Interaction between ammonium heptamolybdate and NH_4ZSM-5 zeolite: the location of Mo species and the acidity of Mo / HZSM-5

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Received 3 March 1995; accepted 26 July 1995

Mo/HZSM-5 catalysts show high reactivity and selectivity in the activation of methane without using oxidants. Mo/HZSM-5 catalysts with Mo loading ranging from 0 to 10% were prepared by impregnation with an aqueous solution of ammonium heptamolybdate (AHM). The samples were dried at 393 K, and then calcined at different temperatures for 4 h. The interaction between Mo species and NH_4ZSM-5 zeolite was characterized by FT-IR spectroscopy, differential thermal analysis (DTA) and temperature programmed decomposition (TPDE) and NH_3-TPD at different stages of catalyst preparation. The results showed that if Mo/HZSM-5 catalysts were calcined at a proper temperature, the Mo species will interact with acid sites (mainly with Brønsted acid sites) and part of the Mo species will move into the channel. The Mo species in the form of small MoO_3 crystallites residing on the external surface and/or in the channel, and interacting with Brønsted acid sites may be responsible for the methane activation. Strong interaction between Mo species and the skeleton of HZSM-5 will occur if the catalyst is calcined at 973 K. This may lead to the formation of MoO_4^{2-} species, which is detrimental to methane activation.

Keywords: Mo/HZSM-5; NH_4ZSM-5; zeolite; Brønsted acid sites; methane activation

1. Introduction

Recently, catalytic chemists in the world have paid much attention to zeolite supported transition metal and oxide catalysts because, either from the point of view of industries or from the point of view of catalysis science, these catalysts will have many advantages and unique properties for their potential application [1,2]. We have first reported that methane can be activated over Mo modified HZSM-5 catalysts without using oxidants for the production of benzene and toluene in 1993 [3,4]. We have also revealed that ethylene is the initial product of the reaction. In

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contrast to the oxidative coupling of methane (OCM), for which the catalyst basicity is an important factor for high reactivity and selectivity to C_2 [5,6], the reactivity and selectivity of this reaction on Mo/HZSM-5 catalysts are closely dependent on the acidity and the channel structure of the zeolite used. The acidity, which has already been demonstrated in many cases in homogeneous catalysis, is an important factor in methane activation [7–9]. Therefore, the methane activation over Mo/HZSM-5 catalyst without using oxidants is of importance in offering a new example that methane can also be heterogeneously activated by acid since HZSM-5 zeolite can be recognized as a solid acid medium. We call this acid-assisted heterolytic splitting of methane (forming CH_3^+ and H^-) in this case in order to differentiate it from basicity-assisted heterolytic splitting of methane (forming CH_3^- and H^+) in the OCM. A possible mechanism for methane dehydrogenation and aromatization has been proposed in which both the heterolytic splitting of methane in a solid acid environment and a molybdenum carbene-like complex as an intermediate are of significance [10]. Therefore, the Brønsted acid sites and the channel structure of HZSM-5 zeolite, and the location and state of Mo species in the zeolite play a key role in the reaction.

In this paper, we focus our attention to the interaction between AHM and NH_4ZSM-5 zeolite at different preparation stages by using differential thermal analysis (DTA), Fourier transform infrared spectrometer (FT-IR), temperature programmed decomposition (TPDE) and NH_3-temperature programmed desorption (NH_3-TPD) techniques in order to offer some understanding of the function of the acidity of HZSM-5 zeolite and the location of Mo species on methane activation.

2. Experimental

2.1. CATALYST PREPARATION

The ZSM-5 zeolite was supplied by Nankai University with SiO_2/Al_2O_3 ratio of 50. It was first converted into its ammonium form (NH_4ZSM-5) by repeated ion exchange (four times) with a 1 N NH_4NO_3 aqueous solution at 368–373 K for 2 h, and was then dried at 393 K. Mo/HZSM-5 catalysts with 2, 6, and 10% Mo loadings respectively were prepared by wet impregnation techniques from NH_4ZSM-5 zeolite with aqueous solutions of ammonium heptamolybdate (AHM). The samples were first dried at 343 K, and then heated up to 393 K. They were finally calcined at 573, 773, 973 K for 4 h separately. The catalysts are referred to hereafter as XMo/HZ-Y, where X and Y denote the corresponding Mo content and the calcination temperature used, respectively.

