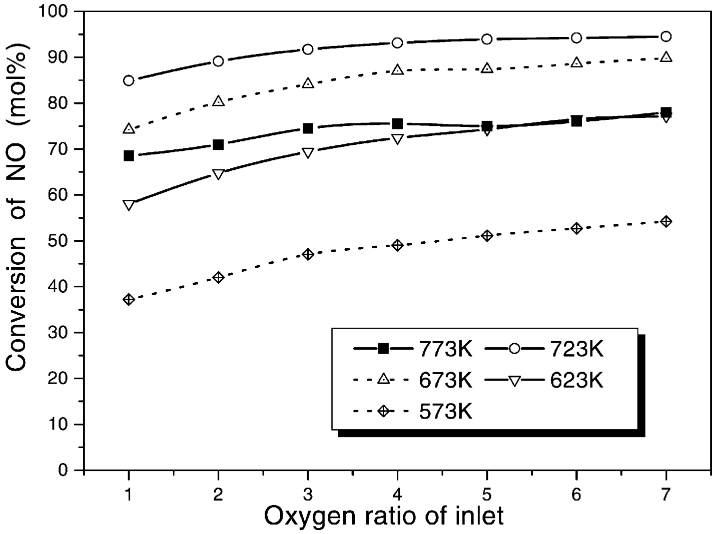

Fig. 1. The correlation between the oxygen ratio of inlet and the conversion of NO at various temperatures on V_2O_5–MoO_3–WO_3/TiO_2/Al_2O_3/cordierite-honeycomb (SV = 6000 h^{-1}, NH_3/NO = 1.0).

3.1.1.4. Effect of space velocity. Fig. 4 shows the effect of space velocity on the conversion of NO. The increase in SV resulted in the decrease of the conversion at the temperature higher than 573 K, while the situation at 573 K was an exception.

3.1.2. Performances of V_2O_5–MoO_3–WO_3 monolithic catalysts supported on Al_2O_3/cordierite honeycomb and TiO_2/cordierite honeycomb

In order to study the influence of the supports (TiO_2, Al_2O_3 or TiO_2/Al_2O_3) on the performance of

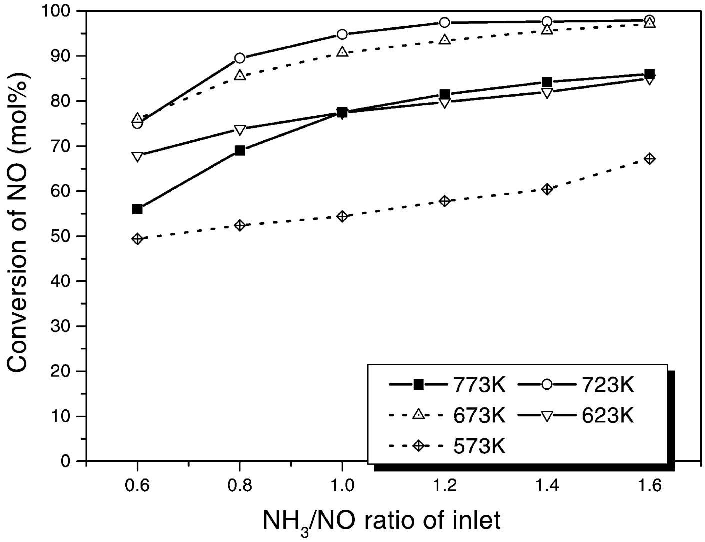

Fig. 2. The correlation between the NH_3/NO ratio of inlet and the conversion of NO at various temperatures on V_2O_5–MoO_3–WO_3/TiO_2/Al_2O_3/cordierite-honeycomb (SV = 6000 h^{-1}, oxygen ratio = 5%).

