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Coke Relocation and Mo Immobilization in Donut-Shaped Mo/HZSM-5 Catalysts for Methane Dehydroaromatization

Ming Cheng^{a,†}, Hugo Cruchade^{b,†}, Ludovic Pinard^b, Eddy Dib^b, Honghai Liu^c, Jiujiang Wang^c, Xinmei Liu^a, Zi-Feng Yan^a, Zhengxing Qin^{a,*}, Svetlana Mintova^{b,*}

Molybdenum-modified HZSM-5 catalysts are widely used for methane dehydroaromatization (MDA) but suffer from rapid deactivation due to coke formation. The limited diffusion in zeolitic catalysts promotes coke accumulation in micropores, creating concentration gradients of reactants and products within the crystals. In this study, we propose a synthesis approach to evaluate the impact of removing the crystal core in the Mo/HZSM-5 catalyst on the MDA performance. To achieve this, a parent zeolite (Z_p) comprising a silicalite-1 core encased by an HZSM-5 crystal is subjected to two distinct treatments: fluorine (Z_F) and alkaline (Z_{OH}). These treatments dissolve the silicon-rich core, creating a central macropore in the crystals leading to the formation of donuts-shaped catalysts. The alkaline treatment further generates additional mesopores and silanols by leaching atoms from the zeolite framework. The MDA reaction on molybdenum-impregnated zeolite catalysts (Z_p, Z_F, and Z_{OH}) at 973 K was carried out. Interestingly, the "donut"-shaped catalysts modify the nature of the coke deposition, relocating the coke from the micropores to the macropores. Consequently, the removal of the crystal core effectively mitigates catalysts deactivation caused by coke formation. Moreover, the alkaline-treated catalyst exhibits additional beneficial properties, such as increased silanols and higher surface area, which help to limit the sintering of molybdenum carbides during the MDA reaction. The new strategy improves the performance and stability of Mo/HZSM-5 catalysts in methane dehydroaromatization.

1. Introduction

Methane dehydroaromatization under non-oxidative conditions (MDA: $6CH_4 \rightleftharpoons C_6H_6 + 9H_2$) over bifunctional Mo/HZSM-5 catalysts has raised the hope of the scientific community over the last decades as a new potential energy source.¹ Indeed, MDA allows hydrogen production while capturing the carbon from methane by forming valuable petrochemical products (*e.g.* aromatics). Therefore, it appears as a more sustainable alternative to energy production through natural gas and biogas combustion. However, the challenging conditions of MDA, the diverse presence of molybdenum and carbon species, and their constant evolution throughout the reaction pose significant difficulties in elucidating the underlying mechanisms.^{2,3} Hence, the industrial development of MDA is still impeded by (i) a relatively low benzene yield, limited by thermodynamics at about 12.5% (700 °C), and (ii) a rapid catalyst deactivation due to coke formation.^{4,5} Catalyst development is one of the strategies identified to address such challenges.^{3,6} Different ways of catalysts improvement have been reported such as Mo/Al balance tuning,^{7–9} variation of molybdenum loading approach,^{10,11} pretreatment,^{12–14} metallic promoter addition,^{15–17} or crystal engineering.^{18–21} The latter represents an extensive research topic for hydrocarbon processing catalyzed by acidic-microporous materials since the diffusional limits in zeolites lead to coke accumulation and

mitigate the efficiency of the crystal core.²² In this sense, the decrease of the diffusion pathway in MDA catalysts has been studied through hierarchization and crystal nanosizing.^{18,19,23}

The shortening of the crystal size favors the desorption of the products but enhances the molybdenum carbides migration on the external surface. On the contrary, a long diffusional pathway enhances the condensation of products within the micropores but mitigates the sintering of molybdenum carbides. Therefore, certain nanosized Mo/HZSM-5 does not show higher stability than micron-sized catalysts. Thus, diffusion in MDA catalysts is crucial, challenged by the dual mode of deactivation governing MDA involves the molybdenum sintering and coke deposition.

Hollow type zeolites can be considered as intermediates between the micron-sized zeolites (*i.e.* high diffusion pathway and low external surface) and nanosized zeolites (*i.e.* low diffusion pathway and high external surface). They show an extended lifetime compared to commercial HZSM-5.^{24–26} The variable wall thickness of the hollow type zeolites may enhance diffusion and help inhibiting coke deposition. As an intermediate material a crystal with a big central hole can be considered. A selective dissolution of silicon-rich part of silicalite-1-Core/HZSM-5-Shell material or HZSM-5 zeolites synthesized by the seed-assisted method through post-treatments has been reported.^{20,27} Core/shell materials made with silicalite-1 and HZSM-5 allow tuning of catalysts reactivity. The diffusion pathway is not shortened, but the absence of

