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Effect of Mo contents on properties of Mo/ZSM-5 zeolite catalyst for NOx reduction

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Abstract: Mo/ZSM-5 catalysts with different Mo content were prepared by impregnation method. The effect of Mo content on the property of Mo/ZSM-5 catalysts and their performance for selective catalytic reduction(SCR) of NO with ammonia was investigated by XRD, ICP, XPS and NO-TPD respectively. The results showed that the catalytic activity of Mo/ZSM-5 for SCR of NO is strongly influenced by the Mo loading in HZSM-5 zeolites. The NOx conversion reached the highest value of 64.2% at 375℃ when Mo content is about 10.9%, and the temperatures at which the maximum of NOx conversion obtained were declined with the increase of Mo content. From XRD results, it can be seen that it exhibits the distinct interaction between Mo and HZSM-5 when Mo content is about 10.9%. This may result in a suitable phase structure in Mo/ZSM-5 catalyst, which is advantageous for NO reduction. XPS and NO-TPD results also showed that the catalytic activity of Mo/ZSM-5 may be related to the Mo percent on the surface.

Keywords: Mo/ZSM-5; Mo content; nitrogen oxides; selective catalytic reduction

Introduction

The pollutants from gasoline-fueled cars can be almost completely transformed to carbon dioxide, water, and dinitrogen in a three-way catalyst. However, the exhaust from a diesel and lean-burn engines contains a large surplus of oxygen which prevents the reduction of nitrogen oxides. The selective catalytic reduction of nitrogen oxides(NOx) in the presence of excess O_2 can be applied in the removal of gaseous pollutants from diesel and lean-burn engines (Heinrich, 2002). By now a number of works in this field have been reported. The effect of key parameters on the characteristics of barium oxide-based NOx storage catalysts was systematically investigated by Fridell and co-workers (Fridell, 1999). And the catalysts based on ZSM-5 zeolites have also been extensively studied in selective catalytic reduction (SCR) of NOx. Copper ion-exchanged ZSM-5 zeolites was reported to have exceptionally high activity for the NO decomposition and selective catalytic reduction of NO by hydrocarbons (Xiao, 1999). And the activity and selectivity are strongly influenced by the copper loading in ZSM-5 zeolites, the activity of 100% exchanged CuZSM-5 was 100 times more than that of the 80% exchanged one (Campa, 1994). There are however no catalysts as yet that combine sufficient activity and stability to commercial applications(Heinrich, 2002).

In our previous work(Li, 2002), the catalysts doped with different metal oxides on HZSM-5 have been studied, and the results showed that the Mo/ZSM-5 catalyst is the best one for the NO decomposition and catalytic reduction. And Luiza *et al*. have studied the reduction of NO with ethanol over Pd-Mo/ZSM-5 catalyst(Luiza, 2003), it was found that the Pd-Mo/ZSM-5 was more active at higher temperature than Pd/HZSM-5, due to a molybdenum promotion. The present study focuses on the basic understanding still lacking with respect to the effect of Mo content on surface properties of Mo/ZSM-5 catalysts and their catalytic performance for selective catalytic reduction of nitrogen oxides. The Mo/ZSM-5 catalysts were prepared by wet impregnation method, and the bulk-phase and surface compositions of the catalysts are determined by XRD, ICP, XPS and NO-TPD respectively.

1 Experimental

1.1 Preparation of Mo/ZSM-5 catalysts

A series of Mo/ZSM-5 catalysts with different Mo content were prepared by wet impregnation method. HZSM-5 powders were impregnated with aqueous solutions given amount of ammonia heptamolybdate, then dried at 60℃ and 100℃ for 8 and 12 h, respectively. After calcinations at 500℃ for 5 h, the catalysts were crushed and sieved to 40—60 mesh granules.

