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Methane dehydroaromatization over Mo/HZSM-5: A study of catalytic process

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The deactivation process of methane dehydroaromatization (MDA) reaction has been followed by various physical chemistry methods.

KEY WORDS: methane dehydroaromatization; Mo/HZSM-5; MAS NMR; TG; XPS; deactivation.

1. Introduction

Natural gas (mainly methane) is known as a potential energy resource and promising raw material for chemical industry in the 21st century. Direct conversion of methane into valuable chemicals has been a highlight in heterogeneous catalysis during the past decades [1]. In 1993, we reported for the first time the transformation of methane into aromatics on Mo/HZSM-5 catalyst under nonoxidative condition [2]. As a novel route for direct conversion of methane, methane dehydroaromatization reaction has attracted great attention in the past decade [3,4]. Although remarkable progresses have been achieved on this reaction, many problems are yet to be solved. Among them the deactivation process is of particular importance to understand the nature of this reaction. The present paper reports a study on the deactivation process of MDA reaction with multinuclear solid-state NMR and other techniques.

2. Experimental

2.1. Sample preparation

HZSM-5 zeolite with a Si/Al of 30 was provided by Nankai University. Mo/HZSM-5 catalyst with Mo loading of 6 wt.% was prepared by impregnating 10 g HZSM-5 with 10 ml aqueous solution which contained the desired amount of ammonium heptamolybdate (AHM). Then, the samples were dried at room temperature for 24 h. A further drying at 373 K for 3 h was followed by calcination at 773 K for 5 h. MDA reaction was conducted at 973 K for different time [5]. The used catalysts are denoted as 6Mo (x h), x is the reaction time.

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2.2. Characterization

^{27}Al MAS NMR and ^{13}C MAS NMR measurements were performed on a Bruker DRX-400 spectrometer with a BBO MAS probe using 4 mm ZrO_2 rotors. For ^{27}Al MAS NMR, pulse width was 1.5μs for $\pi/12$ and 500 scans were accumulated with a 2 s recycle delay. Samples were spun at 8 kHz and the chemical shifts were referenced to 1 M Al^{3+} aqueous solution. Prior to ^{27}Al MAS NMR measurements, all samples were fully hydrated in a desiccator with saturated NH_4NO_3. For ^{13}C MAS NMR, pulse width was 3.3μs for $\pi/6$ with a 4 s recycle delay. Samples were spun at 6 kHz and the chemical shifts were referenced to adamantane. ^{13}C CP/MAS NMR measurements were performed on a Varian Infinity-Plus 400 spectrometer. The Hartmann–Hahn condition was established using HMB.

XRD patterns were obtained on a Rigaku Miniflex diffractometer using Cu Kα radiation at room temperature. The instrument settings are 30 kV and 15 mA. The data of the samples were recorded from 5° to 50° at a scanning rate of 5°/min.

TG/DTG measurements were conducted on a PE Diamond instrument. About 25 mg coked samples were charged and heated from room temperature to 1023 K at a heating rate of 10 K/min in an air stream with a flow rate of 100 ml/min.

BET measurements were carried out on an AUTOSORB-1-MP equipment.

XPS measurements were performed in a Leybold LHS 12 MCD system. Binding energies were calibrated by the zeolitic Si 2 p peak at 102.8 eV [6].

3. Results and discussion

^{27}Al MAS NMR has proved to be an efficient tool to study zeolite structure, i.e., discriminating different

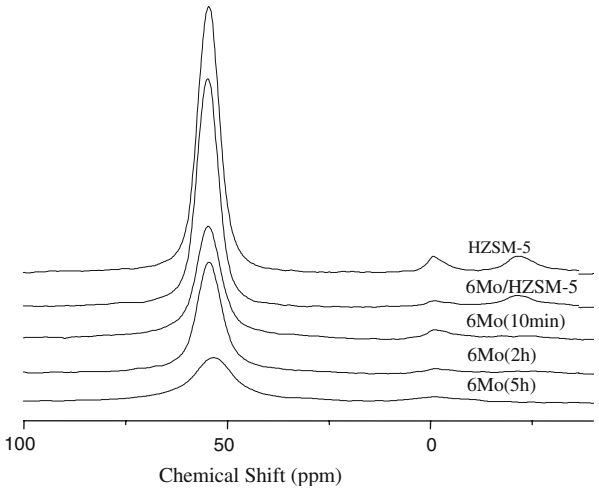

Figure 1. ^{27}Al MAS NMR spectra of parent HZSM-5, fresh catalyst and reacted catalysts (with different reaction times).

