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Citation for published version (APA):

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DOI:
10.1016/j.ces.2018.09.023

Document status and date:
Published: 28/04/2019

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
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Gallium-promoted HZSM-5 zeolites as efficient catalysts for the aromatization of biomass-derived furans

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Highlights

- High dispersion of Ga in HZSM-5 zeolite is achieved via reductive treatment.
- Gallium decreases Brønsted acidity and forms Lewis acidic (GaO)x+ species.
- Enhanced BTEX selectivity in aromatization of 2,5-dimethylfuran with ethylene.
- The role of ethylene: alkylation and transfer-de(hydrogenation) enabled by Ga.
- The catalysts retain activity under multiple reaction-regeneration cycles.

Abstract

The development of novel technologies to convert renewable biomass feedstocks to fuels and chemicals is of increasing interest for making our chemical industry more sustainable. Plant biomass or its biomass-derived platform molecules are typically over-functionalized, requiring substantial modification to produce the chemicals currently demanded by industry. Furanic compounds are intermediates in the catalytic fast pyrolysis of lignocellulosic biomass or sugar dehydration and can in principle be further converted to aromatics. While upgrading of furanics by zeolite-catalysed aromatization typically results in a large loss of carbon due to coke deposition, carbon laydown can be mitigated by the addition of ethylene and by the modification of the zeolite with Lewis acid Ga sites. Here, we investigate the influence of the Ga loading on the physicochemical properties of Ga-modified HZSM-5 zeolite and its performance in the gas-phase aromatization of 2,5-dimethylfuran with ethylene. Characterization of the morphological, textural and acidic properties were carried out to understand the role of Brensted and Lewis acid sites on the catalytic reaction. We demonstrate a crucial role of the dispersion of Ga-species and the resulting Lewis acidity of the Ga/ZSM-5 catalysts; and show means how to control both parameters by adjusting the synthesis method.

1. Introduction

The potential of zeolite catalysts for the production of sustainable chemical building blocks from biomass has attracted widespread attention in the last decade (Corma et al., 2007; Graaff...
et al., 2016; Kubiška and Kikhtyanin, 2015; Rezaei et al., 2014; Williams et al., 2012). Bio-based platform molecules are small molecules obtained preferably from lignocellulosic biomass that can be utilized as building blocks for higher-value chemicals and in this way help to introduce alternative, sustainable feedstock in the value chain of the chemical industry (Ennaert et al., 2016; Sheldon, 2014). Oxygenated bio-derived compounds, such as furan, 2-methylfuran and 2,5-dimethylfuran, can be thought to constitute a class of such renewable platform molecules. These furanics can be converted into light aromatic hydrocarbons, such as benzene, toluene, ethylbenzene and xylenes (further denoted as BTEX), for example by selective Diels-Alder addition with ethylene in the liquid phase (Rohling et al., 2018; Settle et al., 2017; Williams et al., 2012). Another route prominently investigated in recent years is catalytic fast pyrolysis (CFP) of raw biomass to bio-oil, with furanics thought to play a crucial role, particularly, in the production of the aromatic components of the oil (Cheng and Huber, 2011; Ramirez-Corredores, 2013). Carlson et al. proposed a reaction pathway for the CFP of cellulose over HZSM-5 catalysts involving dehydration of sugar fragments derived from cellulose to form anhydro sugars and then furans (Carlson et al., 2009). Further deoxygenation reactions of furans lead to aromatics, light olefins and coke (Cheng and Huber, 2011). Recently, we demonstrated that the conversion of methylated furans, namely 2-methylfuran and 2,5-dimethylfuran (2,5-dMF), results in significantly higher selectivity to aromatics than the conversion of furan (Uslamin et al., 2018). Despite these promising developments in the aromatization of furanic compounds, the overall process remains problematic, primarily due to the low selectivity for the production of valuable alkylated benzenes and strong catalyst deactivation.

In recent studies, Huber and co-workers discussed Diels-Alder pathways as a main reaction mechanism of furan aromatization (Cheng et al., 2012; Cheng and Huber, 2011). Based on these insights, co-feeding of light dienophiles, such as ethylene and propylene, has been explored to enhance the reaction selectivity. The BTEX selectivity was indeed enhanced upon addition of ethylene, with the addition of olefins, especially propylene, additionally improving deoxygenation by dehydration, resulting in less carbon loss as COx (Cheng and Huber, 2012). Addition of Ga to ZSM-5 was demonstrated to improve the BTEX yield during furan aromatization and CFP of saw dust (Cheng et al., 2012). The authors speculated that Lewis acid Ga sites promote aromatics yields by increasing Diels-Alder reaction rates. In these studies, the acidic and morphological properties of the zeolite catalysts were not evaluated in detail. To gain deeper understanding into the governing structure-performance relationships and ultimately with the purpose of designing novel catalysts with improved performance, model studies using well-defined catalytic materials are required.

