A Highly Selective and Coking-Resistant Catalyst for Methane Dehydrocondensation

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Acid reflux-dealuminated HMCM-22 supported Mo catalyst exhibits highly selective and coking-resistant catalytic performance for methane dehydrocondensation reaction, compared with conventional catalysts. The excellent catalytic stability of the dealuminated catalyst is based on the remarkable suppression of coke formation owing to the effective decrease of Brönsted acid sites, which are demonstrated by TPO, ^{1}H NMR and NH_3-TPD methods.

The catalytic dehydrocondensation of methane towards benzene and naphthalene for the petrochemical feed stocks and bulky hydrogen for the fuel cell has attracted significant attention. It has been reported that Mo or Re supported on selected microporous zeolites with pore size of 5–6 Å and protonic acid sites exhibit the effective performance for methane aromatization reaction.[1–8] Nevertheless, the obvious decrease in catalytic activity with time-on-stream due to the coke accumulation on catalyst surface is still the main obstacle for the potential industrialization of this process. To solve this problem, we have previously reported that the addition of a few percent CO and CO_2 to methane feed made a dramatic enhancement of the catalyst stability on Mo/HZSM-5 and Re/HZSM-5.[3,9,10] Here we report an alternative but simple method to suppress the coke formation by pre-dealumination of HMCM-22 zeolite using an acid reflux treatment. Significant improvement in catalytic stability and selectivity towards benzene has been realized on this dealuminated HMCM-22 supported Mo catalyst owing to the efficient suppression of coke formation.

The parent MCM-22 zeolite was synthesized using hexamethyleneimine as a template.[7] The dealumination treatment of HMCM-22 zeolite was performed with aqueous 6 M HNO_3 solution at reflux temperature.[11] As a result; the Si/Al atomic ratio increased from 15 to 19. Six weight percent loading of Mo supported with parent and dealuminated HMCM-22 zeolite were prepared by wet impregnation method,[7] and denoted as 6% Mo/HMCM-22 and 6% Mo/HMCM-22-(D), respectively. The methane dehydrocondensation reaction was carried out in a continuous flow system at 973–1023 K, 0.3 MPa and 15 ml min^{-1} of methane flow rate. All the products were on-line analyzed by two GCs with FID and TCD as described in previous report.[3,9,10] ^{1}H MAS NMR spectra of samples were measured on a Bruker DRX-400 spectrometer fitted with a MAS probe using 4-mm ZrO_2 rotors at spinning rate of 8 kHz.[12,13] A sodium 4,4-dimethyl-4-silapentane sulfonate was taken as references for ^{1}H chemical shifts.

XRD patterns of synthesized MCM-22 were consistent with that reported previously.[7] After dealumination treatment, the intensities of peaks were comparable to those of the original MCM-22. In addition, the surface area and micropore volume of dealuminated HMCM-22 did not change as compared to those of the parent zeolite. Accordingly, it is suggested that the microporous structure of HMCM-22 zeolite was unchanged before and after dealumination treatment.

It is worthy to note that the dealumination of HMCM-22 and HZSM-5 exert a significant effect on the catalytic performance in the methane aromatization as shown in Table 1. Compared with 6% Mo/HZSM-5 and 6% Mo/HMCM-22 catalysts, the acid reflux-dealuminated HMCM-22 and HZSM-5 supported Mo catalysts give much higher benzene formation selectivity owing to the lower coke formation. Figure 1 shows the formation rates of benzene, naphthalene, hydrogen, C_2 hydrocarbons and methane

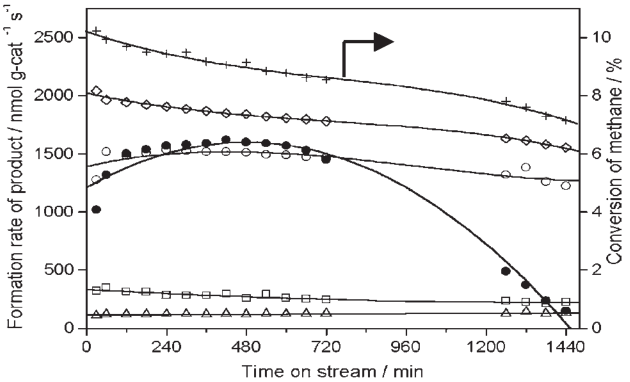

Figure 1. Catalytic performance of 6% Mo/HMCM-22-D catalyst at 1023 K, 0.3 MPa and 2700 ml g^{-1} h^{-1} versus time on stream; +, ○, □, △, and ◇ represent methane conversion, formation rates of benzene, naphthalene, C_2 hydrocarbons, and hydrogen (×1/2), separately. Solid circle (●) represents formation rate of benzene on 6% Mo/HMCM-22 catalyst under same reaction conditions.