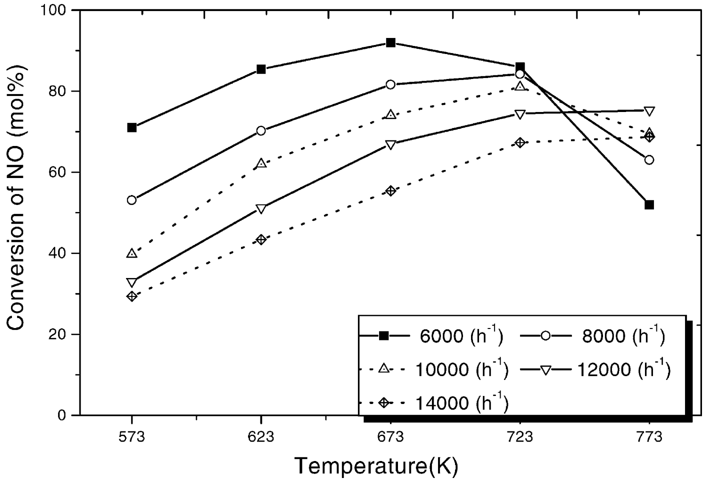

Fig. 3. The correlation between reaction temperature and the conversion of NO at various SV on V_2O_5–MoO_3–WO_3/TiO_2/Al_2O_3/cordierite-honeycomb (oxygen ratio = 5%, NH_3/NO = 1.0).

this monolithic sort of catalysts, two other kinds of cordierite honeycomb-supported catalysts have been tested under the same condition for comparison. The testing results of V_2O_5–MoO_3–WO_3/Al_2O_3/cordierite and V_2O_5–MoO_3–WO_3/TiO_2/cordierite exhibit a significant difference, as shown in Fig. 5. First, the binary oxides/cordierite honeycomb-supported catalyst had much higher activity in the SCR reaction than that of the two single-oxide/cordierite honeycomb-supported catalysts. Meanwhile, the performance of V_2O_5–MoO_3–WO_3/Al_2O_3/cordierite was better than that of V_2O_5–MoO_3–WO_3/TiO_2/cordierite, especially at the temperature higher than 630 K. It is remarkable to note that, both the two kinds of TiO_2 contained catalysts could obtain their best performance at lower temperature, that is to say, the catalysts containing TiO_2 are liable to work at lower temperature.

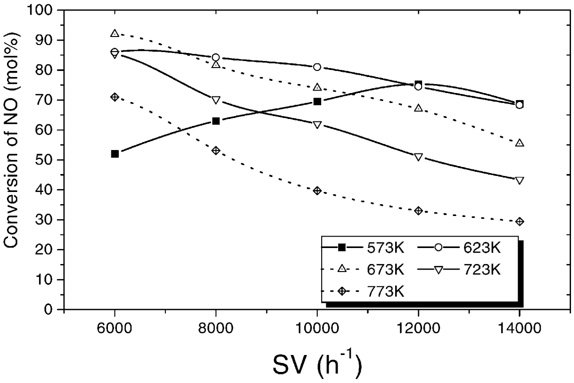

Fig. 4. The correlation between space velocity and the conversion of NO at various temperatures on V_2O_5–MoO_3–WO_3/TiO_2/Al_2O_3/cordierite-honeycomb (oxygen ratio = 5%, NH_3/NO = 1.0).

3.1.3. Performances of V_2O_5–WO_3–MoO_3/TiO_2/Al_2O_3 and V_2O_5–WO_3–MoO_3/TiO_2 pellet catalysts

In order to compare our novel cordierite-supported catalyst with non-cordierite-supported catalysts, the performance of V_2O_5–WO_3–MoO_3/TiO_2/Al_2O_3 and V_2O_5–WO_3–MoO_3/TiO_2 pellet catalysts were observed with the testing results in Fig. 6 which, obviously shows that the supported pellet catalysts had much lower catalytic activity than that of the supported monolithic catalysts.

3.1.4. Performances of V_2O_5–WO_3–MoO_3–TiO_2–Al_2O_3, V_2O_5–WO_3–MoO_3–TiO_2 and V_2O_5–WO_3–MoO_3–Al_2O_3 pellet catalysts made in co-precipitation method

Fig. 7 compares the performances of three pellet catalysts made by means of co-precipitation under the condition of SV = $15 \times 10^4\ cm^3\ g^{-1}\ h^{-1}$, 5% in oxygen content and 1.0 in NH_3/NO ratio. It was found that these pellet catalysts performed their catalytic activity in the order of V_2O_5–WO_3–MoO_3–TiO_2 > TV_2O_5–