2.2. FT-IR CHARACTERIZATION

FT-IR spectra of Mo/HZSM-5 catalysts, in the vibrational region between 400 and 2000 cm^{-1}, were recorded with a BIO-RAD FT-7S infrared spectrometer by using the conventional KBr disk technique. The wafers were prepared with a ratio of XMo/HZ-Y : KBr = 1 : 200 under a pressure of 90 kgf/cm^2.

2.3. DIFFERENTIAL THERMAL ANALYSIS (DTA)

Differential thermal analysis data were recorded with a Perkin-Elmer 1700 thermal analysis station under air atmosphere with a flow rate of 40 ml/min and a heating rate of 10 K/min in the temperature range from room temperature to 873 K.

2.4. TEMPERATURE PROGRAMMED DESORPTION (TPDE) AND NH_3-TPD

TPDE profiles of samples were obtained in a flow reactor system attached to a multichannel mass spectrometer. The sample charge was 200 mg with a particle size of 40–60 mesh. The TPDE experiment was performed under He atmosphere at a heating rate of 16 K/min from room temperature to 873 K. The decomposition species, H_2O ($m/e = 18$) and NH_3 ($m/e = 16$), were monitored and recorded with a multichannel TE-150 mass spectrometer. The data were recorded and processed with an IBM computer.

NH_3-TPD measurements were performed in a conventional set-up using a TCD as detector. The catalyst charge was 140 mg (particle size 40–60 mesh). The sample was first flushed with He (20 ml/min) at 873 K for 1 h and then cooled down to room temperature. After NH_3 adsorption at room temperature and saturation to equilibrium, the sample was flushed with He again until the baseline was stable. NH_3-TPD was then promptly started at a heating rate of 24 K/min.

2.5. CATALYTIC EVALUATION

The catalytic evaluation of methane aromatization over Mo/HZSM-5 catalysts was performed in a flowing reactor system as described in our previous paper [10].

3. Results and discussion

3.1. THE NATURE AND DISPERSION OF Mo SPECIES OF Mo/HZSM-5 CATALYST

Fig. 1a shows the FT-IR spectra recorded on Mo/HZSM-5 zeolite catalysts calcined at different temperatures. The FT-IR spectra of AHM and MoO_3 samples are also shown in fig. 1b for comparison. The FT-IR spectrum of AHM shows bands at about 896 cm^{-1} with two small bands at 843 and 920 cm^{-1} respectively for the Mo=O vibration, and an NH_4^+ band at 1405 cm^{-1} [11]. The sample of pure MoO_3 gives characteristic bands at 860 and 997 cm^{-1}, which can be attributed to crystalline MoO_3 vibrational modes [12,13].

