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Reversible Nature of Coke Formation on Mo/ZSM-5 Methane Dehydroaromatization Catalysts

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Abstract: Non-oxidative dehydroaromatization of methane over Mo/ZSM-5 zeolite catalysts is a promising reaction for the direct conversion of abundant natural gas into liquid aromatics. Rapid coking deactivation hinders the practical implementation of this technology. Herein, we show that catalyst productivity can be improved by nearly an order of magnitude by raising the reaction pressure to 15 bar. The beneficial effect of pressure was found for different Mo/ZSM-5 catalysts and a wide range of reaction temperatures and space velocities. High-pressure operando X-ray absorption spectroscopy demonstrated that the structure of the active Mo-phase was not affected by operation at elevated pressure. Isotope labeling experiments, supported by mass-spectrometry and ^{13}C nuclear magnetic resonance spectroscopy, indicated the reversible nature of coke formation. The improved performance can be attributed to faster coke hydrogenation at increased pressure, overall resulting in a lower coke selectivity and better utilization of the zeolite micropore space.

Methane dehydroaromatization (MDA) over Mo-containing zeolite catalysts is a promising reaction for the direct conversion of natural gas to a mixture of liquid BTX aromatics (mainly benzene) and hydrogen.^[1] This thermodynamically limited non-oxidative reaction requires temperatures as high as 600–800 °C to achieve a significant methane conversion. A major challenge in the realization of a practical MDA process is the rapid deactivation of Mo/ZSM-5 catalysts. Recent advances in our understanding how these catalysts work at the atomic level can aid in strategies to reduce the coking deactivation. First, it has been demonstrated that the mechanism involves a pool of (radical) hydrocarbon reaction intermediates relevant to the formation of aromatics.^[2] Second, the structure of the active molybde-

num centers has been thoroughly studied by means of ^{95}Mo NMR,^[3] operando Raman^[4] and XAS spectroscopy,^[5] and other techniques.^[6] There is a growing consensus that the active centers are monomeric or dimeric molybdenum (oxy)-carbide species which are stabilized inside the zeolite pores, while larger Mo_2C species on the external surface are mere spectators.^[7] Further, various methods to enhance the activity and stability of Mo/ZSM-5 catalysts have been developed as well and they include: 1) Application of hydrogen-selective membranes to remove hydrogen from the reaction zone and shift the equilibrium towards aromatic products.^[8] 2) Adsorptive or oxidative scavenging of hydrogen for the same purpose.^[9] 3) Periodic pulsing of small amounts of oxygen for the selective coke combustion.^[10] 4) Use of oxygen-permeable membranes for a controlled supply of a small amount of oxygen for removal of coke species.^[11] 5) Reaction-regeneration cycling by combustion or reduction of coke.^[12] Finally, the influence of such parameters as temperature and space velocity of methane^[13] and continuous co-feeding of hydrogen,^[14] oxygen,^[15] and oxygenates^[16] has been studied in great detail.

The reaction pressure remains a poorly explored parameter. Nearly all laboratory MDA studies have been performed at atmospheric pressure. In fact, to the best of our knowledge the only reports on the effect of pressure were by Ichikawa and co-workers in the early 2000 s^[17] and, more recently, by Fila et al.^[18] It was found that applying reaction pressures in the 3–6 bar range results in a more stable catalytic performance at the expense of the maximum attainable benzene yield. The results of a recent computational modelling study performed by Kee et al. demonstrated that increasing pressure should result in a higher benzene selectivity over naphthalene, the latter being generally considered a coke precursor.^[19]

According to Le Chatelier's principle, the equilibrium of methane dehydroaromatization reaction is shifted towards methane at increasing pressure:



We also note that coke formation should be suppressed stronger by increasing pressure (as nearly two times more molecules are produced than converted):



To illustrate this point, Figure S1 in the supporting Information shows the results of a thermodynamic analysis. The maximum thermodynamic yields of the main MDA

