Co-aromatization of furan and methanol over ZSM-5: a pathway to bio-aromatics

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Co-Aromatization of Furan and Methanol over ZSM-5—A Pathway to Bio-Aromatics

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ABSTRACT: Aromatization of furan and substituted furans over zeolite catalysts is a promising reaction to convert cellulose-derived compounds into valuable aromatic hydrocarbons and light olefins. A lack of understanding of the reaction mechanism however hinders further development of this process. Here, we propose the reaction mechanism, underlying the chemistry of furan and methanol co-aromatization over HZSM-5 zeolite catalyst. Applying $^{13}$C isotope labeling in a combination with NMR spectroscopy and high temporal resolution gas chromatography-mass spectrometry analysis, we demonstrate that aromatization of furan and methanol are not mechanistically separated and can be described within the dual-cycle hydrocarbon pool mechanism. Cofeeding furan with methanol leads to a significant enhancement of light aromatics selectivity and increased catalyst lifetime.

KEYWORDS: aromatics, biomass, furan, methanol-to-aromatics, zeolite

1. INTRODUCTION

Replacing fossil-based feedstock by renewable alternatives remains a substantial challenge for the chemical industry. Aromatic compounds, which are the basic building blocks for the production of a wide range of polymers, solvents, and fine chemicals, are currently obtained exclusively from petroleum feedstock. As lignocellulosic biomass is considered one of the main sources of renewable carbon, chemical conversion routes to biobased aromatics are highly desirable. Valorization of biomass into chemical commodities requires several separation steps and chemical conversion steps, including depolymerization and oxygen removal. A common approach is to convert biomass into platform molecules from which a wider range of chemical applications can be targeted.1−3 One of the promising methods involves depolymerization of cellulose into glucose followed by its isomerization and dehydration to obtain furanic platform molecules. Furans can be converted to aromatics at high temperature in the presence of zeolite catalysts.4,5 Typically, shape-selective MFI-type (ZSM-5) zeolite is used as catalyst for aromatization processes, because its optimal pore size leads to high benzene, toluene, and xylene (BTX) selectivity.5,6 Besides, it has been shown that furan can serve as a representative model compound for catalytic fast pyrolysis (CFP) of raw woody biomass.5,8 A major drawback of the aromatization of furans is the rapid deactivation of the zeolite catalyst and the relatively low aromatic selectivity.9,10 Diels−Alder (DA) chemistry is commonly thought to form the mechanistic basis for the conversion of furanics to aromatics over zeolites. Furans and reaction intermediates formed via deoxygenation during pyrolysis may act simultaneously as dienes and dienophiles.5,11,12 On the basis of this idea, ethylene and propylene cofeeding during pyrolytic upgrading has been explored. In such studies, it has been observed that the selectivity to BTX is improved when olefins are added to the feed.11,13−15 In practice, such olefins are however too expensive to facilitate the production of aromatics via this route. Recently, it has been suggested that methanol cofeeding can also enhance the BTX selectivity in the zeolite-catalyzed upgrading processes, presumably because methanol is rapidly converted to olefins on the same zeolite catalysts.16,17 In this work, we study the effect of methanol addition on the aromatization of furan over zeolite catalysts. By applying isotopic labeling and NMR spectroscopy, we elucidate the different mechanistic pathways that underlie the coaromatization of furan and methanol. A major insight is that this process does not involve DA chemistry and is predominantly based on the hydrocarbon pool mechanism. On the basis of our findings, we optimized this process, which may link the renewable
energy storage via carbon dioxide hydrogenation to liquid methanol with renewable biomass for the manufacture of important chemical intermediates.18–20

2. EXPERIMENTAL PROCEDURES

2.1. Catalyst Characterization. The ammonium form of zeolite ZSM-5 with Si/Al ratio of 40 (obtained from Alfa Aesar) was calcined at 550 °C for 5 h in static air (heating rate 5 °C/min) to obtain the proton form HZSM-5.

The chemical composition (Si/Al ratio) of zeolite was determined by elemental analysis using inductively coupled plasma optical emission spectrometry (ICP-OES). A Spectro CIROS CCD ICP optical emission spectrometer with axial plasma viewing was used for these measurements. Prior to analysis, the zeolite samples were dissolved in a 1:1:1 mixture by weight of HF (40%), HNO3 (60%), and H2O.

