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# Ammonia-basified 10 wt% Mo/HZSM-5 material with enhanced dispersion of Mo and performance for catalytic aromatization of methane



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| Keywords:<br>Methane aromatization<br>10 wt% Mo/HZSM-5<br>Ammonia basification<br>Catalytic performance<br>Mo dispersion<br>Dealumination | Mo/HZSM-5 is an excellent catalyst for nonoxidative aromatization of methane, but it tends to deactivate rapidly due to severe coking. To date much effort has been devoted to enhancing activity and stability of Mo-impregnated HZSM-5 zeolite with Mo loading of 6 wt% or lower in methane aromatization. For this aromatization reaction, this work first reports a significant improvement in the catalytic performance of 10 wt% Mo/HZSM-5 material after preparation via impregnating HZSM-5 zeolite with ammonia-basified molybdate aqueous solution and pretreatment with a CH <sub>4</sub> /Ar/He (9:1:10, v/v) mixture. After 38 h of continuous reaction at 700 °C and 1500 mL g <sup>-1</sup> h <sup>-1</sup> (90 vol% CH <sub>4</sub> /Ar), this 10 wt% Mo-impregnated catalyst is still able to give an aromatic yield of 7% and a CH <sub>4</sub> conversion of 9.1%. This enhanced catalytic performance of this 10 wt% Mo sample is attributed to the ammonia basification of impregnating solution in catalyst preparation, which leads to a larger amount of highly dispersed Mo species in the zeolitic channels and a less amount of Brønsted acid sites remained on the Mo/HZSM-5 |

#### 1. Introduction

Direct nonoxidative aromatization of methane, a very abundant fossil fuel resource distributed widely around the globe, is a promising process simultaneously producing COx-free hydrogen and value-added aromatic hydrocarbons. Mo/HZSM-5 is an excellent catalyst that can catalyze methane aromatization to near-equilibrium levels at much lower temperatures, e. g., 700 °C, than 1000 °C, showing a great potential for industrial application [1-4]. However, during the reaction, this acidic catalyst tends to deactivate rapidly due to severe coking, and CH4 conversion and formation rates of aromatics, such as benzene and naphthalene, drastically decreases after a few hours on-stream [5]. Since the pioneering work of Wang et al. [5] much effort has been devoted to enhancing the activity, especially the stability of Mo/HZSM-5 catalyst in the methane dehydro-aromatization for the commercial viability of this process [1-4]. For this Mo-based catalyst, calcination temperature of 500 °C, zeolitic Si/Al ratio of 10-25, and impregnation technique are gradually accepted as the most suitable essential preparation conditions [6,7]. Further strategies to suppress the coke formation and increase aromatic yield include adding promotor [8-15], adjusting pH value of impregnating solution [16], modifying zeolitic surface via dealumination/desilication [17,18] or silanation [19], and optimizing zeolitic synthetize [20]. By far the most widely studied catalysts are those based on Mo/HZSM-5 materials with Mo loadings of 2-6 wt%, which were reported to be the most suitable loading for the catalytic performance of this Mo-modified HZSM-5 zeolite [6,21–25]. However, enhancing the catalytic activity and stability of Mo/HZSM-5 with Mo loading of 10 wt% or higher in methane aromatization has rarely been conducted because these high Mo loadings were shown in multiple studies to have lower catalytic activity values for this aromatization reaction.

Usually, a catalyst is calcined and/or preactivated at a temperature slightly higher than reaction temperature for its better stability in a catalytic reaction. In this case, the optimum calcination temperature of Mo/HZSM-5 is, however, 200 °C lower than the reaction temperature of methane aromatization. The large temperature difference between them will promote the influence of pretreatment method on the catalytic performance of the Mo catalyst. Previous activations of Mo/HZSM-5 material prior to the aromatization reaction were mostly conducted in oxygen/air [5,21] or inert gas such as helium [6,7,23,24] and argon [25]. Recent research showed that the Mo/HZSM-5 sample could exhibit better catalytic performance in this reaction after prereduction in 80 vol% CH<sub>4</sub>/He [26,27] and 10 vol% CH<sub>4</sub>/H<sub>2</sub> [28,29] than preactivation in inert helium or oxidative air atmosphere. To avoid rapid release of reaction heat and product water from MoO3 reduction by CH4 in this activation of catalyst, the author developed a pretreatment method of Mo/HZSM-5 with a diluted CH<sub>4</sub> with 55 vol% inert gases He/ Ar, which could remarkably improve the performance of Mo/HZSM-5

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with Mo loading of 10 wt% or higher for the catalytic aromatization of methane [30]. On the other hand, it has been demonstrated that basification of ammonium heptamolybdate (AHM) aqueous solution with ammonia in catalyst preparation was favorable for formation of tetrahedral Mo species rather than octahedral ones on surface of  $MOO_3/Al_2O_3$  [31,32]. In this work, after preparation via impregnating HZSM-5 zeolite with NH<sub>3</sub>-basified AHM aqueous solution and pretreatment in CH<sub>4</sub>/Ar/He (9:1:10, v/v), 10 wt% Mo-impregnated HZSM-5 zeolite exhibited significantly enhanced performance in the catalytic dehydroaromatization of methane. For an insight into the novel catalytic behaviors of this Mo/HZSM-5 material, the effect of ammonia treatment/basification on the dispersion of Mo species as well as the surface structure of the zeolite were then investigated.

