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Stable Mo/HZSM-5 methane dehydroaromatization catalysts optimized for high-temperature calcination-regeneration

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Abstract
Dehydroaromatization of methane is a promising reaction to directly convert methane into aromatics and hydrogen. The main drawback of this reaction is the rapid deactivation of the Mo/HZSM-5 catalyst due to coking. Regeneration at high reaction temperature by air calcination is not possible due to extensive dealumination of the zeolite. We investigated the structural and textural stability of HZSM-5 as a function of the Mo loading in air at high temperature (550–700 °C) and demonstrated that lowering the Mo loading below 2 wt% greatly improves the oxidative stability of Mo/HZSM-5. At low Mo loading (1–2 wt% Mo), Mo is predominantly in the zeolite micropores as cationic mono- and dinuclear Mo-oxo complexes irrespective of the calcination temperature. At higher loading, most of the initially aggregated Mo-oxide at the external surface is dispersed into the micropores upon calcination above 550 °C, resulting in reaction of mobile MoO 3 species with framework Al, aluminum molybdate formation and irreversible damage to the zeolite framework. A DFT-based free energy analysis indicates that water formation from reaction of MoO 3 with Brønsted acid sites and high concentration of Mo during MoO 3 migration causes aluminum molybdate formation. The high oxidative stability of Mo/HZSM-5 with low Mo loading makes them suitable candidates for a novel isothermal (700 °C) reaction – air regeneration protocol of methane dehydroaromatization. Whereas a 5 wt% Mo/HZSM-5 rapidly lost its initial activity, an optimized 2 wt% Mo/HZSM-5 catalyst retained more than 50% of its initial activity after 100 reaction-regeneration cycles (1 week) with a substantially improved total aromatics yield.

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1. Introduction
Abundant reserves of natural gas together with improved technologies of its production make it important to find efficient ways to convert methane to more valuable hydrocarbons such as liquid fuels and chemical building blocks. The commercial processes of natural gas conversion are indirect, involving reforming of methane into a syngas (mixture of CO and H 2 ) followed by, for instance, Fischer-Tropsch or methanol syntheses. The indirect route, however, is only economical at a large scale, which is hampering monetizing the abundant small- and middle-sized gas fields around the globe. Direct processes of methane conversion, applicable at smaller scale, would therefore be very attractive to the chemical industry [1–4].

Among few available alternative approaches to methane valorization [5–9], its dehydroaromatization (MDA) is one of the more promising ones, as it provides a means to directly convert natural gas into a mixture of valuable aromatic hydrocarbons (mainly benzene) and CO 2 -free hydrogen [10–12]. MDA is an endothermic reaction and, accordingly, it requires high temperatures in combination with selective catalysts to obtain sufficient yield of aromatics. The benchmark catalyst for this reaction is molybdenum supported on the proton form of 10-membered ring zeolites (such as HZSM-5 and H-MCM-22) [13]. This catalyst is usually prepared by dispersion of Mo(VI)-oxo compounds (MoO 3, (NH 4 ) 6Mo 7O 24 ) on the external surface of the zeolite and further high-temperature treatment to promote the migration of MoO 3 species inside the zeolite micropores, which results in their reaction with acidic protons releasing water and forming dispersed [MoO 2 ] 2+ monomers [14] and [Mo 2 O 7 ] 2-- dimers [15]. The nature of the dispersed MoO 3 species strongly depends on Mo loading and the zeolite Si/Al ratio [16]. At high Mo loading, some Mo will be inevitably present as large surface oxide aggregates [17]. Upon exposure of the catalyst to methane at relevant temperatures (650–800 °C) Mo(VI) is reduced to molybdenum (oxy)carbides (MoO xCy), which are located in the micropores and at the external surface [18]. Although the exact structure of these (oxy)carbides has not been resolved yet, it is widely accepted that they are the active sites
for the MDA reaction as follows from $^{95}$Mo MAS NMR [19], CH$_2$-TPSR [20,21], XPS [22], EXAFS [23], and more recently a combination of operando X-ray methods [24].