Ga-promoted zeolites are well known as effective catalysts for the aromatization of other feeds, such as alkanes, alkenes and methanol to aromatics (Bhan and Delgass, 2008; Hagen and Roessner, 2000; Lalik et al., 1992; Qiu et al., 1998). Depending on the preparation method used, different Ga species can be obtained with the Ga/ZSM-5 system, strongly affecting catalyst performance in aromatization. The exact nature of the gallium species formed with the Ga/ZSM-5 system, strongly affecting catalyst performance in aromatization, the samples were exposed to oxygen at 150 °C (heating rate 2 °C/min) under 30% H2 in Ar) for 7 h to enhance the metal dispersion. After reduction, the samples were exposed to oxygen at 150 °C (30 vol% O2 in Ar, 1 h). These samples after reduction – oxidation treatment are denoted as Ga(x)RO. Additionally a sample was prepared by physically mixing Ga2O3 (Alfa Aesar, 99.9% metal based) with a parent zeolite followed by calcination at 550 °C (heating ramp rate 2 °C/min) and denoted as Ga(8)PM.

2.2. Catalyst characterization

The elemental composition (Si/Al ratio and Ga content) of the zeolite catalysts was determined by ICP-OES (Spectro CIROS CCD ICP optical emission spectrometer with axial plasma viewing). Prior to analysis, the zeolite samples were dissolved in a 1:1:1
(by weight) mixture of HF (Merck, 40% for trace analysis), HNO₃ (Merck, 85% for trace analysis) and H₂O (18.2 mΩ·cm).

Scanning electron microscopy (SEM) and Energy Dispersive X-Ray analysis (EDX) were performed to determine the presence and morphology of gallium over the surface of the zeolites. Measurements were carried out with a FEI Helios Nanolab 600 FIB-SEM instrument at 15.0 kV acceleration voltage. Energy Dispersive Spectroscopy (EDS) was performed using a Silicon Drift Detector (SDD) X-MAX from Oxford Instruments coupled to the Helios Nanolab.

NH₃ temperature-programmed desorption (TPD) experiments were carried out in a Micromeritics AutoChem II equipped with a TCD detector. Approximately 100 mg sample was placed in the reaction chamber and the sample was dried up at 600 °C in a He flow. Then, the chamber was cooled to 100 °C in a He flow and held at 100 °C for 2 h. A flow of 10 ml/min of 10 vol% NH₃/He was fed into the chamber to saturate the sample with NH₃. Thereafter, the sample was kept at 100 °C in a He flow for 2 h, followed by heating to 600 °C at 10 °C/min.

FTIR spectroscopy of adsorbed pyridine and carbon monoxide was carried out to probe the acid sites. Spectra were taken in the 4000–1000 cm⁻¹ range using a Bruker Vertex 70v spectrometer. First, a zeolite sample was pressed into a self-supporting wafer (5–10 mg, diameter 13 mm) and then placed in an environmental transmittance IR cell. Samples were first pre-treated in a O₂/N₂ flow at 550 °C (heating rate 5 °C/min) to eliminate adsorbed species, followed by cooling in dynamic vacuum (~10⁻⁵ mbar). For pyridine adsorption experiments, the sample was exposed to an excess of pyridine at 150 °C. Spectra were then recorded at different temperatures (150–450 °C) under dynamic vacuum. Heating was done at a rate of 5 °C/min followed by a dwell of 1 h before recording a spectrum. For the quantification of Brønsted and Lewis acid sites the integral molar extinction coefficients (IMEC, E) of 0.73 cm³/μmol and 1.11 cm³/μmol respectively were used (Datka, 1992; Emeis, 1993). For the CO adsorption experiments, the cell was cooled with liquid nitrogen to a temperature of ~183 °C in dynamic vacuum. Small pulses of CO (10 μmol) were then admitted to the IR cell, whilst recording IR spectra. Prior to CO dosing the cell was pressurized with a few mbar of He to enhance thermal conductivity and eliminate possible temperature gradients.

