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Quantifying the impact of dispersion, acidity and porosity of Mo/HZSM-5 on the performance in methane dehydroaromatization

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ABSTRACT

The catalytic performance of the bifunctional catalyst Mo/HZSM-5 for methane dehydroaromatization (MDA) depends on the Mo dispersion and on zeolite acidity. Here we separately quantify the effect of dispersion and the effect of acidity on aromatic yields and coke selectivity. Also, the effect of porosity on the same is quantitatively assessed. For that, a suite of 17 samples with varying Mo dispersion were synthesized by means of several methods, including chemical vapor deposition with MoCl\textsubscript{5}, MoO\textsubscript{2}Cl\textsubscript{2} and Mo(CO)\textsubscript{6} as precursors and the conventional methods, incipient wetness impregnation and solid ion exchange. These catalysts were characterized by pyridine IR-spectroscopy, XPS, UV–vis spectroscopy, N\textsubscript{2} adsorption, XRD, TGA and \textsuperscript{27}Al MAS NMR. The combined results yielded a measure of how much Mo is anchored to the zeolite as well-defined cationic species and how much is present as bigger clusters on the outer surface of the zeolite. Through relating these characterization results to the catalytic behavior of the catalysts, it was found that the maximum instantaneous benzene and naphthalene yields as well as the integral selectivities during methane dehydroaromatization linearly increase with the amount of Mo present as mono- or dimeric species. At the same time, the selectivity to coke increases with the amount of Mo present as bigger clusters or nanoparticles on the outer surface of the zeolite. The number of Mo cationic sites is the most important factor determining the activity of Mo/HZSM-5 for low loadings of Mo. But at higher loadings, the high rate of aromatics formation requires an easily accessible pore structure as well.

1. Introduction

Converting methane to aromatics, an important building block of many consumer goods and pharmaceuticals, is desirable because this small and very stable hydrocarbon is highly available [1]. For valorizing methane, steam reforming combined with Fischer-Tropsch synthesis is one of the indirect routes already applied industrially. However, there is great commercial interest in directly converting methane to aromatics, an important building block of many consumer goods and pharmaceuticals. A process that can achieve this without the addition of oxidants is preferred, as the production of CO and CO\textsubscript{2} can be avoided and carbon efficiency is superior in that case. Thermodynamically, however, the direct non-oxidative conversion of methane to benzene is limited, with values for \(\Delta G^\circ = +104 \text{ kcal mol}^{-1}\) and \(\Delta H^\circ = +127 \text{ kcal mol}^{-1}\) [2–4]. Thus, considerable conversion of methane and yields of benzene (7.8–21.5 mol\%\textsuperscript{a}) can only be achieved at high temperature, practically between 923 and 1073 K, while coke formation is much less limited at these temperatures. This usually leads to fast deactivation of the catalyst. Catalyst deactivation and regeneration is the biggest concern when designing a catalyst for the methane dehydroaromatization (MDA) reaction. The best performing catalysts for this system, Mo/HZSM-5 and Mo/MCM-22 [5–9] almost reach the thermodynamic limit in the beginning of the reaction operation, but their activity immediately decreases once it reached its maximum [2,3].

The most important aspects that were found to influence catalytic activity and stability were Mo dispersion, acidity [10–14] and porosity [15,16] of the zeolite support. The catalyst is believed to be most active when Mo is anchored to the framework Al inside the pores of the zeolite via oxygen bridges, (partially) replacing the proton of the Brunsted acid site (BAS) [17–19]. Mo was found to be either mono- [17] or dimeric...

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2. Experimental

2.1. Catalyst synthesis

Mo was introduced into the H-form of a commercial HZSM-5 zeolite (PQCorporation, CBV 5020E) with Si/Al = 24 (denoted HZ) using IWI, SIE or CVD. Samples are denoted as yMoHZ-x, where y denotes the Mo/Al ratio and x the synthesis method. Catalysts were prepared with Mo/Al = 0.3 and 1. If a precursor other than MoCl₅ is used for the synthesis, this is specifically indicated. The synthesis methods are described in detail in the Supplementary information.