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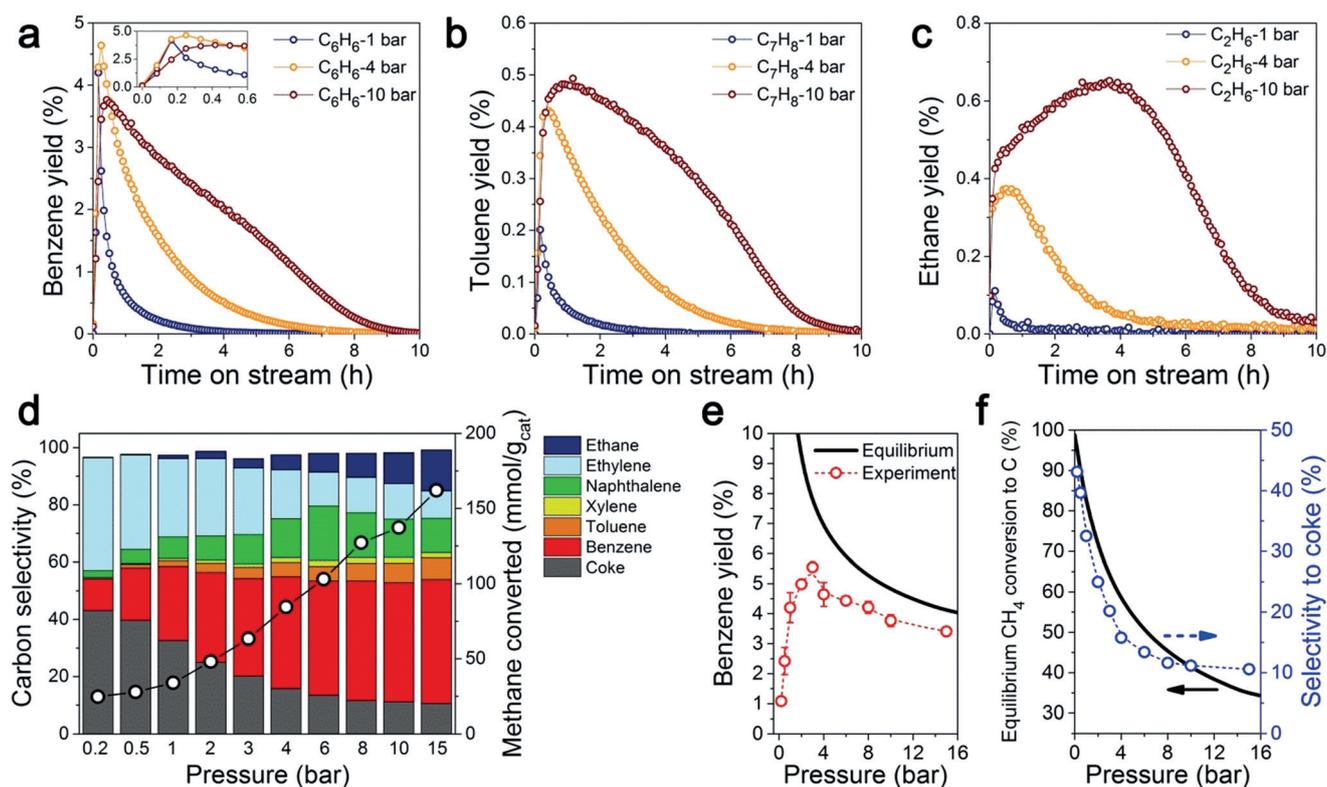


Figure 1. Effect of pressure on catalytic performance of 2% Mo/ZSM-5 catalyst. a) Yields of benzene (with inset highlighting the induction period), b) toluene and c) ethane. d) Overall product distributions and total amounts of converted methane. e) Equilibrium and maximum observed yields of benzene. f) Equilibrium yield of graphite plotted with observed total coke selectivity. Reaction conditions: 700 °C, GHSV 15 000 h⁻¹, 900 min.