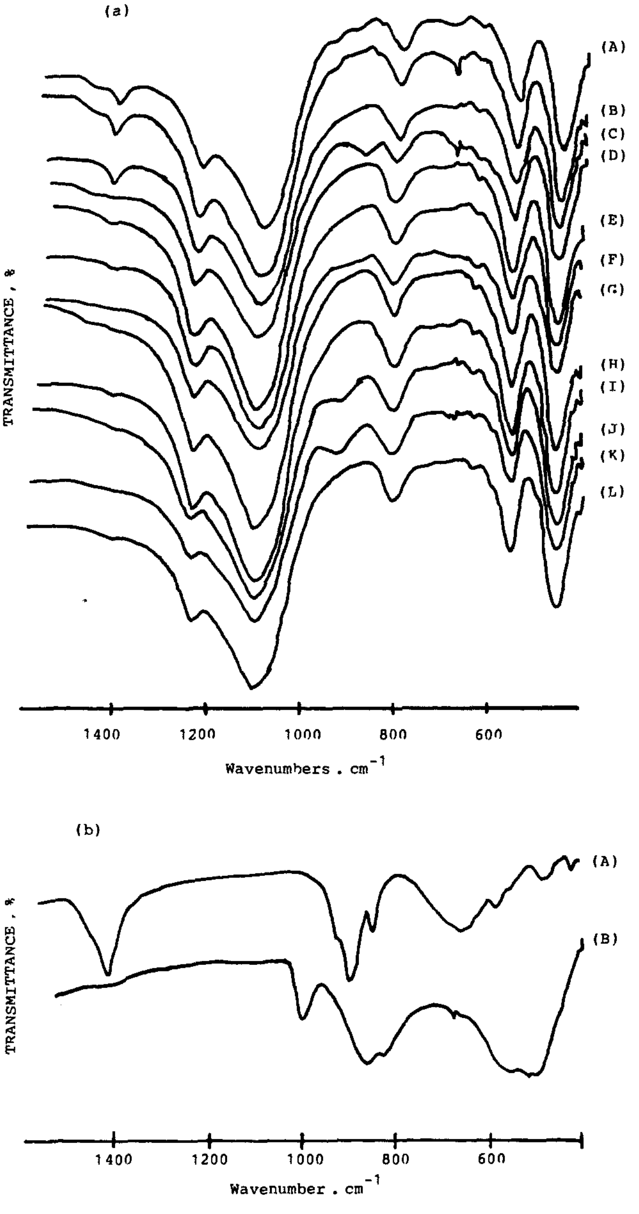

Fig. 1. (a) FT-IR spectra of Mo/HZ catalysts dried and calcined at different temperatures. (A) 10Mo/HZ-393; (B) 6Mo/HZ-393; (C) 2Mo/HZ-393; (D) 10Mo/HZ-573; (E) 6Mo/HZ-573; (F) 2Mo/HZ-573; (G) 10Mo/HZ-773; (H) 6Mo/HZ-773; (I) 2Mo/HZ-773; (J) 10Mo/HZ-973; (K) 6Mo/HZ-973; (L) 2Mo/HZ-973. (b) FT-IR spectra of AHM (A) and MoO_3 (B).

The NH_4ZSM-5 zeolite shows five characteristic bands at 453, 548, 800, 1092 and 1227 cm^{-1}, respectively, as reported in the literature [11,12]. It also shows an NH_4^+ vibrational band at 1407 cm^{-1}. The FT-IR spectra recorded from Mo/NH_4ZSM-5 catalysts after drying at 393 K show that the framework vibration of

Mo/HZSM-5 at this stage is similar to that on NH_4ZSM-5. A band characteristic of NH_4^+ vibrational bands at about 1400 cm^{-1} can be obviously detected. In addition, there is only a small difference observed in the region of 800–900 cm^{-1} for the Mo/HZSM-5 sample, in which very weak bands are located in the region of the AHM bands. This is an indication that Mo species are still in the form of AHM on the Mo/NH_4ZSM-5 samples after drying at 393 K.

The FT-IR spectra of Mo/HZSM-5 samples calcined at 573 K show that the NH_4^+ bands at 1400 cm^{-1} for all three samples diminish strongly. This suggests that most of the AHM and NH_4ZSM-5 zeolite are decomposed after the samples were calcined at 573 K. For the 10Mo/HZ-573 sample there are two new bands at 869 and 1006 cm^{-1} in the FT-IR spectrum, which can be attributed to vibrational modes of MoO_3 crystallites. This is evidence that MoO_3 crystallites are formed at this stage. No such peaks can be detected on 2Mo/HZ-573 and 6Mo/HZ-573, because of the relatively low loading of Mo. From fig. 1 we notice that the band at around 800–900 cm^{-1}, characteristic of AHM, has also disappeared. The other bands of the Mo/HZSM-5 sample after calcining at 573 K, characteristic of HZSM-5 zeolite, have not changed at all. This is an indication that the skeleton of HZSM-5 zeolite is not distorted by impregnation and calcination of Mo species at 573 K.

After calcining at 773 K for 4 h, the FT-IR spectra of Mo/HZSM-5 samples are almost the same as those of HZSM-5. This suggests that at this stage NH_4ZSM-5 is totally converted into HZSM-5. The 10Mo/HZ-773 sample does not show any band at 869 and 1006 cm^{-1}. This suggests that with increasing calcination temperature part of the MoO_3 is now well dispersed on the external surface, and part of the small crystallites of MoO_3 may move into the channels of HZSM-5 zeolite. The dispersion of MoO_3 is too high to be detected by FT-IR technique.

The FT-IR spectrum of the 2Mo/HZ-973 catalyst after calcining at 973 K is similar to that of HZSM-5 zeolite. After calcining at 973 K, there is a new band at 917 cm^{-1} for both 6Mo/HZ-973 and 10Mo/HZ-973 catalysts. The band at 917 cm^{-1} does not correspond to the characteristic bands at 860 and 997 cm^{-1} for MoO_3 crystallites. This may be ascribed to Mo=O bond vibrations in MoO_4^{2-}.