In situ UV–Vis Diffuse Reflectance Spectroscopy (DRS) experiments were carried out in a Linkam FTIR600 in situ cell equipped with a temperature controller. All UV–Vis DRS spectra were collected using an AvaSpec-2048L spectrometer and an AvaLight DH-SBAL fibre probe (Avantes). Samples were pressed over a quartz slide and 15 μl 4-fluorostyrene (99%, Sigma Aldrich) was added to the materials. Afterwards, they were heated to 120 °C while collecting UV–Vis DRS spectra to monitor oligomer formation over time.

Confocal fluorescence microscopy (CFM) measurements were carried out using a Nikon ECLIPS 90i upright confocal laser scanning fluorescence microscope equipped with a 100 × 0.73NA dry objective lens and a pinhole value of 1.2 μm. Fluorescence microphotographs were collected using 488 nm and 561 nm laser lights. The emission was measured in a range of 510–670 nm when using 488 nm laser light and in a range of 580–700 nm when using 561 nm laser light by the A1R scanning head equipped with a spectral detection unit consisting of a diffraction grating and a 32-photonmultiplier tube array. The catalysts were analysed in situ by CFM after staining the samples by 4-fluorostyrene oligomerization. All the materials were heated to 120 °C and held at that temperature for 5 min. Subsequently, 15 μl 4-fluorostyrene was added and after 15 sec. the heating was turned off. After cooling to room temperature, the stained samples, these were illuminated by specific wavelength lasers causing the oligomeric species to fluoresce.

Zeolite crystallinity was evaluated by powder X-ray diffraction (XRD) method. XRD measurements were performed on a Bruker D2 powder diffraction system (Cu Kα radiation, scan speed 0.01°/s, 2 0 range 5 – 60°). The relative crystallinity of samples normalized to a parent HZSM-5 was evaluated by comparing of the integral areas of the reflections (Miller indices in parentheses) at 23.1° (0 5 1), 23.3° (5 0 1), 23.7° (5 1 1), 24.0° (0 3 3), and 24.4° (3 1 3).

The texture of the zeolites was determined by argon porosimetry, carried out at -186 °C using a Micromeritics ASAP-2020 apparatus. The samples were degassed at 500 °C prior to measurements. The micropore volume was determined by the t-plot method in a thickness range from 3.5 to 4.5 Å.

X-ray Photoelectron Spectroscopy (XPS) spectra were taken using a Thermo Scientific K-alpha spectrometer equipped with a monochromatic Al Kα X-ray source and a 180° double-focused hemispherical analyser with a 128-channel detector.

2.3. Catalytic activity measurements

Catalytic performance in the aromatization of 2,5-dimethylfuran (2,5-dMF) in the presence of ethylene was carried out in a fixed bed quartz reactor. In a typical catalytic run, 0.5 g of the sieved catalyst fraction (250–500 μm) was placed into the reactor and held between quartz wool plugs. Calibrated thermal gas mass-flow controllers (Brooks) were used to feed the gases into the reactor. To feed 2,5-dMF a thermostated glass saturator was used. Reaction products were analysed using online GC (Trace 1300, Thermo) and MS (Pfeiffer Omnistar GSD 301 T3) instruments. The gas flow from the reactor was sent directly to the GC injection system equipped with a 100 μl sample loop mounted on a 6-way valve. The MS capillary entrance was installed just below the reactor bed exit. The GC was equipped with two columns and detectors. A TCD detector with an RT-Q-Bond column (1.20 m; i.d. 0.32 mm; d.f. 10 μm) was used for the analysis of the light fraction of the reaction products. Aromatics and other heavier products (including substituted naphthalenes) were analysed on a Stabilwax-DB column (length 30 m; i.d. 0.25 mm; d.f. 0.25 μm) coupled with a FID. Identification of the compounds was done based on the retention time compared to standards. The reaction selectivity, conversion and yield were calculated as:

\[ X_\text{in}(t) = \frac{n_\text{out}}{n_\text{in}} \]  \hspace{1cm} (I)

\[ S_k(t) = \frac{n_\text{in}^\text{out}}{n_\text{in}} \times \left| \frac{\mu_k}{\mu_i} \right| \]  \hspace{1cm} (II)

\[ X_k(C_{\text{based}}) = \sum_i \mu_i \times \int_0^t (n_i^\text{in} - n_i^\text{out}) \, dt \]  \hspace{1cm} (III)

\[ S_k = \frac{\mu_k}{\mu_i} \times \int_0^t n_i^\text{out} \, dt \]  \hspace{1cm} (IV)

\[ Y_k = \mu_k \times \int_0^t n_i^\text{out} \, dt = S_k \times X_k \]  \hspace{1cm} (V)

where (I) – conversion at t; (II) – C based selectivity to a product k; (III) – overall C based conversion at t; (IV) – overall C based selectivity to a product k; (V) – overall C based yield of a product k. Cumulative (overall) parameters were calculated at t such that \[ x(t) = 90\%. \] Both ethylene and 2,5-dimethylfuran are included in the overall carbon balance.
3. Results and discussion