1.2 TPD procedure

For the NO-TPD experiments, 0.5 g Mo/ZSM-5 was loaded in the reactor and was pretreated *in situ* in a N_2 stream(30 ml/min) at 550℃ for 1 h, and then cooled to 30℃ in the same stream. The pretreated sample was then exposed to a gas mixture containing NO and N_2 at a flow rate of 50 ml/min for 20 min. After steady state was reached, the Mo/ZSM-5 surface was purged with N_2 of 100 ml/min for 1 h to remove the physically adsorbed species. Typically, TPD was carried out in a N_2 stream of 300 ml/min at a heating rate of 5℃/min from 30℃ to 600℃. The effluent was continuously monitored for NO and NO_2 during the whole adsorption/desorption process.

1.3 Catalyst characterization

Chemical composition of the Mo/ZSM-5 catalysts was determined by an ICP spectrometer(plasma, ICP Q-1000). X-ray diffraction patterns were obtained with the help of Rigaku 2304-Xay diffraction(Cu, Ka, Ni-filter). After being pressed into slice, measurements of the samples were carried out in the range 2θ of 5—40°, with a scanning rate 2θ of 5°/min. The XPS spectrum of fresh and post reaction samples was obtained by a XSAM800 spectrometer from KRATOS, Al Ka radiation($h\upsilon$ = 1486.6) was the X-ray source. Working power was 120 W(12 kV × 10 mA), and the vacuum in sample chamber was 1.3×10^{-6} Pa. Specific surface areas of catalysts were determined by nitrogen adsorption according to the BETmethod(CE, SORPTOMATIC1990).

1.4 Catalytic measurement

The catalytic activity for NO reduction of Mo/ZSM-5 catalysts was measured in a conventional fixed-bed quartz reactor of 8 mm i.d. and 350 mm in length. Before entering the reactor, four feed gases($NO + N_2$, $NH_3 + N_2$, air, N_2) controlled separately by mass flow controllers were mixed in a chamber filled with glass wool. The compositions of the feed and effluent of the reactor were continuously analyzed using an online Combustion Gas Analyser (KM9006 Quintox, Kine International Limited), which is capable of monitoring NO, NO_2, O_2, and CO simultaneously.

2 Results and discussion

2.1 Active test

Fig. 1 shows the dependence of NO conversion on reaction temperature for NO reduction over Mo/ZSM-5 catalysts. With the increase of Mo content, the catalytic activity for NO reduction was improved, and the NOx($NO + NO_2$) conversion reaches the highest value of 64.2% at 375℃ when Mo content is about 10.9%. The results also showed that the temperatures at which the maximum of NOx conversion obtained were declined with the increase of Mo content. Thus Mo/ZSM-5 catalyst exhibits the best catalytic performance for NO reduction when Mo content is about 10.9%.

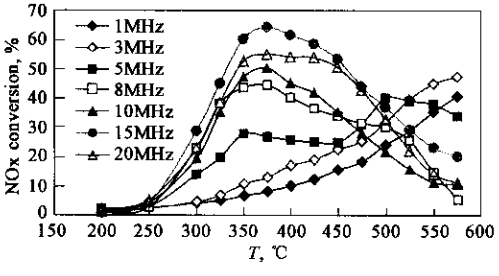

Fig. 1 Effect of temperature and Mo contents on NOx($NO + NO_2$) conversion over Mo/ZSM-5 catalysts

2.2 X-ray diffraction(XRD)

X-ray diffraction patterns of different Mo/ZSM-5 catalysts are shown in Fig. 2. With the increase of Mo content, the peaks of 8.04°, 9.04°, 23.46° assigned to HZSM-5 become weak, while the peaks of 13.2°, 27.3°, 33.8° belong to MoO_3 is being stronger. The peaks of MoO_3 were appeared when Mo content exceeds 4.43%, and the peaks of HZSM-5 had an obviously drop. When the Mo content reached to about 10.9(wt%)(Fig.2d), it exhibits a particular structure property. Except for the peak of 27.3°, the peaks for HZSM-5 are not stronger than that of 20 MHZ, and the peaks for MO_3 are not stronger than that of 10 MHZ. This indicated that there may be a strong interaction between Mo and HZSM-5 phases when Mo content is 10.9% and it is a suitable for NO catalytic reduction. There is no new structure observed in Mo/ZSM-5 catalysts.