There are many different interpretations and assignments to MoO_4^{2-} species in/on zeolites in the literature. Dai and Lunsford attributed a band at 900 cm^{-1} to oxo-molybdenum complex ions located at S_{II} sites [14]. Gallezot et al. [15] interpreted a transmittance band at 895 cm^{-1} in $Mo(CO)_6$ adsorbed on HY zeolite to Mo---O vibrations and took this as evidence for the formation of Mo^{n+}–O^{2-} bonds. Cid et al. considered that it is more reasonable to assign the band at 890 cm^{-1} to a Mo=O bond vibration of monomeric MoO_4^{2-} species attached to the Y-zeolite framework [16]. Dong et al. claimed that the band at 910 cm^{-1} observed in their MoO_3-HZSM-5 system may be attributed to non-crystalline surface Mo species, which were partly in tetrahedral coordination and partly in octahedral coordination [12]. Mitchell and Trifirò [17] pointed out that the frequency of an Mo=O bond vibration depends upon the coordination number and the number of terminal oxygen atoms on the Mo atom. The tetrahedral cis-dioxo molybdenum complexes have Mo=O frequencies in the ranges of 873–913 and 919–943 cm^{-1}. The new band at 917 cm^{-1} is just in this range. We think it may be more reasonable to assign the band at 917 cm^{-1} as due to a Mo=O vibration between Mo species and oxygens of the zeolite. This indicates that for a high Mo loading catalyst, after calcining at a temperature as high as 973 K, a strong interaction between Mo species and the oxygen species of the skeleton of ZSM-5 zeolite will occur.

On the basis of the FT-IR studies, we can see that AHM undergoes the following changes at the various stages of preparation: firstly, AHM decomposes and forms MoO_3 crystallites outside of the zeolite channel after drying and calcination at 573 K; secondly, part of the MoO_3 crystallites move into the channel and part of that well disperse on the external surface of the zeolite after calcining at 773 K; thirdly, the MoO_3 crystallites interact with the oxygens of the zeolite to form MoO_4^{2-} species after calcining at 973 K.

3.2. THE INTERACTION BETWEEN Mo SPECIES AND HZSM-5 ZEOLITE

Table 1 lists the DTA results obtained from various samples after drying at 393 K. The DTA of AHM exhibits three endothermic peaks at 403, 514 and 619 K, respectively. The peak at 403 K is due to the desorption and decomposition of crystalline water in AHM and the peaks at 514 and 619 K show that the decomposition of AHM occurs via two steps. The DTA of NH_4ZSM-5 zeolite only had two peaks, one endothermic peak is at 378 K, which is due to the desorption of water, and the other exothermic peak at 727 K, which is caused by the decomposition of NH_4ZSM-5 and the oxidation of NH_3 evolved during the experiment. The peak temperatures from DTA obtained from 2, 6 and 10Mo/HZ-393 samples are very interesting. There is an exothermic peak at 517 K for the 2Mo/HZ-393 sample. No such exothermic peak could be detected for both 6 and 10Mo/HZ-393 samples. Since only NH_4ZSM-5 zeolite has an exothermic peak, we believe that the exothermic peak observed on 2Mo/HZ-393 is also caused by the decomposition of NH_4ZSM-5 and the oxidation of NH_3 evolved. The oxidation of evolved NH_3 dur-

Table 1
The peak temperatures of DTA profiles obtained on Mo/NH_4ZSM-5 samples

Sample	Peak temperature (K)			
	T_1	T_2	T_3	T_4 [a]
AHM	403	514	619	
NH_4ZSM-5	378	–	–	727
2Mo/HZ-393	372	–	–	517
6Mo/HZ-393	376	584	–	–
10Mo/HZ-393	377	579	–	–

[a] Exothermic peak recorded during DTA.

ing the decomposition of NH_4ZSM-5 is possibly accelerated by the presence of Mo species so that the exothermic peak moves to a temperature as low as 517 K.

The TPDE profiles of NH_4ZSM-5 and 2Mo/HZ-393 and 6Mo/HZ-393 catalysts are presented in fig. 2. There is a peak of H_2O ($m/e = 18$) at 464 K and a peak of NH_3 ($m/e = 16$) at 703 K. This is evidence that NH_3 is evolved from the decomposition of NH_4ZSM-5 and AHM.

