Production of Jet Fuel Intermediates from Biomass Platform Compounds via Aldol Condensation Reaction Over Iron-Modified MCM-41 Lewis Acid Zeolite

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Liquid fuel intermediates could be produced via aldol condensation reaction between furfural or 5-hydroxymethylfurfural (HMF) and acetone. It was found that iron-modified MCM-41 zeolite can be an effective Lewis acid catalyst for C—C bond formation via aldol condensation of furfural or HMF with acetone. The 4-(2-furyl)-3-buten-2-one and 1, 5-di-2-furanyl-1, 4-pentadien-3-one (FAc and FAc, or 1, 5-di-2-furanyl-1, 4-pentadien-3-one and 1, 5-bis[5-hydroxymethyl]-2-furanyl]-1, 4-pentadien-3-one (HAc and HAc), as two main condensation products of furfural with acetone or HMF with acetone, were observed. After 24 h at 160 °C, 86.9% conversion of furfural with 60.0% yield of the FAc and 88.9% conversion of the HMF with 41.1% yield of the HAc as well as 3.5% yield of the HAc were achieved. Although furfural or HMF conversion was almost same after 24 h at 160 °C, iron-modified MCM-41 zeolite catalyst displayed an enhanced selectivity to condensation products of furfural with acetone. In addition, catalysts showed an improved selectivity to the FAc and HAc at higher reaction temperature. The reusability and regeneration studies showed that iron-modified MCM-41 zeolite catalyst could not be reused directly, but could be regenerated by calcination in air, and the catalytic performance of regenerated catalyst was acceptable.

1. Introduction

In the past decade, remarkable efforts had been devoted to explore the production of drop-in biofuels from renewable biomass resources, which was arisen from increasing serious environmental pollution issues (Stöcker, 2008; Zinoviev et al., 2010; Kubička et al., 2013). Among these extraordinary efforts, the C—C bond formation reaction, like aldol condensation reaction, had drawn widespread attention and been considered as a key step because low carbon containing platform chemicals such as furfural or 5-hydroxymethylfurfural (HMF) derived by lignocellulosic biomass recourses could be transformed into high carbon chain length intermediates and these precursors could be subsequently hydrodeoxygenated into fuel level alkanes (Bohre et al., 2015a; 2015b). Many aldol condensation reactions between furfural or HMF and ketones had been systematically and radically investigated. In general, acetone was used as a most common feedstock to react with furfural or HMF to yield fuel intermediate (Barrett et al., 2006; West et al., 2008; Xing et al., 2010; Faba et al., 2011; Sádaba et al., 2011; Faba et al., 2012; Sádaba et al., 2012; O’Neill et al., 2014; Yang et al., 2014). For example, Huber et al. (2005) researched aldol condensation reaction between furfural or HMF and acetone by Mg-Al-oxide catalyst. Shen et al. (2011) studied the catalytic performance of MgO-ZrO\textsubscript{2} and nitrogen-substituted NaY in aldol condensation of furfural or HMF with acetone or propanal where about 32% yield of condensation product of HMF-acetone was obtained. However, above researches were almost studied under basic conditions. It was known that basic catalysts were facing several important issues containing corrosion, enhanced self-condensation, high cost of neutralizing generated waste water steam and poor product selectivity (Barrett et al., 2006). Therefore, other kinds of catalysts should be studied and be applied to aldol condensation reaction of furfural or HMF with ketones.

