Synthesis and Xylene Isomerization Properties of Hierarchical Eu-1 Zeolite

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Abstract. A series of hierarchical EU-1 molecular sieves with different mesoporous/microporous ratios were prepared by adding water-rich gelatinized starch into the synthesis system of EU-1 molecular sieves. The effects of the amount of gelatinized starch on the crystallization process and the physicochemical properties of the final product were investigated. The synthesized EU-1 molecular sieve was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), N2-adsorption desorption and ammonia temperature programmed desorption (NH3-TPD). The catalytic performance of the synthesized EU-1 molecular sieve in the Xylene Isomerization reaction was studied. The results show that the introduction of gelatinized starch is beneficial to the formation of intergranular mesopores, and the regular changes of mesoporous/micropore volume ratio can be regulated by the amount of gelatinized starch. The amount of gelatinized starch gradually increases from 0% to 6%, and the mesoporous/micropore volume ratio of EU-1 molecular sieve gradually increases from 1.55 to 4.44. The equilibrium concentration of p-xylene and the yield of C8 increased with the increase of the mesoporous/microporous volume ratio of EU-1 molecular sieve in the Xylene Isomerization reaction. The equilibrium concentration of p-xylene gradually increased from 23.35% to 23.85%, and the yield of C8 gradually increased from 95.76% to 97.15%.

Keywords: EU-1 zeolite; gelatinized starch; Xylene Isomerization reaction.

1. Introduction

EU-1 Zeolite is a novel medium pore zeolite which was first synthesized by Casci et al in 1981[1]. It has one-dimensional channel along the [001] direction with 10-T ring apertures of oxygen atoms with a cross-section of 0.58 × 0.41 nm in the main channels and 12-T ring apertures with a cross-section of 0.68 × 0.58 nm and 0.8 nm deep leading to the attached side pockets[2]. Due to its peculiarities of pore dimension and pore structure, EU-1 molecular sieve exhibits very high activity and selectivity in xylene isomerization reaction and is recognized as a new generation of xylene isomerization zeolite [3]. However, it is the biggest problem that diffusion is poor for the one-dimensional micropore structure of EU-1 molecular sieve[4]. Based on this, researchers have done a lot of optimization work. Up to now, the construction of hierarchical pore structure is considered to be the best solution to improve the diffusion problem [5-8].

Starch is a biological homopolymer, whose molecular formula is (C6H10O5)n. It is mainly composed of highly branched amylopectin (crystallized region) and basically linear amylopectin (amorphous region) in a spiral structure arrangement. Gelatinization is one of the basic properties of starch. After the starch particles are treated with moisture and heat, the internal molecules are rearranged to form water-rich compounds. During this process, the starch particles and crystal structure may undergo various changes, such as the disintegration of the double helix structure in the amorphous region and the destruction of the crystal structure of the particles. The recombination of starch chains will occur in intermolecular and intramolecular[9-11].

At present, the influence of gelatinized starch for EU-1 zeolite synthesis, which is rich in water in its own structure, has not been reported. Based on this, gelatinized starch was introduced into the synthesis system of EU-1 zeolite and a series of multiporous EU-1 zeolite with different
mesoporous/microporous ratios were prepared. The effects of addition amount on the 
physicochemical properties of multiporous EU-1 zeolite and its xylene isomerization performance 
were investigated, and the causes were analyzed and discussed.

2. Experimental section

2.1 Materials

Silica sol (25wt%SiO2), Sodium aluminate (41%wtAl2O3,25wt%Na2O), Sodium hydroxide 
(96wt% NaOH), Soluble starch(87wt%), Hexamethonium bromide (98wt%HMBr2), M-xylene 
(98wt%) . All reagents were used without further purification. The demonized water wasmade in 
our own laboratory.

2.2 EU-1 zeolite preparation

The synthesis of multiporous EU-1 zeolite is carried out in two steps: first, the seed guide agent 
is synthesized, and then other raw materials are added to the seed guide agent for crystallization. 
The specific steps are as follows:

2.2.1 Preparation of the seed guide agent

The seed guide agent of EU-1 zeolite was synthesized using the gelwith the molar composition of 
1.0Al2O3:58.3SiO2:8.8Na2O:13HMBr2:800H2O. Typically, 46.3g Silica sol and 18.8 g hexamethonium bromide were mixed with 23.8g deionized water and stirred for 30 min, followed by 
the addition of 1.0g sodium aluminate. 2.6g sodium hydroxide was dissolved in the mixture until 
the homogeneous gel was obtained. The preparedgel was transferred to a 100 mL autoclave reactor 
and the seed guide agent was obtained after crystallization at 180°C for 24h.