The TPDE profile of NH_3 obtained on 2Mo/HZ-393 is similar to that of NH_4ZSM-5 but there is an obvious decrease in the peak area corresponding to NH_3 desorption. With increasing Mo loading, the peak temperature corresponding to NH_3 desorption moves down to the low temperature side. The peak temperatures corresponding to NH_3 desorption are 577 and 655 K, respectively. The former peak is mainly from the decomposition of AHM and the latter from the decomposition of NH_4ZSM-5. Three water peak temperatures are recorded with peak temperatures at 480, 577 and 655 K, respectively. Because there are two ammonia peaks with peak temperatures at 577 and 655 K and these two peak temperatures are consistent with the two water peak temperatures, we come to the conclusion that the NH_3 evolved during TPDE is partially oxidized. Clearly the surface properties of 2Mo/HZ-393 are quite similar to NH_4ZSM-5 because the impregnated amount of Mo is so small that it cannot significantly affect the surface composition of NH_4ZSM-5. The TPDE profiles of 2Mo/HZ-393 and NH_4ZSM-5 provide evidence that the exothermic peak observed on 2Mo/HZ-120 in DTA experiments comes from the NH_4ZSM-5 zeolite.

NH_3-TPD data for Mo/HZSM-5 catalysts are shown in fig. 3. Clearly Mo species mainly interact with the Brønsted acid sites. With increased Mo loading, the Brønsted acid sites diminish more severely than do the Lewis acid sites. The interac-

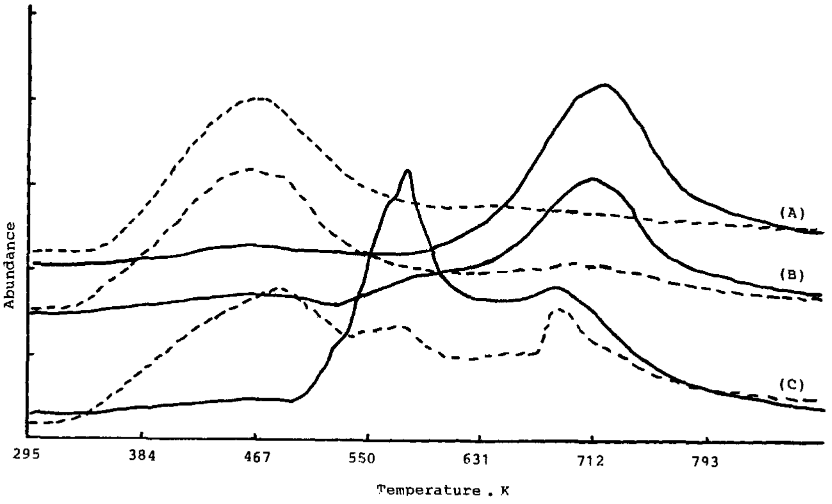

Fig. 2. The TPDE profiles of NH_4ZSM-5 (A) and 2Mo/HZ-393 (B), 6Mo/HZ-393 (C) catalysts. Solid line for NH_3 ($m/e = 16$) and dotted line for H_2O ($m/e = 18$), respectively.

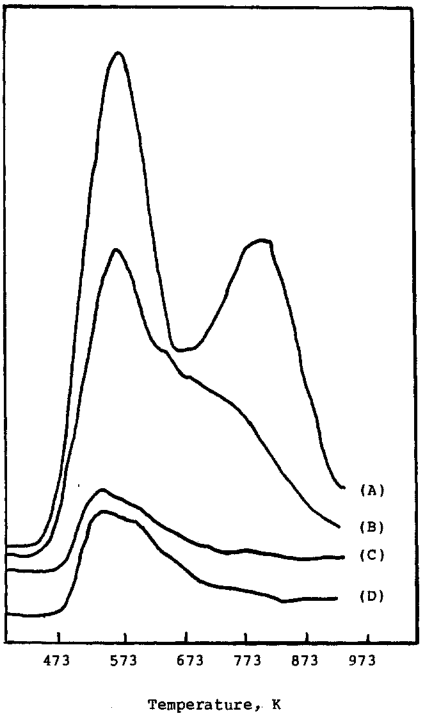

Fig. 3. The NH_3-TPD profiles of Mo/HZ-973 zeolite catalysts. (A) NH_4ZSM-5; (B) 2Mo/HZ-973; (C) 6Mo/HZ-973; (D) 10Mo/HZ-973.

tion between Mo species and the Brønsted acid sites will be significantly enhanced on increasing the calcination temperature, as we can see from fig. 4.