- 54 Brønsted acid sites in the silicalite-1 part reduced 108
 55 probability of further transforming the products into heavy 109
 56 compounds. An acidic (NH₄F) or alkaline (NaOH) treatment 110
 57 zeolite catalysts may dissolve the silicon-rich core of 111
 58 crystals. Moreover, the nature of the post-treatment 112
 59 modify the textural and chemical properties of 113
 60 catalysts.^{28–30} 114
- 61 This study reports how reducing diffusion pathways 115
 62 removing the crystal core affects catalysts behavior during 116
 63 methane dehydroaromatization (MDA). To achieve this, 117
 64 novel synthesis strategy was developed to create coreless 118
 65 Mo/HZSM-5, named donut-shaped catalysts. Fluorine and 119
 66 alkaline post-treatments were applied to the silicalite-1 120
 67 Core/HZSM-5-Shell material to selectively dissolve its core. The 121
 68 textural and chemical properties of the fresh catalysts were 122
 69 characterized and their catalytic performance in MDA was 123
 70 evaluated. Furthermore, catalyst deactivation and coke 124
 71 mechanisms were explored through post-reaction 125
 72 characterization. This comprehensive approach provided 126
 73 insights into the role of the crystal core in the MDA process 127
 74 and its impact on catalyst performance. 128
- 75 **2. Experimental** 129
- 76 **2.1. Materials synthesis** 130
- 77 The reagents used for the preparation of ZSM-5 zeolite are 131
 78 Tetraethyl orthosilicate (TEOS, 28.8 % calculated as SiO₂), 132
 79 Tetrapropylammonium hydroxide (TPAOH, 25% w/w aqueous 133
 80 solution, AR), Aluminum sulfate (Al₂(SO₄)₃·18H₂O, AR), Sodium 134
 81 hydroxide (NaOH, Granular, AR), Tetrapropylammonium 135
 82 bromide (TPABr, AR), Ammonium fluoride (NH₄F, AR), 136
 83 Ammonium Chloride (NH₄Cl, AR), Ammonium molybdate 137
 84 ((NH₄)₆Mo₇O₂₄·4H₂O, AR). All chemicals were purchased from 138
 85 Sinopharm Chemical Reagent Corporation and used directly 139
 86 without further purification. 140
- 87 **2.1.1. Silicalite-1 seeds** 141
- 88 Silicalite-1 was synthesized to be used as seeds for the 142
 89 crystallization of the parent zeolite (Z_p). An aqueous 143
 90 suspension of TPAOH and TEOS resulting in a precursor 144
 91 suspension with a molar composition of 0.35 TPAOH : 1 SiO₂ : 145
 92 19 H₂O was prepared and stirred at room temperature for 146
 93 12 h. Then, the suspension was hydrothermally treated at 147
 94 373 K for 24 h in a polypropylene bottle. The solid 148
 95 collected after cycles of centrifugation and washing with 149
 96 ultrapure water until reaching a pH value of the supernatant 150
 97 7. 151
- 98 152
 99 153
- 100 **2.1.2. Parent zeolite (sample Z_p).** 154
- 101 The parent zeolite was synthesized from a gel with a molar 155
 102 composition of 0.033 Al₂O₃ : 1.0 SiO₂ : 0.13 TPABr : 0.56 NH₄F : 156
 103 23.13 H₂O. First, an aqueous suspension of Al₂(SO₄)₃·18H₂O 157
 104 and TPABr was prepared in a polypropylene bottle and kept 158
 105 under stirring at room temperature for 30 min. Then, TEOS 159
 106 was added, and the resulting gel was kept under stirring at 160
 107 ambient temperature overnight. The silicalite-1 seeds 161
 162 synthesized (see the procedure above) were added to reach 15
 wt.% of the total silica source of the gel. After 2 h of stirring,
 NH₄F and water were added, and the gel was kept under
 stirring for 2 h. The mixture was hydrothermally treated in a
 Teflon-lined stainless-steel autoclave for 3 days at 373 K. The
 solid product was recovered after successive centrifugation
 and washing with ultrapure water until reaching a pH value of
 the supernatant of 7. Then, the product was dried at 353 K for
 10 h and calcinated at 823 K under static air for 12 h with a
 ramp of 2 K min⁻¹.
- 2.2. Donut-shaped zeolite catalysts**
- 2.2.1. Donut-shaped zeolite catalysts prepared by fluorine treatment (Z_F).**
- The Z_F sample was prepared by mixing the Z_p with an aqueous
 solution of NH₄F (40 wt.%) with a solid/liquid ratio of 1 : 20.
 The mixture was kept under stirring for 1 h at 323 K. Then the
 product was separated by centrifugation, washed with
 deionized water, and dried at 353 K overnight and calcined at
 823 K in static air for 12 h with a ramp of 2 K min⁻¹.
- 2.2.2. Donut-shaped zeolite catalysts prepared by alkaline treatment (Z_{OH}).**
- The Z_{OH} sample was prepared by mixing the Z_p with an
 aqueous solution of NaOH at 0.2 mol L⁻¹ with a solid/liquid
 ratio of 1 : 30. The mixture was kept under stirring for 0.5 h at
 353 K. The treated zeolite was separated by centrifugation,
 washed with deionized water, and dried at 353 K overnight.
 The dried sample was NH₄⁺-exchanged three times with an
 NH₄Cl solution (1 mol L⁻¹) at 358 K for 3 h under stirring using a
 solid/liquid ratio of 1 : 30. Then, the sample was washed with
 deionized water, dried at 353 K overnight and calcinated at
 823 K in static air for 12 h with a ramp of 2 K min⁻¹.
- 2.2.3. Molybdenum impregnation of parent (Z_p) and donut-shaped (Z_F and Z_{OH}) catalysts**
- The parent (Z_p) and donut-shaped samples (Z_F and Z_{OH}) were
 wet impregnated with molybdenum. 2 g of the zeolite sample
 was mixed with an aqueous solution containing 0.147 g of
 (NH₄)₆Mo₇O₂₄·4H₂O and 1.6 mL of ultra-pure water. Then, the
 samples were calcined at 823 K in static air for 4 h with a ramp
 of 2 K min⁻¹. The molybdenum impregnated samples were
 denoted [Mo]-Z_p, [Mo]-Z_F and [Mo]-Z_{OH}.
- 2.3. Characterization**
- The X-ray diffraction (XRD) patterns of the zeolite samples
 were collected from 3 to 50° on a Bruker D8 Advance
 diffractometer equipped with Cu and K_α radiation (λ = 1.5418
 Å) at 40 kV and the scanning speed 0.8° min⁻¹.
- The porosity of zeolite samples was analyzed on a 3Flex
 Micromeritics instrument at 77 K. Before the measurement,
 the samples were degassed at 573 K under vacuum for 4 h. BJH
 model was applied to the adsorption branch of the isotherms
 to evaluate the pore size distribution (PSD). The specific
 surface area was determined using BET method, and the
 micropore volume and external surface area from the t-plot
 method.
- The morphology of the samples was determined using a JSM-
 7900F JEOL scanning electron microscope (SEM) equipped with