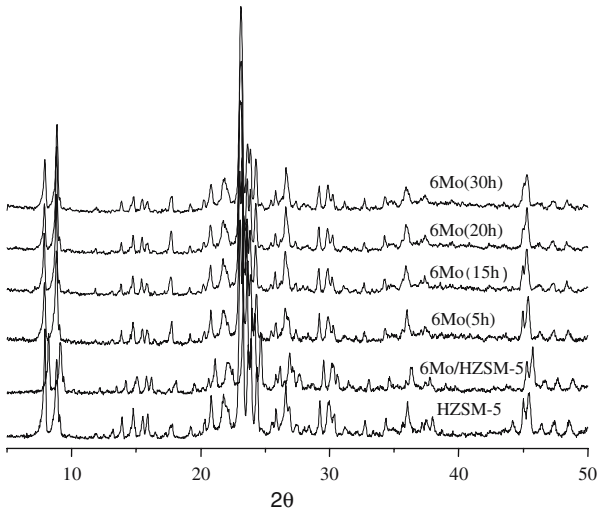

Figure 2. XRD patterns of parent HZSM-5, fresh catalyst and reacted catalysts (with different reaction times).

aluminum species in zeolite such as framework aluminum species and nonframework aluminum species [7]. As shown in Figure 1, the resonance peak at about 55 ppm is assigned to tetrahedral Al_F (framework aluminum). Comparing the spectra of HZSM-5 and 6 Mo/HZSM-5, it is obvious that the intensity of Al_F remains almost unchanged. However, a remarkable decrease of the intensity of Al_F has been observed at the very beginning of the reaction, accompanied with peak broadening. This trend goes further with further reaction. Simulation results of ^{27}Al MAS NMR spectra are listed in Table 1. Compared with HZSM-5, the peak intensity of 6 Mo/HZSM-5 decreases by only 5%, whereas that of 6 Mo (10 min) decreases to 51%. After 5 h reaction, the peak intensity decreases to 30% with the FWHM (the full width at half maximum) increasing from about 730 Hz (HZSM-5) to 1300 Hz. XRD results shown in Figure 2 and Table 2 reveal that there is no significant loss of zeolite crystallinity during the reaction. The decrease of Al_F peak intensity and the peak broadening cannot be attributed to the collapse of zeolite framework, but to the local geometry change of tetrahedral Al species during the high temperature MDA reaction instead.

^{13}C CP/MAS NMR spectra presented in Figure 3 demonstrate the formation and deposition of aromatic products. A weak peak centered at around 128 ppm appeared after 30 min MDA reaction. It can be ascribed to benzene produced during reaction, or carbonaceous species deposited on the surface of catalyst. The intensity of the peak increased with the increase of the reaction time. Judging from the line width of the peak, this signal could be assigned to the carbonaceous species.

In the corresponding ^{13}C MAS NMR spectrum of 6 Mo (5 h) shown in Figure 4, a peak around 286 ppm can be resolved which could be attributed to the carbon in molybdenum carbide, the active center of MDA reaction [8].

A complementary evidence for the formation of molybdenum carbide species is given by XPS spectrum at C1s region. As show in Figure 5, the peak at the binding energy of 281.1 eV is carbidic carbon in molybdenum carbide [6]. The peak at 283.8 eV is due to the carbonaceous contaminants in the vacuum system. As Meinhold et al. pointed out, the deposition of carbonaceous species on zeolitic surface will lead to the

Table 1
Relative intensity of Al_F (results given by simulation of ^{27}Al MAS NMR spectra)

	HZSM-5	6 Mo/HZSM-5	6 Mo (10 min)	6 Mo (2 h)	6 Mo (5 h)
Intensity(%)	100	95	51	50	31
FWHM(Hz)	730	730	790	770	1270

Table 2
Relative crystallinity of parent HZSM-5, fresh catalyst and reacted catalysts (results given by XRD measurements)

	HZSM-5	6 Mo/HZSM-5	6 Mo(5 h)	6 Mo(15 h)	6 Mo(20 h)	6 Mo(30 h)
Crystallinity(%)	100	87	83	82	79	78