2.2.2 Preparation of multiporous EU-1 zeolite

The multiporous EU-1 zeolite was synthesized using the gelwith the molar composition of 
1.0Al2O3:58.3SiO2:10.3Na2O:6.6HMBr2:800H2O. Typically, 9.1g Silica sol and 41.5g seed guide 
agent were mixed with 4.7g deionized water and stirred for 30 min, followed by the addition of 0.2g 
sodium aluminate. 0.7g sodium hydroxide was dissolved in the mixture. Finally, gelatinized starch 
solution (10wt%)was added until the homogeneous gel was obtained. The preparedgel was 
transferred to a 100 mL autoclave reactor for crystallization, which is divided into two steps: first at 
140°C for 12h, and finally at 180°C for 48h. After the crystallization, the products were washed, 
centrifuged , dried, and roasted at 550°C for 6h. The roasted EU-1 zeolite powder was first 
exchanged twice with 1mol • L-1 ammonium nitrate solution in a water at 90°C , and then the 
ammonium was removed at 450°C to obtain multiporous H-EU-1 zeolite powder, which was then 
pressed and crushed. The catalytic performance of 20–40 mesh zeolite was evaluated. The 
multiporous zeolite was synthesized with the number S1, S2, S3, S4 and S5 indicating that the 
amount of gelatinized starch added was 0%, 2%, 4%, 6% and 8% of the dry base mass of silicon 
source, respectively.

2.3 Characterization

The phase and crystallinity of zeoliteswere determinedby powder X-ray diffraction (XRD) using 
a Bruker D8 Advance diffractometer with Cu Karadiation (λ= 1.5406Å). For phase identification, 
XRD patterns were collected in a continuous scanning mode from5-50°(2θ) at a scanning rate of 
8°/min.For relative crystallinity and cell parameter calculation, XRD patterns were collected from 
18-28°(2θ) at a scanning rate of 0.5°/min. The relative crystallinity of samples was calculated by the 
peak intensityof 20 at 19°,20.8°, 22.2°,23.2° and 23.9°. The morphology ofthe obtained samples was 
examined using a JEOLJSM-6700F scanning electron microscope (SEM). Transmission Electron 
Microscope(TEM) images were performed on a JEM-2010 electron microscope operated at 200 
Kv.Acidityof thesamples were determined by NH3-TPD using a TL-5076 typeII Multi-purpose
adsorbent (Tianjin Xianquan Corporation, China). The axial grain crushing strength was tested by crushing strength tester (DL4, Dalian Peng hui Corporation, China). 60 shaped catalysts were tested and the average values were used for comparison. The specific surface area of the samples was determined by using nitrogen adsorption-desorption isotherms recorded at -196 °C on an ASAP2000 automatic physical adsorption analyzer (Micromeritics instrument Corp., USA). The total specific surface area was calculated by the BET (Brunauer-Emmett-Teller) formula, pore size distribution was calculated by the BJH (Barrett-Joyner-Halenda) model, and the micropore volume and micropore specific surface area were determined by using the t-plot method.

2.4 Catalytic test

The hydroisomerization reaction was performed in a fixed-bed reactor. The filling amount of catalyst was 1g, the reaction temperature was 360 °C, the reactant was m-xylene and the m-xylene weight hourly space velocity (GHSV) was 4.5h⁻¹. After the operation was stable, sample was collected from the product tank once every 3 hours. The products were analyzed by gas chromatography using an Agilent 6820, and an Agilent Cerity QC-QA chromatography workstation (Agilent Corporation, USA) was used for processing data. In this study, the equilibrium concentration (PX/∑X) of P-xylene was used as the activity index, while the yield of C8 was used as the selective index. The formulas for the two indexes are shown from Eq. (1) to Eq. (2).

\[ \frac{\text{PX}}{\sum \text{X}} = \frac{w(\text{PX})}{w(\text{PX}+\text{MX}+\text{OX})} \times 100\% \quad (1) \]

\[ Y(\text{C8}) = \frac{w(\text{PX}+\text{MX}+\text{OX}+\text{EB})}{100\%} \quad (2) \]

Where,

- \( w (\text{PX}) \) is the mass fraction of PX in the products, wt%;
- \( w (\text{MX}) \) is the mass fraction of MX in the products, wt%;
- \( w (\text{OX}) \) is the mass fraction of OX in the products, wt%;
- \( w (\text{EB}) \) is the mass fraction of EB in the products, wt%.