Due to its unique shape selectivity, tunable catalytic active sites and acceptable stability, zeolites had received extensive attention and been applied to many domains of biomass conversion such as isomerization of glucose, hydrolysis of biopolymers...
and catalytic fast pyrolysis (Kruger et al., 2012; Chang et al., 2014; Li et al., 2016; Guo et al., 2017). Recently, not a few applications of Lewis acid zeolite into aldol condensation reaction between aromatic aldehyde and ketones were investigated (van de Vyver et al., 2015; Muller et al., 2016; Tolborg et al., 2016; Wang et al., 2016). However, the most prominent and early studied Lewis acid zeolites were microporous zeolites, such as MFI and Beta zeolites (Lewis et al., 2015; Su et al., 2017). These microporous zeolites had some limitations, such as the too small microporous environment that prevented the contact of the reactants with active catalytic sites, and diffusion limitations. Thus, the zeolite with large pore sizes, like order mesoporous MCM-41 zeolite, had been developed as an alternative. Besides, many metals, such as Sc, Ti, and Sn, could be immobilized on the MCM-41 zeolite because of its high surface areas, and ease of surface functionalization, which made metal-modified MCM-41 zeolites potential heterogeneous Lewis acid catalysts. Among these metal-modified MCM-41 zeolites, iron-modified MCM-41 zeolite was cheap, hypotoxicity, and easily accessible. Furthermore, a series of iron-modified MCM-41 zeolite catalysts had been applied to many catalytic fields, and results proved that the iron-modified MCM-41 zeolite was a great Lewis acid zeolite catalyst (Cara et al., 2017; Chen et al., 2018; Chiang et al., 2018; Salviano et al., 2018; Ulu et al., 2018; Xu et al., 2018a; Zhang et al., 2019). These researches indicated that the iron-modified MCM-41 zeolite could be used as an efficient solid Lewis acid catalyst for aldol condensation reaction of furfural or HMF with acetone.

Herein, the iron-modified mesoporous zeolite, Fe-MCM-41, was synthesized by a simplified postgrafting method and used as an efficient solid Lewis acid catalyst to transform furfural or HMF into fuel intermediates via aldol condensation reaction. The effects of introduction of iron on phy-chemical properties of MCM-41 zeolite were characterized in details. Some experimental parameters were investigated to obtain an optimal yield of fuel precursor. The recyclability and regeneration of catalyst were also carried out.

2. Materials and Methods

2.1. Materials

The 5-Hydroxymethyl-2-furaldehyde (HMF, 99%), furfural (AR, 99%), tetraethyl orthosilicate (TEOS, 98%), iron (III) acetylacetonate (Fe(acac)₃, 98%) and hexadecyl trimethyl ammonium bromide (CTAB, 99%) were purchased from Aladdin Industrial, Inc. (Shanghai, China). Acetone (AR) and ammonia solution (NH₄OH, AR, 25%–28%) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All reagents were used as received.

2.2. Catalyst preparation

(1) Synthesis of MCM-41 support

The MCM-41 zeolite was prepared according to previous literature (Savidha et al., 2003). Typically, 0.24 g CTAB was firstly dissolved in 12 mL deionized water at room temperature under stirring, followed by adding 1 mL NH₄OH. After a few minutes, 1 g TEOS was added into above solution and the mixture was stirring for two hours. The mixture was transformed into Teflon-lined autoclave and aged at 100 °C for three days. The obtained solids was washed throughout by deionized water and dried at 80 °C overnight. The MCM-41 support was obtained finally after calcination at 550 °C for five hours in air.

(2) Synthesis of iron-modified MCM-41 zeolite

The Fe-MCM-41 was prepared by modified solid postgrafting method (Xu et al., 2018b). In typical, the desired amount of Fe(acac)₃ and MCM-41 were mixed together and pestled for 30 min. The obtained mixture was calcinated at 550 °C for three hours in air. The obtained powder was named as xFe-MCM-41, where x represented the mass percent of Fe(acac)₃/MCM-41.

2.3. Catalyst characterization

Powder X-ray diffraction (XRD) patterns of samples were measured by a Smartlab X-ray diffractometer equipped with a Cu-Kα source. The textual properties of samples were determined by an Autosorb Q (Quantachrome). The scanning electron microscop (SEM) images for samples were determined with ZEISS GeminiSEM 500 scanning electron microscope from Germany. Transmission electron microscopy (TEM) images for samples were determined with JEM-2100F transmission electron microscope from Japan. The acidity of samples were determined by Fourier transform infrared spectroscopy (FT-IR) adsorbed by pyridine on ThermoFisher Nicolet IS200 from the United States. The X-ray photoelectron spectra (XPS) for sample was performed on Thermo ESCALAB 250 with a monochromated Al Kα X-ray source from the United States.
2.4. Catalytic reaction and analysis methods

Aldol condensation reaction between furfural or HMF and acetone was carried out in a Synthware thick-walled pressure bottle. In typical, 1.25 mmol furfural or HMF and 25 mmol acetone were mixed into glass reactor with 0.1 g catalyst. Afterwards, the reactor was immerged into oil-bath preheated at 80, 100, 120, 140 and 160 °C for 0–24 h. After reaction, the reactor was cool down by ice-bath and the spent catalyst was recovered by centrifugation. Finally, the solution was transferred into a gas chromatography (GC) vial and analyzed by Agilent 7890A GC equipped with a flame ionization detector (FID) detector.