2.2. Catalyst characterization

Pyridine transmission FTIR spectroscopy was performed on a Nicolet 6700 spectrometer with a MCT/B detector. A 10 mm wafer using 50 mg sample is pressed using 4.29 bar. The sample was first activated in vacuum at 400 °C for 16 h to remove adsorbed species. After activation, the pyridine gas was fed to the pellets until saturated and further evacuated at 160 °C for 2 h. Spectra were recorded in 1000–4000 cm⁻¹ range at 4 cm⁻¹ resolution and co-addition of 128 scans. The spectra shown represent the subtraction result of the spectra collected before adsorption of pyridine from the one taken afterwards. All spectra were normalized by the framework absorbance at 1873 cm⁻¹. The decrease in peak area characteristic for Brønsted acidity (BAS) at 1455 cm⁻¹ is expressed by Eq. (1), where A represents the area of the absorbance with a certain vibration of either the catalyst containing Mo or the bare zeolite.

\[
\begin{align*}
\frac{\text{Mo} / \text{Al})_{\text{Py}}}{\text{FTIR}} &= 1 - \left( \frac{A_{1455 \text{cm}^{-1}, \text{sample}}}{A_{1455 \text{cm}^{-1}, \text{bare zeolite}}} \right) \quad (1) \\
\frac{\text{Mo} / \text{Al})_{\text{Py}}}{\text{FTIR}} &= \text{a measure for how many BAS protons got replaced by Mo.}
\end{align*}
\]

The UV–vis diffuse reflectance spectra (UV–vis-DRS) were collected on a Perkin–Elmer Lambda 900 spectrophotometer equipped with an integrating sphere ("LabSphere") in the 200–800 nm range. The bare zeolite was used as a white standard. Before measurement, the samples were degassed at 400 °C under dynamic vacuum for 12 h and then transferred to the sample holders in the glovebox. The absorption intensity is expressed by the Schuster-Kubelka-Munk equation (Eq. (3)).

\[
F(R_m) = (1 - R_m)^2 / 2R_m 
\]

The edge energy (Eg) was determined by fitting a straight line to \((F(R_m)hv)^2\) plotted against the incident photon energy hv in the low energy rise region [27].

Chemical composition of the samples in terms of Mo, and Al content was measured by digestion of approximately 50 mg sample in 4.5 ml 30% HCl + 1.5 ml 65% HNO₃ + 0.2 ml 40% HF using a microwave. The digestion time in the microwave was 60 min at 1000 W for 8 samples and 1300 W for 14 samples. After digestion, the samples were diluted to 50 ml with MQ and analysed with ICP-OES on a PerkinElmer Optima 5300 (torch:Si + saffire injector). For Na a PerkinElmer AAS Modell AAAnalyt was used.

X-ray photoelectron spectroscopy (XPS) analysis was performed in order to identify any agglomeration of Mo on the zeolite surface. A Thermo Scientific K-alpha spectrometer equipped with a monochromatic Al Ka X-ray source and a 180° double-focusing hemispherical analyzer with a 128-2 channel detector was used. Measurements were performed at ambient temperature and chamber pressure of about 10⁻⁸
mb. The spot size was 400 mm. A flood gun was always used for charge compensation. The spectra were analyzed and processed by using Thermo Advantage v5.903 software (Thermo Fisher Scientific). Smart background (derived from the Shirley background) was used over the peak width. (Mo/Al)XPS was determined by quantifying the amount of Mo and Al from the XPS measurement as an average of two measurement points.

**Catalytic testing** was performed in a quartz reactor tube with an inner diameter of 6 mm, using 500 mg catalyst pelletized and sieved to 212–355 μm. A weight hourly space velocity (WHSV) of 1.21 h⁻¹ was used for CVD, while MoO₃ and MoCl₅ were used for SIE and IWI. Three different precursors, MoCl₅, MoO₃, and Mo(OH)₂ were used for CVD, while MoO₃ and MoCl₅ were tested for SIE and AHM for IWI. A detailed description and discussion of the methods perform, because it is hard to disperse Mo at the limit of how much Mo can be anchored inside the pores. The reactor was brought to reaction temperature under the same flow with a heating rate of 10 °C/min. Product yields were calculated according to Eq. (4), where \( j \) denotes the molar flow of molecule \( n \), the number of carbons and \( y \) the number of hydrogens in a product molecule. The integral over the whole time on stream (TOS) is plotted against the ratio, the integrated peak area from the peak width.

Sampled spent catalysts were analysed for porosity by N₂ adsorption and their coke content by thermogravimetric analysis (TGA, heating in air at 10 K/min, see section A5.7 in the SI).