163 a field emission gun. The acceleration voltage, beam current
164 and work distance were 4 kV, 2 nA, and 10 mm, respectively.
165 Transmission electron microscopy (TEM) study was performed
166 on a JEM-2100 JEOL microscope with an acceleration voltage
167 of 200 kV.

168 The Si/Al ratio of samples was determined based on ^{29}Si NMR
169 spectroscopy; the spectra were acquired at 120 MHz.
170 Additionally, ^1H NMR spectra of the zeolite samples using
171 11.7 T Bruker Avance 500 spectrometer at 40 kHz were
172 collected. Prior to the ^1H NMR measurements, the samples were
173 degassed at 573 K for 4 h, and kept in Ar atmosphere.
174 The molybdenum content was measured by inductively
175 coupled plasma mass spectrometry (ICP-MS) on a 7900 ICP-MS
176 (Agilent) device.

177 The Fourier transform infrared spectroscopy (FTIR)
178 characterization of samples was performed on a NEXUS Series
179 (Nicolet) spectrometer at 4 cm^{-1} optical resolution. Prior to IR
180 measurements, the zeolites were pressed into self-supporting
181 discs ($\sim 20\text{ mg}$) and pretreated in the IR cell attached to
182 vacuum line (10^{-6} Torr) at 823 K ($3.5\text{ K}\cdot\text{min}^{-1}$) for 4 h. Then the
183 adsorption of pyridine was performed at 423 K until an
184 adsorption equilibrium was reached, then the cell was
185 evacuated at 523 K in order to remove the physisorbed
186 species. All spectra were normalized to 20 mg zeolite sample
187 (self-supported wafer). The amount of pyridine adsorbed on
188 Brønsted and Lewis sites at different temperatures was
189 determined using the integrated area of the bands at 1540 cm^{-1}
190 and 1490 cm^{-1} , respectively. The extinction coefficients used
191 in this study were $\epsilon(\text{B}) 1545 = 1.02\text{ cm mol}^{-1}$ and $\epsilon(\text{L}) 1454 =$
192 0.89 cm mol^{-1} .^{27,31}

193 2.4. Catalytic test

194 Methane dehydroaromatization (MDA) reaction was
195 performed on molybdenum containing samples in a fixed bed
196 reactor at atmospheric pressure and 973 K. 0.5 g of catalyst
197 with particles size in the range of 0.25 - 0.5 mm were packed in
198 a quartz tube reactor (7 mm internal diameter). Prior to the
199 reaction, the catalyst was heated from room temperature to
200 973 K with a heating rate of 5 K min^{-1} under an argon flow
201 15 ml min^{-1} . MDA reaction was carried out at a WHSV of 1.2 h^{-1}
202 with a feed gas mixture of 90 vol.% CH_4 and 10 vol.% N_2 . The
203 gas composition at the reactor outlet was characterized by
204 online gas chromatography (Chromatec, Crystal 9000) using
205 nitrogen as an internal standard.

206 2.5. Characterization of spent catalysts

207 After 10 h of reaction, the spent catalysts were recovered and
208 characterized, and the samples were named $[\text{Mo}]\text{-Z}_p\text{-Spent}$,
209 $[\text{Mo}]\text{-Z}_F\text{-Spent}$ and $[\text{Mo}]\text{-Z}_{\text{OH}}\text{-Spent}$. The coke content on the spent
210 catalysts was measured by thermogravimetric analysis on a
211 SETSYS (SETERAM, Caluire, France) thermobalance. The
212 samples were heated in an alumina crucible from room
213 temperature to 1273 K at a heating rate of 10 K min^{-1} under a
214 flow of air of 40 ml min^{-1} .

215 The pore volume of the spent catalysts was determined by N_2
216 adsorption at 77 K using a Micromeritics 3Flex device. The
217 samples were degassed at ambient temperature for 4 h.

3. Results and discussions

3.1. Material synthesis and characterization

3.1.1. Z_p zeolite sample

To study the impact of zeolite crystal core removal on MDA
performance, donut-shaped zeolite samples were prepared by
a post-synthetic treatment of the parent ZSM-5 zeolite sample
(Z_p). The Z_p was synthesized using aluminum-containing gel
through the seed-assisted method in fluoride media. The
silicalite-1 used as seeds were prepared with a particle size of
about 80 nm (**Figure 1**) and a high crystallinity (**Figure SI. 1**).

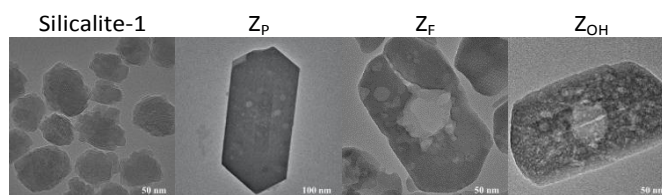


Figure 1. Transmission electron microscopy images of silicalite-1 seeds, Z_p , Z_F and Z_{OH} zeolite samples.