A typical composition of a promising catalyst for the MDA reaction is 5 wt% Mo on HZSM-5 with Si/Al ratios in the range of 15–40. Such material would allow converting approximately 10–12% of a methane feed to aromatics with a benzene selectivity of 60–80% with other products being naphthalene, toluene, ethylene and coke. Coke is a mixture of heavy carbonaceous deposits of graphitic nature, which block the zeolite micropores and the active MoO$_4$C$_x$ centers, thus leading to the inevitable decline in catalytic performance [25–27]. It is relatively high rate of deactivation of Mo/HZSM-5 catalysts in this reaction that hinders its commercialization. Effective catalyst regeneration is thus necessary to turn MDA into a commercially viable process. In the last two decades many studies have been devoted to developing regeneration protocols, which can be divided into reductive and oxidative approaches, i.e., hydrogenation of coke to methane or its combustion into carbon oxides and water [28–34]. A general finding is that the MoO$_3$–HZSM-5 composite is not stable under oxidative conditions at typical temperatures employed for the MDA reaction. Therefore, all reported air regeneration protocols include a cooling step to typically 500–550 °C for regeneration, followed by reheating to the reaction temperature before the reaction is restarted [35–37]. Such temperature cycling is time-consuming and inefficient in fixed-bed reactors and moving-bed reactors are considered a costly alternative. Recently we reported that it is possible to mitigate the deactivation of the 5%Mo/HZSM-5 catalyst at constant reaction temperature of 700 °C by supplying short pulses of oxygen to the methane feed [38]. Another approach would to develop a more stable catalyst that can be completely regenerated at reaction temperature. The main cause of catalyst deactivation during regeneration at high-temperature calcination is the collapse of the zeolite framework due to strong dealumination occurring when volatile MoO$_3$ reacts with tetrahedral Al atoms [39–43]. Methanation of coke is an approach that does not degrade the structure of the zeolite nor that of the Mo component [44], yet complete removal of coke requires substantial amounts of valuable hydrogen [45,46].

In this work, we characterize in detail the stability of Mo/HZSM-5 under oxidative conditions. We focus on the influence of the Mo content and characterize the structural and textural properties of Mo/HZSM-5 after calcination at 550 °C, 625 °C, and 700 °C. Combined with a thermodynamic analysis of the stability of different cationic Mo complexes and aluminum molybdate (the product of dealumination of the zeolite framework) based on quantum-chemical DFT calculations, we gain deeper understanding into the kinetic and thermodynamic stability of Mo/HZSM-5. The novel insight provided by the combined experimental and computational efforts is that at low Mo content the zeolite composite is much more stable during air calcination at 700 °C than at high Mo content. This opens the possibility to calcine the partially coked catalyst at reaction temperature and, in this way, to improve drastically the catalytic stability. Irreversible catalyst deactivation due to collapse of the framework is greatly suppressed, while short regenerative periods of air exposure are sufficient to completely remove carbonaceous deposits. This strategy holds great promise for the development of a scalable methane dehydroaromatization process based on in situ regeneration of the catalyst.

2. Experimental

2.1. Catalyst preparation

Mo-containing zeolite catalysts were prepared from HZSM-5 (Si/Al = 13, Süd-Chemie, now Clariant) by incipient wetness impregnation using an aqueous solution of ammonium heptamolybdate tetrahydrate ($\left(\text{NH}_4\right)_6\text{Mo}_7\text{O}_{24}\cdot\text{H}_2\text{O}$, Merck). The concentration was chosen such to arrive at Mo loadings in the 1–8 wt% range. The impregnated zeolites were dried overnight at 383 K and then calcined in air at 550 °C, 625 °C or 700 °C. For clarity, the obtained samples are designated as x%-y°C (e.g., 2%-700 °C stands for 2 wt% Mo on HZSM-5 calcined at 700 °C).

2.2. Characterization

Bulk chemical composition was analyzed by ICP-OES (inductively coupled plasma optical emission spectroscopy) by a Spectro CIROS CCD ICP spectrometer with axial plasma viewing. Prior measurements the samples were dissolved in an 1:1:1 (by weight) mixture of HF (40%):HNO$_3$ (60%):H$_2$O.

