Effect of Mo/H-MCM-22 with various Si/Al_2 ratios on methane dehydroaromatization

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Abstract: A series of Mo(5)/H-MCM-22 catalysts with various Si/Al_2 ratios were synthesized by using hydrothermal synthesis and impregnation method. The catalysts were applied to MDA reaction and various characterizations such as N_2 adsorption-desorption, ICP-AES, XRD, SEM, NH_3 TPD, XPS, UV-Raman and TPO. In this study, we examined the migration of Mo oxide species into the micropore of zeolite with varying the Si/Al_2 ratios of MCM-22 zeolite and, in addition, investigated the effect of such characteristics on MDA reaction.

Keywords: Mo/H-MCM-22, Methane dehydroaromatization, Si/Al_2 ratio

1. Introduction

Methane has been receiving considerable attention as an alternative fuel by directly converting methane to more valuable hydrocarbon products under nonoxidative condition. Among various nonoxidative reactions, methane dehydroaromatization (MDA) reaction is regarded as more promising way since it is more thermodynamically favorable in converting methane into benzene than other products[1].

The performances of MDA reaction over molybdenum impregnated medium pore zeolites such as ZSM-5 and MCM-22 have been frequently studied because their micropore diameter is close to kinetic diameter of benzene molecule (about 6.0 Å). MCM-22 has two independent multidimensional pore systems. One is 2 dimensional 10-Membered Ring (MR) sinusoidal channel system (4.0 × 5.0 Å) and the other is 3 dimensional 12-MR supercage system interconnected by 10-MR windows (4.0 × 5.5 Å)[2]. Such unique structure and smaller pore size of MCM-22 than other medium pore zeolites can lead to high accommodation ability of carbonaceous deposit and high production rate of benzene under shape-selective environment during MDA reaction.

Migration of Mo oxide species into the microchannel of zeolite are known to play a key role in the performance of MDA reaction[3]. Most previous studies suggested that Mo oxide species present on the external surface mainly diffuse and migrate into the micropore of zeolite while exchanging with the acidic H atom located at Brønsted acid site (BAS) during the calcination above their Tamman temperature. During the initial stage of MDA reaction, Mo oxide species are carburized to Mo carbide species like Mo_2C (or MoO_xC_y) which are known as an active site of methane activation. Thus, we aimed at investigating the migration of Mo oxide species into the micropore of zeolite specifically with changing the Si/Al_2 ratios of MCM-22 zeolite and, moreover, examining the effect of such characteristics on MDA reaction.

2. Experimental

MCM-22 was synthesized with various Si/Al_2 ratios of 21, 45 and 91 via hydrothermal synthesis method[4]. 5 wt% of Mo was impregnated on the H-MCM-22 zeolites with various Si/Al_2 ratios by using an aqueous solution of ammonium heptamolybdate and then the resulting samples calcined in a muffle furnace at 500 °C for 4 h, which are denoted as Mo(5)/H-MCM-22 (X) catalysts.

The catalysts were applied to MDA reaction and various characterizations such as N_2 adsorption-desorption, ICP-AES, XRD, SEM, NH_3 TPD, XPS, UV-Raman and TPO. The MDA reaction was carried out over 0.2 g of the catalyst having 20-40 mesh size under atmospheric pressure in a fixed-bed quartz reactor. 10% N_2/CH_4 mixture gas was fed to the reactor as a reactant. The reactants and reaction products were analyzed by an on-line gas chromatograph equipped with a thermal conductivity detector and flame ionization detector.

3. Results and discussion

Figure 1 shows methane conversion rate and benzene formation rate of all Mo(5)/H-MCM-22 catalysts. The methane conversion rate and benzene formation rate increase when the Si/Al_2 ratio decreases and the descending order is as follow: Mo(5)/H-MCM-22 (21) > Mo(5)/H-MCM-22 (45) > Mo(5)/H-MCM-22 (91).

The amount of desorbed ammonia and Mo/(Si+Al) ratio of all catalysts are obtained from NH_3 TPD and XPS results as summarized in Table 1. It evidently exhibits that the amount of BAS in the MCM-22 samples increases with decreasing Si/Al_2 ratio. In case of Mo containing samples, a new peak located at about 281 ℃ appears, which is designated as Medium strength acid site (MAS) while the amount of BAS decreases. Thus, it can be seen that a large amount of MAS is produced from the catalyst which has a large amount of BAS when Mo is impregnated, thus leading to that Mo oxide species are mainly anchored to BAS.

As shown in Table 1, the ratios of Mo/(Si+Al) decrease when Si/Al_2 ratio decreases. Here, the different ratios of Mo/(Si+Al) signify the relative amount of Mo atom present on the zeolite surface because XPS is a surface analysis technique. Thus, it is confirmed that the migration of Mo atom from surface into microchannel of zeolite increases with decreasing Si/Al_2 ratio. In addition, it is verified that monomeric Mo oxide species are present on the surface more abundantly than polymeric Mo oxide species as the Si/Al_2 ratio decreases through a UV Raman analysis. Consequently, BAS stabilizes monomeric Mo oxide species, thus facilitating to migrate Mo oxide species into the microchannel of zeolite. Therefore, an increment in BAS enhances the dispersion of Mo oxides, thus leading to the improved methane conversion rate and benzene formation rate.

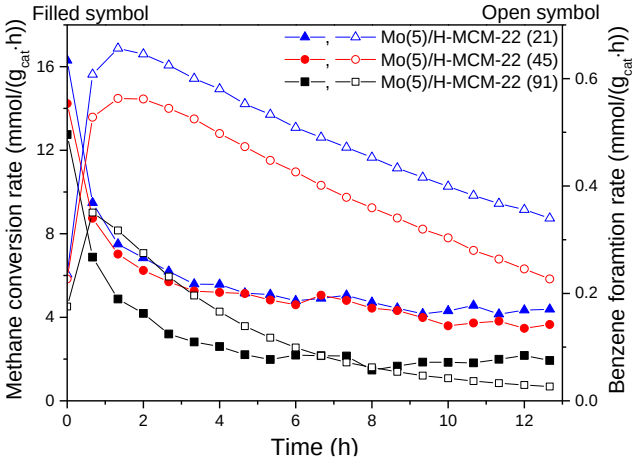

Figure 1. Methane conversion rate and benzene formation rate of all Mo(5)/H-MCM-22

Catalyst	Amount (mmol/g)			Mo/(Si+Al) ratio
	WAS	MAS	BAS	
MCM-22 (21)	0.89	-	0.80	-
MCM-22 (45)	0.49	-	0.49	-
MCM-22 (91)	0.36	-	0.25	-
Mo(5)/H-MCM-22 (21)	0.83	0.26	0.61	$2.54 \cdot 10^{-2}$
Mo(5)/H-MCM-22 (45)	0.63	0.19	0.32	$2.65 \cdot 10^{-2}$
Mo(5)/H-MCM-22 (91)	0.47	0.15	0.17	$3.27 \cdot 10^{-2}$

Table 1. Amount of desorbed ammonia and Mo/(Si+Al) ratio results of all MCM-22 and Mo(5)/H-MCM-22 catalysts obtained from NH_3 TPD and XPS, respectively.

4. Conclusions

The combined NH_3 TPD, XPS and UV Raman results clearly shows that BAS, determined by Si/Al_2 ratios, stabilizes monomeric Mo oxide species and thus facilitating to migrate Mo oxide species into the microchannel of zeolite and, therefore, an increase of BAS can improve methane conversion rate and benzene formation rate.

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