products, except for ethane, decrease with increasing pressure. The effect of pressure on product formation increases in the following order: ethane (no effect) \ll ethylene = xylene < toluene < benzene < naphthalene \ll graphite (coke). Accordingly, this thermodynamic analysis suggests that performing the reaction at elevated pressure might lead to a decreased coke selectivity and, therefore, higher catalyst productivity.^[20]

In this work, we show that operation of the MDA reaction at elevated pressure is an efficient way to increase catalyst lifetime and total hydrocarbon productivity, by decreasing the coke selectivity. Transient kinetic measurements using ¹³C-labelled methane evidence the reversible nature of coke formation during the MDA reaction. At elevated pressure, coke hydrogenation becomes faster, effectively resulting in a slower build-up of carbonaceous deposits. We also present operando high-pressure X-ray absorption near-edge structure (XANES) spectroscopy results, demonstrating that the speciation of the active Mo species is not affected by high-pressure operation.

For the experiments, we used a 2% Mo/ZSM-5 (Si/Al 13, see Table S1 in the Supporting Information for physicochemical properties). Earlier, we have shown that in such a catalyst nearly all Mo atoms are dispersed inside the pores and involved in the MDA reaction.^[2a] MDA activity measurements were performed at 700 °C in a quartz reactor (i.d. 4 mm, o.d. 8 mm), which can be safely operated up to a pressure of

20 bar. The catalytic results (Figure 1 and Table S2 in the supporting Information) demonstrate that raising the reaction pressure results in a higher catalyst productivity. The cumulative yield of aromatic products is substantially higher at elevated reaction pressure. For instance, the cumulative amount of benzene, toluene and xylenes obtained at 15 bar is about one order of magnitude higher than that at 1 bar. About four times more methane could be converted at 15 bar than at atmospheric pressure. We observed that with increasing pressure the formation of ethane is promoted owing to the fact that its production is least influenced by pressure. The main reason for the enhanced hydrocarbon product yields is a decreased total coke selectivity (from 32.6% to 10.6%) when the pressure is increased from 1 to 15 bar. Next, we investigated how the Mo weight loading, the reaction temperature, and the space velocity influence the catalytic performance by carrying out reaction experiments at 1 bar and 10 bar. Figure S2 and Table S3 in the Supporting Information emphasize that for all Mo loadings a higher total productivity is obtained at 10 bar. At low Mo loading a significantly higher coke selectivity is observed in line with previous studies.^[12b] Also, a higher productivity is observed at all temperatures in the 600–800 °C range (Supporting Information, Figure S2 and Table S4). While the coke selectivity gradually increased with temperature at 1 bar, at 10 bar the coke selectivity was around 10% between 600 °C and 700 °C and then significantly increased when the temperature was raised to above 750 °C.

Overall, the beneficial effect of higher reaction pressure on (lower) coke selectivity became smaller at higher reaction temperature. Given that the total amount of coke formed at temperatures above 700 °C was much larger than the maximum amount of coke that can be accommodated inside the pores (Supporting Information, Figure S3), we infer that radical reactions of methane decomposition to carbon on the external surface are likely to play a significant role at higher temperature. Finally, we established that operation at 10 bar is beneficial in a wide GHSV range from 3000 h⁻¹ to 22 500 h⁻¹ (Supporting Information, Figure S2 and Table S5). This finding is particularly important, because for an equilibrium-limited reaction such as MDA it is favorable to operate at a high space velocity to maximize the space-time yield of products.

To investigate the effect of pressure on the structure of Mo-species, we carried out a XANES study. The catalyst samples were exposed to the methane feed at different pressures (from 0.5 to 5 bar), whilst increasing the temperature from ambient to 700 °C (ramp rate of 5 °C min⁻¹) followed by an isothermal period of 1 h. The XANES spectra recorded at 1 bar and 5 bar and represented as heat maps as a function of temperature (Figure 2a,b) display several important features. As expected, Mo reduction starts at significantly lower temperature at higher methane pressure (ca. 500 °C at 5 bar and ca. 600 °C at 1 bar), as manifested by the disappearance of the pre-edge feature and the shift of the rising edge feature to a lower energy. Furthermore, we note that neither spectra before reduction started (that is, at 400 °C) nor those at the final reduction temperature of 700 °C changed as a function of the pressure (Figure 2c). This finding indicates that there are no substantial structural changes in the Mo species before and after the catalyst activation with varying pressure.