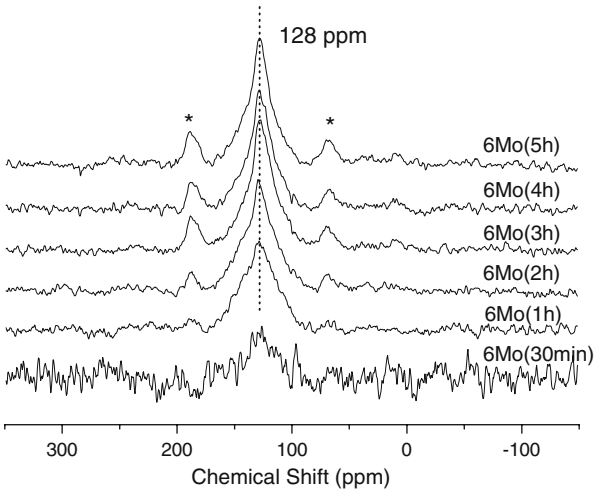

Figure 3. ^{13}C CP/MAS NMR of reacted catalysts (* denotes the spinning side bands).

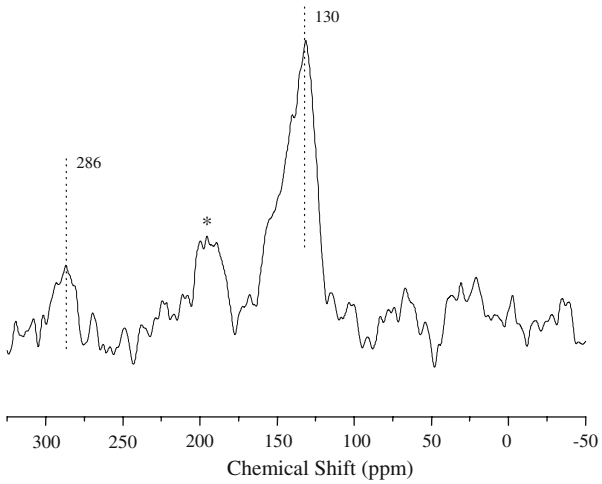

Figure 4. ^{13}C MAS NMR of 6Mo (5 h) (* denotes the spinning side bands).

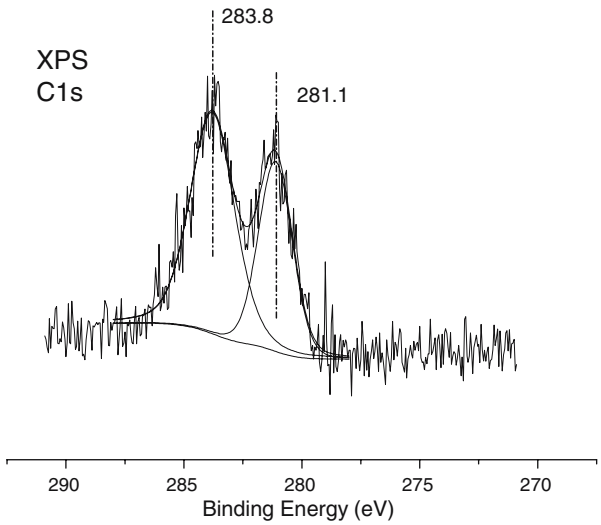

Figure 5. XPS spectrum of C1s region of 6Mo (5 h).

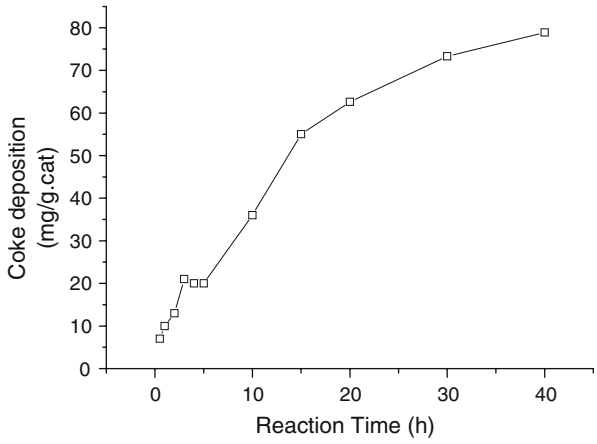

Figure 6. Amount of coke deposition with different times on stream.

local geometry transformation of framework tetrahedral aluminum species [9]. In our study, the observed broadened peak line width and decreased intensity of tetrahedral Al_F species can be attributed to a lower symmetry of aluminum tetrahedron. And in some cases, part of the aluminum species becomes "NMR invisible" or be expelled from the framework [10,11].