#### 2. Experimental

#### 2.1. Catalyst preparation

HZSM-5 zeolite with a molar Si/Al ratio of 25 was supplied by Nankai University, People's Republic of China. Both conventional Mo/ HZSM-5 and Mo/HZSM-5(ZA) samples were prepared by impregnation of HZSM-5 zeolite with ammonium heptamolybdate tetrahydrate (AHM, Sigma-Aldrich) aqueous solution. Before preparation of Mo/ HZSM-5(ZA), the zeolite (6 g) was impregnated by 100 mL basified water with 6 mL 28% aqueous ammonia at room temperature in a beaker whose mouth was closed with a sheet of polythene for 24 h and then dried at 120 °C in an oven. Mo/HZSM-5(MA) sample was prepared by impregnation of HZSM-5 zeolite with ammonia-basified AHM aqueous solution. For preparing the Mo-based catalysts mentioned above, each 6 g portion of original or ammonia-treated HZSM-5 zeolite was impregnated with 100 mL of AHM aqueous solution or basified AHM aqueous solution with 6 mL 28% aqueous ammonia, containing the required amount of molybdenum, at room temperature for 24 h. The impregnation process for Mo/HZSM-5(MA) was conducted in a closed beaker with a sheet of polythene. The resulting materials were dried in an oven at 120 °C and then calcined in a furnace at 500 °C in air for 6 h. The freshly prepared Mo/HZSM-5 catalysts were pressed, crushed and sieved to 20-40 mesh for catalytic reaction. An overview of the different preparations of the Mo-impregnated samples mentioned above was provided in Table S1.

#### 2.2. Catalyst evaluation

Catalytic reaction was carried out in a continuous fixed-bed flow reactor (i.d. 7 mm, quartz) system (Fig. S1) at 700 °C and atmospheric pressure. Typically, 0.5 g catalyst, giving a catalyst-bed depth of ca. 1.5 cm, was heated in the reactor to 700 °C at a ramp rate of about  $22 °C min^{-1}$ . During this pretreatment, a gas mixture of CH<sub>4</sub>/Ar/He (9:1:10, v/v) was introduced into the reactor at 25 mL min<sup>-1</sup> to prereduce the catalyst but also rapidly remove adsorbed and/or produced water from the catalyst. As the temperature reached 700 °C, another gas mixture of 90 vol% CH<sub>4</sub> and 10 vol% Ar in place of the pretreatment gas mixture was introduced at 12.5 mL min<sup>-1</sup> into the reactor through a mass flow controller (Brooks 5850E) and the catalyst test started. All gases used in this test were UHP grade.

All reactants and products were analysed with two Agilent 5820 online gas chromatographs equipped with flame ionization (FID) and thermal conductivity (TCD) detectors, where argon added in reactant methane was used as an internal standard. Reactor outlet pipelines as well as gas sampling valves were kept above 160 °C to prevent condensation of aromatic products. CH<sub>4</sub> and higher hydrocarbon products, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>6</sub>H<sub>6</sub>, C<sub>7</sub>H<sub>8</sub>, and C<sub>10</sub>H<sub>8</sub>, were separated by a Porapak-P packed column, and then analysed using the FID. H<sub>2</sub>, Ar, CO, CH<sub>4</sub>, and CO<sub>2</sub> were separated by an activated carbon packed column, and then analysed using the TCD. Methane conversion and carbon-containing product selectivity/yield were calculated on a carbon number basis.

Disappearance rate of methane was calculated based on carbon balance, and was expressed as nmol/( $g_{cat.}$  s).

#### 2.3. Catalyst characterization

Nitrogen adsorption-desorption measurements of the parent and Mo-impregnated HZSM-5 zeolites at -196 °C were conducted using a Micromeritics automatic surface area and pore analyser (TriStar II 3020). Prior to the analysis, all the samples were outgassed under vacuum at 350 °C for 5 h. The specific surface area was evaluated using the Brunauer-Emmett-Teller (BET) method, while the external surface area, micropore surface area, and micropore volume were determined according to the *t*-plot method.

Temperature-programmed desorption of ammonia (NH<sub>3</sub>-TPD) was performed to determine the acidic properties of the parent and Momodified HZSM-5 zeolites. A 0.1 g sample was first activated at 550 °C for 40 min, and then cooled to 50 °C in helium. After exposure to a gas mixture of ammonia/helium (2:23, v/v) for 40 min at 50 °C, the sample was purged with pure helium at 100 °C for 1.0 h to remove the part of NH<sub>3</sub> physically adsorbed on the sample. The TPD measurements were conducted within a temperature range of 100–650 °C at a heating rate of 10 °C min<sup>-1</sup>. A thermal conductivity detector was used to monitor the amount of desorbed ammonia in the reactor effluent.

The Mo content of Mo/HZSM-5 sample was determined by ICP-AES (Optima 7300DV). The solutions for analysis were prepared by digesting ca. 0.25 g of the Mo-loaded sample, dried at 120 °C for 6 h, in a 10 mL concentrated nitric acid, followed by adding 15 mL concentrated hydrofluoric acid solution at 0 °C and then some deionized water up to 50 mL.

X-ray powder diffraction (XRD) patterns of the parent HZSM-5 zeolite and Mo/HZSM-5 catalysts were obtained on a diffractometer (ARL X'TRA) using Cu K $\alpha$  radiation at 40 mA and 40 kV. Powder diffractograms were recorded in the scanning angle (2 $\theta$ ) range of 5–70° at a scan rate of 5° min<sup>-1</sup>.

X-ray photoelectron spectroscopy (XPS) measurement was performed using a spectrometer (Thermo ESCALAB 250) equipped with a monochromatic Al K $\alpha$ X-ray source (1486.6 eV) operated at 15 kV and 150 W and a hemispherical energy analyzer. The base pressure inside the analysis chamber was  $1 \times 10^{-9}$  Torr. The XPS measurement was carried out at a detector take-off angle of 90°. The spectra were recorded with pass energy of 30 eV, X-ray spot size of 500  $\mu$ m, and step size of 0.05 eV. The Si 2p line at 103.4 eV was taken as a reference for binding energy calibration. Near-surface atomic concentrations of the Mo/HZSM-5 samples were calculated according to peak areas and sensitivity factors.

Diffuse reflectance UV-vis spectroscopy (UV-vis DRS) was used to assess Mo dispersion on Mo/HZSM-5 sample. UV-vis DRS spectra were recorded at room temperature on a Shimadzu DUV-3700 UV-vis spectrophotometer using BaSO<sub>4</sub> as standard.

Al magic-angle spinning nuclear magnetic resonance (<sup>27</sup>Al MAS NMR) was carried out using a Bruker AVANCE III 400 WB spectrometer at a magnetic field of 9.4 T and a H/X/Y CPMAS probe. The hydrated sample was packed in a 4 mm zirconia rotor. The MAS sample rotation speed was 15 kHz. The spectra were recorded at a resonance frequency of 104.3 MHz with a relaxation delay of 1 s and 2048 scans. External Al  $(H_2O)_6^{3+}$  with a chemical shift of 0 ppm was used as a reference.