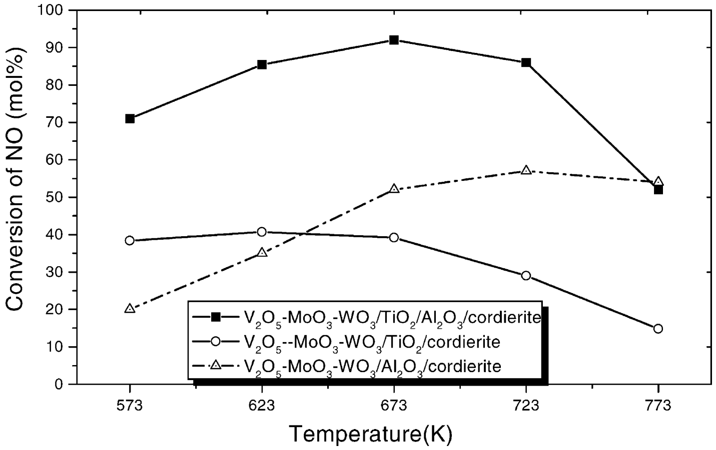

Fig. 5. The correlation between reaction temperature and the conversion of NO on various supported monolith catalyst (SV = 6000 h^{-1}, oxygen ratio = 5%, NH_3/NO = 1.0).

WO_3–MoO_3–TiO_2–Al_2O_3 > V_2O_5–WO_3–MoO_3–Al_2O_3. And specifically, the performance of V_2O_5–WO_3–MoO_3–TiO_2 under this condition obtained the NO conversion higher as that of V_2O_5–WO_3–MoO_3–TiO_2/Al_2O_3/cordierite catalyst.

3.2. BET surface area and pore size

The results of BET and BJH surface area and pore size measurements are listed in Table 2. It can be seen that, for the cordierite honeycomb-supported monolithic type, the BET surface area and pore volume of cordierite honeycomb is pretty low. The addition of Al_2O_3 as the carrier can remarkably increase the surface area and pore volume, while the BET surface area and pore structure of cordierite-coated with TiO_2 did not make any difference. Specifically, our TiO_2/Al_2O_3/cordierite honeycomb-supported catalyst owned a much larger BET surface area and pore volume similar to that of the impregnation pellet. As for the co-precipitation pellet, also those added Al_2O_3 gained higher BET surface area and pore volume,

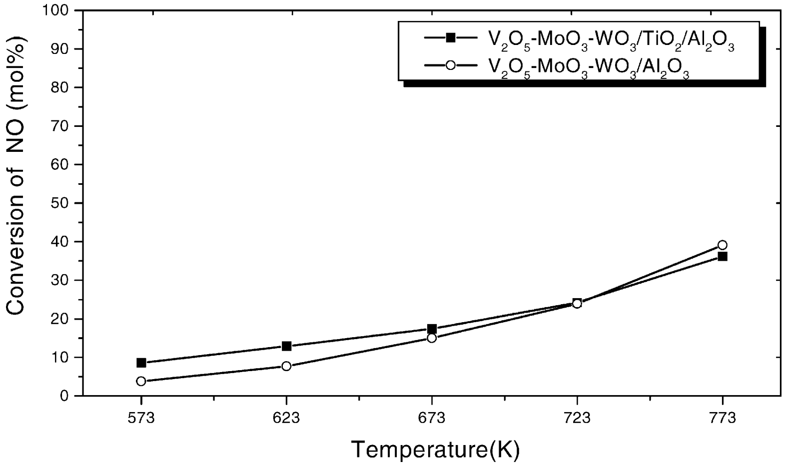

Fig. 6. The correlation between reaction temperature and the conversion of NO on various supported pellet catalyst (SV = 15 × 10^4 cm^3 g^{-1} h^{-1}, oxygen ratio = 5%, NH_3/NO = 1.0).