The catalytic performance of catalyst was evaluated by furfural or HMF conversion, 4-(2-furyl)-3-buten-2-one (FAc) or 1, 5-di-2-furanyl-1, 4-pentadien-3-one (HAc) yield and 1, 5-di-2-furanyl-1, 4-pentadien-3-one (F2Ac) or 1, 5-bis[(5-hydroxymethyl)-2-furanyl]-1, 4-pentadien-3-one (H2Ac) yield. The formula was defined as follows:

**Furfural conversion (%)**
\[
\text{Furfural conversion (%) } = \frac{\text{moles of furfural reacted}}{\text{moles of starting furfural}} \times 100\%
\]

**FAc yield (%)**
\[
\text{FAc yield (%) } = \frac{\text{moles of FAc}}{\text{moles of starting furfural}} \times 100\%
\]

**F2Ac yield (%)**
\[
\text{F2Ac yield (%) } = \frac{\text{moles of F2Ac}}{\text{moles of starting furfural}} \times 100\%
\]

**FAc selectivity (%)**
\[
\text{FAc selectivity (%) } = \frac{\text{moles of FAc}}{\text{moles of reacted furfural}} \times 100\%
\]

**F2Ac selectivity (%)**
\[
\text{F2Ac selectivity (%) } = \frac{2 \times \text{moles of F2Ac}}{\text{moles of reacted furfural}} \times 100\%
\]

**HMF conversion (%)**
\[
\text{HMF conversion (%) } = \frac{\text{moles of HMF reacted}}{\text{moles of starting HMF}} \times 100\%
\]

**HAc yield (%)**
\[
\text{HAc yield (%) } = \frac{\text{moles of HAc}}{\text{moles of starting HMF}} \times 100\%
\]

**H2Ac yield (%)**
\[
\text{H2Ac yield (%) } = \frac{\text{moles of H2Ac}}{\text{moles of starting HMF}} \times 100\%
\]

**HAc selectivity (%)**
\[
\text{HAc selectivity (%) } = \frac{\text{moles of HAc}}{\text{moles of reacted HMF}} \times 100\%
\]

**H2Ac selectivity (%)**
\[
\text{H2Ac selectivity (%) } = \frac{2 \times \text{moles of H2Ac}}{\text{moles of reacted HMF}} \times 100\%
\]

3. Results and Discussion

The XRD patterns of MCM-41 and iron-modified MCM-41 at low diffraction angles (2θ = 1°–10°) range, as well as high diffraction angles (2θ = 10°–60°) range, were displayed in Fig. 1. As shown in the wide diffraction angles spectra, without modification, only a broad diffraction peak at around 22° was observed, which was assigned to the amorphous feature of framework of MCM-41. On the contrary, compared with the bare MCM-41, for all iron-modified MCM-41 samples, the broad peak at 22° was hardly seen. It was reported previously that the metal-acetylacetonate precursors can interact with silica support surface by two methods (Xu et al., 2018b). Firstly, metal-acetylacetonate compounds could connect with silica surface through H-bond. Secondly, covalent metal-O-Si bond could be formed between metal-acetylacetonate compounds and silanol groups through ligand exchange. Therefore, the disappearance of the broad peak at 22° might be ascribed to the interaction between Fe(acac)₃ precursor and abundant silanol groups of MCM-41 support, forming rich Fe—O—Si bond. Besides, a diffraction peak at 2θ = 35°, which was corresponding to Fe species, was clearly seen for all iron-modified MCM-41 samples, and with iron loading increasing, the intensity of this peak increased correspondingly. This phenomenon revealed that small iron oxide clusters or nanoparticles was formed either inside the mesopores or on the external surface with Fe content increasing. The bare MCM-41 and iron-modified MCM-41 samples were also characterized by Low-angle XRD measurements. As shown in the low diffraction angles spectra, compared with the bare MCM-41, the diffraction peak at around 2° of all iron-modified MCM-41 samples shifted to a lower angle region, suggesting a slight framework expansion of MCM-41 zeolite after iron modification. This framework
expansion might be attributed to the electrostatic attraction interaction between iron and lattice oxygen atom, and the insertion of a fraction of iron into the silica matrix after iron modification, which affected the hexagonal unit cell parameters of MCM-41 zeolite. The diffraction peak at about 2° of all iron-modified MCM-41 samples was still observed, indicating that the mesoporous structure of iron-modified MCM-41 was preserved after the Fe species were inserted. However, the diffraction peaks lying in the 2θ range of 3°–5° of 20Fe-MCM-41 broadened, revealing a slight decrease of the structural regularity of iron-modified MCM-41 with the content of Fe increasing.