The fraction of extra-framework Al was assessed by 27Al NMR spectroscopy. The measurements were performed using an 11.7 T Bruker DMX500 NMR spectrometer with a 2.5 mm MAS probe head spinning at 25 kHz. The sample was hydrated prior to NMR measurements. 27Al NMR spectra were recorded with a single pulse sequence with an 18 μs, interscan delay of 1 s.

The acidic properties were determined by IR spectroscopy of adsorbed pyridine. Spectra were taken in the 4000–1000 cm−1 range using a Bruker Vertex 70v Fourier-transform infrared spectrometer. Samples were pressed into self-supporting wafers (10–15 mg, diameter 1.3 cm) and placed in an environmental cell. The wafers were first pretreated in O2/N2 (1:4 volume (vol) ratio) flow at 550 °C (heating rate 5 °C/min) to remove contaminants followed by cooling to 150 °C under dynamic vacuum (p < 1 × 10−5 mbar). Pretreated wafers were then exposed to excess pyridine vapor. After evacuation, IR spectra were recorded at different temperatures (150–450 °C) under vacuum. For the quantification of Bronsted and Lewis acid sites, integral molar extinction coefficients (IMEC) of 0.73 and 1.11 cm/mol, respectively, were used.21,22

Textural properties of the zeolites were determined from Ar physisorption isotherms, which were recorded at 87.3 K using a Micromeritics ASAP-2020 apparatus. The sample was outgassed at 450 °C prior to physisorption. The microporous volume was determined by the t-plot method using a thickness range from 3.5 to 4.5 Å.

2.2. Catalytic Activity Measurements. Catalytic activity measurements were performed in a tubular quartz fixed-bed downstream reactor (i.d. = 4 mm, length l = 20 cm). In a typical experiment, 0.5 g of catalyst (sieve fraction of 250–500 μm) was held between two quartz wool plugs. Prior to the measurements, zeolite was pretreated under O2/He (1:4 vol ratio) flow at 550 °C (heating rate 5 °C/min) to remove water and any possible organic contaminants and then cooled to the reaction temperature. Calibrated thermal mass-flow controllers (Brooks) were used to feed carrier gases to the saturators and to the reactor. Furans (Sigma-Aldrich, ≥99%), 2,5-dimethylfuran (2.5-dMF, Sigma-Aldrich, 99%), and methanol (VWR chemicals, 99.9%) were introduced in the feed by leading a gas flow through thermostated saturators. For isotope labeling experiments 13C ethylene (Eurisotop, 98%, 99% 13C) and 13C methanol (Cambridge Isotope Laboratories, 98%, 99% 13C) were used.

Reaction products were analyzed with online mass spectrometry (Pfeiffer Omnistar GSD 301 T3MS) and gas chromatography (Trace GC 1300, Thermo) instruments, placed consecutively downstream from the reactor. A thermal conductivity detector (TCD) equipped with an RT-Q-Bond column (length 20 m; i.d. 0.32 mm; film thickness 10 μm) was used to analyze the light fraction of the reaction products including water, CO2, and C1–C4 hydrocarbons. Aromatic products were analyzed with a flame ionization detector (FID) coupled with Rxi-Sil MS column (length 30 m; i.d. 0.32 mm; film thickness 0.25 μm). For qualitative analysis and identification of individual compounds, the reaction products were collected in a cold trap (cooled with liquid nitrogen) and then analyzed with a GC-MS instrument (Shimadzu MS GCMS-QP 5050a). A mixture of GC standards was used to confirm the assignment of the main components. The reaction selectivity, conversion, and yield were calculated as follows:

\[
x(t) = \frac{n_{i}^{out}}{n_{i}^{in}}
\]

(1)

\[
s_{k}(t) = \frac{n_{k}^{out}}{n_{k}^{in} - n_{k}^{out}} \times \frac{\mu_{i}^{out}}{\mu_{k}^{out}}
\]

(II)

\[
X_{k}(C_{based}) = \sum_{i} \mu_{i} \times \int_{0}^{t} (n_{i}^{in} - n_{i}^{out}) dt
\]

(III)

\[
S_{k} = \frac{\mu_{k} \times \int_{0}^{t} n_{k}^{out} dt}{X_{i}}
\]

(IV)

\[
Y_{k} = \mu_{k} \times \int_{0}^{t} n_{k}^{out} dt = S_{k} \times X_{i}
\]

(V)

where (I)—conversion at time t; (II)—carbon-based selectivity to a product k at time t, where ni is concentration of the product ki and μk is number of carbon atoms in the product k; (III)—overall carbon-based conversion at time t; (IV)—overall carbon-based selectivity to a product k; and (V)—overall carbon-based yield of a product k. Cumulative parameters were calculated up until time t such that x(t) = 75%.