3.1. Catalyst characterization

As solvated Ga$^{3+}$ ions are too large to enter the ZSM-5 micropores, the direct exchange of Brønsted acid sites (BAS) with Ga during wet impregnation is limited (Fricke et al., 2000). Therefore, wet impregnation leads to the predominant deposition of aggregated Ga-oxide on the external zeolite surface. A different, more effective method to substitute ZSM-5 BAS for Ga involves their gas phase reaction with volatile Ga compounds, such as Ga(CH$_3$)$_3$ or GaCl$_3$. However, this method is only applicable to prepare model catalyst systems at a small scale. A high degree of gallium-proton exchange can also be achieved by a high-temperature reductive treatment of a Ga/HZSM-5 zeolite sample prepared via conventional wet impregnation or wet ion-exchange methods. Reduction leads to the formation of mobile Ga$_2$O, which can migrate into the micropores and react with BAS. This procedure is sometimes called reductive solid state ion exchange. Subsequent oxidation in oxygen results in the formation of well-dispersed GaO$^+$ ions, which are considered catalytically active (Kazansky et al., 2004; Rane et al., 2008):

$\text{Ga}_2\text{O}_3 + 2\text{H}_2 \xrightarrow{\text{780°C}} \text{Ga}_2\text{O} + 2\text{H}_2\text{O},$

$\text{Ga}_2\text{O} + 2\text{ZO}^- \cdots \text{H}^+ \xrightarrow{} 2\text{ZO}^- \cdots \text{Ga}^+ + \text{H}_2\text{O},$

$2\text{ZO}^- \cdots \text{Ga}^+ + \text{O}_2 \xrightarrow{} 2\text{ZO}^- \cdots \text{GaO}^+.$

A drawback of this approach is that repeated calcination and reductive treatments at 550°C result in damage to the zeolite framework due to water formation. Moreover, volatile Ga species might be removed from the solid catalyst. Accordingly, we investigated the texture, structure and composition of Ga/ZSM-5 after the reductive treatment step followed by the re-oxidation. It should be noted though that the XRD patterns show that neither the presence of Ga nor the high-temperature reductive and oxidative treatments affected the crystal structure of zeolite, even for the highest Ga loading of 8 wt% (Fig. S1). Quantification of the relative crystallinity confirms that the MFI framework remained intact (Table 1). The observed shift of the XRD reflections can be attributed to a slight increase of the zeolite unit cell dimensions, induced by the intra-zeolite Ga species. (Wu et al., 1979)

The presence of a bulk gallium oxide phase (particles > 30 nm) can be inferred from XRD reflections at 31.75° and 35.25° 2θ. (Fricke et al., 2000) Fig. 1a shows that such bulk Ga$_2$O$_3$ reflections are absent in the XRD patterns of the impregnated and treated catalysts, while they are apparent for the physical mixture of Ga$_2$O$_3$ and ZSM-5. XPS analysis of the zeolite samples, which mainly probes the external surface of the crystals, shows how the reductive treatment affects the Ga distribution. After impregnation and calcination a large amount of Ga-species was found to reside at the external surface (Fig. 1b). Reduction resulted in the complete disappearance of the Ga 3d signal for Ga(1)RO and Ga(2)RO. This implies that most of the Ga-oxide has dispersed inside the zeolite pores during reduction. A Ga 3d signal remains for Ga(4)RO,

$$\text{Ga}_2\text{O}_3 + 2\text{H}_2 \xrightarrow{\text{780°C}} \text{Ga}_2\text{O} + 2\text{H}_2\text{O},$$

$$\text{Ga}_2\text{O} + 2\text{ZO}^- \cdots \text{H}^+ \xrightarrow{} 2\text{ZO}^- \cdots \text{Ga}^+ + \text{H}_2\text{O},$$

$$2\text{ZO}^- \cdots \text{Ga}^+ + \text{O}_2 \xrightarrow{} 2\text{ZO}^- \cdots \text{GaO}^+.$$