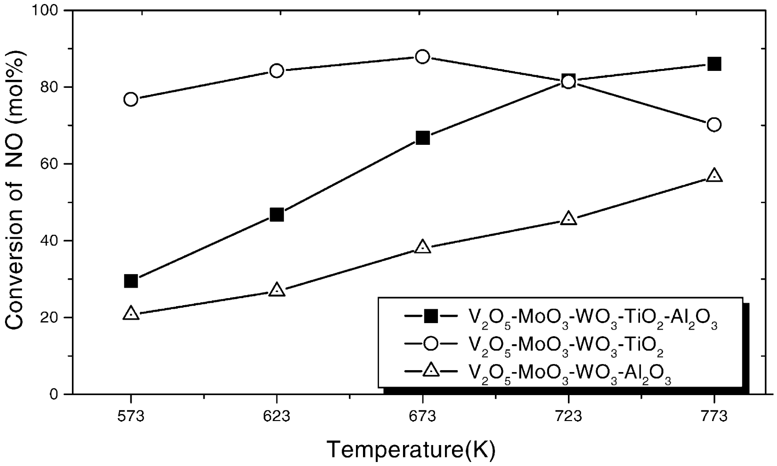

Fig. 7. The correlation between reaction temperature and the conversion of NO on various supported powder catalyst (SV = 15×10^4 $cm^3\,g^{-1}\,h^{-1}$, oxygen ratio = 5%, $NH_3/NO = 1.0$).

Table 2
Surface area, pore volume and pore size of catalysts (m^2/g)

	Samples[a]		
	BET surface area (m^2/g)	BJH total pore volume (cm^3/g)	BJH mean pore size (Å)
Catalysts			
$M/TiO_2/Al_2O_3/CC$	36.4159 (223.2521)[b]	0.051637 (0.314799)	50.3342
$M/TiO_2/CC$	2.8755 (10.1919)	0.004992 (0.014805)	69.3309
$M/Al_2O_3/CC$	35.8655 (255.3126)	0.051620 (0.365607)	50.0492
$M/TiO_2/Al_2O_3$	163.9821	0.207922	48.3561
M/Al_2O_3	185.4356	0.209436	44.1016
$M–TiO_2–Al_2O_3$	238.9487	0.370577	53.9715
$M–TiO_2$	103.9100	0.225122	82.0193
$M–Al_2O_3$	263.6692	0.405492	52.0010
Supports			
$TiO_2/Al_2O_3/CC$	35.2566	0.055697	51.7546
TiO_2/CC	3.1233	0.005350	60.5893
Al_2O_3/CC	39.5305	0.062842	50.2399
CC	1.8512	0.002952	66.8341
TiO_2/Al_2O_3	–	–	–
Al_2O_3	216.1840	0.251852	41.8315
$TiO_2–Al_2O_3$	–	–	–
TiO_2	231.5815	0.311647	52.5422
Al_2O_3	216.1840	0.251852	41.8315

[a] M: $V_2O_5–MoO_3–WO_3$; CC: ceramic cordierite honeycomb.

[b] The values in the brackets are the results corrected by excluding the effect of CC.