Figure 2d compares the trends in the edge positions derived from XANES and simultaneously recorded mass spectrometry traces of benzene (*m/z* = 78). Although the reduction of the Mo-phase occurs faster at elevated pressure, the induction (time for benzene yield to reach the maximum) is significantly slower. In our previous work, we distinguished two processes: 1) activation involving the reduction of Mo-oxo species to active Mo-centers and 2) induction involving the formation of proton-deficient aromatic intermediates stabilized inside the pores.^[2a] These intermediates are involved in the catalytic cycle and necessary for the MDA reaction to occur. The longer induction period at elevated pressure suggests that, similar to the coke species, the polyaromatic hydrocarbon pool precursors are formed slower.

To probe the processes occurring on the surface of the catalyst during MDA reaction we performed an isotope labelling study as illustrated by Figure 3. In these experiments we first pre-heated the catalyst until 700 °C in a flow of ¹²CH₄ and then switched the feed to labelled ¹³CH₄ to form ¹³C-enriched carbon species inside the pores. After 20 min in ¹³CH₄ flow we either quickly cooled the catalyst (Figure 3a) or switched to ¹²CH₄ and kept the catalyst at 700 °C for additional 100 min to study the removal of surface ¹³C atoms upon exchange with gas-phase ¹²CH₄ (Figure 3b).

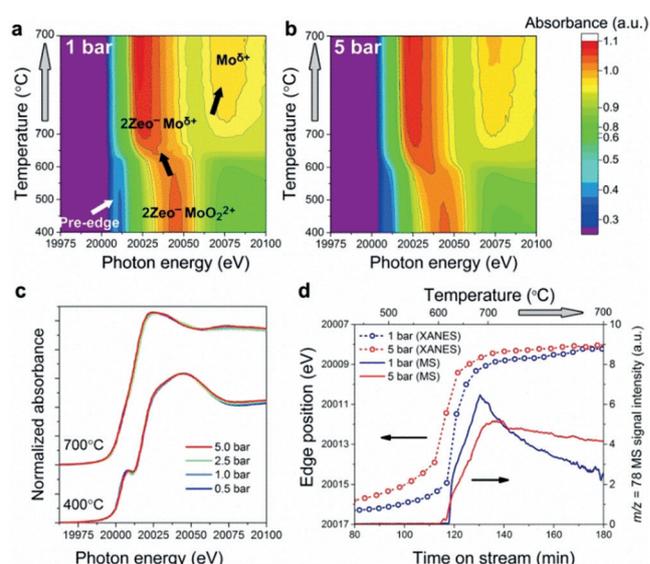


Figure 2. Operando XANES analysis of the effect of pressure on the reduction of initial Mo^{VI} phase. Intensity contour maps constructed from spectra recorded during programmed CH₄ reduction at a) 1 bar and b) 5 bar. Indicated are pre-edge region, rising edge region related to the reduction of Mo^{VI}-oxo precursors to active Mo-species and region at 20075 eV related to a gradual agglomeration of the Mo-species. c) XANES spectra of 2% Mo catalysts recorded at different pressure during CH₄ TPR at 400 °C and 700 °C. d) Intensity of the detected benzene *m/z* = 78 MS signal during the operando experiments together with the edge energies (defined as energies at half-edge) in 1 bar and 5 bar experiments.