3. Results

3.1. Effect of Mo loading

17 catalysts were prepared using several CVD methods found in literature as well as SIE and IWI. Three different precursors, MoCl₅, MoO₃, and Mo(OH)₂ were used for CVD, while MoO₃ and MoCl₅ were tested for SIE and AHM for IWI. A detailed description and discussion of the synthesis methods and the catalytic performance achieved can be found in the Supplementary information sections A1–A3. While a better dispersion was achieved with CVD compared to IWI it also has to be noted that the synthesis was hard to reproduce and more consistent results were obtained with IWI.

Samples with two different loadings of Mo were prepared with Mo/Al = 0.3 and 1.0. The high loading corresponds to the theoretical limit of Mo incorporation, because each Al can theoretically anchor one Mo. This high loading was used to test how well the different synthesis methods perform, because it is hard to disperse Mo at the limit of how much Mo can be anchored. Generally, a better dispersion is achieved for Mo/Al = 0.3 as is evident from XPS as well as UV–vis (vide infra). The integrity of the zeolite is also less impaired by the synthesis method for Mo/Al = 0.3 compared to when the catalysts are prepared with Mo/Al = 1. This is concluded from the N₂ adsorption isotherms, XRD and \(^{27}\)Al MAS NMR. For Mo/Al = 0.3, the N₂ adsorption isotherms (Fig. S8a) retain the same shape as the isotherm for the bare zeolite, while for catalysts prepared with Mo/Al = 1 a decrease in BET surface area is observed accompanied with, in some cases, increased mesoporosity (Fig. S8b). XRD patterns (Fig. S9) also show a more significant decrease in crystallinity for Mo/Al = 1 than for Mo/Al = 0.3. The diffraction peaks characteristic for MoO₃ are observed for more catalysts with Mo/Al = 1 than for Mo/Al = 0.3 showing that there is a higher chance of Mo agglomeration for high Mo loadings. \(^{27}\)Al MAS NMR (Fig. S10) shows that some samples with Mo/Al = 1 experienced significant extraction of framework Al, while only moderate extraction is observed for Mo/Al = 0.3. Both EFAI as well as Al₂(MoO₃)₃ are observed especially for Mo/Al = 1. EFAI leads to an increase in LAS, which in some cases was shown to have a beneficial effect on catalyst lifetime [42], while Al₂(MoO₃)₃ was generally agreed to be inactive for MDA [37,43,44]. At the same time BAS are removed leading to a lower acidity, which was shown to decrease the formation of coke [10–14]. Generally, extraction of Al from the framework leads to a decrease in crystallinity, because some microporous structures are destroyed. This can also result in mesoporosity as observed in the N₂ adsorption measurements. Some mesoporosity can be beneficial for the reaction, but there seems to be an optimum of how many mesopores should exist [16,45–47]. Finally, catalytic performance varies more at higher loadings (compare Figs. S2 and S3), also because it becomes harder to disperse Mo.

3.2. Effect of dispersion

3.2.1. Measuring dispersion

A combination of Py IR, XPS and UV–vis is used to elucidate the nature of Mo species present on the catalysts after synthesis. Py IR indirectly probes the amount of cationic sites of Mo inside the pores of the zeolite particles, XPS only probes the outer surface of the zeolite and UV–vis is a bulk technique giving an average of all Mo species present on the catalyst. Thus a combination of all three techniques is insightful for distinguishing between bigger clusters of Mo on the outer surface of the zeolite particle and Mo anchored inside the pores.

