

# The study on citric acid-modified HUSY catalyzed alkylation of phenol with cyclohexanol

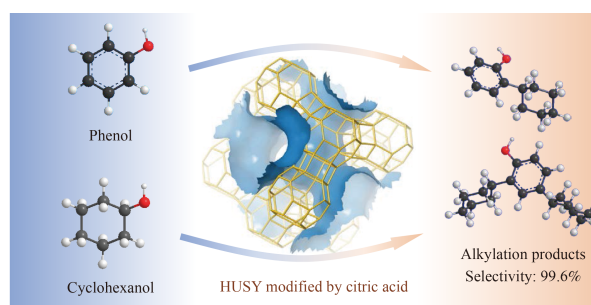
HUA Canhao<sup>1</sup>, WU Jingfeng<sup>1</sup>, ZHU Lingjun<sup>1,\*</sup>, XU Guangwen<sup>2</sup>, WANG Shurong<sup>1,2,\*</sup>

<sup>1</sup> State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou 310027, China;

<sup>2</sup> Key Laboratory on Resources of Chemicals and Materials of Ministry of Education, Shenyang University of Chemical Technology, Shenyang 110142, China

**Abstract:** Lignin-derived oxygenated aromatics, particularly phenols and aromatic ethers obtained through depolymerization, represent promising feedstocks for synthesizing high-density and high-heat-sink aviation fuels via alkylation-hydrogenation processes. This study systematically evaluates the catalytic performance of various zeolites (H $\beta$ , HZSM-5, MCM-41 and HUSY) in the alkylation reaction of phenol with cyclohexanol. Characterization results demonstrate that HUSY zeolite showed superior catalytic activity compared to other zeolites, attributable to its favorable pore architecture and well-balanced acid site distribution that synergistically facilitate molecular diffusion and catalytic transformations. To further enhance the catalytic properties, HUSY zeolite was modified with citric acid at various concentrations and compared with those treated with NaOH and oxalic acid. The results revealed that citric acid treatment preserved the crystallinity of the zeolite while modulating its acid distribution and pore structure. All modified zeolites enhanced phenol alkylation activity. Notably, the HUSY-0.5M catalyst, which exhibited the highest medium-strong acid to total acid ratio, achieved superior catalytic performance, 80.4% conversion of phenol and 99.6% selectivity for alkylation products. The catalyst also exhibited high activity in the alkylation of various lignin-derived compounds, demonstrating its broad applicability. This work provides a new strategy for the valorization of lignin-derived phenols into high-value fuel precursors through alkylation.

**Key words:** citric acid modification; HUSY; phenolic alkylation; aviation fuel



With the increasing consumption of fossil fuels, environmental issues such as the greenhouse effect have intensified. To mitigate carbon emissions, the development of renewable and environmentally friendly fuels has attracted significant attention<sup>[1]</sup>. Lignocellulosic biomass, a ternary matrix of cellulose, hemicellulose, and lignin, stands as the exclusive renewable carbon feedstock in nature, characterized by its carbon-neutral lifecycle and extensive reserves<sup>[2–3]</sup>. Consequently, it holds great promise for producing green fuels and has been extensively studied for transportation fuel applications, including gasoline<sup>[4–5]</sup>, bio-jet fuel<sup>[6]</sup>, and biodiesel<sup>[7]</sup>. Given that the aviation sector's energy demand cannot be readily met by electrification in the near term, the development of biomass-derived

sustainable aviation fuels (SAFs) is a critical pathway to reducing aviation-related carbon emissions.

The primary bio-oil from thermochemical conversion of biomass is rich in organic compounds, and its upgrading into high-value liquid fuels is a critical route for biomass energy utilization<sup>[8]</sup>. However, most components in crude bio-oil are monocyclic molecules, such as lignin derived phenolic compounds (e.g., guaiacol, phenol, catechol, and 2,6-dimethoxyphenol)<sup>[9]</sup> and cellulose/hemicellulose-derived ketones (e.g., cyclohexanone and cyclopentanone)<sup>[10]</sup>. After hydrodeoxygenation (HDO), these low-carbon-number monocyclic structures typically exhibit densities below 0.77 g/mL, failing to meet the requirements for high-density aviation fuels. In contrast,

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\* Corresponding author. Tel: 0571-87952801, E-mail: lingjun\_zhu@zju.edu.cn, srwang@zju.edu.cn.

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polycyclic hydrocarbons, known for their high-density properties, can be synthesized through C–C coupling reactions to construct multi-ring fuel precursors<sup>[11]</sup>. Depending on the reactants, common C–C coupling strategies include alkylation<sup>[12]</sup>, aldol condensation<sup>[13]</sup>, oligomerization<sup>[14]</sup>, and Diels-Alder cycloaddition<sup>[15]</sup>. Notably, lignin-derived phenolics and cyclic alcohols (e.g., cyclohexanol and cyclopentanol) can be converted into bicyclic and tricyclic fuel precursors via alkylation<sup>[16]</sup>.

Zeolites, with tunable surface area, acidity, and pore structure, have been widely employed in alkylation research. Liu et al.<sup>[17]</sup> investigated zeolite-catalyzed alkylation of phenolic compounds and found that, compared to conventional solid catalysts, zeolites with active sites confined within molecular-sized channels exhibited superior catalytic activity. Moreover, the pore size of zeolites was identified as a critical factor influencing the extent of alkylation reactions. The adjustment of the silica-to-alumina ratio (SAR) during synthesis serves as a key strategy for modulating zeolite acidity and pore characteristics. Yang et al.<sup>[16]</sup> systematically studied the alkylation of phenols with cyclopentanol over HY zeolites with varying SARs. Their results demonstrated a gradual decline in catalytic activity as the SAR increased from 5.3 to 40.

Zeolites can also be modified through various post-synthesis treatments such as chemical dealumination<sup>[18]</sup> and hydrothermal aging<sup>[19]</sup> to optimize their acidity distribution and pore structure, thereby enhancing catalytic performance. These post-treatment methods are particularly valuable for catalytic reactions requiring improved mass transfer, as they can create hierarchical pore structures combining both micro- and mesopores. Among these modification approaches, chemical dealumination offers distinct advantages by enabling partial and controlled framework dealumination under relatively mild conditions through judicious selection of dealuminating agents. Matias et al.<sup>[20]</sup> investigated the effects of acid treatment on the acidity of HMCM-22 zeolite, demonstrating that dealumination primarily depends on aluminum accessibility, with non-framework aluminum species being more readily removed. Huang et al.<sup>[21]</sup> systematically compared the dealumination efficiency of hydrochloric acid, oxalic acid, and citric acid on HUSY zeolite for olefin removal from aromatics. Their results revealed that catalysts modified with hydrochloric or oxalic acid exhibited lower activity than those treated with citric acid. This difference was attributed to: (1) the strong acidity of hydrochloric acid causing framework collapse; (2) the strong chelating ability of oxalic acid inducing framework distortion; whereas (3) citric acid could selectively remove both framework and extra-framework aluminum while preserving structural integrity, thereby effectively tuning acidity distribution and pore architecture. These findings establish citric acid treatment as a promising strategy for precisely modulating zeolite properties. Notably, the application of citric acid-modified zeolites in phenolic alkylation reactions remains unexplored in the literature to date.