### 3. Results

#### 3.1. CH<sub>4</sub> aromatization over NH<sub>3</sub>-basified 2-16 wt% Mo/HZSM-5

Table 1, and Figs. 1 and 2 show methane conversion and yield/ selectivity of hydrocarbon products in methane dehydro-aromatization at 700 °C and space velocity 1500 mL  $g^{-1}h^{-1}$  (90 vol% CH<sub>4</sub>/Ar) over Mo-impregnated HZSM-5 zeolite after pretreatment in a diluted CH<sub>4</sub> with 55 vol% Ar/He. In all cases, hydrocarbon products included

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#### Table 1

| 0                       |                                   |   |                    |          |          |          |             |                   |
|-------------------------|-----------------------------------|---|--------------------|----------|----------|----------|-------------|-------------------|
| Mo target loading (wt%) | CH <sub>4</sub> Conversion (mol%) | Disappearance rate of $CH_4$ (nmol/g <sub>cat.</sub> s) | Selectivity (%) of |          |          |          |             |                   |
|                         |                                   |   | $C_2H_4$           | $C_2H_6$ | $C_6H_6$ | $C_7H_8$ | $C_{10}H_8$ | Coke <sup>b</sup> |
| 2                       | 5.5                               | 928   | 11.2               | 2.9      | 44.1     | 3.2      | 10.8        | 27.8              |
| 2 (MA)                  | 8.7                               | 1455  | 5.7                | 2.1      | 61.6     | 4.1      | 11.0        | 15.5              |
| 6                       | 8.9                               | 1493  | 5.0                | 2.1      | 62.1     | 3.9      | 11.7        | 15.2              |
| 6 (MA)                  | 10.8                              | 1801  | 3.4                | 1.5      | 67.9     | 3.7      | 12.2        | 11.3              |
| 10                      | 10.1                              | 1682  | 3.5                | 1.8      | 67.4     | 3.9      | 12.1        | 11.3              |
| 10 (MA)                 | 11.8                              | 1979  | 2.3                | 1.3      | 70.7     | 3.5      | 12.9        | 9.3               |
| 10 (ZA)                 | 10.7                              | 1791  | 2.9                | 1.6      | 69.1     | 3.6      | 13.7        | 9.1               |
| 16                      | 11.4                              | 1905  | 2.8                | 1.5      | 71.9     | 3.7      | 10.5        | 9.6               |
| 16 (MA)                 | 11.6                              | 1935  | 2.5                | 1.4      | 70.3     | 3.5      | 12.8        | 9.5               |
|                         |                                   |   |                    |          |          |          |             |                   |

Catalytic activities of Mo/HZSM-5, Mo/HZSM-5(MA), and Mo/HZSM-5(ZA) samples with various Mo target loadings in methane aromatization at 700  $^{\circ}$ C and 1500 mL g<sup>-1</sup>h<sup>-1a</sup>.

<sup>a</sup> Data were recorded after 10 h of reaction time.

<sup>b</sup>  $S_{Coke} = 100\% - \Sigma S_i$  (*i*, carbon-containing product detected).

mainly benzene and naphthalene, and a small amount of toluene, ethylene and ethane (selectivity/yield ratio of  $C_2H_4/C_2H_6 > 1$ ). For conventional Mo/HZSM-5 sample, its catalytic activity and stability were enhanced with increasing the targeted loading of Mo from 2 to 16 wt%. Compared with the conventional Mo/HZSM-5, corresponding Mo/HZSM-5(MA), prepared by impregnating HZSM-5 zeolite with NH<sub>3</sub>-basified molybdate aqueous solution, provided higher CH<sub>4</sub> conversion and selectivity to aromatics, and lower selectivity to C<sub>2</sub>-hydrocarbon and selectivity/yield ratio of  $C_2H_4/C_2H_6$  (Table 1), and showed better catalytic stability in the aromatization of methane (Fig. 1). However, the enhanced effect of NH<sub>3</sub>-basification on the catalytic performance of the Mo catalyst gradually diminished with increasing the Mo target loading from 2 to 16 wt% (Fig. 2a).

The catalytic activities of Mo/HZSM-5(MA) samples during a 10-h test were shown in Fig. 1b. After 10 h of reaction, the 2 wt% Mo loaded catalyst gave a CH<sub>4</sub> conversion of 8.7%, an aromatic yield of 6.7%, and a C2-hydrocarbon yield of 0.7%. The selectivity/yield ratio of C2H4/ C<sub>2</sub>H<sub>6</sub> was 2.6. The CH<sub>4</sub> conversion and aromatic yield increased with an increase in Mo loading and reached maximum values of 11.8% and 10.3%, respectively, at the targeted Mo loading of 10 wt%. At the same time, C<sub>2</sub>-hydrocarbon yield and selectivity/yield ratio of C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> decreased to 0.4% and 1.8, respectively. By further increasing the targeted loading of Mo to 16 wt%, both CH<sub>4</sub> conversion and aromatic yield slightly decreased, while C2-hydrocarbon yield as well as selectivity/ vield ratio of  $C_2H_4/C_2H_6$  slightly increased. On the other hand, of those Mo/HZSM-5(MA) catalysts investigated, the 10 wt% Mo-impregnated sample exhibited the best catalytic stability in this aromatization reaction. After 38 h of continuous reaction at 700 °C and space velocity 1500 mL  $g^{-1}h^{-1}$ , this catalyst was still able to provide an aromatic yield of 7% and a CH<sub>4</sub> conversion of 9.1% (Fig. 2b). For comparison, the aromatization of methane over 10 wt% Mo/HZSM-5(ZA) catalyst, prepared by conventional impregnation of NH<sub>3</sub>-treated HZSM-5 zeolite with unbasified molybdate aqueous solution, was also investigated under the same reaction conditions. The result indicated that the ammonia treatment of the zeolite before the Mo-impregnating process could also improve the catalytic performance of the Mo sample, but its effect on this performance was weaker than that of ammonia basification of impregnating solution in catalyst preparation (Figs. 1 and 2a).