![Fig. 1 The XRD patterns of MCM-41 and iron modified MCM-41 in the low angle range (a) and high angle range (b)](image)

The FT-IR results of pure MCM-41 and iron-modified MCM-41 sample (20Fe-MCM-41 as represent) are shown in Fig. 2. It is found that vibration peak at about 3500 cm\(^{-1}\), which was assigned to Si—OH, weakened obviously. This phenomenon proved the interaction between Fe precursor and silanol groups of MCM-41 support.

The N\(_2\) adsorption-desorption isotherms of bare MCM-41 and iron-modified MCM-41 samples, as well as the pore size distribution of bare MCM-41 and iron-modified MCM-41 samples, are displayed in Fig. 3. The textural properties of bare MCM-41 and iron-modified MCM-41 samples are summarized in Table 1. It can be seen that all iron-modified MCM-41 samples appeared the type-IV isotherms and hysteresis loops at P/P\(_0\) regions of 0.45–0.90, which was similar with pure silica support, MCM-41. It indicated that the iron modification could not destroy the well-defined mesoporous structure of MCM-41 support. The pore size distribution showed that the pore size of iron-modified MCM-41 distributed widely in the range of 2–4 nm, but the pore size of pure MCM-41 distributed narrowly at around 3 nm. As summarized in Table 1, pure silica MCM-41 support exhibited high BET surface area (899 m\(^2\)/g) and large total pore volume (0.84 cm\(^3\)/g) respectively. However, after insertion of iron into MCM-41 support, the BET surface area and total pore volume of all iron-modified MCM-41 samples decreased significantly. In the case of 20Fe-MCM-41, the BET surface area and total pore volume decreased to 797 m\(^2\)/g and 0.50 cm\(^3\)/g, respectively, which might be attributed to the existence of iron oxide clusters or nanoparticles on the external surface or inside the pore of iron-modified MCM-41 with high iron loading.

The SEM and high-resolution TEM were employed to investigated the morphology and detailed structure characteristics of iron-modified MCM-41 (20Fe-MCM-41 as representative sample), respectively. As shown in Fig. 4, 20Fe-MCM-41 displayed an irregular, layered morphology. The TEM image showed uniform and parallel channels of samples, which confirmed that the insertion of iron species into MCM-41 support could not destroy the mesoporous structure.

The FT-IR after pyridine adsorption was employed to study the acidic properties of iron-modified MCM-41 catalysts and results are shown in Fig. 5. Compared with the bare MCM-41 samples, all iron-modified MCM-41 samples showed an obvious adsorption peak at 1445 cm\(^{-1}\), which was ascribed to pyridine-Lewis acid adduct. In addition, the adsorption peak of pyridine...
adsorbed on Bronsted acid sites was not observed at 1540 cm\(^{-1}\) for all iron-modified MCM-41 samples. These phenomena revealed the acidity of iron-modified MCM-41 originated mainly from Lewis acid sites. In addition, with iron loading increasing, the intensity of the adsorption peaks increased correspondingly, which indicated that the Lewis acidity of iron-modified MCM-41 sample increased with iron content of sample increasing. When iron content of sample was high, a new adsorption peak at about 1490 cm\(^{-1}\) was observed, which could be ascribed to the chemisorbed pyridine on both Lewis acid and Bronsted acid sites. This phenomenon suggested that the acid sites distribution of iron-modified MCM-41 changed slightly when iron content of sample was high. The result indicated that the iron-modified MCM-41 catalyst might be a potential, beneficial catalyst in aldol condensation of furfural/HMF with acetone.