The silicalite-1 crystals act as seeds providing surfaces for the
growth of the zeolite crystals³² and control the crystallization
kinetics of the ZSM-5 phase in fluoride media²⁷. The resulting
material has a pure MFI framework structure (**Figure SI. 2**) and
depicts a coffin shape morphology with a crystal size of about
350 nm (**Figure 1**).

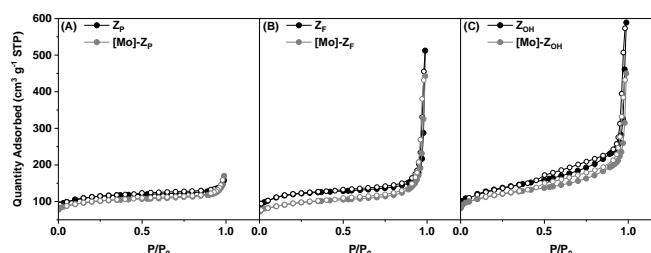
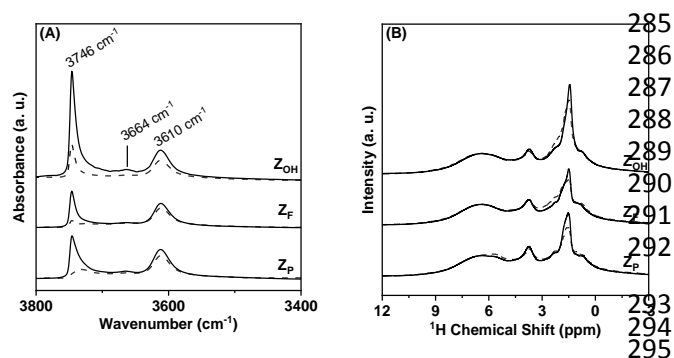


Figure 2. Nitrogen adsorption/desorption isotherms of parent Z_p (A), Z_F (B), and Z_{OH} (C) (black circles) and molybdenum-impregnated $[\text{Mo}]\text{-Z}_p$, $[\text{Mo}]\text{-Z}_F$ and $[\text{Mo}]\text{-Z}_{\text{OH}}$ (grey circles) zeolite samples.

The Z_p sample was characterized by nitrogen physisorption and
the isotherm is presented in **Figure 2**. The micropore and total
pore volume of $0.16\text{ cm}^3\text{ g}^{-1}$ and $0.21\text{ cm}^3\text{ g}^{-1}$, respectively for
the Z_p sample are measured (**Table 1**). Further the
hydrophobicity of the sample was measured by FTIR; the IR
spectra of samples in the $3800\text{-}3400\text{ cm}^{-1}$ region are depicted
in **Figure 3 A**.



249 **Figure 3.** Infrared spectra (A) in the $\nu(\text{OH})$ region of 3800–3400 cm^{-1} and ^1H NMR
 250 spectra (B) of parent Z_p , Z_f , and Z_{OH} (solid line) and
 251 molybdenum-impregnated $[\text{Mo}]\text{-}Z_p$, $[\text{Mo}]\text{-}Z_f$ and $[\text{Mo}]\text{-}Z_{\text{OH}}$
 252 zeolite samples.

253 The peak at 3610 cm^{-1} corresponds to bridged hydroxyls
 254 present in the Z_p sample. Despite the large crystal size, the Z_p
 255 contains isolated silanols confirmed by the presence of a band
 256 at 3746 cm^{-1} .³³ ^1H NMR spectra (**Figure 3 B**) reveal the non- H -
 257 bonded silanols, *i.e.* isolated silanols appearing at 1–3 ppm and
 258 Brønsted acid sites appearing at 4 ppm.^{34,35} These silanols
 259 possibly localized within the crystal core are due to the
 260 presence of silicalite-1 nanocrystal core.^{34,36,37} The Z_p sam-
 261 ple exhibits a heterogeneity with a silicon-rich core surrounded by
 262 an aluminum-rich shell. The Si/Al ratio of the Z_p sample is 38.1
 263 (**Table 2**), corresponding to a theoretical aluminum
 264 concentration of 405 $\mu\text{mol g}^{-1}$. However, the Brønsted acid
 265 concentration measured by pyridine adsorption using FTIR
 266 spectroscopy is lower (**Table 2**) that may be due to the
 267 presence of extra-framework aluminum (**Figure 3 A**, peak at
 268 3664 cm^{-1}) resulting in Lewis acidity (**Table 2**).

269 **Table 1.** Textural properties of the parent Z_p , Z_f , and Z_{OH} and molybdenum
 270 impregnated $[\text{Mo}]\text{-}Z_p$, $[\text{Mo}]\text{-}Z_f$ and $[\text{Mo}]\text{-}Z_{\text{OH}}$ zeolite samples.

Sample	S_{Ext}^a $\text{m}^2 \text{g}^{-1}$	V_{Micro}^a $\text{cm}^3 \text{g}^{-1}$	V_{Tot}^b $\text{cm}^3 \text{g}^{-1}$
Z_p	30	0.16	0.32
$[\text{Mo}]\text{-}Z_p$	29	0.15	0.26
Z_f	47	0.17	0.79
$[\text{Mo}]\text{-}Z_f$	47	0.13	0.68
Z_{OH}	180	0.13	0.91
$[\text{Mo}]\text{-}Z_{\text{OH}}$	132	0.12	0.69

271 ^at-plot, ^bvolume adsorbed at $P/P_0 = 0.99$.