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Summary of the Ga/HZSM-5 physical-chemical properties.</th>
</tr>
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<td>Catalyst</td>
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<tr>
<td>Ga/Al mol$^+$</td>
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</tr>
<tr>
<td>NH$_3$ TPD total, mmol/g</td>
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<td>NH$_3$ TPD weak, T (°C)</td>
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<tr>
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<td>NH$_3$ TPD strong, T (°C)</td>
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<tr>
<td>NH$_3$ TPD strong, mmol/g</td>
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<tr>
<td>v(CO - HO)$^+$, cm$^{-1}$</td>
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</tr>
<tr>
<td>Crystallinity$^d$</td>
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</tbody>
</table>

Measured by (a) ICP; (b) FTIR CO adsorption; (c) FTIR pyridine adsorption; (d) XRD.

Fig. 1. (a) XRD patterns of the parent HZSM-5, Ga(8)RO, Ga(8) and Ga(8)PM; (b) XPS spectra of Ga(x)RO (dashed lines) and Ga(x) (solid lines).
showing that not all Ga can be dispersed inside the zeolite at a higher Ga content.

Elemental analysis showed that the total Ga loading does not change upon reductive treatment (Fig. S1b), confirming that all Ga is retained by the zeolite during high-temperature reduction. Considering that Ga is not visible in the XPS spectra of Ga(1)RO and Ga(2)RO, and just a 10% fraction of Ga remains on the surface for Ga(4)RO, it is clear that Ga is (nearly) quantitatively located inside the zeolite pores at loadings below 4%.

SEM-EDX was used to determine the presence and morphology of the Ga species over the surface of the promoted materials. In order to get an insight into the physical appearance and elemental composition of the Ga/HZSM-5 catalysts, SEM-EDX analysis was performed for the samples before and after reductive treatment. The micrographs of those samples and EDX mapping of the elements are shown in Fig. 2.

SEM images show that incorporation of Ga did not introduce any significant morphological changes in zeolite crystal habit. In line with expectation, EDX mapping showed the presence of Ga conglomerates for Ga(4) and Ga(8) samples. After the reductive treatment the distribution of Ga became significantly more homogeneous. Only Ga(8)RO contained measurable aggregates of Ga. The EDX data is thus in a good agreement with the XRD and XPS data reported above. It confirms the importance of the reductive treatment on the Ga distribution and indicates that, at a Ga loading higher than 4%, a larger fraction of Ga remains on the zeolite outer surface.

The acidity of the samples was probed by different methods. NH₃ desorption traces are shown in Fig. S2, revealing the two main features typical for acidic zeolites. The low temperature desorption feature with a maximum at 220–230 °C (l-peak) is associated with ammonia adsorbed on weak acid sites or physically adsorbed ammonia. The feature at high temperature (h-peak) is attributed to ammonia adsorption on strong acid sites (Sandoval-Díaz et al., 2015; Topsøe et al., 1981). Introduction of Ga led to significant changes in the NH₃ desorption traces. The h-peak became broader with the maximum shifting to lower temperature with increasing Ga loading. The broadening indicates that there are different acid sites associated with h-peak including strong Brønsted acid sites and Lewis acid sites. In contrast, the l-peak remains similar in shape and position. The ratio between l- and h-peaks decreases upon increasing Ga content. Introduction of Ga most likely decreases the number and strength of the remaining strong acid sites, which can be attributed to the partial exchange of Brønsted acid sites and formation of Ga-associated Lewis acid sites. The quantity, nature and strength of the acid sites was further characterized by IR spectroscopy of adsorbed pyridine at 150 °C and CO at −196 °C. Analysis of the pyridine IR spectra (Fig. 3) shows that the exchange degree of Brønsted acid sites increases proportionally with Ga loading between 0 and 4 wt%, before
reaching a plateau. These data are supported by the EDX-mapping and XPS results, where we found that agglomerated Ga starts to form at a Ga loading above 4 wt%. It is also important to note that the disappearance of BAS is accompanied by a proportional increase in Lewis acidity (Fig. 3). The stoichiometry implies that the composition of Ga species formed is different in the samples with different loading. At low Ga loading formation of \((\text{GaO})_2^{2+}\) can be anticipated while at higher loading the ions with the composition \((\text{GaO})_x^{x+}\) are the dominant species. These observations are in line with previously reported theoretical studies detailing the formation and self-organization of such multinuclear clusters, particularly \((\text{Ga}((\text{m-O})_2\text{Ga})^{2+}\) (Pidko et al., 2012; Pidko et al., 2009).