NMR spectra of the reaction products were measured on Bruker 400 Avance II and Agilent 400-MR DD2 spectrometers. All measurements were performed using identical concentrations and sample collection times to ensure adequate comparison between reaction mixtures, produced with 13C labeled and nonlabeled ethylene and methanol substrates. Samples were prepared by diluting the collected reaction mixture with 1 mL of CDCl3, which provided nearly identical 1H spectra for natural and 13C-enriched mixtures. The connectivity of 13C atoms in the reaction products was studied using 13C–13C homonuclear correlation NMR spectroscopy (Incredible Natural Abundance Double QUantem Transfer Experiment (INADEQUATE)). In all cases, nonenriched samples did not produce detectible INADEQUATE signal. The acquisition time of an INADEQUATE experiment for 13C methanol sample was shortened to 64 increments (64 scans each) to ensure absence of interference from naturally abundant 13C atoms.

2.3. Coke Characterization. In situ IR spectroscopy was used to follow the deposited coke using a Bruker Vertex 70v Fourier-transform infrared spectrometer. For this purpose, a
The proton form of ZSM-5 zeolite (Si/Al 40) was used for all experiments. The material was thoroughly characterized for its physicochemical properties (see Table S1). Catalytic tests were performed in a fixed-bed quartz reactor coupled with online gas chromatography. Other experimental details can be found in the Supporting Information. The catalytic results show that aromatization of furan yields a mixture of light hydrocarbons (CH₄, C₂−C₄ compounds), BTX, and other substituted benzenes (e.g., ethylmethylbenzenes, trimethylbenzenes), heavier bicyclic aromatic compounds (indanes, indenes, naphthalenes), as well as water and CO₂ (Figure 1). The numerical data of these tests are collected in Table S2.

As shown in Figure 1a, the conversion of furan is initially close to 100% and rapidly decreases, reaching 50% already after 20 min of reaction due to coke deposition. Addition of methanol to the feed substantially lowers the rate of deactivation, and this effect becomes more pronounced when more methanol is added relative to furan. The total furan conversion increases from 4.5 mmol C/gcat for only furan to 10 mmol C/gcat for a methanol/furan molar ratio of 15. The total cumulative carbon conversion with cofed methanol increases by more than an order of magnitude to 50 mmol C/gcat. Along with the improved lifetime, the addition of methanol significantly changes the product distribution. Figure 1b,c shows that the (carbon-based) BTX selectivity improves with increasing methanol/furan ratio from 10% (pure furan) to 35% (for methanol/furan = 5−5). At the same time, the fraction of the most valuable compounds in the BTX mixture, that is, xylenes, increases from 8% to 64%. When the methanol/furan ratio is further increased, the BTX selectivity becomes lower and eventually approaches the value obtained with pure methanol feed. On the one hand, the higher concentration of xylenes and other methylated benzenes in the product mixture suggests that alkylation of benzene and toluene with methanol occurs. On the other hand, the formation of heavier bicyclic products such as indanes, indenes, and naphthalenes is suppressed in the presence of methanol. This change in the product distribution can explain the observed slower deactivation rate, as polycyclic aromatics are considered to be coke precursors (see Figure S1 for the complete distribution of the reaction products). Addition of methanol to the feed significantly changes during the progress of the reaction. 

**3. RESULTS AND DISCUSSION**

The proton form of ZSM-5 zeolite (Si/Al 40) was used for all experiments. The material was thoroughly characterized for its physicochemical properties (see Table S1). Catalytic tests were performed in a fixed-bed quartz reactor coupled with online gas chromatography. Other experimental details can be found in the Supporting Information. The catalytic results show that aromatization of furan yields a mixture of light hydrocarbons (CH₄, C₂−C₄ compounds), BTX, and other substituted benzenes (e.g., ethylmethylbenzenes, trimethylbenzenes), heavier bicyclic aromatic compounds (indanes, indenes, naphthalenes), as well as water and CO₂ (Figure 1). The numerical data of these tests are collected in Table S2.