3.3. DEPENDENCE OF THE REACTIVITY OF Mo/HZSM-5 CATALYST ON THE STATE OF Mo SPECIES

Table 2 lists the catalytic performances of Mo/HZSM-5 catalysts calcined at different temperatures. Clearly, the calcination temperature is a crucial factor for the reaction. If the calcination temperature was set at 773 K, the Mo loading has no distinct effect on the catalytic performance of either fresh or regenerated catalysts. The 6Mo/HZ-773 catalyst gives the highest reactivity. If Mo/HZSM-5 are calcined at 973 K, the catalytic performances of the catalysts will severely decrease in reactivity for the methane aromatization with increasing Mo loading, as shown in table 2. For the 6 and 10Mo/HZ-973 catalysts, FT-IR observations show that the band at 917 cm^{-1} is characteristic of the MoO_4^{2-} species formed between Mo species and oxygen ions of the zeolite. The strong interaction between Mo species and the oxygen species of the skeleton of HZSM-5 zeolite is the most detrimental factor for the activation of methane. 6Mo/HZ-973 catalyst shows the lowest reactivity, since this Mo loading, after calcining at 973 K, will cause the strongest interaction

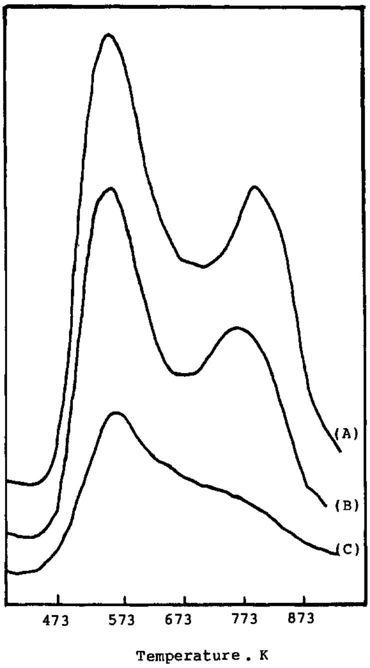

Fig. 4. The NH_3-TPD profiles on 2Mo/HZSM-5 catalysts calcined at different temperatures. (A) 2Mo/HZ-773; (B) 2Mo/HZ-873; (C) 2Mo/HZ-973.

Table 2
The catalytic performance of Mo/HZSM-5 catalysts calcined at 773 or 973 K for 4 h [a]

Catalyst	Conv. (%)	Selectivity (%)		
		C_2	C_3	aromatics
2Mo/HZ-773				
fresh	5.1	7.0	0.2	92.9
regenerated	4.9	7.8	0.2	92.0
6Mo/HZ-773				
fresh	5.8	6.8	0.2	92.9
regenerated	6.5	5.5	0.2	94.4
10Mo/HZ-773				
fresh	5.7	7.2	0.2	92.5
regenerated	5.3	7.9	0.2	91.8
2Mo/HZ-973	4.7	9.3	0.3	90.4
6Mo/HZ-973	1.0	39.6	2.7	58.2
10Mo/HZ-973	2.2	20.4	1.0	78.4

[a] Reaction temperature: 973 K; catalyst charge: 200 mg; flow rate of CH_4: 1450 ml/h; the data were taken after 100 min running of the reaction.

between Mo species and oxygen species of the skeleton of the HZSM-5 zeolite. Some free MoO_3 crystallites may be formed with further increasing of the Mo loading.

4. Conclusions

(1) The decomposition of AHM occurs via two steps at 514 and 619 K. MoO_3 is the decomposition product in the form of aggregates. The higher the calcination temperature, the stronger the interaction between MoO_3 and the zeolite. The MoO_3 crystallites disperse on the surface of HZSM-5 zeolite and migrate into its channels and at last form MoO_4^{2-} species at 973 K.

(2) The characteristic peak for MoO_3 aggregation on 2Mo/HZ-573 and 6Mo/HZ-573 catalysts disappeared from the FT-IR spectra. This suggests that the dispersion of MoO_3 in Mo/HZSM-5 is too high to be detected by FT-IR techniques. For the 10Mo/HZ-573 catalyst, MoO_3 crystallites can be formed at this stage.

(3) A strong interaction between MoO_3 and zeolite can occur for the 6Mo/HZ-973 and 10Mo/HZ-973 catalysts after calcining at 973 K. This strong interaction will cause the formation of MoO_4^{2-} species produced from Mo species and lattice oxygen in the HZSM-5 zeolite framework and will lead to a sharp decrease in catalytic performance.

Acknowledgement

The financial support from the Natural Science Foundation of China (NSFC) is gratefully acknowledged.

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