#### 3.2. Mo content and structure analyses of Mo/HZSM-5

For understanding of this novel catalytic performance of 10 wt% Mo/HZSM-5(MA), this work investigated physicochemical properties of those 10 wt% Mo/HZSM-5, prepared by various methods, and dispersion of Mo species on the support zeolite and interaction between them. For comparison, these features of conventional 6 wt% Mo/HZSM-5, the most widely studied catalyst, was also included. Mo content analyses (Fig. 3a) showed that difference between nominal and measured Mo

loading of the Mo-doped sample increased with increasing the targeted Mo loading value to 10 wt%, at which the difference between nominal and measured Mo loading of Mo/HZSM-5(MA) was, however, less than those of conventional Mo/HZSM-5 and Mo/HZSM-5(ZA), implying that there were more Mo species adsorbed or interacted with the zeolite on the Mo/HZSM-5(MA). XRD patterns of HZSM-5 zeolite and Mo/HZSM-5 catalysts prepared via different methods are presented in Figs. 3b and S2. All samples exhibited typical ZSM-5 zeolite structure. The zeolitic crystallinity of conventional Mo catalysts decreased with increasing Mo loading (Fig. S2a), indicating an interaction between Mo species and the zeolite. After NH<sub>3</sub> treatment/basification of the zeolite or the impregnating solution in catalyst preparation, further decrease in the zeolitic crystallinity of Mo/HZSM-5 was observed. Meanwhile, the intensities of peaks at low angles of 8 and 9° decreased significantly relative to those at angles of 22.5-25°, implying that there was a gradual transformation from orthorhombic to monoclinic symmetry in the zeolite entities [33,34]. Compared with Mo/HZSM-5(ZA), Mo/HZSM-5(MA) showed less symmetry transformation and better zeolitic crystallinity. On the other hand, orthorhombic  $\alpha$ -MoO<sub>3</sub> (2 $\theta$  = 12.7, 25.7, and 27.3°) (JCPDS 05-0508) crystallite was detected on all the Mo samples investigated. Among the 10 wt% Mo-impregnated HZSM-5 zeolites, Mo/HZSM-5(MA) prepared with ammonia-basified impregnating solution exhibited the weakest intensities of these signals of orthorhombic  $\alpha$ -MoO<sub>3</sub> (Fig. S2b and d).

The surface areas and porous textural properties of HZSM-5, conventional and ammonia-treated/basified Mo/HZSM-5 samples with Mo loadings of 6 and 10 wt% were measured by nitrogen adsorption (Fig. 4 and Table 2). The parent zeolite exhibited a type-I isotherm with a small identified hysteresis loop at high  $p/p_0 = 0.44-1.0$ , which was typical for microporous materials containing a small amount of meso and macropores with a broad pore-size distribution centered around approximately 80 nm (Figs. 4b and S3). Application of the t-plot method showed that 79% of the surface area of the zeolite was contributed by its micropores (Table 2). Introduction of 6 wt% Mo to the HZSM-5 zeolite via conventional impregnation led to losses in surface area (BET) and microporous volume, but increases in mesoporous volume and average pore size of the zeolite. The substantial increment of the external surface area and mesoporous volume of the Mo-doped sample demonstrated the dissolution of the framework and the formation of mesopores during the catalyst preparation, which was further confirmed by a clear exhibition of mesopore at ca. 18 nm in the BJH adsorption pore size distribution (Fig. 4b). Meanwhile, the decrement of microporous volume more than the increment of the mesoporous volume implied the migration of part of the loaded Mo species into the micropores of the zeolite. All the surface area and porous properties diminished with increasing Mo target loading from 6 to 10 wt%. The decreased volume of mesopores with increasing Mo loading implied that the migrated Mo species deposited in the mesopores in addition to



**Fig. 1.** Catalytic aromatization of methane at 700 °C and space velocity 1500 mL  $g^{-1}h^{-1}$  (90 vol% CH<sub>4</sub>/Ar) over (1) conventional, and (2) NH<sub>3</sub>-treated/basified Mo/HZSM-5 materials with various Mo target loadings: (a) CH<sub>4</sub> conversions, (b) aromatic yields, (c) C<sub>2</sub>-hydrocarbon yields, and (d) selectivity/yield ratios of C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>6</sub>.

the micropores of the zeolite.

At Mo target loading of 10 wt%, the BET surface area and average pore size of Mo/HZSM-5(MA) were similar to those of the conventionally prepared Mo/HZSM-5, while the micro and mesoporous volumes of Mo/HZSM-5(MA) were obviously less and more, respectively, than those of the conventional Mo/HZSM-5 (Table 2). Meanwhile, for Mo/HZSM-5(MA), the pore size distribution derived from the adsorption branch (Fig. 4b) clearly evidenced that the formed mesopores showed a broad distribution centered around ca. 18 nm (Fig. 4b). Compared with Mo/HZSM-5(MA), Mo/HZSM-5(ZA) exhibited



**Fig. 2.** Catalytic activities of conventional and NH<sub>3</sub>-treated/basified Mo/HZSM-5 materials with various Mo target loadings after methane aromatization for 10 h (a), and catalytic performance of 10 wt% Mo/HZSM-5(MA) material for methane aromatization (b). *Note*, reaction temperature, 700 °C; space velocity, 1500 mL g<sup>-1</sup> h<sup>-1</sup> (90 vol% CH<sub>4</sub>/Ar).

less BET surface area and microporous volume, and larger average pore size. In addition, the isotherms of the latter showed a small hysteresis loop at low  $p/p_0 = 0.03 - 0.35$  whose exhibition was attributed to presence of a large amount of extra-framework Al species, probably blocking micropores of the HZSM-5 zeolite [35,36].