3. Results and Discussion

3.1 Effect of gelatinized starch addition amount on product

The XRD pattern of the samples is shown in Fig. 1. It can be seen from Fig. 1 that the characteristic diffraction peaks of EUO topology appear at 20=19°, 20.8°, 22.2°, 23.2° and 23.9° of samples S1-S4, indicating that pure phase EU-1 zeolites were obtained. When the amount of gelatinized starch is 8% of the dry base mass of silicon source, the synthesized sample S5 crystal phase is amorphous. As can be seen from Table 1, with the increase of gelatinized starch addition, the crystallinity of EU-1 zeolite sample is 100%, 99%, 98%, 96% and 0 in turn, with a general downward trend. The reason is that gelatinized starch has strong water absorption, which affects the effective solvation ability of water after adding to zeolite crystallizing gel. The solubility and reactivity of reactants are reduced, which is not conducive to the rearrangement and dissolution of the primary gel initially generated, and ultimately affects the improvement of nucleation rate and crystallization rate.

![Fig. 1 XRD patterns of EU-1 zeolite samples](image-url)
### Table 1. Crystallinity of EU-1 zeolite samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Amount of gelatinized starch</th>
<th>Crystalline phase</th>
<th>Relative crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0%</td>
<td>EU-1</td>
<td>100%</td>
</tr>
<tr>
<td>S2</td>
<td>2%</td>
<td>EU-1</td>
<td>99%</td>
</tr>
<tr>
<td>S3</td>
<td>4%</td>
<td>EU-1</td>
<td>98%</td>
</tr>
<tr>
<td>S4</td>
<td>6%</td>
<td>EU-1</td>
<td>96%</td>
</tr>
<tr>
<td>S5</td>
<td>8%</td>
<td>Amorphous</td>
<td></td>
</tr>
</tbody>
</table>

3.2 Analysis of morphology

Fig. 2 is the SEM image of the samples. It can be seen from the Fig. that each sample is an irregular aggregate composed of nanometer sized grains. According to the SEM image, the addition amount of gelatinized starch have little influence on the crystal morphology of the sample.

![Fig. 2 SEM images of hierarchical EU-1 zeolite samples](image)

In order to further observe the ultra-structure of the sample, TEM characterization was performed, as shown in Fig. 3. Compared with sample S1 synthesized without gelatinized starch, there are certain intercrystalline pore between the grains of the sample synthesized with gelatinized starch. Moreover, with the increase of gelatinized starch, the intercrystalline pore became more and more obvious, indicating that the addition of gelatinized starch is conducive to the formation of intergranular mesoporous and the dispersion of agglomerated zeolite grains.

![Fig. 3 TEM images of hierarchical EU-1 zeolite samples](image)

3.3 Pore property analysis

Fig. 4(a) shows the N2 adsorption-desorption isotherm of the synthesized samples. Compared with the sample S1 prepared without gelatinized starch, the samples S2, S3 and S4 prepared with gelatinized starch have higher N2 adsorption capacity in the low P/P0 zone and the middle P/P0 zone. The growth of zeolite crystals is inhibited due to the addition of gelatinized starch, which results in the formation of aggregated nanoparticles [12]. The above TEM results further confirm that intergranular mesoporous pores are formed among nanoparticles. Moreover, it can be seen that the nitrogen absorption and desorption curves of the samples do not coincide within the range of 0.4 < P/P0 < 1.0 for the samples S2 to S4. A relatively obvious hysteresis loop was found, and the hysteresis loop gradually became larger, indicating that the mesoporous number of the sample increased gradually.

Fig. 4(b) shows the BJH pore size distribution of the synthesized samples, which further confirms the above results. The peak position of the aperture distribution curve of the four samples is gradually increasing, indicating that the aperture is gradually increasing. Specifically, the peak position of pore size distribution gradually increases from 2.0 nm, 2.5 nm, 3.0 nm to 5.0 nm with the increase of gelatinized starch addition, indicating that the pore size of synthesized zeolite is gradually increasing.
Table II lists the pore structure parameters of the four samples. It can be seen that the mesoporous pore volume of the sample increases gradually, from 0.17 cm³/g to 0.40 cm³/g, and the ratio of mesoporous/microporous also increases gradually, from 1.55 to 4.44 with the increase of gelatinized starch addition, indicating that the introduction of gelatinized starch into the EU-1 zeolite synthesis system is conducive to the formation of mesoporous pores. The mesoporous content of the synthesized sample can be controlled by controlling the amount of gelatinized starch. At the same time, the microporous specific surface area of the sample gradually decreases, which is related to the gradual decrease of the above-mentioned zeolite crystallinity. Moreover, the outer specific surface area is also gradually increasing, which is due to the gelatinized starch is conducive to the dispersion of agglomerated zeolite grains.