IR analysis of adsorbed CO shows that the presence of Ga at exchange sites did not change the acid strength of the remaining BAS. The band positions related to bridging OH groups and CO adsorbed to this bridging OH group were similar for the parent HZSM-5 and the Ga(2)RO and Ga(4)RO samples (Fig. 4). At low partial pressure of CO, only a band at 2174 cm\(^{-1}\) was observed in the CO stretching region, corresponding to \(\nu(\text{OH}--\text{CO})\). With increasing CO pressure, a band at 2140 cm\(^{-1}\) appeared, which is due to physisorbed CO. No bands are observed in the 2200–2300 cm\(^{-1}\) region, showing that reduced Ga species are absent after the re-oxidation treatment. (Kazansky et al., 2004) A summary of the acidity characterization results is given in Table 1.

As demonstrated by NH\(_3\)-TPD and IR measurements, an increase of the Ga loading leads to a lower Brønsted acidity. To gain further insight into the nature and location of acid sites in the Ga-exchanged zeolites, these samples and the parent HZSM-5 reference were analysed with in situ UV–Vis spectroscopy and fluorescence micro-spectroscopy using the BAS-catalysed oligomerization of 4-fluorostyrene as a probe reaction. In previous works, reactivity and distribution of Brønsted acid sites of different porous zeolitic materials have been studied in combination with micro-spectroscopy techniques and acid-catalysed oligomerization reactions (Arumburo et al., 2013; Kox et al., 2008). 4-Fluorostyrene oligomerization yields conjugated cyclic and linear dimeric carboxcatic species as well as higher oligomeric carbocationic species, which serve as BAS-selective reporter molecules (Fig. 5) (Buurmans et al., 2012; Sprung and Weckhuysen, 2015). Sprung and Weckhuysen observed that linear dimeric carboxcations predominantly occupy straight MFI channels, while the cyclic carboxcations can be formed either in the intersections or close to the external surface.

The data (Fig. 5) show the linear dimeric carboxcations, likely occupying the straight channels, to dominate the spectra, as indicated by the intense absorption band at 550 nm found for all catalysts. Modification of zeolite with Ga led to the suppressed formation of the cyclic dimeric (510–515 nm) and the higher oligomeric carboxcations (600 nm), which are located in the intersections of the MFI framework and the zeolitic external surface, respectively. This implies a reduction in Brønsted acidity or hindered accessibility of the acid sites in these positions. The most noticeable decrease in intensity of the linear and cyclic dimeric carboxcations is observed between the parent ZSM-5 zeolite and the Ga(2)RO sample. A drop in intensity is only observed for the 600 nm absorption band of the Ga(8)RO catalyst, which is attributed to the large amount of Ga species agglomerated after the reduction step on the surface. This result is in line with the XPS...
and SEM analyses shown above. The absorption band around 400 nm decreases in intensity as well with increasing Ga loading. This band is assigned to the formation of methyl-substituted benzene carbocationic species (Aramburo et al., 2011; Bjørgen et al., 2003). Furthermore, as shown in Fig. 5, introduction of Ga into MFI also increased the onset temperature for the oligomerization reaction. Specifically, 4-fluorostyrene oligomerization over the HZSM-5 material (Fig. 5a) already yielded the cyclic and linear carbocations after 50 s of reaction. In contrast, for Ga(8)RO (Fig. 5d) the linear dimeric carbocation is detected only after 200 s of reaction, attributed to the lower BAS content and reduced accessibility, in line with the above reasonings.

For a more detailed visualization of the decrease in the formation of oligomeric species by increasing Ga content, absorption spectra of all samples at 300 s are shown in Fig. 6a. It can be observed that an increase in the Ga loading leads to a decrease in the intensity of all the absorption bands. Furthermore, the 400, 510, 550 and 600 nm absorption bands have been plotted over time to see if there is any difference between the ratio of formation of the different oligomeric species (Fig. 6b–e). The absorption difference between the linear and the cyclic carbocations is larger among HZSM-5 and Ga(4)RO, however for sample Ga(8)RO their difference in intensity is smaller revealing a significant reduction of BAS. Concerning the higher oligomeric carbocationic species, their difference in the absorption intensities between the linear carbocations increases as well. Both evidences indicate the decrease in the amount and strength of BAS, which are in line with the TPD data discussed above.