![Fig. 3](image-url)  The N\(_2\) adsorption-desorption isotherms (a) and pore size distribution (b) of MCM-41 and iron modified Fe-MCM-41

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET surface area (m(^2)/g)(^a)</th>
<th>Total pore volume (cm(^3)/g)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCM-41</td>
<td>899</td>
<td>0.84</td>
</tr>
<tr>
<td>5Fe-MCM-41</td>
<td>871</td>
<td>0.75</td>
</tr>
<tr>
<td>10Fe-MCM-41</td>
<td>834</td>
<td>0.67</td>
</tr>
<tr>
<td>20Fe-MCM-41</td>
<td>797</td>
<td>0.50</td>
</tr>
</tbody>
</table>

Notes: a, multipoint BET; b, determined from the amount adsorbed at \(P/P_0\) = 0.95.

![Fig. 4](image-url)  The SEM (top) and TEM (down) images of 20Fe-MCM-41

The XPS was used to distinguish the chemical composition of Fe on the surface of 20Fe-MCM-41. According to previous literature, four peaks can be obtained after deconvolution of Fe 2p spectrum. As shown in Fig. 6, the binding energy (BE) of four deconvolution peaks were considered at 711.7, 717.3, 725.4 and 733.6 ev, respectively. The BE at 711.7 ev was corresponded to Fe 2p\(_{3/2}\) and the BE at 725.4 and 733.6 ev were associated with Fe 2p\(_{1/2}\), which was ascribed to the existence of iron (III). It was widely reported that the BE of pure iron oxide was usually observed at 710.6 and 711.2 ev. Therefore, the different BE for Fe 2p\(_{3/2}\) in 20Fe-MCM-41 was an evidence for the interaction between Fe species and framework of silica MCM-41 support. In the meantime, the BE at 717.3 ev was an implication of the existence of isolated Fe\(^{3+}\) bound to surface O atoms.

The catalytic performances of two representatives of different types of catalysts were shown in Table 2. As the representative
of mixed metal oxide catalysts, MgO-ZrO$_2$ showed 59.9% furfural conversion with 100% selectivity to aldol products. The furfural conversion of 20Fe-MCM-41 was much higher than that of MgO-ZrO$_2$, but the selectivity of 20Fe-MCM-41 was lower than that of MgO-ZrO$_2$. This difference of selectivity between 20Fe-MCM-41 and MgO-ZrO$_2$ could be due to the pore structure of zeolite. More side reaction might occur within the pore of 20Fe-MCM-41 compared with outer surface of MgO-ZrO$_2$. As the representative of zeolite catalysts, Sn-MFI showed 90.0% furfural conversion, which was almost the same as 20Fe-MCM-41. However, the selectivity of 20Fe-MCM-41 was much higher than that of Sn-MFI. The possible reason was that F$_2$Ac could escape from the mesopore of 20Fe-MCM-41 but could not escape from the micropore of Sn-MFI.

![Fig. 5](image1.png)  
**Fig. 5** The FT-IR spectra of iron modified MCM-41 after pyridine adsorbed

![Fig. 6](image2.png)  
**Fig. 6** The XPS spectra of 20Fe-MCM-41

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Furfural conversion (%)</th>
<th>Product selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20Fe-MCM-41</td>
<td>86.9</td>
<td>86.3</td>
</tr>
<tr>
<td>MgO-ZrO$_2$</td>
<td>59.9</td>
<td>100.0</td>
</tr>
<tr>
<td>Sn-MFI</td>
<td>90.0</td>
<td>66.6</td>
</tr>
</tbody>
</table>