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of the reaction as well (Figures S2 and S3). At prolonged reaction times, a gradually increasing fraction of the catalyst becomes deactivated by coke deposits, resulting in a shortening of the effective contact time. Thus, the reaction time-on-stream profiles provide valuable information about the reaction intermediates.28,29 The formation of methylated furans, including 2-methylfuran and 2,5-dimethylfuran (2,5-dMF), was observed at a later stage of the reaction (Figure S4). As we previously showed, such methylated furans can undergo aromatization on zeolites by forming reaction intermediates with a lower C/H ratio upon initial deoxygenation (see Figure S5).30 This results in a lower rate of coke formation and, therefore, a higher total BTX yield as compared to the conversion of unsubstituted furan. Besides, this is in line with the observed shift in deoxygenation pathway from dehydration/decarbonylation/decarboxylation to mainly dehydration (see Table S2 for the distribution of oxygen-containing products), which was previously observed during conversion of methyl-substituted furans.30

To evaluate the importance of furan methylation and DA chemistry (pathways I and III in Scheme 1) on the overall reaction performance, we performed additional catalytic experiments with (i) 2,5-dMF and (ii) furan with cofeeding ethylene and (iii) 2,5-dMF with cofeeding ethylene. The carbon stoichiometry of these feeds was the same as for the co-reaction of furan with 2 equiv of methanol (iii) (see Figure 2 for the product distribution and yield).

Strikingly, for the aromatization of furan in the presence of ethylene, we observe that both the absolute yield and the carbon selectivity to BTX were very close to values obtained for pure furan. A small increase in substituted aromatics production can be attributed to alkylation of the reaction products with ethylene.31 On the other hand, aromatization of pure 2,5-dMF led to a significantly higher aromatics selectivity (~35%) and absolute product yield. However, the distribution of aromatic products is different from that obtained when furan was cofed with 2 equiv of methanol. Both the absolute yield and the fraction of xylenes are higher when methanol is cofed to furan. These findings imply that the positive influence of methanol cannot be solely attributed to either furan methylation followed by aromatization or to DA cycloaddition between furan and ethylene produced from methanol. Clearly, other reactions must be involved that lead to the strongly improved BTX selectivity and longer catalyst life when methanol is cofed.

Isotope labeling was applied to understand the role of cofed methanol and ethylene in furan aromatization. Furan was cofed with either 13C-labeled ethylene (H2; 13C(CH2)) or 13C-labeled methanol (13CH3OH). The liquid reaction products collected in an LN2 trap were analyzed by GC-MS and NMR. GC-MS analysis reveals that the 13C atoms from ethylene and methanol are included in the reaction products. Figure 3 shows MS spectra of toluene obtained after the reaction of furan with labeled ethylene and methanol. The initial 13C content in the feed was 30%, which corresponds to ethylene/furan molar ratio of 1 and methanol/furan molar ratio of 2. After the reaction of furan with 13C-ethylene the 13C content of toluene was 8.4%, and after the reaction of furan with 13C-methanol—26.8%. The 13C content of other aromatic products, produced in cofeeding experiments, was similar to these values (MS spectra of benzene, xylenes, and naphthalenes are shown by Figures S6 and S7; 1H and 13C NMR spectra can be found in Figures S8–S11). Since the 13C contents of the reaction mixture and obtained aromatic products are the same, we can conclude that coaromatization between furan and methanol occurs. A more detailed analysis of the GC-MS data shows that the distribution of 13C labels in toluene is not random (Figure

Scheme 1. Possible Reaction Pathways Involving Methanol in Furan Aromatization Reaction

(1) DA pathway; (II) methylation of furan followed by aromatization; and (III) DA reaction with ethylene.

Figure 2. Overall (a) carbon selectivity and (b) absolute yields in pure furan aromatization reaction as compared to furan with cofeeding of 2 equiv of methanol and to furan with cofeeding ethylene and 2,5-dimethylfuran. Conditions: reactor temperature 450 °C; p(furan) 0.6 kPa; atmospheric pressure; carrier ~100 mL/min He.
The fraction of toluene molecules containing four unlabeled atoms is significantly higher than the expected value, and this difference from a random distribution is also observed for the other aromatic molecules. In contrast to the methanol case, ethylene incorporation into the reaction products is limited. In this case, for aromatics we observe a strong tendency to either remain unlabeled or to contain two $^{13}$C atoms.