Building on the optimized zeolite selection, this study employed citric acid modification of HUSY zeolite. The effects of different citric acid concentrations on the acidity, pore structure, and framework silicon/aluminum species of HUSY were systematically investigated using comprehensive characterization techniques including Brunauer-Emmett-Teller (BET), X-ray diffraction (XRD), Nuclear Magnetic Resonance (NMR) and NH<sub>3</sub> temperature programmed desorption (NH<sub>3</sub>-TPD). Subsequently, the citric acid-modified HUSY catalysts were applied to the alkylation of phenol with cyclohexanol to evaluate the influence of citric acid concentration on catalytic performance. Finally, the optimal catalyst (HUSY-0.5M) was tested in the alkylation of lignin-derived phenolic compounds and ethers to assess its substrate versatility.

## 1 Experimental

### 1.1 Materials

All chemicals were used as received without further purification. Phenol, cyclohexanol, dodecane, guaiacol, citric acid, and HUSY zeolite (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 20–30) were purchased from Macklin Biochemical Co., Ltd. (Shanghai, China). *p*-Cresol and anisole were obtained from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). 1,4-Dioxane was supplied by Sinopharm Chemical Reagent Co., Ltd.

The zeolite catalysts, including HZSM-5 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 25), HUSY (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 11) and H $\beta$  (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 25), were procured from Nankai University Catalyst Co., Ltd. (Tianjin, China). MCM-41 was purchased from XFNANO Materials Technology Co., Ltd. (Jiangsu, China).

### 1.2 Preparation of catalysts

2 g sample of HUSY zeolite was added to 20 mL of citric acid solution (0.5 mol/L) and treated in an oil bath at 90 °C for 4 h. The sample was thoroughly washed with deionized water until the filtrate reached neutrality. The filter cake was dried at 110 °C for 12 h, followed by calcination at 500 °C for 4 h. The resulting sample was labeled HUSY-0.5M. For comparison, catalysts were prepared under identical conditions using 0.5 mol/L NaOH solution and 0.5 mol/L oxalic acid solution, designated as HUSY-SH and HUSY-OA, respectively. Subsequently, the citric acid concentration was varied (0.1, 0.3, 1.0 mol/L) while repeating the above steps. The obtained samples were named HUSY-*x* (where *x* denotes concentration). Prior to use, all zeolites were calcined at 500 °C for 4 h.

### 1.3 Characterization

The crystallinity and crystal structural parameters of the catalyst powders were analyzed using an X-ray

diffractometer (Rigaku SmartLab) with Cu  $K\alpha$  radiation ( $\lambda = 0.15406$  nm, 40 kV, 40 mA). The measurement range is  $2\theta = 5^\circ\text{--}80^\circ$ , the step size is  $0.01^\circ$ , and the scanning speed is  $10^\circ/\text{min}$ . The relative crystallinity of the samples was calculated based on the diffraction peaks at  $2\theta = 6.32^\circ$  (111),  $10.36^\circ$  (220),  $12.12^\circ$  (311),  $15.96^\circ$  (331),  $19.08^\circ$  (333),  $20.8^\circ$  (440),  $24.12^\circ$  (533) and  $27.6^\circ$  (642)<sup>[22]</sup>. Textural properties (specific surface area, pore volume, and pore size) were measured using a fully automated surface area analyzer (Micromeritics 3Flex, USA) with  $N_2$  as the adsorbate at  $-196^\circ\text{C}$ . Prior to analysis, samples were degassed under vacuum at  $300^\circ\text{C}$  for 8 h. Morphological features were observed by field-emission scanning electron microscopy (SEM, Sigma 360). The coordination environments of Si and Al in the zeolites were investigated by solid-state NMR (Bruker 400WB Avance III).  $^{29}\text{Si}$  NMR: Resonance frequency 79.56 MHz, referenced to the silicon signal of Q8M8 (methyl group-attached Si, 12.1). Data were acquired using a  $30^\circ$  single pulse ( $1.5\ \mu\text{s}$  @ 273 W) with a 15 s relaxation delay.  $^{27}\text{Al}$  NMR: Resonance frequency 104.34 MHz, referenced to a 1 mol/L  $\text{Al}(\text{NO}_3)_3$  solution. Spectra were collected with a  $10^\circ$  single pulse ( $0.11\ \mu\text{s}$  @ 188 W), 0.4 s acquisition interval. Acidic properties were evaluated using a chemisorption analyzer (Microtrac BELCat II). Samples were pretreated in He flow (50 mL/min) at  $300^\circ\text{C}$  ( $10^\circ\text{C}/\text{min}$ ) for 1 h, cooled to  $50^\circ\text{C}$ , and saturated with 10%  $\text{NH}_3/\text{He}$  (50 mL/min, 1 h). Weakly adsorbed  $\text{NH}_3$  was removed by He purging (50 mL/min, 1 h), followed by desorption from  $50^\circ\text{C}$  to  $800^\circ\text{C}$  ( $10^\circ\text{C}/\text{min}$ ) under He flow. Evolved gases were detected by thermal conductivity detector (TCD).

#### 1.4 Catalytic tests

The alkylation experiments were conducted in a 150 mL stainless steel reactor (EasyChem E150) equipped with a magnetic stirring system. Based on previous literature<sup>[16,23–24]</sup>, the reaction conditions were as follows: 50 mL dodecane (solvent), 25 mmol phenol, 25 mmol cyclohexanol, and 0.2 g catalyst were loaded into the reactor. The system was purged with  $N_2$  three times and pressurized to 1 MPa, followed by reaction at  $140^\circ\text{C}$  for 4 h with continuous stirring. After cooling to room temperature, a known amount of 1,4-dioxane was added as an internal standard. The reaction products were analyzed using an

Agilent GC-MS system (8890-5977C) equipped with both a flame ionization detector (FID) and mass spectrometer (MS). Qualitative and quantitative analyses were performed on HP-5 MS capillary columns ( $30\text{ m} \times 0.25\text{ mm} \times 0.25\ \mu\text{m}$ ) for both GC-MS and GC-FID channels. Complex product distributions were determined using the internal standard method combined with the effective carbon number (ECN) approach<sup>[25]</sup>. The reaction network involved two primary pathways: (1) Dehydration of cyclohexanol to form cyclohexene, (2) alkylation of phenol. The main detected products included: Cyclohexylphenol (CHPs): 2-cyclohexylphenol (2-CHP), 4-cyclohexylphenol (4-CHP); Dicyclohexylphenol (DCHPs): 2,4-dicyclohexylphenol (2,4-DCHP), 2,6-dicyclohexylphenol (2,6-DCHP); Cyclohexene, Cyclohexyl phenyl ether, Cyclohexylcyclohexene. Product selectivity calculations considered all above-mentioned products. Conversion and selectivity were calculated using the following formulas (for polycyclic products, the mole number was multiplied by the number of rings):

$$\text{Conversion}(\%) = \frac{\text{mol}(\text{reactant converted})}{\text{mol}(\text{original reactant})} \times 100\% \quad (1)$$

$$\text{Selectivity}(\%) = \frac{\text{mol}(\text{a product})}{\text{mol}(\text{products})} \times 100\% \quad (2)$$

## 2 Catalysts characterization

### 2.1 Analysis of physical structure

The textural properties (specific surface area and pore volume) of zeolites with different structures are summarized in Table 1. Both surface area and pore volume follow the order: MCM-41 > HUSY > H $\beta$  > HZSM-5. MCM-41 exhibits typical mesoporous characteristics, with its high surface area ( $1039\text{ m}^2/\text{g}$ ) and large mesopore volume ( $0.96\text{ cm}^3/\text{g}$ ), indicating a well-developed mesoporous system. In contrast, the surface area of HZSM-5 primarily originates from micropores, and its total pore volume ( $0.27\text{ cm}^3/\text{g}$ ) is significantly smaller. Both HUSY and H $\beta$  show intermediate textural properties between MCM-41 and HZSM-5, with their pore structures being predominantly microporous.