Py IR was used to determine how many active Mo sites are created. Fig. 1a, Figs. S11b and S12b show the absorbance bands of pyridine adsorbed on the acid sites of the bare zeolite and the catalysts containing Mo. Three contributions are observed corresponding to Lewis acid sites (LAS) at 1455 cm⁻¹, a mixture of BAS and LAS at 1490 cm⁻¹ and BAS at 1546 cm⁻¹ [48–50]. In addition, several absorbances are observed between 1612 and 1635 cm⁻¹ that represent a mixture of LAS and BAS as well. The intensity for the BAS absorbance at 1546 cm⁻¹ decreases for the catalysts with Mo, because the Mo cations replace the acidic protons [21]. Through this exchange new Lewis acid sites are created. One of the absorbances around 1635 cm⁻¹ decreases together with the BAS absorbance at 1546 cm⁻¹ and is therefore assigned to BASs. Both the absorbance at 1623 cm⁻¹ as well as at 1612 cm⁻¹ are assigned to LASs. For the bare zeolite, LASs stem from extra-framework Al (EFAI), while on the zeolite containing Mo both LASs from EFAI and from Mo cations are observed. The absorbance at 1612 cm⁻¹ only appears for the zeolite containing Mo, therefore this wavenumber is assigned to LAS arising from Mo cations while the absorbance at 1623 cm⁻¹ likely stems from EFAI [21]. Comparing Figs. S11a and S12a, it can be seen that for Mo/Al = 1, the OH absorption corresponding to Si–OH and Al–OH almost disappeared. This is because Mo is also anchored on those groups for high loadings. A complete table containing the fraction of BAS covered and the amount of extra LAS created for each sample can be found in the SI (Table S1). In Fig. 1b, the amount of additional LASs created, LASₘₐₛₚ is plotted against the ratio of BAS covered, (Mo/Al)ₓ François. Proportionally the more LASs are created, the more acidic protons are replaced by Mo cations. Some EFAI is created during the synthesis of the zeolite, likely during the calcination step, as discussed in the SI, section A3. This explains why the bare zeolite, HZ does not follow the same linear trend as the other samples. The catalysts with Mo however, follow one trend, because the amount
of EFAl created is similar for most samples as shown by $^{27}$Al MAS NMR in Fig. S10. 1MoHZ-CVD1 presents an outlier, as no extra LASs are created in that case during the incorporation of Mo. This indicates that most of the decrease in the characteristic BAS absorbance is not because Mo replaced the acidic proton, but because the BASs got destroyed during the synthesis. Similarly for 1MoHZ-SIE the decrease in BAS is partly due to extraction of FAI and formation $\text{Al}_2(\text{MoO}_4)_3$. In contrast, for 1MoHZ-CVD3(i) and 1MoHZ-CVD3(ii), more EFAl was created during the synthesis compared to other samples.

Since XPS is a surface sensitive technique, which for our specific experimental configuration has a mean escape depth of around 3–4 nm (details in SI section A5.5) [51–53], it can inform about agglomeration and clustering of Mo on the external surface of the catalyst particles. An agglomeration on the outer surface of the zeolite crystal will yield an increased amount of Mo detected by XPS. XPS confirms that Mo does not significantly cluster on the outer surface of the catalyst particle for catalysts synthesized with Mo/Al = 0.3, as the Mo/Al ratios obtained from XPS for those samples are all below 0.33, while they can be as high as 1.44 for catalysts synthesized with Mo/Al = 1 (Table S1). The more Mo anchors to the BAS, the less Mo is expected to be present as bigger clusters and nanoparticles on the outer surface of the zeolite and the lower the expected (Mo/Al)$_{XPS}$.

Fig. 1. a) Py IR spectra of 1MoHZ-x samples with illustration of how the Mo cation replaces the proton at the BAS to create LAS. b) LAS$_{extra}$ as determined by integrating the absorbance at the IR wavenumber characteristic for pyridine adsorption on LAS and subtracting the area of the absorbance at the same location on the bare zeolite plotted against (Mo/Al)$_{Py FTIR}$ as determined by integrating the absorbance at the IR wavenumber characteristic for pyridine adsorption on BAS for a sample containing Mo and comparing it to the area of the same absorbance measured for the bare zeolite. Results for all samples are plotted and outliers highlighted. For all values refer to Table S1.

Fig. 2. a) (Mo/Al)$_{XPS}$ on the outer surface of the catalyst particle as determined by quantifying the amount of Mo and Al from the XPS measurement plotted against (Mo/Al)$_{Py FTIR}$ as determined by integrating the absorbance at the IR wavenumber characteristic for pyridine adsorption on BAS for a sample containing Mo to the same absorbance measured for the bare zeolite. Results for all samples are plotted and outliers highlighted. For all values refer to Table S1. b) Edge energy $E_g$ determined from UV–vis (Fig. S19, Table S1) plotted against LAS$_{extra}$ as determined by integrating the absorbance at the IR wavenumber characteristic for pyridine adsorption on LAS and subtracting the area of the absorbance at the same location on the bare zeolite.
Fig. 3. a) Instantaneous maximum yield to benzene and naphthalene (Table S3). b) The integral selectivity to aromatics (Table S2) plotted against the ratio of BAS covered, (Mo/Al)_{Py FTIR} (Table S1). c) The integral selectivity to coke (Table S2) plotted against the ratio of BAS covered, (Mo/Al)_{Py FTIR} (Table S1).