Because of the higher amount of $^{13}$C, we could study the connectivity of $^{13}$C atoms in the reaction products of furan$-^{13}$C methanol coaromatization, using $^{13}$C-$^{13}$C homonuclear correlation NMR spectroscopy (INADEQUATE, see Figure 3e). Apart from a large number of $^{13}$C-$^{13}$C bonds in the aromatic region of the INADEQUATE spectra, we found that in toluene the $^{13}$C labels can form three $^{13}$C chains starting from the aliphatic methyl group of the molecule (C$_1$−C$_3$ in Figure 3e). This result is in accord with the GC-MS data, implies a certain tendency for the original four-carbon $^{12}$C furan skeleton to remain intact during the coaromatization reaction.

As described above, the addition of methanol to the feed lowers the rate of catalyst deactivation and is therefore expected to affect the structure of intrazeolitic coke deposits. Thermogravimetric (TG) analysis of spent zeolite samples (Figure S12) shows a small shift to lower temperature (~10 °C) of the main combustion peak for samples obtained by furan coaromatization with methanol in comparison to the sample obtained during furan aromatization and furan coaromatization with ethylene. A higher proton content of the coke species is a reasonable explanation for the more facile combustion. By periodically burning the formed coke species in oxygen, we established that the catalyst could be regenerated at least 4 times without obvious changes in activity and selectivity (see Figure S13).

To establish the relation between the structure of carbon deposits and the composition of reactant mixture the catalyst samples after the reaction in pure furan and in mixtures of furan with $^{13}$C-methanol/$^{13}$C-ethylene were studied by MAS NMR spectroscopy. The $^{13}$C$\{^1$H$\}$ cross-polarization and $^{13}$C direct excitation NMR spectra are presented in Figure 4a and

![Figure 3. Isotope distribution in toluene obtained in a reaction of furan with addition of (a) ethylene and (b) methanol; $^{13}$C labeled (c) ethylene and (d) methanol; (e) INADEQUATE NMR spectrum of the reaction mixture obtained in the presence of $^{13}$CH$_3$OH. Cross peaks corresponding to toluene product are labeled on the graph with respective chemical shifts.](https://example.com/figure3.png)

![Figure 4. Formation of coke species in zeolite: (a) $^1$H-$^{13}$C CP MAS NMR of the samples obtained after the aromatization reaction of pure furan and furan$-^{13}$C methanol and furan$-^{13}$C ethylene mixtures; (b) $^1$H-$^{13}$C$\{^1$H$\}$ HETCOR MAS NMR 2D spectrum of zeolite catalysts after furan aromatization reaction with cofeeding of $^{13}$C methanol; IR spectra of 1800–1250 cm$^{-1}$ region recorded under incremental dosing of (b) furan and (c) a mixture of methanol and furan (2:1).](https://example.com/figure4.png)

![Figure S14.](https://example.com/figureS14.png)
in furan/methanol, and it can be assigned to methoxyl groups.\textsuperscript{35} The $^{13}$C DE spectra shown in Figure S14b,c provide quantitative information about these intrazeolite species. When $^{13}$C-ethylene was cofed with furan, we observed an eightfold increase in the total $^{13}$C intensity of coke as compared to the experiment with pure furan. This implies that surface carbon contains $\sim$8% of $^{13}$C atoms (natural abundance of $^{13}$C is 1.1%). Note that a similar $^{13}$C content ($\sim$10%) was observed in liquid reaction products by GC-MS. Besides, the relative intensity of the aliphatic signal at 20 ppm for the reaction with $^{13}$C-ethylene is higher than for $^{12}$C-ethylene, suggesting that ethylene preferentially impacts the aliphatic fraction of coke. A stronger effect was observed when furan was reacted with methanol. The total intensity of NMR signal was $\sim$20 times higher ($^{13}$C fraction of $\sim$20%), while the increase in aliphatic fraction was significantly more pronounced than for the ethylene case. Note that the total coke content of the spent catalysts was similar (Figure S12), confirming that the increase in NMR signals is only related to the isotope enrichment of coke.