272 3.1.2. Z_f and Z_{OH} donut-shaped zeolite samples

273 The post-treatment of the parent zeolite in fluoride (sample Z_f)
 274 and alkaline (sample Z_{OH}) media resulted in donut-shaped
 275 materials (**Figure 1**) while preserving the high crystallinity and
 276 MFI type framework structure (**Figure SI. 2**). Both Z_f and Z_{OH}
 277 zeolite samples keep the coffin shape morphology of the
 278 parent Z_p and feature a central hole with a diameter
 279 corresponding to the size of the silicalite-1 seeds ($\approx 80 \text{ nm}$).
 280 The macropores formed in both samples due to the removal of
 281 the silicalite-1 seeds increase the total pore volume and the
 282 external surface without impacting the micropore volume
 283 (**Table 1**). The decrease of the Si/Al ratio after treatments
 284 confirms the removal of the silicon-rich part of the zeolite

crystals (**Table 2**). The removal of the seeds results in a partial
 breaking of the zeolite crystals (**Figure SI. 3**).

In the case of the fluoride treatment, the removal of silicalite-1
 results in a lower amount of silanols of sample Z_f in
 comparison to the parent sample Z_p (**Figure 3**). On the
 contrary, the alkaline leaching extracts part of the framework
 atoms, creating additional intracrystalline mesopores (**Figure**
SI. 4) and additional silanols defects (**Figure 3**).

Table 2. Chemical composition and acidity of parent Z_p , Z_f , and Z_{OH} and
 molybdenum-impregnated $[\text{Mo}]\text{-}Z_p$, $[\text{Mo}]\text{-}Z_f$ and $[\text{Mo}]\text{-}Z_{\text{OH}}$
 samples.

Sample	(Si/Al) _{Framework} ^a	[Mo] ^b wt. %	[H] ^c $\mu\text{mol g}^{-1}$	[L] ^c $\mu\text{mol g}^{-1}$
Z_p	38.1	/	276	108
$[\text{Mo}]\text{-}Z_p$	36.1	3.2	228	151
Z_f	34.5	/	245	44
$[\text{Mo}]\text{-}Z_f$	32.3	3.3	221	141
Z_{OH}	26.5	/	226	188
$[\text{Mo}]\text{-}Z_{\text{OH}}$	27.0	3.2	200	210

^adetermined by solid-state ^{29}Si MAS NMR, ^bdetermined by ICP-MAS, ^cBrønsted
 ([H⁺]) and Lewis ([L]) acid sites quantified by pyridine desorption at 423 K by FTIR.

3.1.3. Mo-impregnated zeolite samples: $[\text{Mo}]\text{-}Z_p$, $[\text{Mo}]\text{-}Z_f$ and $[\text{Mo}]\text{-}Z_{\text{OH}}$

The three zeolite samples (Z_p , Z_f and Z_{OH}) were wet-
 impregnated with about 3 wt.% of molybdenum (**Table 2**).
Figure 3 A depicts the OH region of the IR spectra for samples
 before and after Mo impregnations. On the three samples, the
 intensity of the bridged hydroxyls band decreases after
 molybdenum loading. Indeed, during the calcination a part of
 the molybdenum migrates within the micropores and reacts
 with the framework aluminum.³⁸ The quantity of molybdenum
 anchored to the framework aluminum ($[\text{Mo}]_{\text{Anch}}$) can be
 estimated from the loss of Brønsted acid sites as determined
 by pyridine adsorption using IR of samples before and after Mo
 loading (**Table 2**). Assuming a stoichiometry of one
 molybdenum atom per aluminum atom^{39,40}, the $[\text{Mo}]_{\text{Anch}}$ is
 estimated to be of 0.4 wt.% and only a half of this value on
 $[\text{Mo}]\text{-}Z_f$ and $[\text{Mo}]\text{-}Z_{\text{OH}}$ samples (**Table 2**). In both IR and ^1H
 NMR spectra (**Figure 3**), the intensity of the isolated silanols
 bands decreases after Mo loading on the 3 samples ($[\text{Mo}]\text{-}Z_p$,
 $[\text{Mo}]\text{-}Z_f$ and $[\text{Mo}]\text{-}Z_{\text{OH}}$). Thus, part of the molybdenum is
 anchored to the zeolite framework on the three samples by
 interacting with the isolated silanols. Mo-mapping of the
 samples $[\text{Mo}]\text{-}Z_p$, $[\text{Mo}]\text{-}Z_f$ and $[\text{Mo}]\text{-}Z_{\text{OH}}$ by EDS reveal the
 homogeneous dispersion of molybdenum located within the
 crystals volume and on the surface (**Figure 4**), except in the
 empty core on $[\text{Mo}]\text{-}Z_f$ and $[\text{Mo}]\text{-}Z_{\text{OH}}$.
 Based on the characterization results presented above, the
 samples can be described as follow: (i) $[\text{Mo}]\text{-}Z_p$ as silicon-core
 /ZSM-5-shell material, (ii) $[\text{Mo}]\text{-}Z_f$ as ZSM-5 zeolite with
 macropores created by seed core removal, and (iii) $[\text{Mo}]\text{-}Z_{\text{OH}}$ as
 ZSM-5 zeolite with high external surface and macropores
 created by seed core removal with intracrystalline mesopores
 and additional external silanols.