Table 1 Specific surface area and pore volume of different molecular sieves

| Catalyst  | BET surface area <sup>a</sup> /( $\text{m}^2 \cdot \text{g}^{-1}$ ) |                   |                  | Total pore volume <sup>a</sup> /( $\text{cm}^3 \cdot \text{g}^{-1}$ ) |                   |                    |
|-----------|---------------------------------------------------------------------|-------------------|------------------|-----------------------------------------------------------------------|-------------------|--------------------|
|           | $S_{\text{micro}}$                                                  | $S_{\text{meso}}$ | $S_{\text{BET}}$ | $v_{\text{micro}}$                                                    | $v_{\text{meso}}$ | $v_{\text{total}}$ |
| MCM-41    | —                                                                   | 1039              | 1039             | —                                                                     | 0.96              | 0.96               |
| HZSM-5    | 338                                                                 | 53                | 391              | 0.14                                                                  | 0.13              | 0.27               |
| H $\beta$ | 517                                                                 | 86                | 602              | 0.20                                                                  | 0.24              | 0.44               |
| HUSY      | 730                                                                 | 58                | 788              | 0.30                                                                  | 0.19              | 0.49               |

<sup>a</sup>: By  $t$ -plot method for the microporous molecular sieves.

Figure 1(a) displays the  $N_2$  adsorption-desorption isotherms of HUSY treated with different modifiers and citric acid at varying concentrations. All three samples, HUSY-0.5M (citric acid), HUSY-SH (NaOH) and HUSY-OA (oxalic acid), exhibit Type I isotherms with H4-type hysteresis loops. However, the hysteresis loop area decreases in the order: HUSY-SH > HUSY-0.5M > HUSY-OA. Compared to pristine HUSY, HUSY-0.5M shows a slight decrease in surface area ( $731 \text{ m}^2/\text{g}$ ) but an increase in pore volume ( $0.52 \text{ cm}^3/\text{g}$ ). In contrast, HUSY-OA demonstrates a dramatic reduction in both surface area ( $389 \text{ m}^2/\text{g}$ ) and pore volume ( $0.32 \text{ cm}^3/\text{g}$ ), suggesting severe framework collapse due to excessive dealumination during oxalic acid treatment.

The isotherms and hysteresis ring shapes of the catalyst samples treated with different citric acid concentrations were consistent with those of pristine HUSY, indicating that the citric acid treatment did not cause significant damage to the catalyst structure. With the increase of citric acid concentration, the area of the hysteresis ring gradually increases, which indicates that the mesoporous structure of the catalyst increases, and the mesoporous structure is conducive to the alkylation reaction and the diffusion of the product. When the concentration of citric acid was  $0.1 \text{ mol/L}$ , the specific surface area of the catalyst sample increased to  $802 \text{ m}^2/\text{g}$ . This might be because, the amorphous aluminum

in the channels and the aluminum species outside the framework were mainly removed, forming new micropores and mesopores at low concentrations<sup>[26]</sup>. However, when the concentration of citric acid was further increased to  $1.0 \text{ mol/L}$ , the specific surface area decreased to  $711 \text{ m}^2/\text{g}$ . This might be because citric acid removed part of the skeletal aluminum, resulting in the destruction of micropores and the formation of mesopores<sup>[27]</sup>. This conclusion is further supported by the observed increase in mesoporous pore volume (from  $0.23$  to  $0.27 \text{ cm}^3/\text{g}$ ) and the decrease in micropore specific surface area (from  $732$  to  $613 \text{ m}^2/\text{g}$ ).

Figure 1(b) shows the micropore size distribution of the catalysts. A clear decrease in micropore structure is observed with increasing citric acid concentration. These results indicate that treatment with a lower citric acid concentration ( $0.1 \text{ mol/L}$ ) effectively removes the extra-framework aluminum, thereby increase the pore volume and specific surface area. Increase in the citric acid concentration leads to an increase in the mesoporous pore volume. However, excessive dealumination at higher concentrations can cause substantial removal of framework aluminum, leading to partial structural collapse of the zeolite. Therefore, selecting an appropriate concentration of citric acid is essential to balance the mesoporous volume and structural-integrity, ensuring optimal catalytic performance.

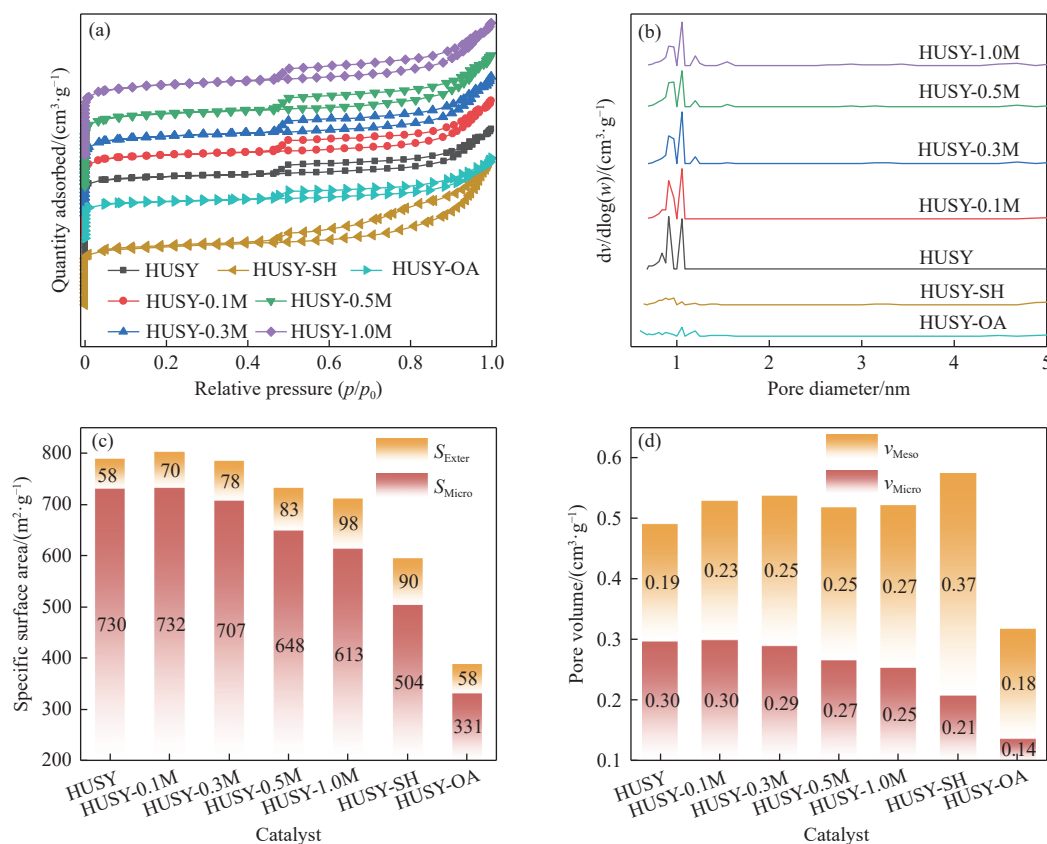


Fig. 1 (a) Nitrogen adsorption-desorption isotherms, (b) pore size distribution (NLDFT model), (c) specific surface area, (d) pore volume of HUSY-x catalysts