The surface of the materials was probed by X-ray photoelectron spectroscopy (XPS) using a Thermo Scientific K-alpha spectrometer equipped with a monochromatic Al Kα X-ray source and a 180° double-focusing hemispherical analyzer with a 128-channel detector. Spectra were obtained using an aluminum anode (Al Kα = 1486.6 eV) operating at 72 W with a spot size of 400 μm and pass energy of 200 eV.

The local environment of Mo in the oxidic precursor was investigated by UV-Vis spectroscopy in diffuse-reflectance mode using a Shimadzu UV-2401 PC spectrometer with BaSO$_4$ as the reference. The powder samples were packed in plastic sample holders and the spectra were recorded in the 150–600 nm range at a resolution of 1 nm$^{-1}$. All spectra of catalysts and reference compounds (Na$_2$MoO$_4$ (Aldrich), MoO$_3$ (Alfa Aesar), Al$_2$(MoO$_4$)$_3$ (Merck) and (NH$_4$)$_6$Mo$_7$O$_{24}$ (Merck)) were recorded at ambient conditions. The position of the absorption edge energy was determined by defining the intercept positions of $\left[F(R_\text{m}) \times h\nu\right]$ vs. $h\nu$ plot, where $F(R_\text{m})$ is the Kubelka-Munk function (see Fig. S1 and [47] for more details).

Chemical speciation of Al was determined by $^{27}$Al magic-angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy using an 11.7 T Bruker DMX500 NMR spectrometer with a Bruker 2.5-mm MAS probe head spinning at 25 kHz. Prior analysis the samples were hydrated overnight in desiccator containing water.

The acidity of the catalysts was characterized by FTIR spectroscopy. The spectra were recorded in the range of 4000–4000 cm$^{-1}$, using a Bruker Vertex 70v spectrometer. The samples were pressed to obtain self-supporting wafers (~10 mg/cm$^2$), which were placed in a controlled-atmosphere cell. After evacuation, the sample was kept at 550 °C for 2 h under vacuum to remove absorbed species. A background spectrum was measured at 150 °C in vacuum. Pyridine was dosed to the sample until saturation was reached. Spectra were then recorded after evacuation at 150 °C for 2 h.

XRD patterns were recorded using a Bruker D2 powder diffraction system. Cu Kα radiation with a scanning speed of 0.01 °/sec was used in a 2θ range of 5–60°. The relative crystallinity of samples (normalized to pristine HZSM-5) was evaluated by summing the area (area was used to reduce the effect of peak broadening) of (001) reflections at 23.1° (051), 23.3° (~501/501), 23.7° (~511/511), 24.0° (033) and 24.4° (~313/313).

SEM images were taken by a FEI Quanta 200F scanning electron microscope at an accelerating voltage of 3–5 keV using aluminum sample holders and without any coating.

Textural properties were analyzed by Ar physisorption, which was carried out at -186 °C using a Micromeritics ASAP-2020 apparatus. The samples were outgassed at 500 °C prior to the measurements. The microporous volume was determined by the t-plot method in a thickness range from 3.5 to 4.5 Å.

Thermogravimetric analysis was done on calcined and spent samples using a Mettler Toledo TGA/DSC 1 instrument. Approximately 25 mg of sample was placed in an alumina crucible and
heated to 1050 °C at a rate of 5 °C/min in a 33/67 (v/v) mixture of O2/He.

2.3. Catalytic activity measurements

The catalyst samples were tested for their activity in the aromatization of methane in a quartz reactor with an internal diameter of 4.0 mm and a length of 400 mm. An amount of 0.3 g catalyst was loaded as 0.25–0.5 mm particles, obtained by pelletizing, crushing and sieving the Mo-containing powder samples. Thermal mass flow controllers (Brooks) were used to supply the gasses into the feed stream. Reactions were performed at atmospheric pressure and 700 °C in a 30 ml/min flow of CH4/N2 95/5 (N2 used as an internal standard) for 16 h. The catalysts were heated to 700 °C at a ramp rate of 10 °C/min in a flow of CH4/N2. The products were analyzed using an online gas chromatograph (Interscience Compact GC) equipped with three separate columns and detectors. A thermal conductivity detector (TCD) coupled with a Molsieve 5 Å column was used to analyze light gases (H2, N2, CH4 and CO). Light hydrocarbons (ethane, ethylene) were analyzed with an RT-Q-BOND column equipped with another TCD, and higher hydrocarbons (benzene, toluene, naphthalene) were analyzed using a flame ionization detector with an Rtx-1 column.