The fluorescence microscopy images of the series of (Ga-exchanged) HZSM-5 catalysts stained with 4-fluorostyrene are shown in Fig. 7. The images were taken after excitation with 488 nm and 561 nm wavelength lasers, respectively.

**Fig. 5.** UV–Vis absorption spectra recorded after the exposure of zeolites to 4-fluorostyrene at 25 °C followed by heating to 120 °C and the main oligomeric species formed with their expected absorption wavelengths (bottom) (a) HZSM-5; (b) Ga(2)RO; (c) Ga(4)RO and (d) Ga(8)RO.
After excitation with the 488 nm laser the predominant species excited are the cyclic dimeric carbocations and to a lower extent the linear dimeric carbocations. As Fig. 7 shows, the fresh HZSM-5 sample expectedly gives the highest fluorescence intensity after excitation with the 488 nm laser followed by Ga(2)RO and Ga(4)RO samples. The overall fluorescence intensity decreases with increasing Ga loading, confirming that the density of BAS is reduced. Moreover, a rather consistent fluorescence intensity is displayed in all the CFM images revealing a homogeneous distribution of the Ga species in all the Ga-exchanged samples, as also shown in the SEM-EDX analyses shown above. Also, after excitation with the 561 nm wavelength laser, the parent ZSM-5 shows the highest fluorescence intensity. The main excited oligomeric species in this case are the linear dimeric carbocations and the larger oligomeric carbocations.

For a more detailed analysis of the fluorescence microscopy measurements we also collected emission spectra, as shown in Fig. S3, for each sample after excitation with 488 nm and 561 nm lasers. After excitation with the 488 nm laser there is one broad shoulder at around 550 nm in the emission spectra, which corresponds to the cyclic dimeric carbocation, and two bands at around 570 nm and 610 nm in the emission spectra, corresponding to the linear dimeric carbocation emission bands. In turn, after excitation with the 561 nm laser there is a band around 630–640 nm, which
can be attributed to the larger oligomeric carbocation. For both sets of spectra we can corroborate that fresh HZSM-5 displays the highest fluorescence intensity, reflecting also its higher reactivity in 4-fluorostyrene oligomerization.

3.2. Aromatization of 2,5-dimethylfuran

To investigate the influence of Ga content and location on the catalytic performance, the different samples were used as catalysts in the co-aromatization reaction of 2,5-dMF with ethylene. We first verified that SiC used as a diluent was not active in this reaction in the 300–600 °C temperature regime (Fig. S4) in line with an earlier study. (Lifshitz et al., 1998) A silica reference was found to convert 2,5-dMF at temperatures of 400 °C. Full conversion was reached at 600 °C and above 500 °C benzene and toluene formation was observed. The low mass balance indicates that most 2,5-dimethylfuran is converted to coke at these high temperatures. Accordingly, we carried out the activity measurements of the zeolites at a temperature of 450 °C to avoid non-selective reactions at the external zeolite surface.

Fig. 8a shows that all catalysts possess a complete conversion of 2,5-dMF at the start of the reaction. After ca. 100 min, the catalysts undergo rapid deactivation. The major deoxygenation product is water for both Ga-modified and pristine zeolites (Fig. S5). Only trace amounts of COx and benzofuran were detected. The product distribution for the various catalysts are displayed in Fig. 8b. The hydrocarbon products are aromatics, mainly benzene and toluene with small amounts of xylenes. The BTEX selectivity shows a considerable increase from ca. 25% on the pristine zeolite to 40% on Ga (2)RO. Further increase in Ga loading from 2 wt% to 8 wt% leads to an increase in BTEX selectivity of ca. 7–8%. The observed trends correlate well with the concentration of LAS as well as with removal of BAS.

In addition, we found that the distribution of aromatic products changes with increasing the Ga loading. The overall carbon selectivity towards benzene and xylenes significantly increased, while the production of toluene stayed on almost the same level. This difference can be attributed to a change in the reaction mechanism due to the presence of Ga. Based on literature reports, we suspect that following reaction pathways might be facilitated by Ga species: (i) Diels-Alder coupling of 2,5-dMF and ethylene, (ii) enhanced aromatization of ethylene via hydrogen transfer reactions (Guisnet et al., 1992), and (iii) interaction of ethylene with some other reaction intermediates, for example (de)alkylation of...
aromatic or olefinic intermediates. To evaluate which of these pathways is important under our conditions, we investigated the behaviour of ethylene in a more detailed way.