The $^1$H–$^{13}$C($^1$H) HETCOR MAS NMR experiments provide additional insights into the structure of retained species. The 2D spectrum shown in Figure 4b reveals complexity of the signal around 130 ppm. This might be attributed to different polyaromatic species interacting with Bronsted acid sites of zeolite. The data show a clear correlation between the aliphatic (20 ppm) and the aromatic (130 ppm) region, which suggests that aliphatic species are present as substituents in the aromatic molecules. We also followed the formation of intrazeolite species with in situ IR spectroscopy (Figure 4c,d IR spectra of 1800–1250 cm$^{-1}$ region, complete spectra in the Supporting Information, Figure S15). For this purpose, a catalyst sample was exposed at 450 °C to either pure furan vapor or a vapor containing methanol and furan in a 2:1 molar ratio. The concentration of reactants in the cell was incrementally increased to 150 $\mu$mol C per Bronsted acid site (Figure S15, peak assignment summarized in Table S3). In both experiments, the dosing procedure led to a gradual disappearance of the bridging hydroxyl IR features at 3610 cm$^{-1}$, assigned to Bronsted acid sites.\textsuperscript{36} Perturbed hydroxyls and water produced during decomposition of furan and methanol give rise to a broad band extending in the 3500–2000 cm$^{-1}$ range (Figure S15). In the experiment with methanol, the disappearance of the unperturbed $\nu$(OH) is much slower than in the experiment with pure furan. The formation of intrazeolite hydrocarbon species is evident from the formation of bands at lower frequencies. These IR bands are very different for the two experiments. During the reaction with pure furan, bands assignable to fused polyaromatics develop. The band at 1610 cm$^{-1}$ evidence formation of highly unsaturated polyaromatic deposits.\textsuperscript{37} Less condensed polycyclic species give rise to bands at 1540–1520 cm$^{-1}$. The bands at 1350–1450 cm$^{-1}$ are due to $\delta$(CH) of unsaturated species.\textsuperscript{37,38} When methanol is cofed, two new bands are observed at 1590 and 1364 cm$^{-1}$, corresponding to $\nu$(CC) and $\delta$(CH) vibrations of polymethylated benzenes.\textsuperscript{39} These results suggest that the intrazeolite species formed during coaromatization of furan with methanol include a substantial amount of highly alkylated aromatic species in contrast to the exclusively sp$^2$ polyaromatics formed in pure furan. On the basis of these results we suggest that the alkyl termination makes it more difficult for the initial coke precursors to fuse into larger polyaromatic species, resulting in the decreased deactivation rate.

On the basis of the presented data we put forward a mechanism for the coaromatization of furanics with methanol (Figure 5). We propose that this reaction shares similarities with the dual-cycle hydrocarbon pool mechanism established for methanol-to-hydrocarbons (MTH) process. In this mechanism, a pool of hydrocarbon species including aromatics (arene cycle) and alkenes (alkene cycle) is responsible for the formation of hydrocarbon products.\textsuperscript{40} In case of coaromatization with methanol, furanic compounds undergo deoxygenation through either dehydration or decarbonylation to form highly proton-deficient intermediates.\textsuperscript{30} Because of their low H/C ratio, these intermediates are directly involved in the aromatic cycle. As indicated by MS and NMR data, methanol and furan undergo coaromatization when cofed, and these processes are not separated mechanistically. An evident increase in the propylene/ethylene ratio and decrease in the alkane/alkene ratio with increasing methanol concentration evidence that the reaction mechanism shifts from the predominant aromatic cycle to the alkene cycle upon increasing the concentration of methanol in the feed. Other important effects, resulting from methanol addition, are methylation of furan, methylation of aromatics in the arene cycle, and methylation of heavier aromatics. Methylation of light aromatics explains the higher selectivity to xylene, while methylation of polycyclic aromatics suppresses polycrystallinity reactions and, in this way, lowers the coke formation rate.
4. CONCLUSIONS

In summary, this work demonstrates a potential of the methanol cofeeding concept to improve the catalytic performance of zeolite catalysts in aromatization of biomass-derived compounds. On the basis of a combination of catalytic, isotope labeling, and spectroscopy data, we put forward a mechanistic proposal for the coaromatization of furan with methanol. In this proposal furan aromatization over zeolites follows a hydrocarbon pool mechanism, previously observed for the MTH processes. Given that both furanics and methanol are potential carbon sources in the future carbon-neutral chemical industry, the cofeeding concept presents a promising way for the sustainable production of aromatics.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.9b02259.

Physico-chemical properties of the catalysts, detailed catalytic activity data and product distribution, isotope distribution for labeling experiments, catalyst deactivation, and coke characterization data (PDF)

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The authors declare no competing financial interest.

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