Aldol condensation reaction between furfural/HMF and acetone was studied by a series of iron modified MCM-41 catalysts and results are shown in Fig. 7. It could be clearly seen that all iron modified MCM-41 catalysts display a significantly improving catalytic activity compared with pure MCM-41 catalyst. This result indicated that Fe species was a feasible Lewis acid catalytic site for aldol condensation reaction. In addition, with Fe loading increasing, the catalytic activity of iron modified MCM-41 increased correspondingly. For furfural, 5Fe-MCM-41 showed 67.7% furfural conversion with 26.8% yield of FAc and 1.5% yield of F$_2$Ac, respectively. When Fe loading increased 20 wt%, furfural conversion achieved 86.9% with 60% yield of FAc and 7.5% yield of F$_2$Ac, respectively. For HMF, when 20Fe-MCM-41 was used as the catalyst, 41.1% yield of HAc and 3.5% yield of H$_2$Ac with 88.9% HMF conversion was achieved. However, when 5Fe-MCM-41 was used as the catalyst, only 25.3% yield of HAc and 0.8% yield of H$_2$Ac with 60.5% HMF conversion was achieved. This enhanced catalytic activity of iron
modified MCM-41 with higher Fe loading was ascribed to more Lewis acid sites possessed by higher Fe loading catalyst according to FT-IR after adsorbed by pyridine. In addition, iron modified MCM-41 showed preferred selectivity to aldol condensation reaction between furfural and acetone, compared with HMF and acetone. As shown in Table 3, in the case of almost same conversion, 20Fe-MCM-41 showed enhanced selectivity to condensation products of furfural compared with HMF. The 69.0% selectivity to FAc as well as 17.3% selectivity to F\textsubscript{2}Ac, 86.3% total selectivity, was achieved, which was much higher than 46.2% selectivity to HAc and 7.9% selectivity to H\textsubscript{2}Ac, 54.1% total selectivity.

Table 3  Selectivity to condensation products between furfural or HMF and acetone over 20Fe-MCM-41

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Conversion (%)</th>
<th>FAc/HAc selectivity (%)</th>
<th>F\textsubscript{2}Ac/H\textsubscript{2}Ac selectivity (%)</th>
<th>Total selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furfural</td>
<td>86.9</td>
<td>69.0</td>
<td>17.3</td>
<td>86.3</td>
</tr>
<tr>
<td>HMF</td>
<td>89.8</td>
<td>46.2</td>
<td>7.9</td>
<td>54.1</td>
</tr>
</tbody>
</table>

Notes: reaction conditions are time, 24 h; temperature, 160 °C; catalyst loading, 0.1 g; and the molar ratio of furfural or HMF to acetone = 1:20.

The effect of reaction time, varying from 3h to 24 h, on aldol condensation of furfural or HMF with acetone over 20Fe-MCM-41 catalyst was investigated. As exhibited in Fig. 8, with reaction time increased from 3 h to 24 h, furfural conversion increased from 35.1% to 86.9% and FAc, as well as F\textsubscript{2}Ac yield, increased correspondingly from 11.4% to 60.0% and from 1.0% to 7.5%, respectively. This result revealed that prolonging reaction time could effectively increase the yield of condensation product between furfural and acetone. The same trend was also observed in aldol condensation of HMF with acetone. The HMF conversion increased from 39.9% to 88.9% with HAc as well as H\textsubscript{2}Ac yield increasing from 15.4% to 41.1% and from 0.6% to 3.5%, respectively, when the reaction time was prolonged from 3 h to 24 h. It was worth noting that after 9 h, HAc yield was exceeded by FAc yield although HMF conversion was still higher than furfural conversion. It possibly was ascribed that more side reaction was occurred in aldol condensation reaction between HMF and acetone, which made that the catalyst was poisoned more seriously, compared with aldol condensation reaction between furfural and acetone. The thermo gravimetric analysis (TGA) results could certify this suppose. The mass loss of spent catalyst after reaction with furfural of acetone was 0.1%, but the mass loss of spent catalyst after reaction with the HMF of acetone was 2.2%. This result lead to the gap of selectivity of catalyst in aldol condensation between HMF with acetone and furfural with acetone. The same trend was also observed in aldol condensation reaction between HMF with acetone and furfural with acetone. However, after 9 h, the selectivity to FAc remained at about 70% but the selectivity to HAc was only about 46%. Different with FAc (HAc) yield, the effect of reaction time on F\textsubscript{2}Ac (H\textsubscript{2}Ac) yield was not remarkable, which was mainly attributed that the competitive adsorption between FAc (HAc) and furfural (HMF) was more difficult than acetone and furfural (HMF) because of high molar ratio of acetone/furfural (HMF). Therefore, the process of production of F\textsubscript{2}Ac (H\textsubscript{2}Ac) was not a major reaction, which made that the influence of reaction time on F\textsubscript{2}Ac (H\textsubscript{2}Ac) yield was not as conspicuous as FAc (HAc) yield.
Reaction conditions: temperature, 160 ℃; catalyst loading, 0.1 g; the molar ratio of furfural or HMF to acetone = 1:20