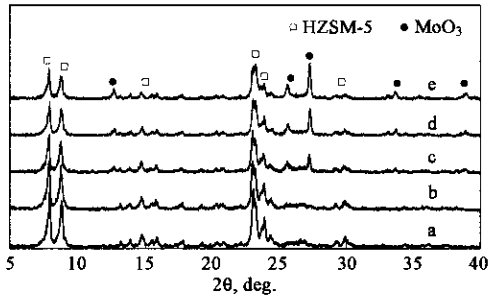

Fig. 2 XRD patterns of the catalysts
a. H/ZSM-5; b. 5 MHZ; c. 10 MHZ; d. 15 MHZ; e. 20 MHZ

To understand the effect of Mo content on phases and crystallinities of Mo/ZSM-5 catalysts, the lattice constants were calculated from peak locations and miller indices(Table 1). The crystal type of standard HZSM-5 is monoclinic, and the deviation, $\triangle a$, $\triangle b$, $\triangle c$ and $\triangle \beta$, with standard HZSM-5 for each sample have also been calculated. The lattice constants, a, b, c, of 15 MHZ shows the lowest value, while the β value is similar with others. This can concluded that when Mo content is about 10.9%, there may be a suitable phases structure caused from the interaction between Mo and HZSM-5, which is advantage for selective catalytic reduction of NO.

Table 1 Lattice constants of Mo/ZSM-5 with different Mo content prepared by wet impregnation method

Catalyst	a	b	c	β	$\triangle a$	$\triangle b$	$\triangle c$	$\triangle \beta$
H*	19.879	20.107	13.369	90.67	–	–	–	–
5 MHZ	19.2773	20.1391	13.3468	92.53	0.6017	0.0321	0.0222	1.86
10 MHZ	14.9936	20.1302	15.0992	126.48	4.8854	0.0232	1.7302	35.81
15 MHZ	14.8946	20.0069	14.9914	126.66	4.9844	0.1001	1.6224	35.99
20 MHZ	14.939	20.0121	15.0482	126.82	4.94	0.0949	1.6792	36.15

Notes: * Standard HZSM-5 from MFI calcined ZSM-5; Reference: van Koningsveld, 1990

2.3 NO-TPD

Fig.3 shows the TPD pattern of NO after the Mo/ZSM-5 with different Mo content was exposed to NO at 30℃ to a steady state. 15 MHZ catalyst exhibits a unique characteristic among the six samples. It has the most amount of NO, and there are three distinct NO desorption peaks, centered at about 366℃, 484℃, and 637℃. Among them the peaks of 366℃ and 484℃ may be responsible for the catalytic reduction of NO over Mo/ZSM-5 catalyst. A similar observation was reported by Zhu *et al*. in the SCR reaction over activated coke based catalyst(Zhu, 2000).

2.4 XPS

To understand the surface properties of Mo/ZSM-5 catalysts with different Mo content, XPS measurement was taken by a XSAM800 spectrometer from KRATOS. The surface composition, bulk phases(Mo) and surface area are shown in Table 2. It can be seen that the percents of Mo on surface are smaller than in bulk phases, this may result from

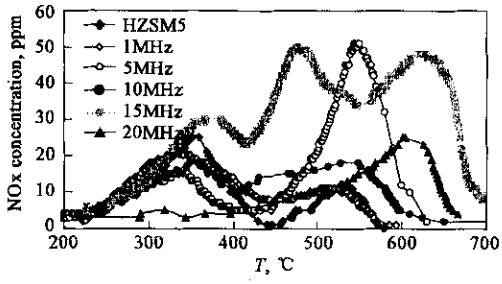

Fig.3 TPD profiles of NO after adsorption on Mo/ZSM-5 catalysts with the different Mo content at 28℃