Both post-treatments of the zeolites in OH^- and F^- media decrease the number of Brønsted acid sites, hence, molybdenum anchored to BAS ($[\text{Mo}]_{\text{Anch}}$).

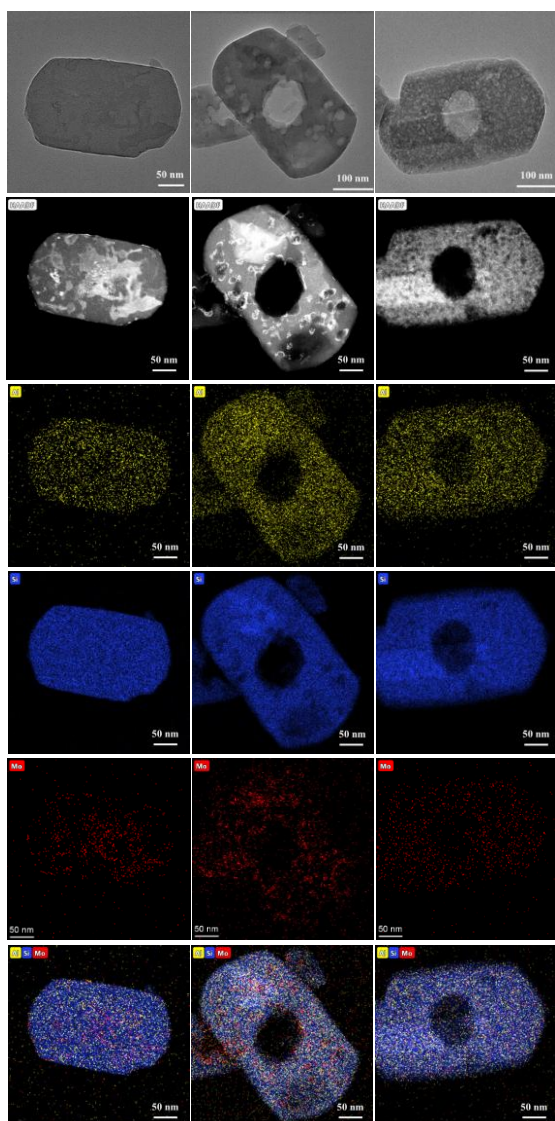


Figure 4. TEM and EDS mapping of $[\text{Mo}]\text{-Z}_p$ (left), $[\text{Mo}]\text{-Z}_f$ (middle) and $[\text{Mo}]\text{-Z}_{\text{OH}}$ (right) zeolite samples.

3.2. Catalytic evaluation of zeolite catalysts in MDA reaction

Methane dehydroaromatization was carried out on parent $[\text{Mo}]\text{-Z}_p$ and donut-shaped $[\text{Mo}]\text{-Z}_f$, $[\text{Mo}]\text{-Z}_{\text{OH}}$ zeolite catalysts at 973 K.

3.2.1. MDA on $[\text{Mo}]\text{-Z}_p$ parent zeolite catalyst

The methane consumption rate on the $[\text{Mo}]\text{-Z}_p$ catalyst sharply decreases with the time on stream, following the same behavior as $\text{Mo}/\text{ZSM-5}$ catalysts with similar Mo content and Si/Al ratio, previously reported in the literature (Figure S1). The gain and loss in methane consumption (Figure 5 A), benzene production (Figure 5 B), and the deactivation constant (k_d) calculated assuming a first-order law (Figure 5 C) over 10 h reaction using the three catalysts are presented. The methane consumption on the $[\text{Mo}]\text{-Z}_p$ catalyst ($31 \text{ mmol}_{\text{cat}}^{-1}$,

Figure 5 A) and the k_d value (0.14 h^{-1}) are in the same order of magnitude as reported in the literature.

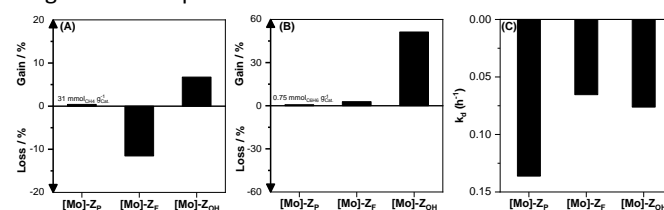


Figure 5. Impact of fluorine ($[\text{Mo}]\text{-Z}_f$) and alkaline treatment ($[\text{Mo}]\text{-Z}_{\text{OH}}$) relative to the parent zeolite ($[\text{Mo}]\text{-Z}_p$) on (A) the CH_4 consumption and (B) the benzene formation on time on stream window of 10 h, and (C) benzene first order deactivation rate (k_d).

The analysis of coke on the spent $[\text{Mo}]\text{-Z}_{p\text{-Spent}}$ catalyst was carried out by thermogravimetry and the content of soft coke and hard coke at combustion temperatures of 722 and 846 K, respectively were measured (Figure 6).

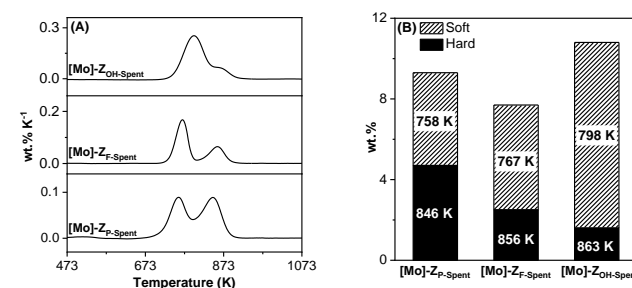


Figure 6. Coke on the spent catalysts ($[\text{Mo}]\text{-Z}_{p\text{-Spent}}$, $[\text{Mo}]\text{-Z}_{\text{OH-Spent}}$ and $[\text{Mo}]\text{-Z}_{f\text{-Spent}}$) after 10 h of reaction represented by derivative curves of thermogravimetric measurements (A) and content of soft coke and hard coke and combustion temperatures determined by thermogravimetric analysis (B).