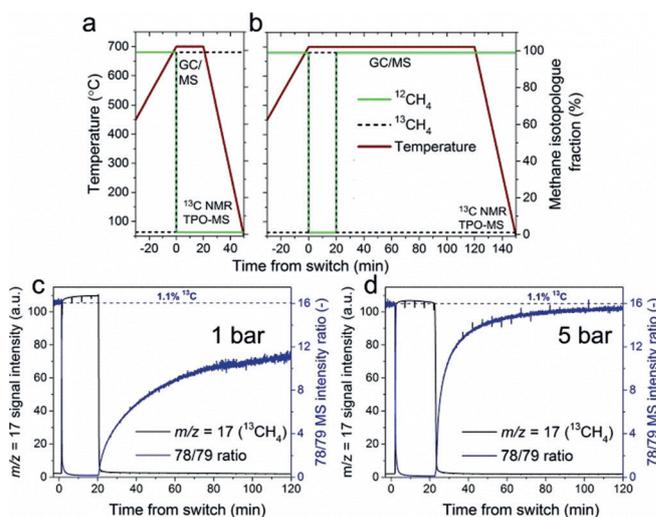


Figure 3. Scheme of isotope labelling experiments when 2% Mo catalyst was preheated in a flow of ¹²CH₄ to 700 °C, then kept under ¹³CH₄ flow for 20 min and finally was either a) quickly cooled down or b) kept under ¹²CH₄ flow for 100 min before cooling down. The moment when the temperature of 700 °C was reached and the switch from ¹²CH₄ to ¹³CH₄ was performed is taken as time = 0. MS-derived intensity of ¹³CH₄ *m/z* = 17 signal and transient response of benzene isotopologues with masses 78 and 79, demonstrating gradual removal of ¹³C from the catalyst surface during c) 1 bar and d) 5 bar labelling experiments.

During the reaction the gas phase composition was monitored by GC and MS analyses (Supporting Information, Figure S4). After the reaction the spent catalysts were collected and characterized by ^{13}C NMR spectroscopy and TPO-MS to determine the surface ^{13}C content before and after exchange with $^{12}\text{CH}_4$. Figure 3c,d demonstrate that it is possible to observe the interaction of surface and gaseous carbon atoms by analyzing the ratio between $m/z = 78$ and 79 MS signals, corresponding to benzene molecules with 0 and 1 ^{13}C labels, respectively. Initially, in the $^{12}\text{CH}_4$ flow the m/z 78/79 ratio of 16 is consistent with the natural abundance of ^{13}C (1.1%). After the switch to $^{13}\text{CH}_4$, the m/z 78/79 ratio decreased, indicating formation of ^{13}C -rich benzene molecules in the absence of gaseous $^{12}\text{CH}_4$. When the flow was switched back to $^{12}\text{CH}_4$, a slow increase of the m/z 78/79 ratio was observed. The transient increase corresponds to the exchange of gas-phase ^{12}C atoms with surface ^{13}C atoms. Based on these data, we can estimate the rate of removal of ^{13}C atoms from the catalyst surface through benzene molecules. We note here that the formation of labelled benzene molecules can occur through two main pathways: 1) direct interaction of labeled hydrocarbon pool molecules with initial products of methane activation and 2) hydrogenation of labelled surface species to ^{13}C methane followed by its aromatization. Both these processes contribute to the observed isotope exchange.

Figure 4a shows that the initial rate of isotope exchange at 5 bar is significantly higher than that at 1 bar (ca. 6 times). This difference points to a higher rate of coke hydrogenation at elevated pressure. The nature and the initial amount of the ^{13}C carbon species were similar at both pressures (see Figure S5 in the Supporting Information for detailed HETCOR ^1H - ^{13}C NMR spectra). Furthermore, quantitative ^{13}C NMR spectroscopy (Figure 4b,c) analysis demonstrated that extensive exchange of sp^2 carbon atoms occurs, that is to say that more than 40% of ^{13}C atoms were removed from the surface after $^{12}\text{CH}_4$ treatment at 5 bar. In line with MS results, a much lower value of 19% was obtained for the 1 bar experiments.