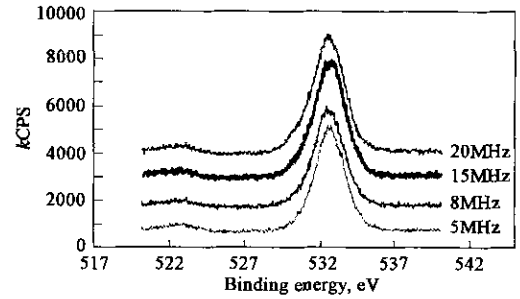

Fig.4 XPS spectra of O(1s) on Mo/ZSM-5 catalysts with different Mo content

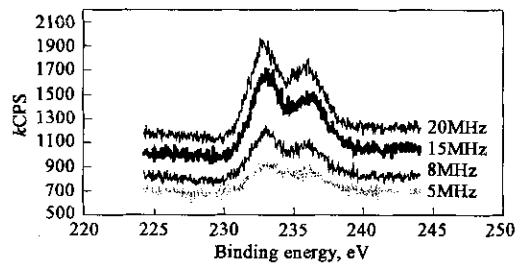

Fig.5 XPS spectra of Mo(3d) on Mo/ZSM-5 catalysts with different Mo content

the accumulation of MoO_3 on the surface. With the increase of bulk mo content, the Mo percent on surface were slowly increased. Considering the catalytic activities of Mo/ZSM-5 catalyst, it can be presumed that the surface Mo percent may be favorable for NO reduction over Mo/ZSM-5. However, the smallest surface area and pore volume may restrain its catalytic activity for 20 MHZ, although it has a largest value of surface Mo percent.

Table 2 The specific surface area, pore volume and compositions of Mo/ZSM-5 catalysts

Catalysts	Surface composition, %			Bulk phase Mo, %	Surface area, m^2/g	Pore volume, cm^3/g
	O(1s)	Si(2p)	Mo(3d)			
HZSM-5	-	-	0	0	314.4	0.3050
5 MHZ	56.03	42.27	1.70	4.43	324.02	0.2913
8 MHZ	56.69	40.33	2.97	-	271.16	0.2284
15 MHZ	56.21	39.89	3.90	10.9	242.81	0.2261
20 MHZ	56.70	38.98	4.32	13.6	234.24	0.1944

XPS spectra of O(1s) on Mo/ZSM-5 catalysts with different Mo content are shown in Fig.4. There is a main peak of O(1s) spectra centered at 532.9 eV, which is attributed to lattice oxygen species on surface of Mo/ZSM-5 catalysts. 10.9% Mo content among them results in a distinct increase in the intensity of O(1s) spectra, and an obvious shoulder at 531.09 eV can be observed, which may be assigned to Mo-O and other oxygen species on the surface. Fig.5 shows the Mo(3d) spectra of Mo/ZSM-5 catalysts. There is only one kind of Mo(3d) spectra centered at 232.6 eV which attributed to Mo^{6+} species on each Mo/ZSM-5 sample, but the intensity of Mo(3d) spectra on 15 MHZ is stronger than others. The results indicated that the catalytic activity of Mo/ZSM-5 may be related to the percent of Mo on the surface, however it is disadvantageous to the catalytic activity that the amount of Mo in bulk phase is too much, which can cause the accumulation of MoO_3 on the surface and reduce the surface area and pore volume(Table 2).

It is also important to note that NO_2 was not detected during the XPS measurement, which is similar to the activity results of SCR of NO over Mo/ZSM-5 catalysts. Then it can be deduced that NO is directly reacted with ammonia to form nitrogen and water on Mo/ZSM-5 catalysts, not through NO_2.

3 Conclusions

From the results above, it can be seen that the catalytic activity of Mo/ZSM-5 for SCR reaction of NO is strongly influenced by the Mo loading in HZSM-5 zeolites. And there is an optimal Mo content under the experiment condition. The NOx conversion reaches the highest value of 64.2% when Mo content is about 10.9%. The results also showed that the temperatures at which the maximum of NOx conversion obtained were declined with the increase of Mo content.

XRD results showed that it exhibits a distinct interaction between Mo and HZSM-5 when Mo content is about 10.9%. This may result in a suitable bulk phase structure in Mo/ZSM-5 catalyst, which is advantageous for NO reduction.

From XPS and NO-TPD results above, it is also shown that there is an unique characteristic on the surface structure of 15 MHZ catalyst and the catalytic activity of Mo/ZSM-5 may be related to the Mo percent on the surface.

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