Selective Catalytic Reduction of NO$_x$ on High Concentration of Vanadium Catalyst at Middle-Low Temperature

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Abstract: A series of high concentration of vanadium catalysts were prepared by the citric acid method and was evaluated for the selective catalytic reduction of NO$_x$ by ammonia (NH$_3$-SCR) at middle-low temperature (180-280°C). Experimental results showed that V-W/SiTiO$_x$ exhibited the good activity on NH$_3$-SCR reactions, N$_2$ selectivity and SO$_2$ durability over a broad temperature range of 180-280°C with the high space velocity. Above 90% conversion of NO$_x$ with 100% selectivity of N$_2$ had been achieved on V$_5$W$_8$SiTi at 220-240°C with the space velocity of 36,000 h^{-1}. X-ray diffraction, BET were adopted for the characterization of the active phase. The high activity of the VW/SiTi mixed oxide catalyst could be main be reason for the strong interaction between V and W.

Introduction

Nitrogen oxides (NO, NO$_2$ and N$_2$O) are a major source of air pollution, contributing to photochemical smog, acid rain, ozone depletion and greenhouse effects[1,2]. The commercial catalysts for this process are V$_2$O$_5$/TiO$_2$ promoted by WO$_3$ or MoO$_3$, and they are preferentially applied in form of monolithic honeycombs due to their low pressure drop[3]. However, the commercial catalysts is still not satisfactory due to some drawbacks, such as the low N$_2$ selectivity at high temperatures, the relatively narrow temperature window of 300-400°C, and the low SO$_2$ sufferance[4].

Many researchers concluded that SO$_2$ had a serious poisoning effect on the activity of catalyst at middle-low temperature[5]. In Li's study[6],V^{3+} had a notable influences for the catalysts activity, when catalysts was used, the vanadium in the new species is most probably V^{5+}. Zhu[7] investigated the decomposition and reactivity of sulfate species formed on the V$_2$O$_5$/TiO$_2$ catalysts by using TPR and TPD. They found the decomposition rate of the formed sulfate species sharply increased with temperature rising in the range of 260-350°C.

The research shows that very few catalyst would be able to have a good catalytic activity and N$_2$ selectivity under the high sulfur condition at middle-low temperature (180-280°C). Therefore, in this paper, high concentration of vanadium catalysts were prepared by citric acid method and used for SCR of NO by NH$_3$ in the presence of high concentration of SO$_2$ at the temperature range of 180-280°C, which still have high activity and good N$_2$ selectivity. Experimental results showed that V and W elements were uniformly distributed in the surface of the catalyst, titanium was used as a support in presence.

Experimental Procedure

Catalyst preparation. The catalyst was prepared by the citric acid method, and titanium of amorphous state was used as the support. V$_a$W$_b$/SiTi (a is the ratio of weight percentage of V$_2$O$_5$/(V$_2$O$_5$+WO$_3$+SiTiO$_x$), b is the ratio of WO$_3$/(V$_2$O$_5$+WO$_3$+SiTiO$_x$)) catalyst was prepared by joining ammonium tungstate (H$_{40}$N$_{10}$O$_{41}$W$_{12}$.xH$_2$O), ammonium metavanadate (NH$_4$VO$_3$) and titanium dioxide to 2mol/L citric acid, then stirred at room temperature for 2h in air, subsequently dried at 120°C for 12h and calcined at 550°C for 2h,after cooling the catalyst, then it was tableted

and sieved to 40-80 mesh. The composition of catalyst was mainly controlled by the concentration and amount of NH_4VO_3 and ammonium paratungstate, which is expected to 1~6wt% V_2O_5, 8 wt% WO_3, 86~91 wt% SiO_2 and TiO_2.