#### 3.3. Dispersion of Mo species on HZSM-5

The near-surface compositions, which is mostly relevant to the external surface of the zeolite and perhaps the channels closest to it, of the parent and Mo-modified HZSM-5 zeolites were measured by means of XPS technique. The near-surface composition analyses (Fig. 5a and b) of conventional Mo/HZSM-5 samples showed that with increasing Mo loading to 10 wt%, there were an increase in surface Mo concentration and decreases in surface Si and Al concentrations, but the increment and decrement of them respectively gradually declined. Surface concentrations of Al and Si, as well as Al/Si ratio of the Mo-doped samples lower than those of the parent HZSM-5 confirmed that part of Mo species covered Si sites, and more preferentially, Al sites after catalyst preparation. At Mo target loading of 10 wt%, the surface Al concentrations of Mo/HZSM-5(MZ) and Mo/HZSM-5(ZA) sample were 0.64% and 0.74%, respectively, which were both higher than that of the conventional Mo/HZSM-5 one, demonstrating that ammonia-treatment of HZSM-5 or impregnating solution in the catalyst preparation could enhance the dealumination of the zeolite. Compared with Mo/HZSM-5

or Mo/HZSM-5(ZA), Mo/HZSM-5(MA) exhibited high surface Si concentration and low surface Mo concentration, consistent with the analyses of the XPS spectra in the Mo 3d (Fig. 5c) and O 1s regions (Fig. S4), implying less amount of Mo remained the external surface of the zeolite after the Mo-doped catalyst preparation.

The dispersion of molybdenum oxides on the Mo/HZSM-5 was further assessed by UV-vis spectroscopy. It was well known that the absorption bands between 200 and 400 nm of MoO<sub>3</sub> were attributed to  $O^{2-} \rightarrow Mo^{6+}$  charge transfer (CT) transitions. The CT bands in the range 220-250 nm and around 280 nm have been commonly assigned to tetrahedrally coordinated Mo-oxo species (MoO<sub>4</sub>) [32,37-39], while those at higher wavelengths of 300-330 nm to Mo-oxo centers in octahedral geometry (MoO<sub>6</sub>) [32,38-41]. Furthermore, while the tetrahedral Mo-oxo species with CT bands at low wavelengths of 220-250 nm was reported to be isolated monomeric [38,40,41], Jezlorowski and Knözinger suggested that the absorption at the band around 280 nm was possibly due to the formation of Mo-O-Mo containing structures [38]. In this case, all the UV-vis spectra of 6 wt% and 10 wt% Mo-impregnated HZSM-5 zeolites investigated contained bands at 230 (sharp) and 255 (broad) in addition to the band in the 300-330 nm range that might be assigned to octahedral Mo (Fig. 5d). Since intense absorbance at 230 nm was not observed in the spectra of both  $MoO_3/SiO_2$ , which exhibited three absorption bands at 220 (weak shoulder), 260 (main), and 320 nm, respectively, [42], and MoO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> with absorption bands at 240, 280-290, and 320 nm [32],the



Fig. 3. Mo contents (a), and XRD patterns (b) of fresh 6 wt% and 10 wt% Mo-impregnated HZSM-5 zeolites prepared by various methods.



Fig. 4. N<sub>2</sub> adsorption and desorption isotherms (a), and BJH adsorption pore size distributions (b) of parent HZSM-5 zeolite, and fresh 6 wt% and 10 wt% Mo-impregnated HZSM-5 zeolites prepared by various methods.

highly intensive band at this wavelength detected on Mo/HZSM-5 might be attributed to isolated tetrahedral Mo adsorbed on Si-O–Al of the support zeolite. The broadened band at ca. 255 nm could be further distinguished into two features, one at 250 nm and another at 260 nm. While the latter was assigned to tetrahedral Mo oxide species on zeolitic Si sites [42], the former with lower intensity than that at 230 nm might be assigned to tetrahedral Mo species on extra-framework alumina

nanoparticles [43] of Mo/HZSM-5 material.

At a high Si/Al ratio of 25, it was reported that the possibility to find two Brønsted acid sites with an adequate distance diminished and the formation of monomeric dihapto  $Mo(=O)_2^{2+}$  species located on the zeolitic framework became difficult [43]. Based on Raman spectra analyses and DFT calculations, Gao et al. [43] suggested this kind of isolated tetrahedral Mo be monomeric monohapto  $Mo(=O)_2(OH)^+$ species that anchored one framework Al atom via two oxygen bridges. Meanwhile, the existence of Al atoms as double anchoring sites in the arrangement Al-O-(Si-O)\_2-Al of HZSM-5 with Si/Al higher than 15 allowed the formation of dimeric  $Mo(=O)_2^{2+}$  species in the channels of the zeolite [43]. When the Si/Al ratio of the HZSM-5 zeolite reached 25 or 40, the  $Mo(=O)_2(OH)^+$  species anchored on single Al-atom sites became the dominant Mo dioxo species on the framework Al sites of the Mo/HZSM-5 catalyst [43].

In this study, the UV-vis spectra (Fig. 5d) showed that with increasing Mo loading from 6 to 10 wt% on the conventional Mo/HZSM-5 sample, the absorptions in the 245-260 nm and 300-330 nm ranges became more intensive, indicating that the formations of tetrahedral Mo species on Al or Si sites and octahedral Mo ones were both enhanced. At the Mo target loading of 10 wt%, the intensity exhibitions of those signals associated with Mo species depended on the preparation method of the Mo/HZSM-5 catalyst. Compared with the spectrum of the conventional Mo/HZSM-5, that of Mo/HZSM-5(ZA) contained slightly more intensive band at about 230 nm, and obviously less intensive ones above 255 nm, implying that pretreatment of HZM-5 zeolite with ammonia prior to impregnating process was unfavourable for the formations of octahedral Mo species. Among these 10 wt% Mo-doped samples investigated, the Mo/HZSM-5(MA) possessed the most amount of tetrahedrally coordinated Mo-oxo species, as reflected in both the enhancement of the intensities in the bands rang 245-265 nm, and the broadening in the signal around 230 nm, which indicated the coexistence of molvbdenum species on normal or distorted Si-O<sup>-</sup>-Al of the zeolite. After comparison of the distribution of Mo species measured by UV-vis with catalytic activity of Mo/HZSM-5, these tetrahedral Mo-oxo species were possibly the precursors of the active Mo phases for methane activation.