3. Results and discussion

3.1. Catalyst characterization

Mo/HZSM-5 samples were prepared with a Mo metal content varying between 1 and 8 wt%. Molybdenum was loaded on zeolite ZSM-5 by impregnation with an aqueous solution of ammonium heptamolybdate followed by drying and calcination at 550 °C, 625 °C, or 700 °C. Before determining the stability of these samples in air at elevated temperature, we characterized their physico-chemical properties in detail. The nature and location of the Mo-oxide phase were investigated by XPS and UV-Vis spectroscopy. As XPS is sensitive only to the surface region of the zeolite crystals (several nm), it can be used to probe the diffusion of Mo-oxides into the micropores of the much larger HZSM-5 zeolite crystals. Based on the XPS-derived atomic Mo/Al ratios shown in Fig. 1a, the samples can be divided into two categories. At low Mo content (1–2 wt%), the Mo/Al ratio is relatively low and does not vary with the calcination temperature. Samples with higher Mo content contain, relatively speaking, much more Mo at the external surface. The calcination temperature affects the location of Mo much more pronouncedly in the high-loaded samples. Samples calcined at 550 °C and with a Mo loading higher than 2 wt% have a surface Mo/Al ratio between 5 and 6, showing that polymolybdates are present at the external surface of the zeolite particles. A Mo/Al ratio of ca. 6 corresponds to the Anderson ion ([Al(OH)6Mo6O18]3+), which has been previously observed on the surface of Mo/alumina [48] and Mo/HY at Mo loading above 3 wt% [49]. However, further characterization is necessary to establish whether Mo is present at the zeolite surface in this form. For these samples, the strong decrease in the Mo/Al ratio with increasing calcination temperature points to the dispersion of Mo-oxide into the zeolite micropores. We confirmed that calcination did not affect the bulk Mo content, that is to say, no sublimation took place, even not during heating in air at 700 °C for 6 h (Table S1). The low and constant Mo/Al ratios observed for the 1 wt% and 2 wt% samples indicate that most of the Mo is already highly dispersed in the micropores after 550 °C calculation.

We then measured the bandgap of the Mo-oxide phase in these samples by UV-Vis spectroscopy. It is well known that the bandgap is sensitive to the local environment of Mo in Mo-oxide, i.e., the bandgap energy is inversely proportional to the number of neighboring Mo atoms [50,51]. Thus, it is possible to obtain information about the nature of MoOx species by comparing the bandgap energies of Mo/HZSM-5 catalysts and reference compounds. For comparison, the bandgaps of a number of reference Mo-oxide compounds were measured. As Fig. 1b demonstrates, we found that Mo/HZSM-5 samples with low Mo content contain predominantly monomeric MoO3 species, as the bandgap is close to that of Na2MoO4 (no Mo-O-Mo bonds). The Mo phase in zeolites containing more Mo (>2 wt%), which was calcined at 550 °C, has a higher agglomeration degree. The number of Mo-O-Mo bonds is close to that in (NH4)6Mo7O24. For the samples of intermediate Mo content (3.3 wt% and 5.5 wt%), there is only a small effect of the calcination temperature on the dispersion. On contrary, calculation at 625 °C and 700 °C strongly increases the bandgap of the two samples with 6.8 wt% and 8 wt% Mo. The resulting bandgap energies are significantly lower than that of Na2MoO4 and correspond much better to that of Al2( MoO4)3. The formation of this compound will be confirmed next by 27Al NMR spectroscopy.