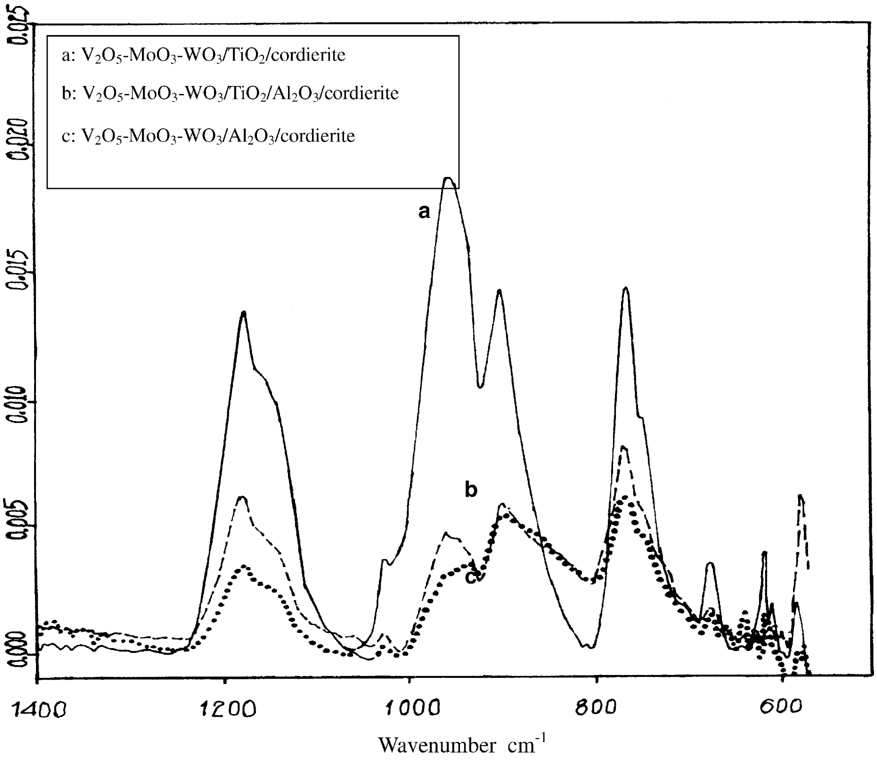

Fig. 8. FT-IR reflectance spectra of various vanadium catalysts.

while that of M-TiO_2 was still higher than that of M/TiO_2/CC and M/Al_2O_3/CC.

3.3. FT-IR spectra

The FT-IR spectra of M/TiO_2/Al_2O_3/CC, M/TiO_2/CC and M/Al_2O_3/CC are reported in Fig. 8. Three intense IR bands at 1180, 960 and 766 cm^{-1}, and two shoulder peaks at 1028 and 900 cm^{-1} were observed. According to literature data [9], the IR peaks at 960 and 760 cm^{-1} attributes to M=O (M: V, Mo and W) and M–O–Ti, and the shoulder peaks at 1030 and 900 cm^{-1} are assigned to V=O in dry conditions and Mo=O. The intensities of the mentioned IR bands of the three catalysts are different from each other, and they are in the order of: V_2O_5–WO_3–MoO_3/TiO_2/CC>CV_2O_5–WO_3–MoO_3/TiO_2/Al_2O_3/CC > V_2O_5–WO_3–MoO_3/Al_2O_3/CC.

The acidic properties of the catalysts were also characterized by using FT-IR spectroscopy with pyridine adsorption. From the results, a IR peak at 1448 cm^{-1} was observed in the spectrum of M/TiO_2/Al_2O_3/CC, which denoted the existence of Louise acid sites on the catalyst surface.

3.4. XPS

Fig. 9a and b shows the XPS patterns of O 1s on the surface of V_2O_5–WO_3–MoO_3/TiO_2/Al_2O_3/cordierite before and after reaction, respectively. From Fig. 9a and b, it can be seen that both the peak height and peak area decreased after reaction, which reveals a significant change of surface oxygen species after reaction, especially, the surface adsorbed oxygen decreased to zero.

From the XPS spectra, the peaks attributed to V and Mo cannot be found probably because their contents were too small. The peaks in the region of W were found, and the peaks at 35, 36 and 36.5 eV^{-1} attributed to W^{4+}, W^{5+} and W^{6+}. Fig. 10a and b show their XPS patterns of W 4f before and after reaction correspondingly.