The change in the micropore volume measured by N_2 adsorption (Figure 7 A), is a deactivation descriptor. Indeed, Hensen *et al.* showed a linear dependence between the coke content and the remaining microporous volume of zeolite catalysts. For the $[\text{Mo}]\text{-Z}_{p\text{-Spent}}$ catalyst, a loss of half of the initial microporous volume corresponding to a total coke content of 9.3 wt.% was measured (Figure 6 B and Figure 7 A). Moreover, the mesopore volume of the $[\text{Mo}]\text{-Z}_{p\text{-Spent}}$ catalyst remains almost unchanged (Figure 7 A), thus one can conclude that the coke is mainly located in the microporous volume (Figure 7 B). The deactivation of the $[\text{Mo}]\text{-Z}_{p\text{-Spent}}$ catalyst during MDA also occurs through molybdenum carbides sintering located on the external surface (Figure 8). Such clusters are mostly localized on the ZSM-5 part of the $[\text{Mo}]\text{-Z}_{p\text{-Spent}}$ catalyst, while Mo species seems to have a better dispersion on the silicalite-1 core. The methane consumption, k_d , and combustion temperatures of soft coke and hard coke, and remaining microporous volume of the parent $[\text{Mo}]\text{-Z}_p$ catalyst are similar to the ones reported for ZSM-5 zeolite earlier. Thus, the parent sample $[\text{Mo}]\text{-Z}_p$ can be considered as a reliable reference in order to understand the behavior of the donut-shaped zeolite catalysts in the MDA reaction.

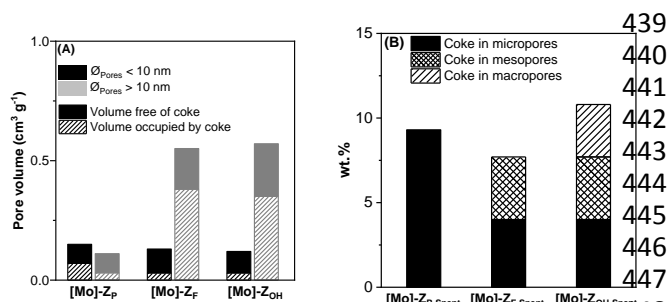


Figure 7. Characterization of [Mo]-Z_p-Spent, [Mo]-Z_f-Spent and [Mo]-Z_{oh}-Spent catalysts after 10 h of reaction: pore volume with and without coke, measured by nitrogen sorption (A) and coke distribution in different pores of zeolite catalysts (B).

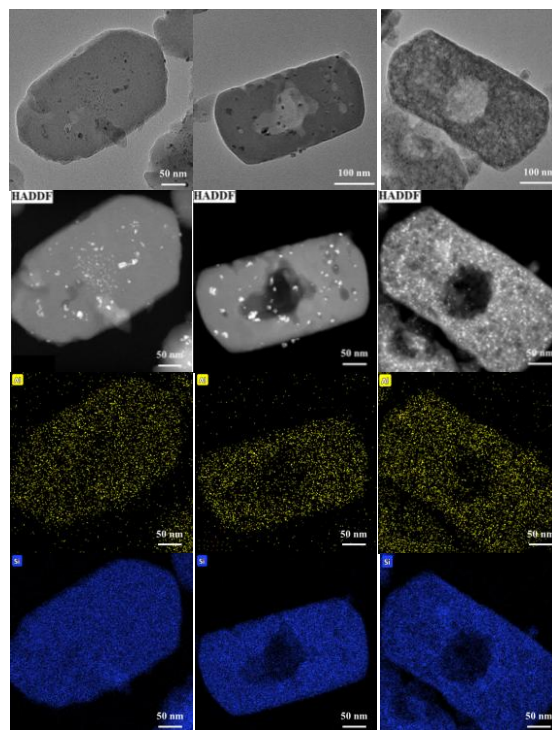
3.2.2. MDA on [Mo]-Z_f and [Mo]-Z_{oh} donut-shaped catalysts

The methane consumption on the [Mo]-Z_f catalyst decreases slightly without any change in benzene production (Figure 5A and B). The NH₄F etching used for the preparation of [Mo]-Z_f leads to a lower amount of [Mo]_{Anch} (see section 3.1.3) considered as a precursor for MDA active sites⁹, thus lowering the methane consumption. However, the presence of the central hole enhances the catalyst stability, probably mitigating the coke deposit within zeolite micropores (Figure 5C and Figure SI. 6). A loss of 0.03 cm³ g⁻¹ of the micropore volume (V_{Micro}) of sample [Mo]-Z_f-Spent shown by the black column (volume occupied by coke) is depicted in Figure 7A. Based on the linear relationship presented elsewhere⁴², a coke content of 4.0 wt.% located in the micropore volume of this sample is calculated. The total coke content of [Mo]-Z_f-Spent measured by TG is 7.7 wt.% (Figure 6) and based on the coke balance, 3.7 wt.% of the coke is located in the macropores (more details on the calculation can be found in the supporting information) due to the presence of a hole in the donut-shaped structure (Figure 7A). After 10 h of MDA, molybdenum carbide was formed and predominantly deposited on the external surface of the catalysts.