It is well established that acidic protons play an important role in the interaction of Mo-oxides with the zeolite surface [52,53]. Mo-oxides can react with the protons to form cationic Mo-oxo complexes, which compensate the negative framework charge. Such interactions can also lead to removal of tetrahedral Al from the framework, giving rise to Al2( MoO4)3 formation. We investigated the interaction between Mo and the zeolite framework in more detail by 27Al (MQ)MAS NMR spectroscopy. The 27Al MAS NMR results (Fig. 2a) show that, upon introduction of Mo, the signal corresponding to framework Al (~55 ppm) decreases in intensity and significantly broadens due to quadrupolar effects.

Fig. 1. Dispersion of MoOx species as determined by (a) determining of the surface Mo/Al atomic ratios (dashes correspond to the bulk Mo/Al ratio derived form ICP) by XPS and (b) adsorption-edge energy values derived from UV-Vis DRS (Fig. S1 demonstrates the principle of obtaining these values).
Framework dealumination becomes more pronounced with increasing Mo content and higher calcination temperature (Fig. 2b). Thus, the 8%-700 °C sample hardly contains framework Al. Aside from the presence of extraframework Al in octahedral coordination (−0 ppm), two signals at −14 and 14 ppm are observed to be assigned to well-dispersed and bulk Al₂(MoO₄)₃ species, respectively [54–58]. However, a signal at 14 ppm might be also partially due to surface Al₂O₃ and Anderson entities [49]. The signals due to extraframework Al and Al₂(MoO₄)₃ grow with increasing Mo content and higher calcination temperature. Thus, addition of Mo leads to framework dealumination and induces formation of extraframework aluminum.

Quadrupolar line broadening can be decreased by carrying out ²⁷Al MQMAS measurements (Fig. 2c–f) [59]. The increased resolution allows resolving the extraframework Al species at about 0 ppm in the 8%-700 °C sample into two distinct Al species. We surmise that a new slightly lower field (2 ppm) signal detected in the severely dealuminated 8%-700 °C sample is related to extracted Al species in octahedral coordination bridged to both Si and Mo. Neither the parent HZSM-5 nor 1%-550 °C sample contains framework Al. Aside from the presence of extraframework Al in octahedral coordination (−0 ppm), two signals at 14 and 14 ppm are observed to be assigned to well-dispersed and bulk Al₂(MoO₄)₃ species, respectively [54–58]. However, a signal at 14 ppm might be also partially due to surface Al₂O₃ and Anderson entities [49]. The signals due to extraframework Al and Al₂(MoO₄)₃ grow with increasing Mo content and higher calcination temperature. Thus, addition of Mo leads to framework dealumination and induces formation of extraframework aluminum.

We used FTIR spectroscopy of adsorbed pyridine in order to follow acidity changes upon interaction of Mo-oxides with the zeolite framework. The Brønsted acid site density is given in Fig. 3a (FTIR spectra in Fig. S2 and Lewis acidity in Table S1). These data show that about a third of the acid sites reacted with Mo species in the 1%-550 °C sample. For the samples calcined at 550 °C, it is seen that the acidity decreases only slightly with increasing Mo content. The much stronger decrease in the acidity for higher calcination temperature indicates the migration of Mo-oxide into the zeolite micropores, which is in accordance with the NMR results. The changes are more pronounced for samples with higher Mo content.

XRD patterns of these samples (Fig. S3) show that air calcination results in a decrease in the zeolite crystallinity (Fig. 3b). The extent of amorphization trends in a similar manner with the Mo content and calcination temperature as does the measured acidity and framework Al content. The crystallinity of the samples with 1 wt% and 2 wt% Mo was hardly affected by calcination, even at the highest calcination temperature. Moreover, at all temperatures the crystallinity decreases when the sample contains more Mo. High calcination temperature results in more severe damage to the framework. We further investigated the texture and morphology of these samples by Ar physisorption and SEM. Expectedly, the damage to the zeolite framework leads to a proportional reduction in microporous volume (Figs. 3c and S4 and Table S1). Furthermore, the damage to the crystal was also visible by SEM. In comparison with the smooth surfaces of highly crystalline parent HZSM-5 and 6.8%-550 °C samples (Fig. 3d and e), the crystals of 6.8%-700 °C (Fig. 3f) are full of pinholes, cracks and other defects.