Table 1. The typical reaction results of Mo supported zeolite catalysts before and after the dealumination treatment[a]

Sample	CH_4 conv./%	Rate of product formation/10^3 nmol g-cat^{-1}·s^{-1}			Selectivity of product/%		
		C_6H_6	$C_{10}H_8$	Coke	C_6H_6	$C_{10}H_8$	Coke
6%Mo/HMCM-22-(D)	6.5	1.1	0.2	0.5	52.0	9.0	22.7
6%Mo/HMCM-22	7.5	1.2	0.1	1.1	46.2	3.7	43.4
6%Mo/HZSM-5-(D)	6.7	1.1	0.4	0.4	47.3	18.2	18.1
6%Mo/HZSM-5	6.9	1.0	0.3	0.8	41.8	13.1	35.1

[a] 973 K, 0.3 MPa, 2700 ml g^{-1} h^{-1}, and the data were taken at the stable period of 240 min time on stream. (D): dealuminated zeolite.

conversion on the 6% Mo/HMCM-22-(D) catalyst at 1023 K, 0.3 MPa and 2700 ml $g^{-1}h^{-1}$, in comparison with those of benzene on the 6% Mo/HMCM-22. As seen, the initial formation rate of benzene on both catalysts is around 1500 nmol g-cat^{-1} s^{-1}. However, the formation rates of benzene on the 6% Mo/HMCM-22 declined drastically after 10 h of time on stream and eventually reached to 10% of its initial value. In contrast, the 6% Mo/HMCM-22-(D) showed quite stable performance by keeping the benzene formation rate at 85% level for the prolonged 24 hours. This high stability of the methane aromatization reaction at high temperature as 1023 K under pure methane feed without any additives such as CO and CO_2 has never been reported before.

TPO experiments of coked 6% Mo/HMCM-22-(D) and 6% Mo/HMCM-22 were conducted and the results are displayed in Figure 2. There are two peaks existed on coked 6% Mo/HMCM-22, the low temperature oxidation peak was attributed to carbon associated with molybdenum while the high temperature peak to the carbonaceous deposits on the zeolite Brönsted acid sites.[3,9] After dealumination treatment, the amount of coke deposited on the Brönsted acid sites decreased greatly and less pronounced.

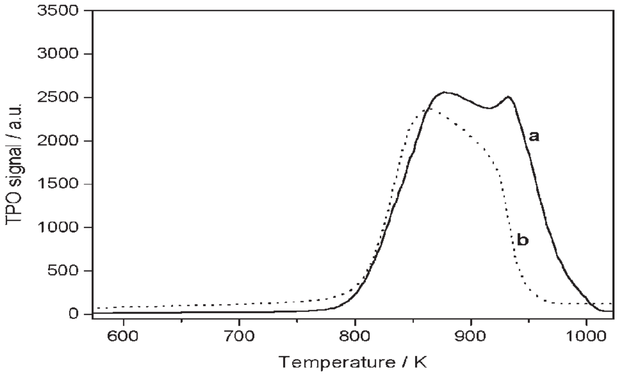

Figure 2. TPO profiles of coked 6% Mo/HMCM-22 (a) and 6% Mo/HMCM-22-D (b) after reaction at 1023 K for 24 h. (TPO experiments were carried out using 30 mg of catalyst at a 10% O_2/He flow rate of 15 ml min^{-1} and temperature raising rate of 10 K min^{-1}.)

^1H MAS NMR experiments were carried out to study the variation of zeolite acidity before and after dealumination treatment, and the corresponding spectra are shown in Figure 3. As presented, HMCM-22 gave peaks at 1.6, 3.7 and 6.0 ppm which were reasonably attributed to silanol group, framework Al(Si)-bridging OH groups (Brönsted acid sites) and water adsorbed on Lewis sites (another kind of Brönsted acid sites), respectively.[12,13] It is demonstrated that the Brönsted acid sites of HMCM-22 are suppressed drastically after dealumination treatment. The following NH_3-TPD experiments also confirmed the effective decrease of strong acid sites after such treatment. Basing on those findings, we can propose that the remarkable suppression of coke formation on the dealuminated HMCM-22 supported Mo catalyst is related to an effective decrease of the Brönsted acid sites.

In conclusion, the acid reflux pre-dealumination treatment for catalyst modification efficiently suppresses the coke formation in methane dehydrocondensation reaction owing to the distinct decrease of the Brönsted acid sites. The higher catalytic activity and longer stability are achieved as compared with conventional catalysts.

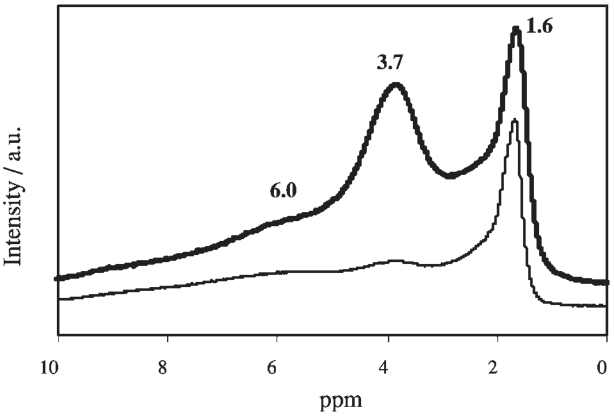

Figure 3. ^1H MAS NMR spectra of parent HMCM-22 (bold line) and dealuminated HMCM-22 (narrow line), respectively.

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