It is noteworthy that the reversible formation of coke at higher pressure does not result in a lower amount of coke formed. Figure 5a shows that, although the coke selectivity significantly decreases with increasing pressure, the actual amount of coke accumulated inside the zeolite pores after complete deactivation increases. At a pressure of 15 bar, nearly 60% more coke was formed as compared to the experiment carried out at 1 bar. Earlier, we found that, during the MDA reaction at 700°C , coke species grow predominantly inside the zeolite pores.^[2] Based on detailed characterization, we proposed that the coke deposits with an overall stoichiometry of about $\text{CH}_{0.4}$ are most likely acenes, occluded in the straight channels (Supporting Information, Figure S9). With a structural coke model outlined in the Figure S9, we estimate the maximum coke capacity of ZSM-5 to be $270 \text{ mg}_{\text{coke}}/\text{g}_{\text{zeolite}}$. Carrying out the MDA reaction at 1 bar does not lead to a complete filling of the zeolite micropores: both our previous work and other literature showed that the typical coke content of spent Mo/ZSM-5 catalysts was limited to $80\text{--}180 \text{ mg}_{\text{coke}}/\text{g}_{\text{catalyst}}$ at atmospheric pressure.^[21] With

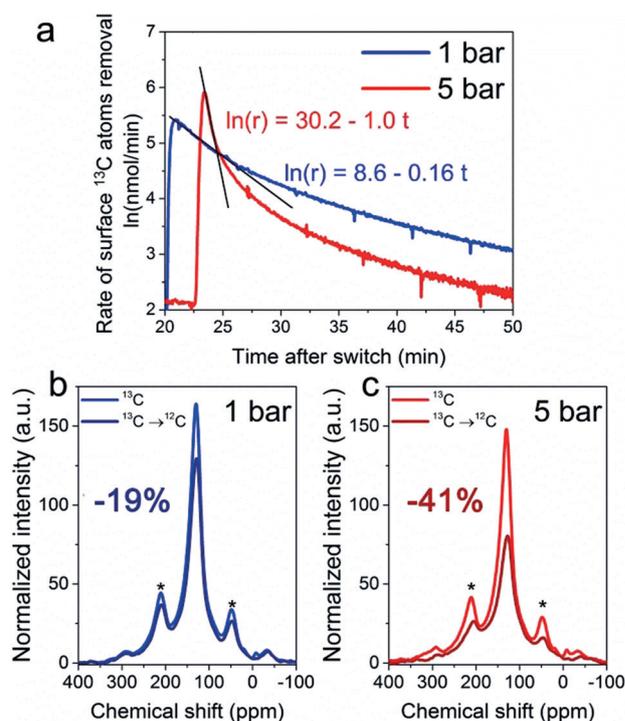


Figure 4. a) Rates of removal of ^{13}C surface atoms with benzene molecules after the switch from $^{13}\text{CH}_4$ to $^{12}\text{CH}_4$ methane feed. Quantitative ^{13}C NMR spectra of 2% Mo catalysts preheated in a flow of $^{12}\text{CH}_4$ to 700°C , then kept under $^{13}\text{CH}_4$ flow for 20 min and immediately cooled down or kept under $^{12}\text{CH}_4$ flow for 100 min before cooling at b) 1 bar and c) 5 bar.

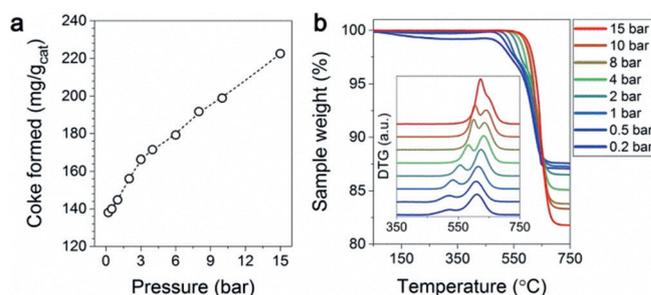


Figure 5. TG analysis of spent samples after MDA reaction at different pressures. a) Total coke content and b) TG and DTG (inset) profiles. Reaction conditions: 700°C , GHSV $15\,000 \text{ h}^{-1}$, 900 min.