Catalytic activity measurement. The activity of the catalysts was investigated using a fixed-bed quartz reactor.V_2O_5-WO_3/$SiTiO_x$ catalyst(40-80 mesh, 2mL) in the reactor was heated from 180^oC to 280^oC, starting from 180^oC, each temperature increase of 20 degrees segment, and stable for 30 min. From the 180^oC the stream was replace by 1000ppm NO, 1000ppm NH_3, 600ppm SO_2, 3% O_2, and the balance by N_2. The total gas flow rate was main trained at 1200mL/min, corresponding to a gas hourly space velocity (GHSV) of 36,000h^{-1}. The compositions of the feed gases and the effluent streams were monitored continuously using on-line sensors with emission monitors: gas analysis (Photon II, Madur, Austria) for NO, NO_2, SO_2, N_2O and O_2. From the concentration of the gases at steady state, the NO_x conversion and N_2 selectivity are calculated according to the following equations:

$$NO_x \ conversion(\%) = \frac{[NO_x]_{in} - [NO_x]_{out}}{[NO_x]_{in}} \times 100 \qquad (1)$$

$$N_2 \ selectivity(\%) = \frac{[N_2]_{out}}{[N_2]_{out} + [N_2O]_{out}} \times 100 \qquad (2)$$

$[NO_x]$=$[NO]$+$[NO_2]$, and the subscripts in and out indicated the inlet concentration and outlet concentration at steady state.

Catalyst characterization. The textures structures of the prepared samples were measured by N_2 adsorption at 77K in a micromeritics ASAP2020 system, and specific surface areas of samples were measured using Brunauer-Emmett-Teller (BET) method. X-ray diffraction (XRD)patterns were obtained by using Cu Kα radiation (Rigaku D/MAX RA) at 40 kV and 150 mA with the angle of 2θ from 5° to 80°.

Results and discussion

NH₃-SCR activity. NH₃-SCR activities of V_aW_b/SiTi catalysts as a function of temperature were evaluated and the results are illustrated in Fig.1. It could be seen that the V_6W_8/SiTi catalyst exhibited the highest NH₃-SCR activity than all of others. Mostly the relatively high vanadium loading contributed to improving the SCR activity, while it was not all the same. As the temperature rising it enhanced NO_x conversion, however V_3W_8/SiTi and V_4W_8/SiTi catalysts effect were reduced. V_5W_8/SiTi and V_6W_8/SiTi catalysts got a better activity since from 200^oC, which the NO_x conversion were over 80%, and from 220^oC to 280^oC, the NO_x conversion on V_5W_8/SiTi and V_6W_8/SiTi catalysts were 90% to 100%. In the whole temperature range the N_2 selectivity were over 97%. Therefore V_5W_8/SiTi and V_6W_8/SiTi were much more active than the low V catalysts. This fact indicated that the relatively higher concentration of vanadium contributed to improving the SCR activity at middle-low temperature, but it is not the higher the better. Comparing the Fig.1 and Fig.2 we found that the presence of excess of tungsten play an inhibitory effect to catalyst.
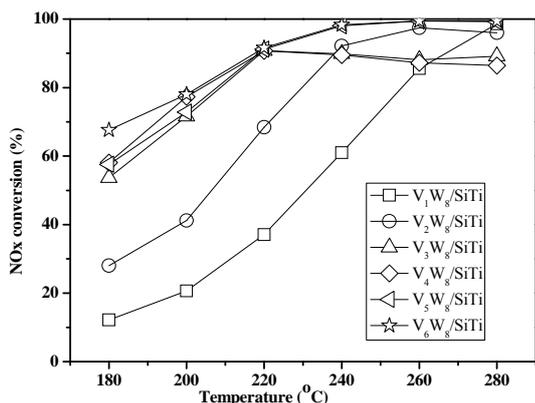
Fig.1.The effect of vanadium content on NO$_x$ conversion over V$_a$W$_8$/SiTi catalysts. Reaction conditions: [NO]=[NH$_3$]=1000ppm, [SO$_2$]=600ppm, [O$_2$]=3%,N$_2$ as balance, GHSV=36,000h^{-1}.
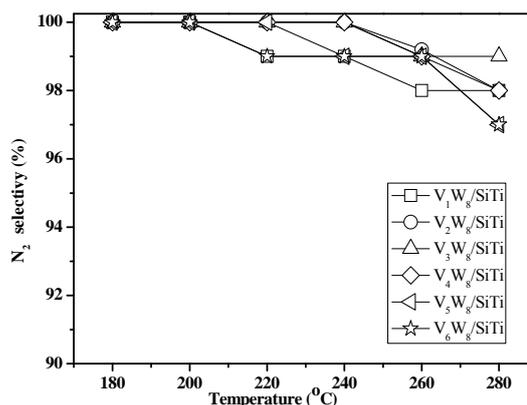
Fig.2.The effect of vanadium content on N$_2$ selectivity over V$_a$W$_8$/SiTi catalysts. Reaction conditions: [NO]=[NH$_3$]=1000ppm, [SO$_2$]=600ppm, [O$_2$]=3%, N$_2$ as balance, GHSV=36,000h^{-1}.
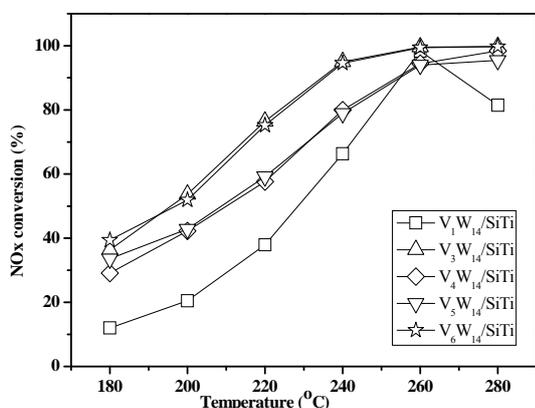
Fig.3. The effect of vanadium content on NO$_x$ conversion over V$_a$W$_{14}$/SiTi catalysts. Reaction conditions: [NO]=[NH$_3$]=1000ppm, [SO$_2$]=600ppm, [O$_2$]=3%,N$_2$ as balance, GHSV=36,000h^{-1}.
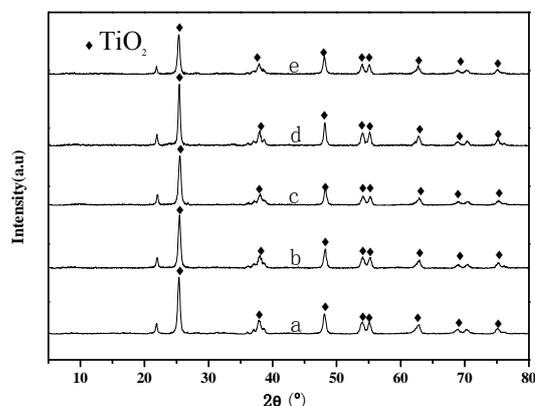
Fig.4. XRD patterns of V$_a$W$_8$SiTi with different V content. (a) V$_1$W$_8$/SiTi, (b) V$_3$W$_8$/SiTi, (c) V$_4$W$_8$/SiTi, (d) V$_5$W$_8$/SiTi, (e) V$_6$W$_8$/SiTi.