3.3. Effect of acidity and porosity

When exchanging the proton at the BAS with Mo, Mo active sites are created while simultaneously decreasing the acidity [30]. That is why it is difficult to separate the effect of more Mo sites from the effect of lowering the amount of acid sites. Although it has been shown that coke selectivity decreases when the Brønsted acidity of the zeolite is lowered [10–14], this is not the sole reason as might be suggested by Fig. 3c. Additionally, the aromatics formation rate increases, because there are more well-dispersed Mo sites on which methane can be activated [22]. This prolongs activation period and results in structural changes (Fig. S8b) and formation of inactive particles on the as-synthesized catalysts. A prolonged activation period leads to an increased coke production already in the beginning of the reaction.

Carburization takes longer, because of the presence of bigger Mo particles on 1MoHZ-CVD3(MoO\textsubscript{2}Cl\textsubscript{2}) and 0.3MoHZ-CVD3(MoO\textsubscript{2}Cl\textsubscript{2}), which are observed as MoO\textsubscript{2} diffraction peaks in the XRD pattern (Fig. S9). Al\textsubscript{2}(MoO\textsubscript{4})\textsubscript{3} is generally a bit lower, generally increases with Mo/Al = 0.3, E\textsubscript{g} is generally between 4.00 and 4.42 (Table S1) suggesting that with such low loadings, Mo is almost exclusively present as mono- or dimeric species [27]. For Mo/Al = 1, E\textsubscript{g} is generally a bit lower, because this ratio is at the limit of how much Mo can be anchored to the BAS of the zeolite framework and Mo oxide polymers will always be present to some extent. Fig. 2b shows that E\textsubscript{g} generally increases with the number of extra Lewis acid sites created compared to the bare zeolite, confirming that these LASs correspond to mono- or dimeric Mo cations. The limitations of using E\textsubscript{g} as an indicator of dispersion however are also clear, as many outliers can be found in Fig. 2b. Even worse correlations were found when trying to correlate the results from UV–vis with results from XPS.

3.2.2. Relating dispersion to catalytic activity

Finally, the measure for dispersion (Mo/Al)_{Py FTIR} determined with pyridine IR can directly be related to catalytic performance. The overall activity is increased when more well-dispersed cationic Mo sites are created. This is evident from the increase in the instantaneous yield of naphthalene and benzene with (Mo/Al)_{Py FTIR} shown in Fig. 3a. More benzene and naphthalene are produced leading to an increased integral selectivity to aromatics (Fig. 3b), and a decreased integrated selectivity to coke (Fig. 3c). 1MoHZ-CVD1 presents an outlier in all three relationships, because of the significant destruction of the zeolite during synthesis as discussed in Section 3.1. The other outliers in the trend for selectivity to aromatics can be explained by the particularly low selectivity to C2–C3 hydrocarbons, effectively increasing aromatics selectivity. The other outliers in Fig. 3c correspond with a prolonged activation period. During the activation period, the oxidic Mo present on the as-synthesized catalysts is carburized to its active phase, which leads to a delay in the onset of aromatics production [54]. This is observed for 1MoHZ-CVD3(MoO\textsubscript{2}Cl\textsubscript{2}) and 0.3MoHZ-CVD3(MoO\textsubscript{2}Cl\textsubscript{2}) (Fig. S3). This prolonged activation period leads to an increased coke production already in the beginning of the reaction.

UV–vis can be used to determine the electronic edge energy (E\textsubscript{g}) of the charge transfer from oxygen to molybdenum. For samples with Mo/Al = 0.3, E\textsubscript{g} is generally between 4.00 and 4.42 (Table S1) suggesting that with such low loadings, Mo is almost exclusively present as mono- or dimeric species [27]. For Mo/Al = 1, E\textsubscript{g} is generally a bit lower, because this ratio is at the limit of how much Mo can be anchored to the BAS of the zeolite framework and Mo oxide polymers will always be present to some extent. Fig. 2b shows that E\textsubscript{g} generally increases with the number of extra Lewis acid sites created compared to the bare zeolite, confirming that these LASs correspond to mono- or dimeric Mo cations. The limitations of using E\textsubscript{g} as an indicator of dispersion however are also clear, as many outliers can be found in Fig. 2b. Even worse correlations were found when trying to correlate the results from UV–vis with results from XPS.