## 2.2 XRD

Figure 2 presents the XRD patterns of the catalyst samples. HUSY-0.5M shows obvious diffraction peaks, while the intensities of the HUSY-SH and HUSY-OA samples are significantly reduced. This indicates that the treatment with NaOH and oxalic acid has caused severe structural damage to the HUSY structure. Assuming that the crystallinity of the untreated HUSY catalyst is 100%, the relative crystallinities of HUSY-SH and HUSY-OA decreased to 54.52% and 19.22%, respectively, compared with 92.93% for HUSY-0.5M (Table 2). The Si/Al ratio of the molecular sieve, calculated from the unit cell constant of the (311) crystal plane, further highlights the difference: HUSY-OA reached 69.06, far higher than 20.77 for HUSY-0.5M. These results confirm that citric acid treatment induces milder dealumination than oxalic acid, enabling gradual removal of aluminum while preserving the zeolite framework. Notably, all the samples treated with citric acid showed diffraction peaks consistent with those of the carrier, indicating that different concentrations of citric acid treatment had no significant effect on the crystal structure of HUSY.

The crystallinity of HUSY-*x* initially increases and then decreases with the increase of citric acid concentration. At 0.1 mol/L, the crystallinity of the catalyst increases to 105.50%. This enhancement may be attributed to two factors: (i) citric acid-induced dealumination promotes the removal of non-framework aluminum or amorphous species from the pores, and (ii) partial reorganization of non-framework aluminum into the lattice may compensate for framework vacancies, thereby preserving crystallinity<sup>[28]</sup>.

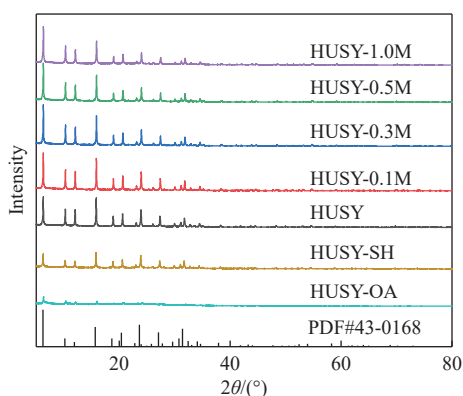


Fig. 2 XRD patterns of HUSY-*x* catalysts

Table 2 The crystallinity, silicon-aluminum ratio and (311) crystal plane unit cell constant of HUSY-*x* catalysts

| Catalyst  | Relative crystallinity/% | SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> | (311) cell constant /Å |
|-----------|--------------------------|--------------------------------------------------|------------------------|
| HUSY      | 100.00                   | 12.96                                            | 24.41                  |
| HUSY-0.1M | 105.50                   | 16.84                                            | 24.37                  |
| HUSY-0.3M | 100.87                   | 20.53                                            | 24.34                  |
| HUSY-0.5M | 92.93                    | 20.77                                            | 24.34                  |
| HUSY-1.0M | 88.18                    | 23.42                                            | 24.32                  |
| HUSY-SH   | 54.52                    | 10.14                                            | 24.46                  |
| HUSY-OA   | 19.22                    | 69.06                                            | 24.23                  |

When the acid concentration was further increased from 0.3 to 1.0 mol/L, the crystallinity of the sample showed a downward trend. This can be attributed to the removal of skeletal aluminum under treatment with a higher concentration of citric acid, resulting in lattice defects<sup>[29]</sup>. This result is consistent with the reduction of pore volume and specific surface area. With the increase of citric acid concentration, the silicon-aluminum ratio of HUSY molecular sieve increased from 12.96 to 23.42, indicating that part of the aluminum in the molecular sieve was successfully removed.

## 2.3 NH<sub>3</sub>-TPD

The acidity of the catalyst is crucial for the alkylation reaction. Figure 3 shows the NH<sub>3</sub>-TPD characterization results of different carriers and citric acid treated catalysts, with the quantitative data summarized in Table 3. It can be seen from Figure 3(a) that the number of acidic sites of HUSY, HZSM-5 and Hβ is approximately the same and much higher than that of MCM-41. In Figure 3(b), peaks below 250 °C are weak acid sites, and those above 250 °C are strong acid sites<sup>[26]</sup>. Compared with the untreated HUSY, citric acid treatment reduced both total acidity and weak acidity. The number of strong acid sites generally decreased with increasing citric acid concentration, except at 0.5 mol/L, where the value increased from 0.670 mmol/g (HUSY-0.3M) to 0.863 mmol/g (HUSY-0.5M). This anomaly can be attributed to an aluminum replenishment effect, where partially leached aluminum species reinserted into framework vacancies, generating new strong acid sites. Yan et al.<sup>[28]</sup> found that when exploring the low-temperature etherification activity of Hβ modified by citric acid, the total amount of acid in the citric acid-treated samples decreased and the proportion of strong acid increased, which was consistent with the phenomenon in this paper. When the concentration of citric acid was further increased to 1.0 mol/L, the number of strong acid sites of the catalyst significantly decreased to 0.445 mmol/g. It indicates that when HUSY samples are treated with a high concentration of citric acid, the strong acid sites in the lattice can be removed, resulting in a decrease in the number of strong acid sites. This is consistent with the reduction in crystallinity of samples treated with high concentration of citric acid in XRD characterization. In addition, the variation trend of the proportion of strong acid sites in the catalyst sample to the total acid sites with the concentration of citric acid is shown in Figure 3(c).