BET surface area and XRD patterns. As we show in Table 1, the BET surface area follow in the order of V$_1$W$_8$/SiTi > V$_2$W$_8$/SiTi > V$_3$W$_8$/SiTi > V$_4$W$_8$/SiTi > V$_6$W$_8$/SiTi > V$_5$W$_8$/SiTi, it exhibited the highest NH$_3$-SCR activity, indicating that synergistic effected between V and W species and the BET surface area did not play a key role in the SCR reaction. Fig.3 showed the XRD patterns of different catalysts. For all the catalysts, the anatase phase was the main phase, and no others phase can be found. The results showed that active constituents of V$_2$O$_5$, WO$_3$ were highly dispersed on the surface of TiO$_2$ and in the presence of amorphous.

Table 1 BET data of catalysts

Entry	Catalysts	BET surface area $(m^2 \cdot g^{-1})$	Pore volume $(cm^3 \cdot g^{-1})$	Pore size (nm)
1	V_1W_8/SiTi (550)	76	0.23	12
2	V_2W_8/SiTi (550)	68	0.23	12
3	V_3W_8/SiTi (550)	65	0.24	13
4	V_4W_8/SiTi (550)	63	0.20	13
5	V_5W_8/SiTi (550)	47	0.17	14
6	V_6W_8/SiTi (550)	52	0.20	14

Conclusions

The catalytic activity for the NH_3-SCR reaction on V_2O_5-WO_3/SiO_2-TiO_2 catalysts was enhanced after V increasing obviously at middle-low temperature. The NO_x conversion over the V_5W_8/SiTi catalyst reached above 90% at the widened temperature range from 220°C to 280°C, and nearly 90% N_2 selectivity in the whole temperature range. A series of high concentration of vanadium catalysts exhibited excellent activity, good N_2 selectivity, and strong resistance to SO_2 poisoning, which were beneficial to the practical application on industrial kiln flue gas denitrification.

Acknowledgements

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