#### 3.4. Dealumination and surface acidic properties of Mo/HZSM-5

Modification of Mo and/or basic ammonia treatment will change the nature and environment of Al species of the HZSM-5 zeolite, most of which can be readily characterized with <sup>27</sup>Al MAS NMR measurement [44,45].As shown in Fig. 6a, the <sup>27</sup>Al NMR spectrum of the parent HZSM-5 zeolite contained a dominant feature at  $\delta = 55$  ppm ( $\delta$ , chemical shift) associated with four-coordinated framework Al (F-Al) atoms and a very small feature at  $\delta = 0$  ppm associated with octahedral extra-framework Al (EF-Al) species, such as  $[Al(OH)_n]^{3-n}$  and [Al (H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> [44]. For the conventional samples, a loading of 6 wt% Mo led to a decrease and broadening of the F-Al signal caused by the proximity of cationic Mo-oxo complexes that replace the protons [45],

Table 2

Surface areas and pore properties of the parent HZSM-5 zeolite, and conventional and NH3-treated/basified Mo/HZSM-5 samples with various Mo target loadings.

| Sample         | $S_{BET} (m^2/g)$ | $S_{\text{external}}^{a}(m^{2}/g)$ | S <sub>micropore</sub> <sup>a</sup> (m/g) | V <sub>total</sub> <sup>b</sup> (cm <sup>3</sup> /g) | V <sub>micropore</sub> <sup>a</sup> (cm <sup>3</sup> /g) | V <sub>mesopore</sub> <sup>c</sup> (cm <sup>3</sup> /g) | Pore size <sup>d</sup> (Å) |
|----------------|-------------------|------------------------------------|---|--|--|---|----------------------------|
| HZSM-5         | 309.4             | 65.6                               | 243.8                                     | 0.153 (PD < 693.1 Å)                                 | 0.113  | 0.040   | 19.75                      |
| 6 wt% Mo       | 277.8             | 98.7                               | 179.1                                     | 0.143 (PD < 708.7 Å)                                 | 0.083  | 0.060   | 20.57                      |
| 10 wt% Mo      | 265.2             | 96.7                               | 168.5                                     | 0.136 (PD < 652.1 Å)                                 | 0.078  | 0.058   | 20.45                      |
| 10 wt% Mo (ZA) | 219.2             | 86.0                               | 133.2                                     | 0.118 (PD < 678.1 Å)                                 | 0.062  | 0.056   | 21.50                      |
| 10 wt% Mo (MA) | 260.5             | 105.5                              | 155.0                                     | 0.134 (PD < 701.3 Å)                                 | 0.071  | 0.063   | 20.65                      |

Note, S, surface area; V, volume.

<sup>a</sup> Calculated by *t*-plot method.

<sup>b</sup> Single point adsorption total pore volume of pores at  $p/p^0 = 0.97$ ; PD, pore diameter.

<sup>c</sup>  $V_{\text{mesopore}} = V_{\text{ads,p/p0}} = 0.97 - V_{\text{micropore}}$ .

<sup>d</sup> Adsorption average pore width (4 V/A by BET).



Fig. 5. Near-surface atomic concentrations (a) and atomic ratios (b), XPS spectra in the Mo 3d region (c), and UV-vis spectra (d) of fresh 6 wt% and 10 wt% Moimpregnated HZSM-5 zeolites prepared by various methods.

and an increase in the intensity of the signal at  $\delta = 0$  ppm. The peak maximum of this resonance associated with F-Al gradually shifted to high field (around 54 ppm). When the targeted loading of Mo increased to 10 wt%, the main <sup>27</sup>Al signal at the chemical shift of about 54 ppm further broadened slightly, while its intensity was similar to that of the conventionally prepared 6 wt% Mo/HZSM-5 (Figs. 6a and S5). Rahman et al. [29] attributed the broadening of the main signal given by framework Al atoms due to increase in Mo loading from 6 to 10 wt% to the

exchange of protons and cationic Mo-oxo complex species. By curvefitting of the <sup>27</sup>Al NMR spectra (Fig. S6), a new band at  $\delta$  = 44.5 ppm, which was possibly associated with the formation of slightly distorted framework Al, could be distinguished from this broadened <sup>27</sup>Al signal of the 10 wt% Mo sample. At the same time, compared with the 6 wt% Mo sample, the 10 wt% Mo one possessed slightly more amount of EF-Al (Fig. S5), implying that extraction of framework Al by Mo species did not strengthen markedly. For Mo/HZSM-5, since zeolitic dealumination



Fig. 6. <sup>27</sup>Al MAS NMR spectra (a), and NH<sub>3</sub>-TPD profiles (b) of parent HZSM-5 zeolite, and fresh 6 wt% and 10 wt% Mo-impregnated HZSM-5 zeolites prepared by various methods.

was reported by multiple research groups as the key factor affecting the structure of the support, this result reasonably explained that the XRD patterns of the 6 and 10 wt% Mo-doped samples were similar (Figs. 3b and S2). Curve fitting analysis (Fig. S6) of this Al spectrum showed that ca. 10.6% of total Al detected was in the form of extra-framework entities. In addition, a weak shoulder at  $\delta = 30$  ppm associated with distorted four or five-coordinated Al species [27,33] became readily distinguished.

At the targeted loading of 10 wt% Mo, the intensity of the signal at  $\delta = 0$  ppm further increased after the HZSM-5 zeolite or impregnating solution was treated or basified with ammonia in the catalyst preparation process. Meanwhile, a new feature at a chemical shift of about -14 ppm due to EF-Al species in the form of Al<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> [44,45] were clearly observed. Compared with Mo/HZSM-5(ZA), Mo/HZSM-5(MA) exhibited obviously low contents of Al<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> and distorted Al species formed during the catalyst preparation. After curve fitting of the spectra (Fig. S6), quantitative analyses showed that the total concentrations of extra-framework Al on the Mo/HZSM-5(MA) and Mo/HZSM-5(ZA) catalysts were about 19.7% and 22.4%, respectively.