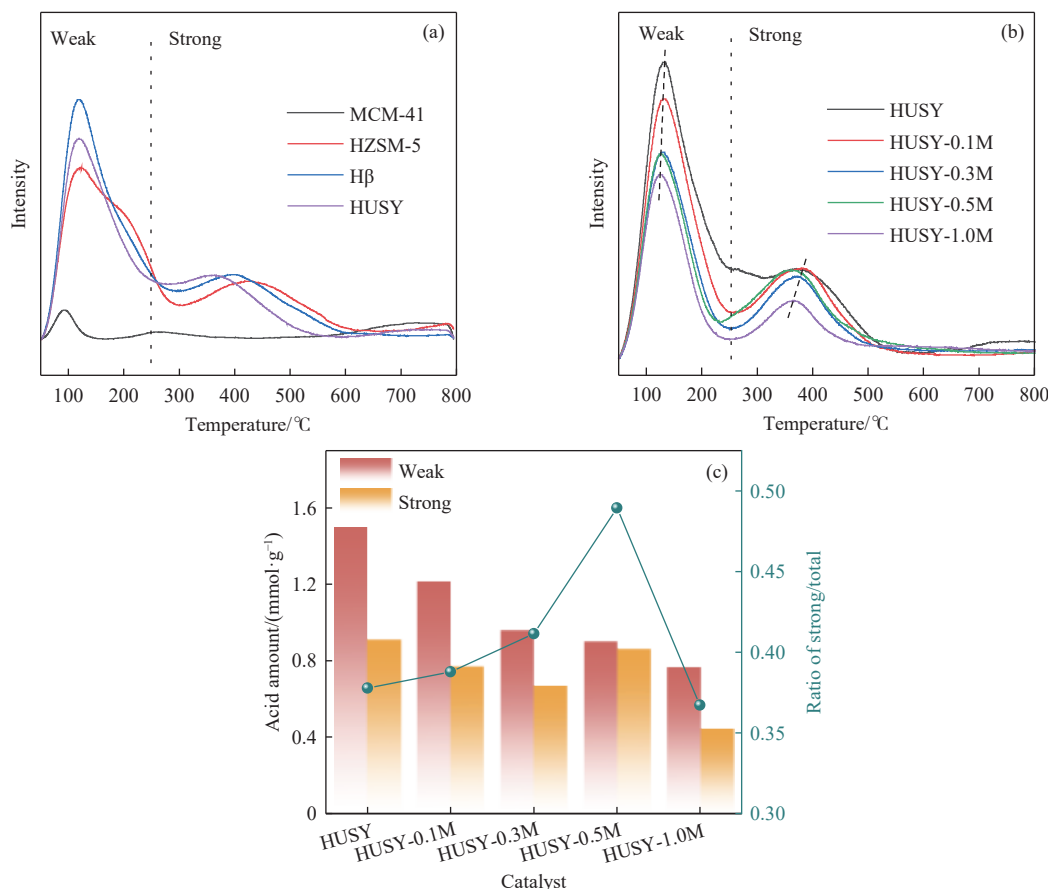


Fig. 3 NH<sub>3</sub>-TPD spectra of (a) different molecular sieves, (b) HUSY-*x*, (c) the ratio of strong acid to total acid of HUSY-*x*

Table 3 The acidic distribution of HUSY-*x*

| Catalyst  | Weak/(mmol·g <sup>-1</sup> ) | Strong/(mmol·g <sup>-1</sup> ) | Total/(mmol·g <sup>-1</sup> ) | Strong/Total |
|-----------|------------------------------|--------------------------------|-------------------------------|--------------|
| HUSY      | 1.499                        | 0.910                          | 2.409                         | 0.377        |
| HUSY-0.1M | 1.217                        | 0.771                          | 1.988                         | 0.387        |
| HUSY-0.3M | 0.958                        | 0.670                          | 1.628                         | 0.411        |
| HUSY-0.5M | 0.900                        | 0.863                          | 1.763                         | 0.489        |
| HUSY-1.0M | 0.767                        | 0.445                          | 1.212                         | 0.367        |

The proportion of strong acid sites at HUSY-0.5M to the total acidic sites was 0.489, which was higher than 0.411 of HUSY-0.3M and 0.367 of HUSY-1.0M. Similar to the selectivity law of alkylation products, it is speculated that strong acid sites may be an important factor affecting the catalytic effect. It is worth noting that, compared with HUSY, the weak acid peaks and strong acid peaks of all citric acid-treated catalysts shifted towards the low-temperature zone, indicating that citric acid treatment reduced the acid strength of the catalysts. The above analysis indicates that appropriate citric acid treatment can regulate the distribution and intensity of HUSY acidity.

## 2.4 NMR

In order to explore the effects of citric acid treatment on Si and Al in the HUSY framework, the catalysts were characterized by NMR. Figure 4(a) shows the <sup>27</sup>Al MAS NMR spectra of the catalysts treated with citric acid at

different concentrations. It can be seen that all samples present two distinct peaks at -2 and 55, as well as a wide peak between them. The peak at -2 corresponds to non-framework six-coordinated aluminum, the peak at 55 is attributed to framework tetra-coordinated aluminum, and the broad signal arises from extra-framework five-coordinated aluminum species. For the tetra-coordinated skeletal aluminum species, the resonance signal intensity shows a decreasing trend with the increase of citric acid concentration, possibly because the acidic centers of the skeletal aluminum species are removed. When the concentration of citric acid is 0.5 mol/L, the signal value is enhanced instead. This is due to the occurrence of the aluminum supplementation phenomenon. Chen et al.<sup>[30]</sup> studied the hydrochloric acid dealumination modification of HZSM-5 and found that the dealuminated HZSM-5 molecular sieve could achieve heavy alumination after being treated with hydrochloric acid solution, and some five-coordinated aluminum species in the outer framework were re-inserted into the framework.

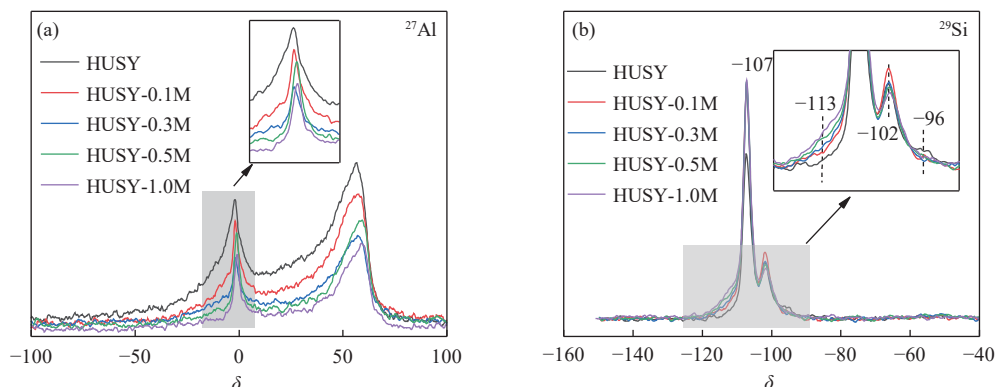


Fig. 4 (a)  $^{27}\text{Al}$ , (b)  $^{29}\text{Si}$  MAS NMR spectra of HUSY- $x$

When the concentration of citric acid continues to increase to 1.0 mol/L, the tetra-coordinated aluminum species in the lattice are removed, resulting in a further decrease in peak intensity. Wang et al.<sup>[31]</sup> conducted NMR characterization on molecular sieves treated with different concentrations of citric acid and found a sudden increase in the peak intensity of skeletal aluminum species, which was consistent with the above-mentioned change pattern. Xie et al.<sup>[32]</sup> also hold that when molecular sieves are modified with citric acid, the dealumination phenomenon and the aluminum supplementation phenomenon occur simultaneously and are related to the concentration of citric acid.

The  $^{29}\text{Si}$  MAS NMR spectra in Figure 4(b) also shows peaks at  $-96$ ,  $-102$ ,  $-107$  and  $-113$ , which belong to Si (2Al), Si (1Al), Si (0Al) and amorphous  $\text{SiO}_2$ , respectively, where Si ( $x\text{Al}$ ) represents the number of aluminum-oxygen tetrahedra connected to silicon<sup>[33–34]</sup>. Due to the relatively high silicon-aluminum content, no peaks of Si (4Al) and Si (3Al) were found. It can be seen from the figure that the citric acid treatment did not change the chemical shifts of

silicon species in each state. With the increase of citric acid concentration, the peak at  $-96$  decreased, and the peak of amorphous  $\text{SiO}_2$  at  $-113$  gradually intensified. This also indicates that the citric acid treatment removed the framework aluminum species.

## 2.5 SEM

Figure 5 shows the SEM profile of HUSY- $x$ . As can be seen from Figure 5 (a), the untreated HUSY molecular sieve is in the form of irregular particles with a particle size of 400–800 nm, and the microscopic surface flatness is relatively high. After citric acid treatment, the particle morphology and overall structure remain largely unchanged; however, surface etching becomes evident. With the increase of citric acid concentration, the etching degree of the microscopic surface of the catalyst gradually intensifies, indicating progressive removal of aluminium species. This etching process contributes to the generation of new pore structures.