We then investigated the thermal stability of the Mo/HZSM-5 samples by thermogravimetric analysis (TGA). The volatility of MoO₃ allows direct probing the Mo-support interaction strength by thermogravimetry [60]. Fig. 4a shows mass changes of the samples during heating to 1050 °C. Most strikingly, the samples with 1 and 2 wt% are stable and only above 1000 °C a small weight loss is recorded. On contrary, the two samples with the highest Mo content already show a small weight loss at 700 °C (which corresponds to water evolved upon interaction of MoO₃ with the Brønsted acid sites), while MoO₃ sublimes between 800 and 900 °C. The weight loss of the samples with intermediate Mo content occurs in the same temperature range. This rather high sublimation temperature corresponds well to the sublimation temperature of MoO₃ from aluminum molybdate (−800 °C, Fig. S5), while pure MoO₃ sublimes at lower temperature (−700 °C). The latter statement is supported by a TGA experiment with MoO₃/SiO₂ (Fig. S5).

The TGA results are consistent with the formation of aluminum molybdate during calcination. That is to say, there is hardly sublimation of MoO₃, presumably due to the relatively stronger interaction of Mo-oxides with the zeolite than with silica, and instead Mo-oxides first induce dealumination of the zeolite followed by decomposition of the formed Al₂(MoO₄)₃ into MoO₃ which then sublimes at high temperature. Fig. 4b shows the correlation
between the relative fraction of Mo sublimed at 1050 °C and the initial Mo content of the sample. Evidently, the tendency for sublimation strongly relates to the Mo content of Mo/HZSM-5. The weight loss of the 1 wt% Mo/HZSM-5 is negligible, while nearly all Mo is lost from the 8 wt% Mo/HZSM-5 sample.

To gain insight into the structure of MoO$_3$-HZSM-5 at elevated temperature, we carried out density functional theory calculations, using periodic models of the ZSM-5, containing different Mo species. The unit cell of our model contained two tetrahedral Al sites placed in a –Al–O–Si–O–Si–O–Al– arrangement in the 10-membered ring of the straight channel of ZSM-5. The negative framework charge is compensated by protons (2H/2Al/Zeo). The Si/Al ratio of the resulting framework was 47. Although this is higher than that of the used zeolite, we can consider such exchange sites as suitable models for the diluted cation-exchange sites in high-silica ZSM-5. We considered cationic two mononuclear and one binuclear Mo complexes, resulting from the interaction of MoO$_3$ with ZSM-5:

$$\text{MoO}_3 + 2\text{H}/2\text{Al}/\text{Zeo} \rightarrow [\text{MoO}_2]^{2+}/2\text{Al}/\text{Zeo} + \text{H}_2\text{O} \quad (1)$$

$$\text{MoO}_4 + 2\text{H}/2\text{Al}/\text{Zeo} \rightarrow [\text{MoO}_2\text{OH}]^{+}/2\text{Al}/\text{H}/\text{Zeo} \quad (2)$$

$$\text{MoO}_4 + 2\text{H}/2\text{Al}/\text{Zeo} \rightarrow 1/2[\text{Mo}_2\text{O}_5]^{2+}/2\text{Al}/\text{Zeo} + 1/2\text{H}_2\text{O} \quad (3)$$

The two monomeric cationic complexes were also considered by Gao et al. [14] Another possibility is that Al$_2$(MoO$_4$)$_3$ is formed by the reaction of framework Al with MoO$_3$. This leads to partial...
collapse of the framework. To model this situation, we assumed that part of the zeolite gives rise to silica formation following the reaction stoichiometry:

\[
\text{MoO}_3 + 2\text{H}_2\text{O} \rightarrow \frac{1}{3}\text{Al}_2(\text{MoO}_4)_3 + 1\text{SiO}_2
\]

\[
+ 2\text{H}_2\text{O} \rightarrow \text{Al}_2(\text{MoO}_4)_3 + \frac{1}{3}\text{H}_2\text{O}
\]

(4)