NH<sub>3</sub>-TPD is a usual tool used to measure the surface acidity of a pure or metal-modified zeolite. In this study, each NH<sub>3</sub>-TPD signal of parent and Mo-doped HZSM-5 zeolites might be deconvoluted into three distinct components (Fig. 6b). For the parent HZSM-5 zeolite, the features at 240 °C (40.6%), 360 °C (19.6%), and 460 °C (39.8%) were attributed to desorptions of chemisorbed NH3 on weak acid site, moderate acid site possibly associated with extra framework Al species, and Brønsted acid site, respectively [46]. With increasing Mo target loading from 6 to 10 wt%, both the amount and strength of surface Brønsted acid of the Mo/HZSM-5 catalyst decreased, as reflected in the reduction of intensity and desorption temperature of the signal at 460 °C of the NH<sub>3</sub>-TPD profiles (Fig. 6b). Ammonia treatment/basification of the HZSM-5 zeolite or impregnating solution in this Mo catalyst preparation process resulted in further decline in the properties of the acids including Brønsted ones. About 43%, 25%, and 21% of zeolitic surface Brønsted acid sites were remained on Mo/HZSM-5, Mo/HZSM-5(MA), and Mo/HZSM-5(ZA) catalysts with the targeted loading of 10 wt% Mo, respectively.

#### 4. Discussion

Two kinds of molybdate ions, monomolybdate (MoO<sub>4</sub><sup>2-</sup>) and polymolybdate ions (Mo<sub>7</sub>O<sub>24</sub><sup>6-</sup> and Mo<sub>8</sub>O<sub>26</sub><sup>4-</sup>), are reported in ammonium heptamolybdate (AHM) aqueous solution [47]. Their concentrations depend on the pH of the AHM solution. After mixing with HZSM-5 zeolite without ammonia basification, the pH value of AHM solution decreased from 6 to about 3. At this pH value, polymolybdate ions such as  $Mo_7O_{24}^{6-}$  were the predominant molybdate ones [47]. Owing to their large sizes, these Mo species distributed on the external surface after impregnation. It was reported that the acidity of the zeolite was not modified and relatively little Mo was present in the channels of ZSM-5 when the Mo-impregnated HZSM-5 material was treated at temperatures as high as 400 °C [48]. After calcination at 500 °C under air, N<sub>2</sub> adsorption measurement clearly demonstrated that part of Mo diffused into the zeolitic channels. Since dealumination was not severe, the diminished acidic property of the zeolite after Mo modification could be mainly attributed to Mo exchange with H<sup>+</sup> of Si-(OH)-Al due to the electronic attraction between the oxygen of MoO<sub>3</sub> and the H<sup>+</sup>. Further UV-vis measurement indicated that those exchanged Mo ions were dominantly present as a kind of tetrahedral Mo-oxo species, which was possibly in the form of  $[Mo(=O_2)(OH)]^+$  anchoring on zeolitic Brønsted acid site as suggested by Gao et al. [43] and Schwach et al. [4]. With increasing Mo loading from 6 to 10 wt%, UV-vis and NH<sub>3</sub>-TPD results showed more exchange of MoO<sub>3</sub> with the H<sup>+</sup> due to the increased concentration difference of Mo between the external and internal surfaces of the zeolite. However, owing to the strengthened electronic repulsion of oxygen atoms of the dispersing and exchanged

MoO<sub>3</sub>, more dispersion of MoO<sub>3</sub> became gradually difficult and the increment and decrements in the surface concentrations of Mo, Al, and Si respectively decreased. Since those exchanged Mo species inside the zeolite pores are reported to be the main precursors of active phases responsible for the activation of methane [2,4,23,49–51], this could reasonably explain the enhanced catalytic activity of Mo/HZSM-5 with suitably increasing Mo loading. On the other hand, although acid sites are needed for the conversion of intermediate ethylene to aromatics, excessive acidic sites would promote dehydrogenation of aromatic products to carbonaceous materials, which would deposit on the active sites. The increased dispersion of Mo species would gradually consume extra acid sites of the support and, hence, enhanced the catalytic stability of the Mo/HZSM-5 material.

For the conventional Mo-impregnated HZSM-5 zeolite, the recent work of the author's [30] indicated that the catalytic behaviors of Mo/ HZSM-5 with Mo loading higher than 10 wt% in methane aromatization were significantly improved after pretreatment of these Mo-based samples with a CH<sub>4</sub>/Ar/He (9:1:10, v/v) gas mixture; a Mo loading of 16 wt% was found to provide the best catalytic activity and stability for this aromatization reaction over Mo/HZSM-5 prepared via conventional impregnation and calcination at 500 °C. Similarly, Rahman et al. [29] reported that the catalytic performance of Mo/HZSM-5 with Mo loading of 10 or higher were remarkably better than those of Mo/ HZSM-5 with Mo loading of 6 wt% or lower in methane aromatization after this Mo-impregnated HZSM-5 zeolite was calcined at 500 °C, and was then pretreated with a CH<sub>4</sub>/H<sub>2</sub> gas mixture. Although the research group of Hensen gave obviously different results [52], their conclusion is not in contradiction to those of the author's [30] and Khatib's group [29] because the Mo/HZSM-5 samples tested by Hensen et al. were calcined at higher temperature (550 °C or higher) during the catalyst preparation, which would lead to a stronger interaction between Mo species and the support zeolite.

The result that catalytic performance of conventional Mo/HZSM-5 was enhanced with increasing Mo target loading to 16 wt% (Fig. 2a) implied the possibility of further improving the catalytic performance of the conventional Mo/HZSM-5 with Mo content less than 16 wt% via enhancing dispersion of Mo and/or declining Brønsted acid sites. In this case, although the dispersion of Mo species was not obviously improved on Mo/HZSM-5(ZA) sample, near-surface atomic concentration and <sup>27</sup>Al NMR measurement demonstrated that ammonia could extract zeolitic framework Al species to form external-framework Al entities. This dealumination was kinetically favourable for the formation of Al<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> with MoO<sub>3</sub> loaded on HZSM-5, which was confirmed by  $^{27}\mathrm{Al}$  NMR of Mo/HZSM-5 (Fig. 6a). The consumption of some  $\mathrm{MoO}_3$ loaded was probably responsible for the weakened intensities of these signals of orthorhombic  $\alpha$ -MoO<sub>3</sub> exhibited in the XRD pattern of Mo/ HZSM-5(ZA) (Fig. 3b). On the other hand, this dealumination led to an additional loss of Brønsted acid sites as well as an increase in the average pore size of the zeolite. For this Mo/HZSM-5(ZA) with Mo target loading of 10 wt% in methane aromatization, the loss of zeolitic Brønsted acid sites caused by ammonia-treatment of HZSM-5 zeolite was responsible for its improved stability, while the increase in the average pore size of the zeolite for the increased selectivity to heavier aromatic product naphthalene.