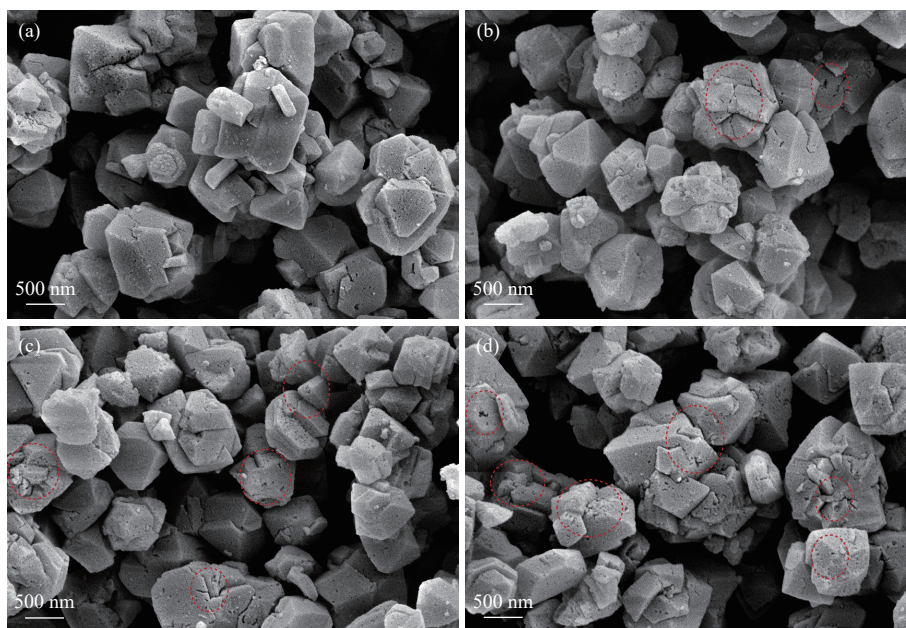


Fig. 5 SEM images (a)HUSY, (b) HUSY-0.1M, (c) HUSY-0.5M, (d) HUSY-1.0M

### 3 Results and discussion

#### 3.1 Alkylation of phenol with cyclohexanol

##### 3.1.1 Influence of different molecular sieves on alkylation

Firstly, the effects of molecular sieves with different acidity and pore structures on the alkylation reaction of phenol and cyclohexanol were studied. Mesoporous MCM-41 with relatively weak acidity was used as the control, and the experimental results are shown in Figure 6. Among the tested molecular sieves, HUSY and H $\beta$  exhibited better catalytic activities, with phenol conversions of 56.3% and 48.0% respectively, while HZSM-5 and MCM-41 showed the lowest phenol conversions. The catalytic performance followed the order: HUSY > H $\beta$  >> HZSM-5  $\approx$  MCM-41. Compared with other molecular sieves, HZSM-5 has the smallest pore size ( $\sim 0.56$  nm), which severely limits the diffusion of reactant molecules within the pores, thereby inhibiting the alkylation reaction, and causing the reaction to remain at the dehydration stage of cyclohexanol and unable to continue the alkylation reaction to generate alkylphenols. Even though the acidity of HZSM-5 is comparable to that of H $\beta$  and HUSY, the selectivity of its product cyclohexene is close to 100%, and the alkylation products are nearly undetectable. Therefore, the pore size is one of the important factors affecting the activity of molecular sieve catalytic alkylation reactions.

In addition to the pore size, acidity is another important factor affecting the catalytic activity of molecular sieves in alkylation reactions. Although the specific surface area of MCM-41 is as high as 1039 m<sup>2</sup>/g, there is only an acid site concentration of 0.160 mmol/g and it is mainly a weak acid site.

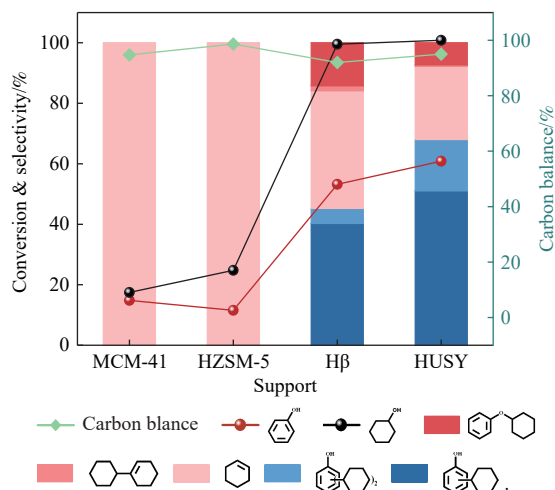


Fig. 6 Different zeolites catalyze the alkylation of phenol and cyclohexanol

Reaction conditions: 140 °C, 25 mmol phenol and 25 mmol cyclohexanol, 50 mL dodecane, 1 MPa N<sub>2</sub>, 4 h, 0.2 g catalyst.

Furthermore, only a portion of the cyclohexanol dehydration products were found, and non-obvious alkylation products were detected. This also indicates that the dehydration reaction and alkylation reaction require the participation of acidic sites. Compared with HUSY, although H $\beta$  has a higher acid site concentration, its relatively small pore size (H $\beta$ : 0.57 nm  $\times$  0.75 nm, HUSY: 0.74 nm) also affects the alkylation efficiency of phenol, resulting in the selectivity of its alkylation product (45.2%) being lower than that of HUSY (67.0%).

##### 3.1.2 Alkylation catalytic performance of citric acid-modified HUSY molecular sieve

The effect of different treatment on activity of molecular sieves in alkylation reactions were further studied. The experimental results show that the citric acid treatment improves the alkylation activity of the catalyst, while the NaOH and oxalic acid treatments only catalyze partial dehydration of cyclohexanol. This might be attributed to the relatively mild process of citric acid treatment, which retains the crystal structure of HUSY while introducing a secondary mesoporous structure. The latter two cause significant damage to the molecular sieve framework, resulting in lower catalytic activity. HUSY molecular sieves were treated with citric acid of different concentrations (0.1, 0.3, 0.5, 1.0 mol/L), and the experimental results of catalytic alkylation of phenol and cyclohexanol are shown in Figure 7(a). As can be seen from the figure, the regulation of the pore structure of HUSY molecular sieve by citric acid modification effectively promotes its alkylation catalytic ability. With the increase of citric acid concentration, the phenol conversion rate and the selectivity of alkylation products show a “volcanic” curve.

It is worth noting that the distribution of monoalkylation products in HUSY-*x* remains relatively constant, while the main variations occur in secondary alkylation products (selectivity: 17.0%, 37.6%, 43.6%, 48.0%, 29.2%), as summarized in Table 4. Due to the electron-donating effect of the phenolic hydroxyl group, the mono-alkylation reaction of phenol mainly occurs at the ortho and para positions, consistent with the relevant literature reports<sup>[17,35]</sup>. For the secondary alkylation products, the selectivity of 2, 4-dicyclohexylphenol is higher than that of 2, 6-dicyclohexylphenol. This might be because the former can be formed from 2-/4-dicyclohexylphenol, while the latter can only be formed from 2-dicyclohexylphenol<sup>[17]</sup>. Catalytic alkylation requires both accessible acid sites and sufficient pore space to accommodate bulky products. The mesoporous pore volume of HUSY-*x* increased compared with that of HUSY, while the proportion of strong acid sites showed the same change curve as the selectivity of alkylation products. When the concentration of citric acid is 0.5 mol/L, the selectivity of alkylation products reaches the highest (99.6%), and the conversion rate of phenol also reaches 80.4%.