To properly determine the stability of the various Mo-containing species at finite temperature and pressure, we make use of the ab initio thermodynamics approach [61,62]. For this purpose, we compute the corresponding reaction Gibbs free energy \(\Delta G(T, p)\) for these four reactions:

\[
\Delta G_{\text{ii}}(T, p) = C_{\text{MoO}_3}^{2-}/\text{zeo} - C_{\text{MoO}_3}^{2-}/\text{zinc} - C_{\text{MoO}_3}^6/\text{H}_2\text{O} + \mu_{\text{H}_2\text{O}}^g
\]

\[
\Delta G_{\text{iii}}(T, p) = \frac{1}{2} C_{\text{MoO}_3}^{2-}/\text{zeo} - \frac{1}{2} C_{\text{MoO}_3}^{2-}/\text{zinc} - C_{\text{MoO}_3}^6/\text{H}_2\text{O} + \frac{1}{2} \mu_{\text{H}_2\text{O}}^g
\]

\[
\Delta G_{\text{iv}}(T, p) = C_{\text{MoO}_3}^{3+}/\text{zeo} - C_{\text{MoO}_3}^{2+}/\text{zinc} - C_{\text{MoO}_3}^{3+}/\text{H}_2\text{O} - C_{\text{MoO}_3}^6/\text{H}_2\text{O} + \frac{1}{3} \mu_{\text{H}_2\text{O}}^g
\]

In this analysis we neglected vibrational and PV contributions of solids and, henceforth, approximated their free energies by their electronic energies obtained by DFT. The chemical potential of solids and, henceforth, approximated their free energies by their isotope exchange by Iglesia and co-workers [63]. For this purpose, we compute the corresponding reaction Gibbs free energy of mononuclear and binuclear Mo species in Mo/HZSM-5 and aluminum molybdate (Eqs. (1)–(4), corresponding to the reactions of a–d) as a function of water chemical potential \(\Delta \mu_{\text{H}_2\text{O}}\). The chemical potential of water is further converted to water partial pressures at different temperatures (axis on the top).

**Fig. 5.** The reaction Gibbs free energy of mononuclear and binuclear Mo species in Mo/HZSM-5 and aluminum molybdate (Eqs. (1)–(4), corresponding to the reactions of a–d) as a function of water chemical potential \(\Delta \mu_{\text{H}_2\text{O}}\). The chemical potential of water is further converted to water partial pressures at different temperatures (axis on the top).

The catalytic performance of the Mo/HZSM-5 samples in the dehydroaromatization of methane was evaluated next. The samples showed the typical time-on-stream behavior of Mo/HZSM-5 with increasing aromatics yield in the first hour followed by slow decrease in the methane conversion and the benzene yield (see Figs. S6 and S7). The cumulative product yields during 16 h reaction are presented in Fig. 7. In all cases benzene is the main product followed by naphthalene and coke. For catalysts calcined at 550 °C the optimal Mo content with respect to benzene yield is 5.5%, which is in good agreement with the preferred Mo loading in many other reports [64–66]. The way that calcination temperature affects catalytic performance depends strongly on the Mo content. Catalysts with more than 2 wt% Mo display lower catalytic performance when the calcination temperature was raised. The higher the Mo content and the higher the calcination temperature, the stronger the observed decrease in performance is (Fig. S8). On
contrary, catalysts with 1 wt% and 2 wt% Mo content exhibit nearly unchanged performance in terms of conversion of methane and product selectivity with respect to calcination temperature. The present results indicate that damage to the zeolite framework (dealumination, $\text{Al}_2(\text{MoO}_4)_3$ formation) caused by high temperature calcination is the main reason for the decline in catalytic performance. On the other hand, samples with 1 wt% and 2 wt% Mo remain stable upon high-temperature calcination, which opens the possibility to use air calcination at reaction temperature to regenerate the catalyst by burning coke deposits. We optimized such an isothermal reaction-regeneration protocol at $700^\circ\text{C}$ and found that reaction for 60 min in methane, followed by a regeneration step in air for 22 min with intermediate He flushing for 3 min to avoid direct contact between methane and air (Fig. S9) significantly improves the long-term performance of the low-Mo-content Mo/HZSM-5.