Fig. 8 Effect of reaction time on aldol condensation reaction with furfural or HMF of acetone over 20Fe-MCM-41 catalyst

The effect of reaction temperature, varying from 80 °C to 160 °C, on aldol condensation of furfural or HMF with acetone over 20Fe-MCM-41 catalyst was also studied. As shown in Fig. 10, furfural conversion increased from 17.8% to 86.9% and FAc yield, increased correspondingly from 1.4% to 60.0%. This result indicated that enhancing reaction temperature could effectively boost the yield of condensation product between furfural and acetone. The same trend was also obtained in aldol condensation of HMF with acetone. The HMF conversion increased from 4.2% to 88.9% with HAc yield increasing from 1.1% to 41.1%, when the reaction temperature was enhanced from 80 °C to 160 °C. In addition, F\textsubscript{2}Ac and H\textsubscript{2}Ac, were only observed when reaction temperature was above 140 °C. This phenomenon revealed that higher reaction temperature would benefit the competitive adsorption of FAc (HAc) with furfural (HMF), which led to higher F\textsubscript{2}Ac (H\textsubscript{2}Ac) yield.

Reaction conditions: time, 24 h; catalyst loading, 0.1 g; the molar ratio of furfural or HMF to acetone = 1:20

Fig. 9 Selectivity to FAc and HAc over 20Fe-MCM-41 catalyst

The reusability and regeneration research of iron modified MCM-41 in aldol condensation between furfural and acetone was investigated. Figure 11 summarized the reusability (run 2) and regeneration (run 3, 4 and 5) studies of 20Fe-MCM-41 catalyst. After the first run, attempt was made to recycle the spent catalyst via just washing with acetone thoroughly and dried at 100 °C. As shown in Fig. 11 (run 2), the catalytic behavior of this as-treated spent catalyst decreased obviously. The furfural conversion decreased from 86.9% to 69.5% and the yield of FAc and F\textsubscript{2}Ac decreased from 60.0% to 36.9% and 7.5% to 3.0%, respectively. The result indicated that 20Fe-MCM-41 catalyst can not be recycled through only washing with acetone after reaction. The regeneration of 20Fe-MCM-41 was performed by calcination at 550 °C in air for five hours after washing with acetone and drying at 100 °C. The regenerated 20Fe-MCM-41 displayed almost the same catalytic behavior compared with the first run. The furfural conversion was 85% with a 58% yield of FAc and a 6.9% yield of F\textsubscript{2}Ac, respectively (run 3). The 20Fe-MCM-41 was
regenerated by washing, drying and calcination in air (the same way as run 3) in the following two runs (run 4 and run 5). Although the furfural conversion and condensation product yield continuously decreased, the catalytic performance of 20Fe-MCM-41 catalyst after regeneration was acceptable. The reusability and regeneration research of iron modified MCM-41 in aldol condensation of HMF with acetone was also studied and the catalytic performance was similar to the result of aldol condensation of furfural with acetone.

4. Conclusions

In this study, iron modified MCM-41 was prepared by a simple solid postgrafting method and was used as an effective Lewis acid catalyst for aldol condensation reaction of furfural or HMF with acetone. High furfural or HMF conversion and condensation products yield were achieved. Compared with condensation products of the HMF with acetone, iron modified MCM-41 catalyst showed preferred selectivity to condensation product of furfural with acetone. The 86.3% total selectivity to condensation products of furfural with acetone was observed, much higher than 54.1% total selectivity to condensation products of HMF with acetone. The reusability and regeneration researches showed iron modified MCM-41 could be regenerated by calcination in air and the catalytic performance of regenerated 20Fe-MCM-41 catalyst was acceptable.

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