From the above observations, it is assured that the carbonaceous deposition has almost no influence on the zeolite crystallinity but will alter one of the reaction centers in the bifunctional catalyst, i.e., the local geometry of Brönsted aluminum species. Thus, it is important to quantify the carbonaceous deposition and couple the result afterwards with NMR observations. TG/DTG is a powerful method to obtain detailed information of carbonaceous deposition. TG results shown in Figure 6 give a correlation between the amount of carbonaceous deposition and the reaction time. At the earlier stage of the reaction, the so-called induction period, the carbonaceous deposition rate is much higher than that of the steady reaction stage, which results from the reduction and carburization of molybdenum oxide [6]. Although the carbonaceous deposits increase during the reaction time, the rate of coke formation gradually slows down. When the reaction time is prolonged to 40 h, the amount of coke reaches a value of about 80 mg/gcat. As presented in Table 3, the surface areas of catalysts decrease tremendously when MDA reaction is carried out, which maybe result from zeolitic channel blockage caused by the carbonaceous deposits on the aperture of the zeolitic channels.

Similar to TPO experiments, DTG measurements shown in Figure 7 give out the information of coke combustion. There are at least two types of carbon deposits on the catalysts which can be revealed from figure 7, the carbon related to molybdenum and the carbon deposited on the acid sites [12–14]. Possibly the carbonaceous deposition on the acid sites could be

Table 3
Surface area of parent HZSM-5, fresh catalyst and reacted catalysts

Samples	HZSM-5	6 Mo/HZSM-5	6 Mo(5 h)	6 Mo(10 h)	6 Mo(20 h)	6 Mo(30 h)	6 Mo(40 h)
Surface are(m^2/g)	319	338	210	169	116	90	75

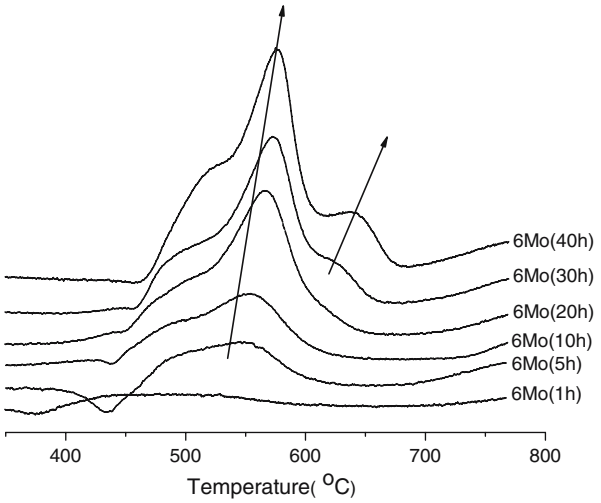

Figure 7. DTG profiles of used catalysts.

regarded as live carbon which could serve as so-called carbon-pool for the aromatics formation. During the reaction, the carbon species deposited on the catalyst surface could be condensed to inert coke at the high temperature. As a result, the temperature of coke combustion elevates with the reaction time. When the reaction time is prolonged to 30 h, there is a new carbon combustion peak emerging at a temperature higher than 600 °C, which maybe resulted from the formation of a large amount of graphitic coke, leading to the final death of the catalyst.

4. Conclusions

It is clearly demonstrated from above results that initially in the MDA reaction, the coke species are mainly aromatic carbonaceous species deposited on the Brönsted acid sites and carbidic carbon in molybdenum carbide. Upon further reaction, the graphitic carbon appears as the result of deep dehydrogenation of above carbon species, and indicates the death of catalyst. The deactivation of MDA catalyst is a combination of several factors, i.e., it comes from the local geometry change of tetrahedral aluminum (then the expelling of aluminum from the zeolitic framework thus the loss of Brönsted centers), the carbonaceous deposits on the Brönsted acid sites and thereafter the blockage of the channels as well as the deep dehydrogenation of live carbonaceous species (the formation of graphitic coke) in the final stage.

Acknowledgments

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