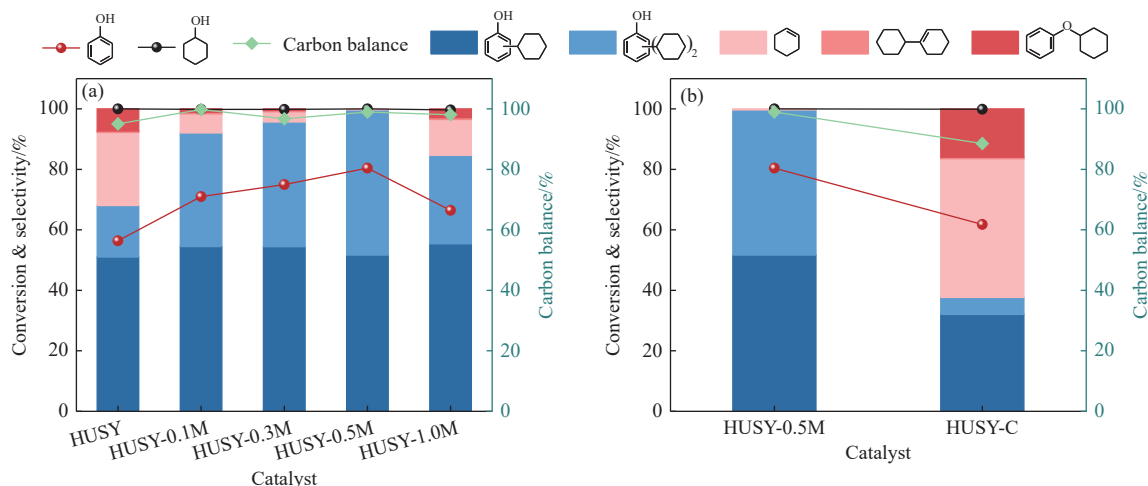


Fig. 7 The alkylation of phenol and cyclohexanol catalyzed by HUSY-x and HUSY-C  
Reaction conditions: 140 °C, 25 mmol phenol and 25 mmol cyclohexanol, 50 mL dodecane, 1 MPa N<sub>2</sub>, 4 h, 0.2 g catalyst.

Table 4 Distribution of alkylation products catalyzed by HUSY-x

| Catalyst  | Alkylation product selectivity/% |       |          |          |
|-----------|----------------------------------|-------|----------|----------|
|           | 2-CHP                            | 4-CHP | 2,4-DCHP | 2,6-DCHP |
| HUSY      | 35.9                             | 15.1  | 11.9     | 5.1      |
| HUSY-0.1M | 39.8                             | 14.6  | 25.6     | 12.0     |
| HUSY-0.3M | 40.6                             | 13.8  | 29.6     | 14.0     |
| HUSY-0.5M | 39.1                             | 12.6  | 32.2     | 15.8     |
| HUSY-1.0M | 41.7                             | 13.7  | 19.7     | 9.5      |

This is attributed to the relatively abundant mesoporous structure and strongly acidic sites of HUSY-0.5M. Compared with HUSY (mesoporous pore volume 0.19 cm<sup>3</sup>/g), HUSY-0.5M formed a secondary mesoporous structure (0.25 cm<sup>3</sup>/g) under the action of citric acid, promoting the diffusion of the product. In addition, citric acid treatment reduced the number of weak acid and strong acid sites of the catalyst, which was particularly obvious on the catalysts treated with 0.1, 0.3 and 1.0 mol/L. However, the number of strong acid sites of HUSY-0.5M (0.863 mmol/g) was much higher than that of the samples treated with citric acid of other concentrations. Moreover, the proportion of HUSY-0.5M strong acid sites was the highest (reaching 48.9%). This is another reason for the high catalytic activity of HUSY-0.5M. When the concentration of citric acid was 1.0 mol/L, both the conversion rate of phenol and the selectivity of alkylation products decreased, which were 66.4% and 84.6% respectively. This might be because the high concentration of citric acid disrupted the structure of HUSY. Although more mesoporous structures were produced, the strongly acidic sites were significantly reduced (only 0.445 mmol/g), and the decrease in the number of alkylation active sites led to a reduction in phenol conversion rate and product selectivity.

Furthermore, to explore the effect of citric acid treatment, commercial HUSY molecular sieves (referred to as HUSY-C) with a silicon-aluminum ratio close to that of HUSY-0.5M were used as the control. The results are shown in Figure 7 (b). The substrate conversion rate and alkylation

selectivity of HUSY-C were lower than those of HUSY-0.5M. This confirms that citric acid treatment not only adjusts the Si/Al ratio but also optimizes pore structure and acidity, collectively enhancing the catalytic performance beyond that of untreated or commercial HUSY.

### 3.1.3 Effects of reaction conditions on alkylation

Further optimization of alkylation conditions using HUSY-0.5M was conducted, and the time-dependent distribution of products (0.5–4 h) is shown in Figure 8(a). At 140 °C, within 0.5 h after the reaction began, cyclohexanol was completely dehydrated, and the generated cyclohexene also reacted with phenol. It is notable that within the time period after 1 h, the selectivity of the single alkylation products remained almost unchanged (45.9%, 50.4%, 55.1%, 51.6%), while the selectivity of the secondary alkylation products increased with the increase of time (13.5%, 19.8%, 35.1%, 48.0%). The reaction that occurs is the alkylation of phenol to form a single alkylation product and its secondary alkylation reaction. The two reaction rates are close, resulting in the selectivity of the single alkylation product remaining stable. Furthermore, when the reaction time was 0.5 h, the by-product cyclohexylphenyl ether (with a selectivity of 12.5%) was also detected in the product. With the increase of time, the selectivity of this product gradually decreased (8.8%, 6.4%, 0).

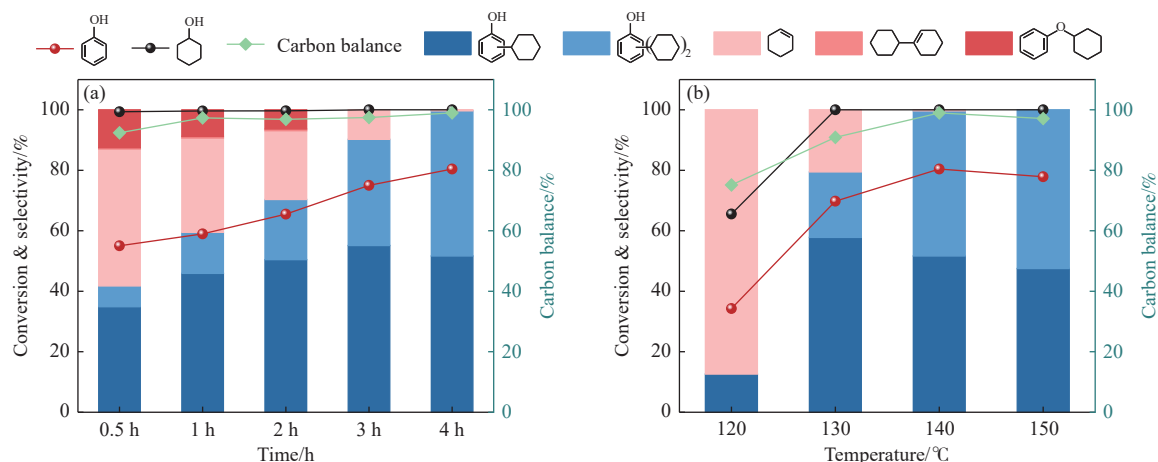


Fig. 8 Effects of (a) time, (b) temperature on the alkylation of phenol with cyclohexanol  
Reaction conditions: 25 mmol phenol and 25 mmol cyclohexanol, 50 mL dodecane, 1 MPa N<sub>2</sub>, 0.2 g catalyst.