The alkaline treatment of the parent zeolite substantially improves methane consumption and benzene production as shown in Figure 5A and B. The higher activity is probably not due to a higher molybdenum-aluminum anchoring since for both samples, [Mo]-Z_{oh} and [Mo]-Z_f, a similar [Mo]_{Anch} is measured. Despite the decrease in the number of active sites of sample [Mo]-Z_{oh} compared to [Mo]-Z_p, the activity gain may result from additional small mesopores connected to the micropore network and better stability of molybdenum carbides present (Figure 8). This can be explained with the high external surface of sample [Mo]-Z_{oh} in comparison to the parent [Mo]-Z_p and [Mo]-Z_f catalysts (Table 1). Moreover, the [Mo]-Z_{oh} contains silanols defects that interact with molybdenum and prevent sintering of molybdenum carbides during the MDA reaction.

The deactivation rate constant (k_d) remains similar for the [Mo]-Z_{oh} sample regardless of the post-treatment procedure applied (Figure 5C and Figure SI. 6). The additional small mesopore network has no impact on the catalyst stability, thus the mitigation of deactivation is only due to the dissolution of

the silicalite-1 seeds resulting in a decrease of the diffusion pathway within the [Mo]-Z_{oh} crystals. For the spent [Mo]-Z_f-Spent and [Mo]-Z_{oh}-Spent donut-shaped catalysts, the losses of V_{Micro} and V_{Tot} are similar no matter the post-treatment applied (Figure 7A). Yet, the total coke content is higher on the [Mo]-Z_{oh}-Spent catalyst than on the [Mo]-Z_f-Spent free of silanols defects (Figure 6). The presence of a hole leads to better accessibility of oxygen to coke during TGA measurements. Thus, a higher amount of soft coke was measured on [Mo]-Z_f-Spent and [Mo]-Z_{oh}-Spent catalysts (Figure 6). Moreover, the presence of mesopores in the [Mo]-Z_{oh} catalyst enhances this phenomenon. A similar shift was previously reported on mesoporous catalysts¹⁹. The location of coke in the [Mo]-Z_{oh}-Spent catalysts can be estimated as follows (more details on the calculation can be found in the supporting information): (i) 4.0 wt.% in the micropores, (ii) 3.7 wt.% in macropores, and (iii) by coke balance 3.1 wt.% in the additional mesopores (Figure 7B). The coke retention in the mesopores can be explained with the presence of silanols known to act as coke traps⁴³⁻⁴⁵. Thus, the retention of soft coke in sample [Mo]-Z_{oh}-Spent is enhanced (Figure 6). Only the coke deposited in the micropores of the [Mo]-Z_{oh}-Spent deactivates the catalyst. The coke in the different pores of the [Mo]-Z_{oh}-Spent catalyst does not directly affect the loss of free total pore volume regarding the [Mo]-Z_f-Spent catalyst, as exemplified in Figure 7B. Yet the soft coke and hard coke combustion occur at higher temperatures (Figure 6), despite the presence of mesopores allowing higher accessibility to oxygen^{18,42}.



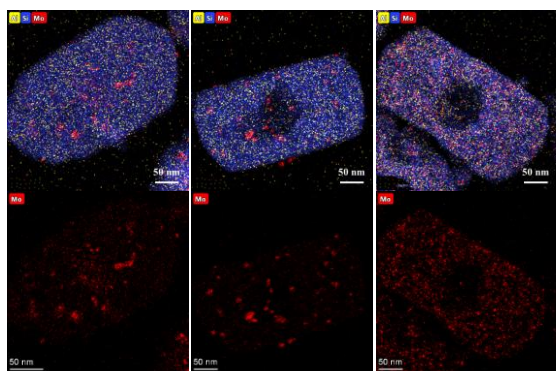


Figure 8. TEM and EDS mapping images of [Mo]-Z_p-Spent (left), [Mo]-Z_f-Spent (middle) and [Mo]-Z_{OH}-Spent (right) catalysts after 10 h of reaction.

469
470

471 4. Conclusions

472 The synthesis of donut-shaped catalysts containing
473 molybdenum was successfully carried out by NH₄F and NaOH
474 post-treatment of silicalite-1-core/HZSM5-shell zeolite
475 composites. Both treatments dissolve the silicon-rich core of
476 the parent silicalite-1-core/HZSM5 sample and the total
477 porosity changed in the order: [Mo]-Z_p < [Mo]-Z_f < [Mo]-Z_{OH}.
478 Both treatments of the parent silicalite-1-core/HZSM5 sample
479 (Z_p) resulted in donut-shaped catalysts however the [Mo]-Z_{OH}
480 contains higher amount mesopores and isolated silanols.
481 The catalytic test of the three samples in MDA reaction
482 revealed deposition of coke in the micropores of the catalysts.
483 While in the donut-shaped catalysts, the decrease of
484 diffusion pathway improves the stability of the catalysts during
485 MDA by shifting the coke location from micropores to
486 macropores. Extra coke deposits in the mesopores of the
487 alkaline-treated catalyst ([Mo]-Z_{OH}) was found but without
488 impacting its deactivation. Moreover, the presence of silanols
489 and the high external surface of the [Mo]-Z_{OH} catalyst mitigate
490 the sintering of molybdenum carbides and lead to higher
491 activity in the MDA reaction.

492 5. Conflicts of interest

493 There are no conflicts to declare.

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508 7. References

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