We further assessed the effect of porosity on catalytic performance.
Pore volume, especially micropore volume decreases with (Mo/Al)Py-FTIR, because more Mo is anchored inside the pores of the zeolite (Fig. 4a). For Mo/Al = 0.3, maximum instantaneous yields to aromatics decrease with pore volume, because more Mo cationic sites are present (orange points, Fig. 4b). In contrast, for a higher loading of Mo, the maximum instantaneous yields to aromatics are higher for higher pore volumes. The rate of aromatics formation for these catalysts with a lot of active Mo sites is very high and thus diffusion of the products starts to impact catalyst performance. A longer catalyst lifetime can also be expected for a higher pore volume, because more coke can be accommodated before access to the active sites of the catalyst is blocked. The total amount of coke deposited after 364 min on stream increases with pore volume (Fig. S16), but this is not due to a complete filling of the pores, since the pore volume of the catalysts decreased by less than 40% during the 364 min on stream and mesopore volume decreased relatively more than micropore volume (Table S6). Total coke amounts instead increase because the concentration of BASs is also higher at higher pore volumes (Fig. 4a). Coke formation is thus clearly associated with acidity. This is supported by the fact that for the catalysts with lower loadings of Mo and thus higher acidity, activity drops around 70% and only by 30–60% for the high loadings. The drop in benzene formation is also much higher than the decrease in pore volume indicating that coking might not be the only cause of deactivation, but agglomeration of Mo could play a role as well, as has been suggested before [17,55]. The integrated aromatic selectivities follow a similar trend as the maximum instantaneous yields (Fig. S17), demonstrating that more cationic Mo sites increase activity at low Mo loadings and that it is important to increase accessibility for high Mo loadings.

4. Conclusions

Comparing and adapting several CVD techniques from literature and using the conventional preparation techniques, IWI and SIE, a suite of 17 catalysts were synthesized, characterized and their catalytic performance tested for MDA. The synthesis method had a greater effect on catalyst performance for the high Mo loading corresponding to a Mo/Al ratio of 1, while the different synthesis methods lead to more similar performance for Mo/Al = 0.3. Mo/Al = 1, which corresponds to a loading of 5.8 wt.% Mo on a zeolite with Si/Al = 25, represents the theoretical maximum of Mo that can be anchored to the framework Al of the zeolite. At this loading, dispersing Mo while avoiding the formation of Mo nanoparticles is difficult to achieve. Full exchange of the acidic protons with Mo is controlled by migration of the Mo precursor into the pores of the zeolite. This migration can be enhanced by using a Mo precursor with a lower melting point.

Characterization with pyridine IR, XPS, UV–vis and $^{27}$Al MAS NMR allowed determining the amount of Mo present as mono- or dimeric species inside the pores of the zeolite as well as the fraction of Mo that formed nanoparticles and bigger clusters on the outer surface of the zeolite. Py IR showed to be the most informative technique in that regard, as XPS shows a high local measurement variation, and edge energies determined from UV–vis do not correlate well with results from other characterization techniques. The information from Py IR can be related well with catalytic behavior. A linear relationship was found between the rate of aromatics formation (benzene and naphthalene) and the concentration of Mo cations inside the channels of HZSM-5. Hence, when more Mo cations are present the integral selectivity to aromatics also increases and at the same time the selectivity to coke decreases due to a simultaneously reduced acidity.

Both the dispersion of Mo as well as overall acidity influence catalytic performance. Thus, it is not sufficient to create a zeolite support with low acidity to enhance aromatic selectivity as has been suggested [47], the amount of well-dispersed Mo sites has to be increased as well. Coking can clearly be associated with the acid sites. In addition, bigger Mo nanoparticles prolong the induction period and the catalyst deactivates faster. Deactivation also occurs because of agglomeration of Mo and thus a decrease in the number of cationic Mo sites. The number of cationic Mo-sites is the most important factor determining the activity of Mo/HZSM-5 for low loadings of Mo, but at higher loadings, catalysts design should also provide for enough porosity to enhance diffusion of products.

Declaration of interest

We declare no conflict of interest.

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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.2019.01.022.

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