increasing pressure, however, a higher coke content of the pores is attained. Furthermore, both combustion peaks in DTG profiles (Figure 5b), corresponding to coke species in close proximity (low temperature peak) and distant from Mo-centers (high temperature peak), shift to higher temperature. The fraction of coke species, whose combustion is catalyzed by Mo, also increases with temperature. We explain these observations by 1) stronger diffusion limitations, experienced by oxygen and combustion products, with increasing occupancy of the zeolite pores with coke species,^[22] and 2) a higher efficiency of Mo-catalyzed combustion at increased temperature. The dependence of total methane conversion capacity on coke selectivity rules out the extensive formation of coke

species on the external surface at 700 °C (Supporting Information, Figure S3). Clearly, reversible growth of carbonaceous species at elevated pressure results in the formation of denser carbon structures and higher pore occupancy.

To summarize, rapid deactivation due to coke deposition is a common feature of Mo/ZSM-5 catalysts used in the dehydroaromatization of methane to aromatics. We demonstrate that performing the MDA reaction at elevated pressure leads to an increased rate of surface species hydrogenation, lower overall coke selectivity, and higher methane conversion capacity. A nearly one order of magnitude increase in the aromatics productivity of 2% Mo/ZSM-5 catalyst was observed by increasing the pressure from 1 bar to 15 bar. The improvement of the catalytic performance at increased pressure is independent of the Mo loading, reaction temperature and methane space velocity. It is also noted that higher pressure results in higher selectivity towards more valuable products such as toluene and xylene. Operando XAS results evidence that, although the Mo-oxide precursor is reduced easier under elevated pressure, the structure of the active sites during the actual reaction is independent of pressure. Notably, the total amount of coke deposits is increased at elevated pressure, showing how reversible growth of coke deposits results in a higher pore utilization. The current finding, that elevated pressure operation has such a strong positive effect on the performance of Mo/ZSM-5, is also important for practical methane valorization, as it eliminates the need to depressurize the natural gas stream before aromatization.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: deactivation · heterogeneous catalysis · methane dehydroaromatization · operando spectroscopy · zeolites

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- [1] a) J. J. Spivey, G. Hutchings, *Chem. Soc. Rev.* **2014**, *43*, 792–803; b) P. Schwach, X. Pan, X. Bao, *Chem. Rev.* **2017**, *117*, 8497–8520.
[2] a) N. Kosinov, A. S. Wijkema, E. Uslamin, R. Rohling, F. J. Coumans, B. Mezari, A. Parastaev, A. S. Poryvaev, M. V. Fedin,