![Fig. 6. Schematic representation of interactions in the MoO$_3$-HZSM-5 composite catalysts. Although only monomeric [MoO]$^{2+}$ species is shown on the scheme, the actual dispersed species are both monomeric and dimeric [Mo$_2$O$_5$]$^{2+}$.](image6)

![Fig. 7. Cumulative product yields obtained during the MDA tests of Mo/HZSM-5 catalysts pre-calcined at (right to left) 550 °C, 625 °C, 700 °C. Conditions: 700 °C, atmospheric pressure, 0.3 g of catalyst, WHSV 2.0 h$^{-1}$, 16 h.](image7)

was found sufficient to remove all coke molecules from the catalysts during every cycle (Fig. S11).

To gain insight into the changes in the catalyst upon cyclic operation, we used XRD (Fig. 9a), $^{27}$Al NMR spectroscopy (Fig. 9b) and Ar physisorption (Fig. 9c) to follow structural and textural properties. Clearly, the cause of the rapid loss in activity of the 5%-550 °C sample is the degradation of the zeolite structure as can be appreciated from the XRD pattern of the spent catalyst. Besides, the much lower Ar uptake at low pressure and loss of framework Al signify the collapse of the microporous zeolite framework. On contrary, these changes are much less pronounced for the spent 1%-550 °C and 2%-550 °C samples. Structural degradation as probed by XRD is minor, while the decrease in micropore volume is small for 2%-550 °C and nearly negligible for 1%-550 °C. Nonetheless, it appears that the framework dealumination of the samples cannot be completely avoided.

We suspect that the formation of water during coke oxidation contributes to dealumination of the Mo/HZSM-5 catalysts at low Mo content. As it is known that zeolites with higher Si/Al ratio are more (hydro)thermally stable [67], we anticipated that increasing the Si/Al ratio of Mo/HZSM-5 may be a good strategy to further improve the stability during the reaction-regeneration cycling. Thus, three catalysts containing 1 wt%, 2 wt% and 5 wt% Mo on HZSM-5 with Si/Al = 30 were prepared and subjected to the same isothermal reaction-regeneration procedure. Fig. 10 confirms that
these catalysts are much more stable than their counterparts prepared at Si/Al = 13, yet follow the same trend with respect to Mo loading. Fig. 10b emphasizes that in the first 10 h the catalytic activity is completely stable. Optimum performance is obtained with the 2 wt% Mo/HZSM-5 sample which retained as much as half of its original activity after 1 week (100 reaction-regeneration cycles). These results emphasize that our approach is valid for the typical range of Si/Al ratios relevant to ZSM-5 based MDA catalysts (Si/Al = 15–25) [16].

4. Conclusions

A systematic investigation shows that the Mo loading is the key parameter in determining structural and textural stability of Mo/HZSM-5 at high temperature in air. It is demonstrated that the stability strongly decreases with Mo loading and calcination temperature. At low Mo loading (1–2 wt % Mo), most of the Mo species are dispersed in the zeolite micropores as cationic mono- and dinuclear Mo-oxo complexes (i.e., $\text{[MoO}_2\text{]}^{2+}$ and $\text{[Mo}_2\text{O}_5\text{]}^{2+}$).
irrespective of the calcination temperature. At higher loading, most of the Mo is present in aggregated form at the external surface after calcination at 550 °C. Oxidative treatment of MoO₃-HZSM-5 composites above 550 °C causes extensive reaction of mobile MoO₃ species with framework Al, which results in aluminum molybdate and irreversible damage to the zeolite framework. A free energy analysis on the basis of DFT-computed stabilities suggests that water formation originating from reaction of MoO₃ with Bronsted acid sites and high concentration of Mo during MoO₃ migration are responsible for extensive deactivation at higher Mo loading. Although the Mo/HZSM-5 samples with low Mo loading exhibit slightly lower initial activity, they are much more stable and are thus candidates for in situ regeneration of spent catalysts by coke burn-off at high temperature. Based on these insights, we have developed a novel isothermal (700 °C) reaction – air regeneration protocol, which was effective in yielding much more aromatics from methane using catalysts with low Mo loading. An optimized Mo/HZSM-5 catalyst retained more than 50% of its initial activity after 100 reaction-regeneration cycles (1 week on stream).

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2016.12.006.

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