Fig. 9a shows that ethylene is produced in the reaction of pure 2,5-dMF on both HZSM-5 and Ga(4)RO catalysts. It contributes about 10% and 5% to the overall carbon selectivity, respectively. No conversion of ethylene is observed when ethylene is co-fed with 2,5-dMF over pristine HZSM-5 catalysts. (Fig. 9b) In contrast, Ga(4)RO catalysts shows 65% conversion at the beginning of the reaction, which dropped in a linear manner to zero. Conversion of pure ethylene over the HZSM-5 zeolite under the same reaction conditions is relatively low (<5%). Modification of the zeolite with Ga substantially improved the conversion up to 85% for Ga(4)RO, yielding mostly benzene and toluene in a nearly equimolar ratio (Fig. 9c). This dramatic effect can be attributed to a high activity of Ga species in C-H bond activation, enabling various transfer-dehydrogenation processes.

Interestingly, the conversion of ethylene which is co-fed with 2,5-dMF is close to zero on HZSM-5, indicating that the conversion of ethylene and the formation of ethylene from 2,5-dMF have nearly equal rates under our reaction conditions (Fig. 9b). Considering that ethylene affected the product distribution (Fig. S6), we infer that ethylene is involved in the further conversion of the primary products from 2,5-dMF conversion. However, the net conversion of ethylene is very low. A thermodynamic basis for similar effects observed during co-aromatization of alkanes with methane over zeolites has been earlier discussed. (Parmon, 1999; Luzgin et al., 2008) When Ga is added to ZSM-5 zeolite, there is a net conversion rate of ethylene. However, as ethylene addition did not lead to a significant increase in xylenes selectivity (the principal product of Diels-Alder coupling of 2,5-dMF with ethylene is p-xylene), it is not likely that a Diels-Alder reaction of 2,5-dMF with ethylene is the predominant reaction by which ethylene is incorporated in the products.

Finally, to evaluate catalyst stability we carried out 10 reaction-regeneration experiments (Fig. 10). Intermediate regeneration was carried out at 550 °C (ramp rate 5°C/min) in 20% O2 in Ar. Although water evolving during the reaction and regeneration might cause dealumination of the zeolite (Kosinov et al., 2017), the catalytic activity remained at the same level after 10 reaction-regeneration cycles. These results indicate that Ga/HZSM-5 is an active and stable catalyst for cyclic reaction-regeneration operation of co-aromatization of furanics with ethylene.

4. Conclusions

By applying SEM-EDX, XPS, NH3-TPD, FTIR and UV–Vis DRS and CFM we showed that Ga-oxide clusters are abundant on the external surface of the HZSM-5 crystals after impregnation. Upon reduction and re-oxidation, these large agglomerates are dispersed into the zeolite micropores and nearly quantitatively exchanged as (GaO)x+ species. A high dispersion and absence of Ga-oxide on the external surface can be achieved in this manner, when the Ga loading is kept below 4 wt%. The cationic Ga species substitute Brønsted acid sites, resulting in a lowering of the Brønsted acidity and an increase of the Lewis acidity Ga/HZSM-5. The evaluation of these catalysts in co-aromatization of 2,5-dMF with ethylene showed a positive role of Ga-promotion on the BTEX productivity. Ga species are involved in the conversion of ethylene. The role of ethylene in the overall reaction is complex and cannot be attributed exclusively to Diels-Alder chemistry. We suggest that ethylene undergoes transfer-dehydrogenation reactions with the intermediates formed from 2,5-dMF under the given reaction conditions. Besides, ethylene most likely participates in alkylation and trans-alkylation reactions, affecting the reaction network and, as a result, the product distribution. The BTEX selectivity increased proportionally to the concentration of exchanged GaO+ sites, implying that Ga LAS play an important role in the reaction. Finally, we found that an optimized Ga(4)RO catalysts is stable during at least 10 reaction – high temperature regeneration cycles, proving the high stability of cationic Ga-oxo-species in Ga/HZSM-5.
Acknowledgment

This work was supported by the Netherlands Center for Multiscale Catalytic Energy Conversion; Funder ID 501100003245 (MCEC), an Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO) Gravitation program funded by the Ministry of Education, Culture and Science of the government of the Netherlands.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ces.2018.09.023.

References