- E. A. Pidko, *Angew. Chem. Int. Ed.* **2018**, *57*, 1016–1020; *Angew. Chem.* **2018**, *130*, 1028–1032; b) N. Kosinov, E. A. Uslamin, F. J. Coumans, A. S. Wijkema, R. Y. Rohling, E. J. Hensen, *ACS Catal.* **2018**, *8*, 8459–8467.
[3] H. Zheng, D. Ma, X. Bao, J. Z. Hu, J. H. Kwak, Y. Wang, C. H. Peden, *J. Am. Chem. Soc.* **2008**, *130*, 3722–3723.
[4] J. Gao, Y. Zheng, J. M. Jehng, Y. Tang, I. E. Wachs, S. G. Podkolzin, *Science* **2015**, *348*, 686–690.
[5] I. Lezcano-González, R. Oord, M. Rovezzi, P. Glatzel, S. W. Botchway, B. M. Weckhuysen, A. M. Beale, *Angew. Chem. Int. Ed.* **2016**, *55*, 5215–5219; *Angew. Chem.* **2016**, *128*, 5301–5305.
[6] I. Vollmer, I. Yarulina, F. Kapteijn, J. Gascon, *ChemCatChem* **2018**, *10*, 1–15.
[7] N. Kosinov, F. J. Coumans, E. A. Uslamin, A. S. Wijkema, B. Mezari, E. J. Hensen, *ACS Catal.* **2017**, *7*, 520–529.
[8] S. H. Morejudo, R. Zanón, S. Escolástico, I. Yuste-Tirados, H. Malerød-Fjeld, P. Vestre, W. Coors, A. Martínez, T. Norby, J. Serra, *Science* **2016**, *353*, 563–566.
[9] a) A. Kumar, K. Song, L. Liu, Y. Han, A. Bhan, *Angew. Chem.* **2018**, *130*, 15803–15808; b) Y. Zhang, H. Jiang, *Chem. Commun.* **2018**, *54*, 10343–10346.
[10] N. Kosinov, F. J. Coumans, E. Uslamin, F. Kapteijn, E. J. Hensen, *Angew. Chem. Int. Ed.* **2016**, *55*, 15086–15090; *Angew. Chem.* **2016**, *128*, 15310–15314.
[11] Z. Cao, H. Jiang, H. Luo, S. Baumann, W. A. Meulenber, J. Assmann, L. Mleczko, Y. Liu, J. Caro, *Angew. Chem. Int. Ed.* **2013**, *52*, 13794–13797; *Angew. Chem.* **2013**, *125*, 14039–14042.
[12] a) Y. Xu, J. Lu, Y. Suzuki, Z.-G. Zhang, H. Ma, Y. Yamamoto, *Chem. Eng. Process.* **2013**, *72*, 90–102; b) N. Kosinov, F. J. Coumans, G. Li, E. Uslamin, B. Mezari, A. S. Wijkema, E. A. Pidko, E. J. Hensen, *J. Catal.* **2017**, *346*, 125–133.
[13] Z. R. Ismagilov, E. V. Matus, L. T. Tsikoza, *Energy Environ. Sci.* **2008**, *1*, 526–541.
[14] J. Bedard, D.-Y. Hong, A. Bhan, *J. Catal.* **2013**, *306*, 58–67.
[15] P. Tan, Y. Leung, S. Lai, C. Au, *Catal. Lett.* **2002**, *78*, 251–258.
[16] J. Bedard, D.-Y. Hong, A. Bhan, *RSC Adv.* **2014**, *4*, 49446–49448.
[17] a) Y. Shu, R. Ohnishi, M. Ichikawa, *J. Catal.* **2002**, *206*, 134–142; b) Y. Shu, H. Ma, R. Ohnishi, M. Ichikawa, *Chem. Commun.* **2003**, 86–87; c) Y. Shu, R. Ohnishi, M. Ichikawa, *Appl. Catal. A* **2003**, *252*, 315–329; d) H. Ma, R. Kojima, S. Kikuchi, M. Ichikawa, *Catal. Lett.* **2005**, *104*, 63–66.
[18] V. Fila, M. Bernauer, B. Bernauer, Z. Sobalik, *Catal. Today* **2015**, *256*, 269–275.
[19] B. Kee, C. Karakaya, H. Zhu, S. De Caluwe, R. J. Kee, *Ind. Eng. Chem. Res.* **2017**, *56*, 3551–3559.
[20] S. S. Arora, D. L. Nieskens, A. Malek, A. Bhan, *Nat. Catal.* **2018**, *1*, 666–672.
[21] a) H. Liu, L. Su, H. Wang, W. Shen, X. Bao, Y. Xu, *Appl. Catal. A* **2002**, *236*, 263–280; b) H. Liu, Y. Li, W. Shen, X. Bao, Y. Xu, *Catal. Today* **2004**, *93*, 65–73; c) C. H. Tempelman, E. J. Hensen, *Appl. Catal. B* **2015**, *176*, 731–739.
[22] M. Milanese, G. Artioli, A. F. Gualtieri, L. Palin, C. Lamberti, *J. Am. Chem. Soc.* **2003**, *125*, 14549–14558.

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