Table 2. Pore structure parameters of hierarchical EU-1 zeolite samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>SBET (m²·g⁻¹)</th>
<th>Smicro (m²·g⁻¹)</th>
<th>SExt (m²·g⁻¹)</th>
<th>Vtotal (cm³·g⁻¹)</th>
<th>Vmicro (cm³·g⁻¹)</th>
<th>Vmeso (cm³·g⁻¹)</th>
<th>Vmeso/Vmicro</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>405</td>
<td>380</td>
<td>25</td>
<td>0.28</td>
<td>0.11</td>
<td>0.17</td>
<td>1.55</td>
</tr>
<tr>
<td>S2</td>
<td>410</td>
<td>328</td>
<td>82</td>
<td>0.33</td>
<td>0.09</td>
<td>0.24</td>
<td>2.67</td>
</tr>
<tr>
<td>S3</td>
<td>408</td>
<td>274</td>
<td>134</td>
<td>0.42</td>
<td>0.10</td>
<td>0.32</td>
<td>3.20</td>
</tr>
<tr>
<td>S4</td>
<td>412</td>
<td>241</td>
<td>171</td>
<td>0.49</td>
<td>0.09</td>
<td>0.40</td>
<td>4.44</td>
</tr>
</tbody>
</table>

3.4 Acid property analysis

The surface acid center intensities and their distributions of different EU-1 zeolites were investigated using NH3-TPD, and the results are shown in Fig. 5 and Table III. As shown in Fig. 5, two desorption peaks appeared at 225°C and 425°C for all samples, and the acid strength is similar. The specific calculation results of NH3-TPD are shown in Table III, which shows that the amounts of strong and weak acids are basically the same. To sum up, the addition of gelatinized starch has little effect on the acid strength and acid content of zeolite.
3.5 Catalytic performance in the m-Xylene Isomerization reaction

The reaction results of xylene isomerization for the synthesis of hierarchical pore zeolite are listed in Table IV. As can be seen from the table, the equilibrium concentration of para-xylene (PX) increased from 23.35% to 23.83% with the increase of the interpore/micropore ratio of the multipore EU-1 zeolite sample, increasing by 0.48%. The hydrocarbon yield of C8 also increased from 95.76% to 97.15%, increasing by 1.39%. The results show that for poor PX raw materials, the isomerization reaction was mainly carried out on the outer surface of zeolite. According to the characterization results of N2-adsorption and desorption and NH3-TPD in this paper, under the condition of constant total specific surface area and total acid content, the outer specific surface area of the synthesized sample increases gradually, and the acid content of the outer surface also increases gradually, which is favorable for the conversion of m-xylene. Meanwhile, the amount of o-xylene and para-xylene in the product unquestionably increase. At the same time, according to the TEM analysis and pore structure parameter calculation results in this paper, the intergranular mesoporous pores of zeolite increase, which makes the isomerized PX on the outer surface of zeolite rapidly diffuse to the reaction phase. Undoubtedly, it reduces the probability of side reaction and improves the selectivity of para-xylene. Finally, the yield of C8 is significantly improved.

Table 4. Data for xylene isomerization of hierarchical EU-1 zeolite samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Vmeso/Vmicro</th>
<th>PX/%</th>
<th>MX/%</th>
<th>OX/%</th>
<th>PX+MX/%</th>
<th>Y(C8)/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>1.55</td>
<td>22.36</td>
<td>52.85</td>
<td>20.55</td>
<td>23.35</td>
<td>95.76</td>
</tr>
<tr>
<td>S2</td>
<td>2.67</td>
<td>22.25</td>
<td>52.01</td>
<td>20.70</td>
<td>23.43</td>
<td>95.83</td>
</tr>
<tr>
<td>S3</td>
<td>3.20</td>
<td>22.86</td>
<td>51.93</td>
<td>21.91</td>
<td>23.64</td>
<td>96.70</td>
</tr>
<tr>
<td>S4</td>
<td>4.44</td>
<td>23.15</td>
<td>51.74</td>
<td>22.26</td>
<td>23.83</td>
<td>97.15</td>
</tr>
</tbody>
</table>

4. Conclusions

(1) The amount of gelatinized starch has an important effect on the crystallization process of EU-1 zeolite and the physical and chemical properties of the final product. The amount of gelatinized starch should not exceed 6%, otherwise it will affect the crystal shape. The addition of gelatinized starch has little effect on the acidity of EU-1 zeolite, but has a great effect on the pore properties and specific surface area. Surprisingly, the gelatinized starch can be changed regularly by controlling the amount added.

(2) In the xylene isomerization reaction, with the increase of the mesoporous/microporous volume ratio of EU-1 zeolite, the equilibrium concentration of PX gradually increases from 23.35% to 23.85%, and the yield of C8 gradually increases from 95.76% to 97.15%, which is attributed to the multi-polarization of EU-1 zeolite. It promotes the diffusion of reactive molecules and increases the active site on the outer specific surface of zeolite.
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References