When the impregnating solution was basified by ammonia, the effect of  $NH_3$  on the surface structure of the Mo/HZSM-5 material became more complex. Under the basic condition,  $MOQ_4^{2-}$  in place of polymolybdate ions such as  $Mo_7O_{24}^{6-}$  became the predominant molybdate ion in the AHM solution [47], which might readily enter the channels of the zeolite due to its small size. After impregnation of the HZSM-5 zeolite with ammonia-basified AHM solution,  $NH_4^+$  would replace the H<sup>+</sup> of the zeolitic acid and be absorbed on the Brønsted acid site. Owing to the electronic attraction, the OH- and  $MOQ_4^{2-}$  trended to approach cationic ammonium ions including the ones absorbed on acidic sites to form loose ion-pairs, e. g.,  $NH_{4ad}^{+}$ ...OH- and  $NH_{4ad}^{+}$ ... $MOQ_4^{2-}$ ...NH<sub>4ad</sub> (or  $NH_{4dissociative}$ ) (Scheme 1). On the other hand,



Scheme 1. The effect of ammonia on the evolution of Mo species during the preparation of Mo/HZSM-5.

according to the NMR analysis (Fig. 6a), Mo/HZSM-5(MA) exhibited less zeolitic dealumination than Mo/HZSM-5(ZA). Since they were prepared using the same original chemicals,  $MOO_4^{2-}$ , formed in the NH<sub>3</sub>-basified AHM solution, should play an important role in diminishing the extraction of zeolitic framework Al of Mo/HZSM-5(MA). As shown in Scheme 1, due to the electronic repulsion between  $MOO_4^{2-}$ and OH-, the  $MOO_4^{2-}$  adsorbed on the  $NH_{4ad}^{+}$  might act as a check to prevent the dissociative OH- from approaching the Al-OH-Si and extracting the framework Al. The decrease in dealumination made it possible that more Brønsted acid sites were remained after impregnation, increasing exchange of the H<sup>+</sup> and Mo in the subsequent calcining process of Mo/HZSM-5(MA).

According to the analyses of ICP-AES and XPS, the Mo/HZSM-5(MA) possessed slightly more content of total Mo but remarkably less surface Mo and O concentrations than the conventional Mo/HZSM-5 and Mo/HZSM-5(ZA). The results combined with BJH adsorption pore size distribution (Fig. 4b) of the Mo catalyst implied that there was more Mo entering the channels of the support after the preparation of Mo/HZSM-5(MA), which originated from the adsorbed or dissociative  $MoO_4^{2-}$  in the zeolitic pores in the impregnating process. The adsorption measurement of perfluorotributyl amine showed that the Brønsted acid sites of the HZSM-5 zeolite were mostly located inside the zeolitic channels [24]. The spatial advantage of the Mo species in the zeolitic channels made them easier for their exchange with the proton of the Al-OH-Si. Thus, the increased amounts of Mo-oxo species in the pores of HZSM-5 and Al-OH-Si remained on the Mo/HZSM-5(MA) catalyst led to more exchanged Mo on Brønsted acid sites, the precursors of the active species, demonstrated by the UV-vis measurements, which was responsible for the enhancement in the catalytic activity of this ammonia-basified catalyst for methane activation. Meanwhile, the enhancement in Mo migration into zeolitic channels driven by NH<sub>3</sub>-basification partly counteracted the increment of the pore volume due to the framework corrosion by ammonia. This part counteracting led to the average pore size of Mo/HZSM-5(MA) slightly larger that of conventional Mo/HZSM-5, but obviously less than that of Mo/HZSM-5(ZA), and, consequently, the same evolutions in the selectivity to heavy naphthalene as well as selectivity ratio of benzene/ naphthalene observed over these shape-selective catalysts in methane aromatization. On the other hand, for Mo/HZSM-5(MA), more exchange of the proton with Mo and extraction of framework Al consumed the extra acid sites of the conventional Mo/HZSM-5 with Mo target loading of 10 wt% for methane aromatization and, consequently, the catalytic stability of the NH<sub>3</sub>-basified Mo sample was significantly improved in this aromatization reaction.

#### 5. Conclusions

After pretreatment with a mixture of CH<sub>4</sub>/Ar/He, (9:1:10, v/v), Mo/ HZSM-5 material with Mo target loading of 10 wt%, prepared by impregnation of HZSM-5 zeolite with NH<sub>3</sub>-basified molybdate aqueous solution, exhibited significantly enhanced activity and stability in catalysing methane to aromatic hydrocarbons in the absence of an added oxidant. After 38 h of continuous reaction at 700 °C and space velocity 1500 mL  $g^{-1}h^{-1}$  (90 vol% CH<sub>4</sub>/Ar), this catalyst was still able to give an aromatic yield of 7% and a methane conversion of 9.1%. This improved catalytic performance was attributed to a larger amount of highly dispersed Mo species in the zeolitic channels, and a less amount of Brønsted acid sites on Mo/HZSM-5, which were caused by the basification of impregnating solution with ammonia in catalyst preparation. Pretreatment with a diluted CH<sub>4</sub> with 55 vol% inert gases Ar/He prior to the reaction is helpful for this Mo-doped catalyst to exhibit its inherent catalytic behaviours via both prereduction of the catalyst with CH₄ and rapid removal of adsorbed/produced water from the catalyst. Up to now, much effort has been devoted to enhancing catalytic activity and stability of Mo/HZSM-5 material with Mo loading of 6 wt% or lower. This work shows a new and highly efficient pathway to improve the catalytic performance of Mo/HZSM-5 material for methane aromatization via increasing Mo loading to 10 wt%, and provides an insight into the effect of ammonia on the surface structure of Mo/HZSM-5 material.

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#### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcata.2019.05.011.

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