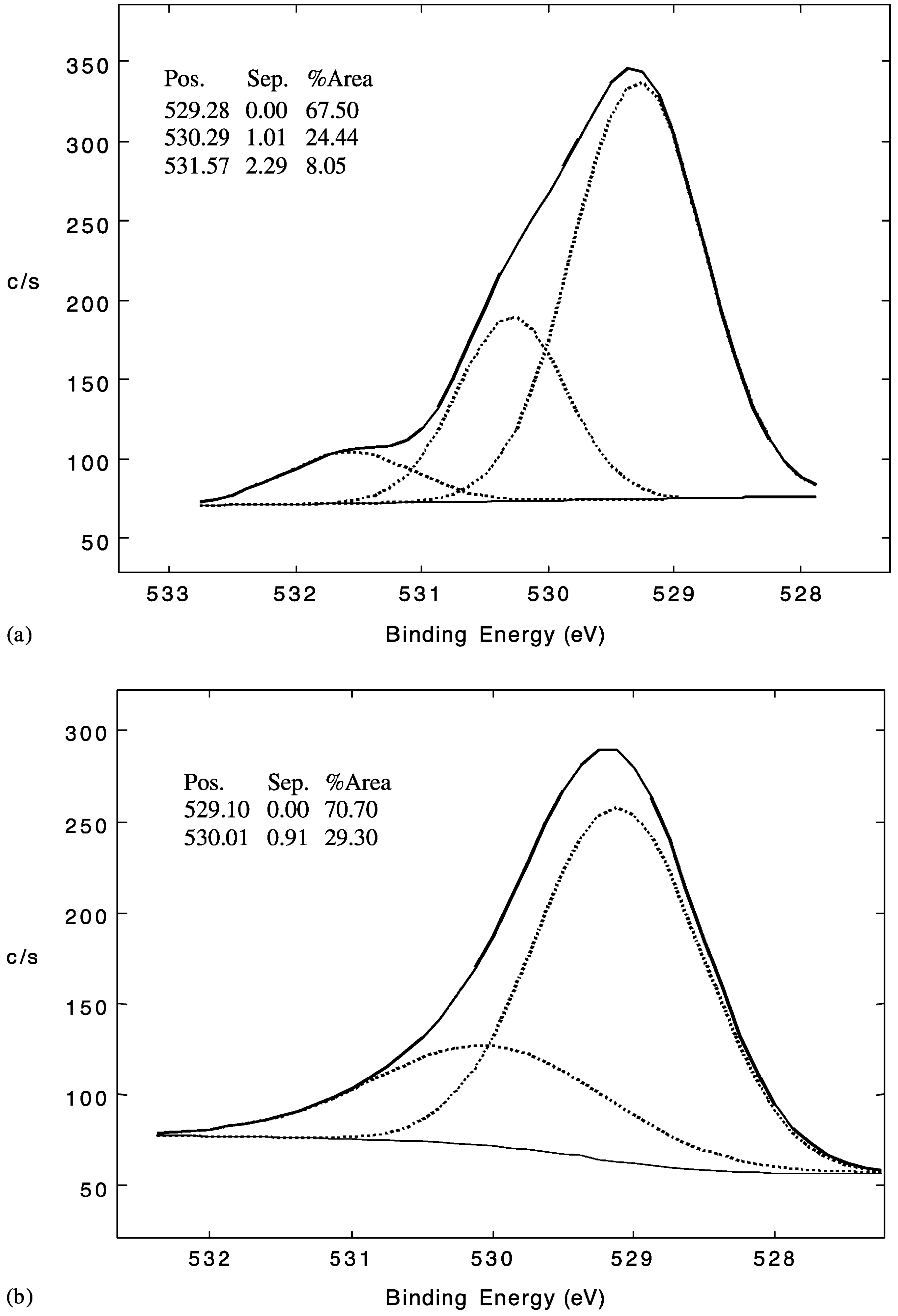

Fig. 9. (a) XPS spectra of V_2O_5–MoO_3–WO_3/TiO_2/Al_2O_3/cordierite in the region of O 1s before reaction, (b) XPS spectra of V_2O_5–MoO_3–WO_3/TiO_2/Al_2O_3/cordierite in the region of O 1s after reaction.

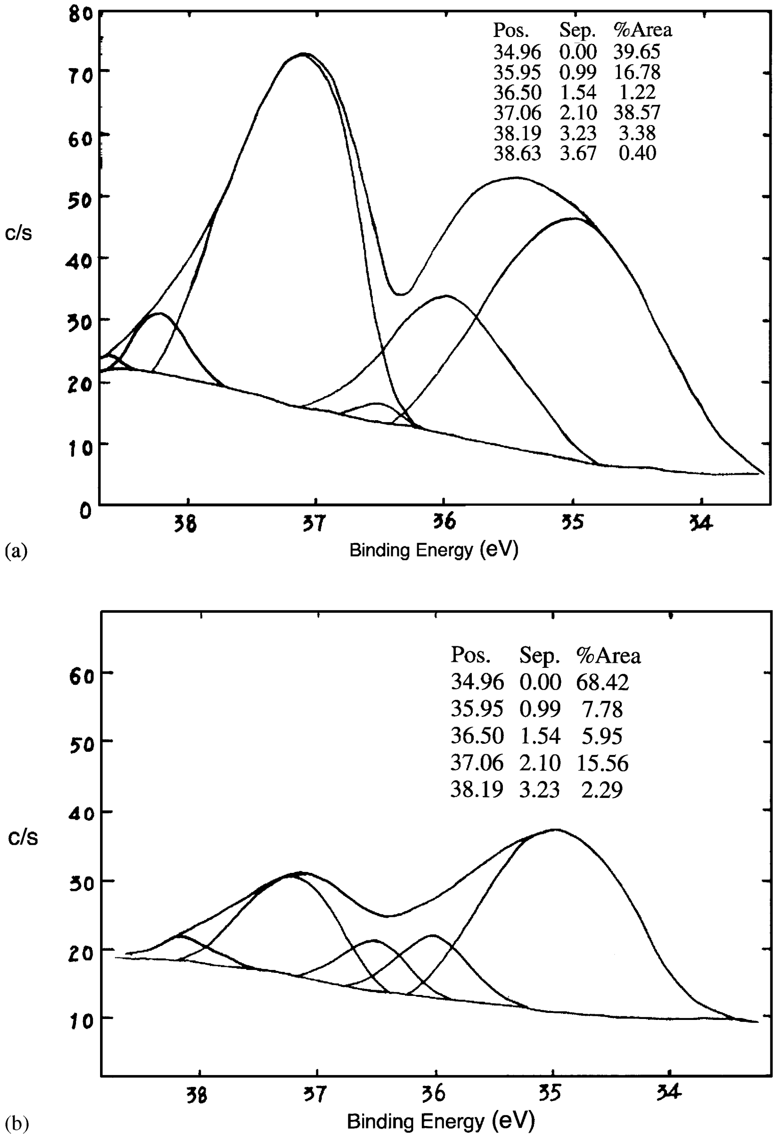

Fig. 10. (a) XPS spectra of V_2O_5–MoO_3–WO_3/TiO_2/Al_2O_3/cordierite in the region of W 4f before reaction, (b) XPS spectra of V_2O_5–MoO_3–WO_3/TiO_2/Al_2O_3/cordierite in the region of W 4f after reaction.

4. Discussion

4.1. *Influence of TiO_2 and Al_2O_3*

All the TiO_2 contained samples, except for V_2O_5–MoO_3–WO_3/TiO_2/cordierite, displayed reasonable SCR activities. Their higher conversion and the lower optimal reaction temperature can be attributed to the interaction between the active phase and TiO_2 support, i.e. the bridging V–O–Ti bond on the surface gives rise to the high activity of the catalyst as reported by Wachs et al. [6]. Acidity of the surface is also another important factor in the reaction [7]. Furthermore, during the preparation of the catalysts, because of the presence of a certain amount of acid sites on the surface of TiO_2 support, the adsorption of vanadium complex anion took place on acid site, which resulted in the good dispersion of active components and then the high catalytic activity. Both the Lewis and Bronsted acid sites on TiO_2 surface are favorable to share the electron pair offered by adsorbing vanadium complex anion during impregnation [8–10].

According to the BET results, TiO_2 has much smaller BET surface area and pore volume than that of Al_2O_3, and also TiO_2 is difficult to be loaded on the cordierite surface, therefore, V_2O_5–MoO_3–WO_3/TiO_2/cordierite catalyst has small BET surface area and pore volume and then resulted in low NO conversion.

In contrast, Al_2O_3 has large BET surface area and can be easily loaded on cordierite surface and formed a tightly combined layer. Consequently, both the catalysts supported on Al_2O_3 and on Al_2O_3-coated cordierite obtained high BET surface area and large pore volume, though they had low NO conversion. The low NO conversion of these catalysts directly supported on Al_2O_3 or Al_2O_3-coated cordierite maybe partially due to the strong interaction between metal oxide and the support, i.e. the strong bridging V–O–Ti bond on the surface gives rise to the low activity of the catalyst [6].

Thus, a conclusion can be drawn that we cannot get the best catalyst if we only use TiO_2 or Al_2O_3 as support. When the support was coated with binary oxides of TiO_2/Al_2O_3, the catalyst cannot only take advantage of the interaction between the active phase and the support, but also can make use of Al_2O_3 to obtain better dispersion of active components and titanium supports on the surface of ceramic cordierite. Thus obtained catalyst can exhibit appropriate acidity and good surface properties, which are required for obtaining high activity. This is in good consistent with the results of the catalytic performances test.

4.2. Influence of the ceramic cordierite

From the results, it can be found that the unsupported sample of V_2O_5–MoO_3–WO_3–TiO_2 also exhibited high NO conversion at the space velocity of $15 \times 10^4\,cm^3\,g^{-1}\,h^{-1}$, which is similar to that of V_2O_5–MoO_3–WO_3/TiO_2/Al_2O_3/cordierite. However, the reaction on monolithic catalyst was taken at SV of $6000\,h^{-1}$, which was as high as $25 \times 10^4\,cm^3\,g^{-1}\,h^{-1}$ in terms of the amount of active component V_2O_5, MoO_3, WO_3, i.e. V_2O_5–MoO_3–WO_3/TiO_2/Al_2O_3/cordierite had a higher conversion than that of pellet catalyst V_2O_5–MoO_3–WO_3–TiO_2 under a much higher space velocity. Through the effective dispersion of active phase on the surface of cordierite, a thin layer of active phase with high surface area and large pore volume can be obtained. Thus, the surface area/volume ratio of active phase increased remarkably. Therefore, for the catalyst of V_2O_5–MoO_3–WO_3/TiO_2/Al_2O_3/cordierite, the spreading of V_2O_5–MoO_3–WO_3 on the TiO_2/Al_2O_3-coated cordierite honeycomb not only can improve the physical and mechanic properties of the catalyst, but also increase the activity of active phase and improve the diffusion of reactant and product.

As for the catalyst simply supported on Al_2O_3 or TiO_2/Al_2O_3 by impregnation, on the contrary, since it did not take advantage of cordierite honeycomb to form a thin layer on the surface, did not make use of the honeycomb channel as the path of gas stream, a good inner and outer diffusion character could not be acquired, which has been testified by the results of catalytic performance.

4.3. Influence of surface active site

From the FT-IR results, surface density of M=O (M: V, Mo and W) and M–O–Ti of three catalysts were in the order of: V_2O_5–WO_3–MoO_3/TiO_2/CC > V_2O_5–WO_3–MoO_3/TiO_2/Al_2O_3/CC>V_2O_5–WO_3–MoO_3/Al_2O_3/CC. It can be easy found that the catalyst with the higher TiO_2 content has the stronger intensity of the IR bands of M=O and M–O–Ti. This result is in a good agreement of the interaction of TiO_2 and metal oxides that we mentioned above. Though the higher TiO_2 content resulted in the stronger intensity of the IR bands of M=O and M–O–Ti, which were responsible for selective adsorption of NH_3 [11], the activities of these catalysts did not be in agreement with the order of surface density of active sites. Taking consideration of surface area, the total number of active sites of these three catalysts were in the order of: V_2O_5–WO_3–MoO_3/TiO_2/Al_2O_3/CC > V_2O_5–WO_3–MoO_3/Al_2O_3/CC>V_2O_5–WO_3–MoO_3/TiO_2/CC, which is as same as the order of catalytic performance. For example, V_2O_5–WO_3–MoO_3/TiO_2/Al_2O_3/CC exhibited highest activity because of its largest surface area and higher surface density of active sites.

The XPS results shown that active O and W were found on the catalysts, in correspondence with the results of FT-IR. As can be seen from the results of XPS experiments on the surface active oxygen shown in Fig. 9, the total amount of surface active oxygen after reaction changed remarkably, especially the surface adsorbed active oxygen amount decreased to zero, which was related to the consumption of oxygen during the reaction.

5. Conclusion

The investigation of three different types of catalysts shows that the monolithic catalyst V_2O_5–MoO_3–WO_3/TiO_2/Al_2O_3/cordierite, which is supported on the binary oxides-coated cordierite honeycomb, had good SCR properties as a whole in contrast with others. The active phase supported on binary oxides-coated cordierite honeycomb takes advantages of the special interaction between the active components with TiO_2, the tight combination of Al_2O_3 and the cordierite support. The spreading of V_2O_5–MoO_3–WO_3 on the TiO_2/Al_2O_3-coated cordierite honeycomb not only can improve the physical and mechanic properties of the catalyst, but also increase the activity of active phase and improve the diffusion of reactant and product.

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