This is because ether products are kinetically stable and will undergo further rearrangement reactions as the reaction proceeds to transform into the thermodynamically more stable alkylated product, cyclohexylphenol<sup>[36–38]</sup>. Subsequently, the influence of reaction temperature on the system was investigated under the condition of 4 h, and the results are shown in Figure 8(b). At 140 °C, the catalyst exhibited optimal performance, affording 99.6% selectivity toward alkylated products. At lower temperatures, the reaction was strongly suppressed: at 120 °C, phenol and cyclohexanol conversions were only 34.3% and 65.5%, respectively, with 12.6% alkylation selectivity. Increasing the temperature to 130 °C improved alkylation selectivity to 79.4%. These results show that both the dehydration process and the alkylation process of cyclohexanol are highly temperature sensitive, requiring sufficient thermal energy to overcome mass transfer limitations and the reaction barrier.

Based on the above experimental results, the reaction pathway for phenol alkylation with cyclohexanol is proposed (Figure 9). Cyclohexanol is first dehydrated at the acidic site to form cyclohexene, which is then activated to a carbocation species<sup>[39]</sup>. Due to the electron-donating ability of the phenolic hydroxyl group, the ortho and para positions of phenol are most reactive toward electrophilic attack. The carbocation can thus attack the aromatic ring to yield cyclohexylphenol or react with the hydroxyl oxygen atom to form cyclohexylphenyl ether.

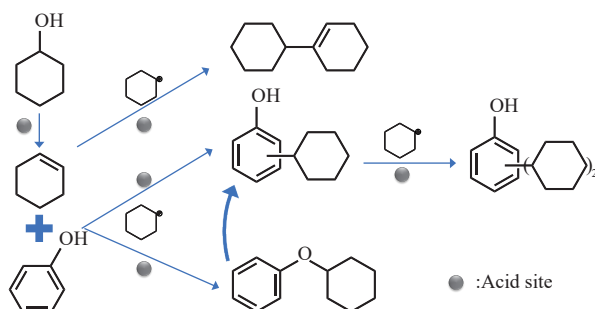


Fig. 9 Alkylation pathway of phenol with cyclohexanol

The ether, however, is only a minor intermediate and undergoes rearrangement to cyclohexylphenol as the reaction proceeds<sup>[40]</sup>. Cyclohexylphenol can also be further alkylated with the carbocation ion to form dicyclohexylphenol.

### 3.1.4 Stability of the catalyst

In order to explore the stability of the HUSY-0.5M catalyst, its cycling performance was tested under the optimized working conditions, and the results are shown in Figure 10. After the catalyst was only dried (80 °C, 6 h) and then subjected to the second cycle, the phenol conversion rate and the selectivity of the alkylation product decreased to 57.4% and 43.2% respectively, probably due to the blockage or deactivation of active sites by physically adsorbed water or reactants<sup>[24]</sup>. When the spent catalyst was regenerated by calcination (500 °C, 4 h), both phenol conversion and alkylation selectivity recovered significantly to 74.4% and 85.8%, respectively.

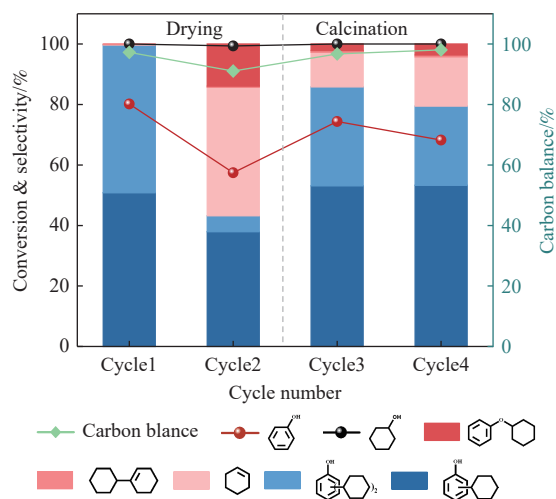


Fig. 10 Stability of HUSY-0.5M catalyst  
Reaction conditions: 140 °C, 25 mmol phenol and 25 mmol cyclohexanol, 50 mL dodecane, 1 MPa N<sub>2</sub>, 4 h, 0.2 g catalyst.

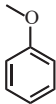
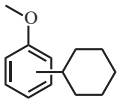
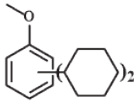
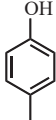
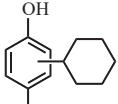
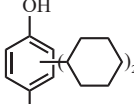
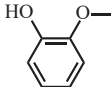
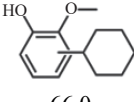
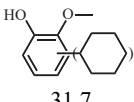
Upon further reuse, the catalyst maintained stable performance, demonstrating that HUSY-0.5M possesses good recyclability after appropriate regeneration.

### 3.2 Alkylation reaction of lignin depolymerization derivatives with cyclohexanol

The real lignin depolymerization derivatives are complex mixed phenol and ether systems. To verify the universality of the catalyst to such feedstocks, the alkylation reactions of aromatic compounds with aromatic substrates and cyclohexanol were further studied using the HUSY-0.5M catalyst. The results are shown in Table 5. When *p*-cresol

and anisole were used as substrates, conversion rates comparable to phenol were obtained (77.2% and 80.7%, respectively), with alkylation product selectivities exceeding 99%. When guaiacol is used as the substrate, its conversion rate can reach 84.9%, and the selectivity of single-ring product is significantly higher than that of anisole and *p*-cresol. This might be because the steric hindrance of the monoalkylated guaiacol makes it difficult to undergo secondary alkylation. The above results indicate that the HUSY-0.5M catalyst has good alkylation catalytic activity for various monomer compounds in lignin bio-oil, providing an important experimental basis for the high-value utilization of lignin.

Table 5 Alkylation reactions of different substrates with cyclohexanol

| Entry          | Reactant                                                                            | Conversion/% | Selectivity/%                                                                                |                                                                                               |
|----------------|-------------------------------------------------------------------------------------|--------------|----------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------|
| 1 <sup>a</sup> |    | 80.7         | <br>51.2   | <br>48.6   |
| 2 <sup>a</sup> |   | 77.2         | <br>52.3  | <br>47.3  |
| 3 <sup>a</sup> |  | 84.9         | <br>66.0 | <br>31.7 |

<sup>a</sup>: The conversion of cyclohexanol was close to 100%; Reaction conditions: 25 mmol substrates, 25 mmol cyclohexanol, 0.2 g HUSY-0.5M, 140 °C, 4 h, 50 mL dodecane.

## 4 Conclusions

In this paper, high-density aviation fuel precursors were prepared *via* the alkylation of phenol with cyclohexanol using citric acid-modified molecular sieves as catalysts. Among the tested molecular sieves (MCM-41, H $\beta$ , HUSY and HZSM-5), HUSY exhibited the best catalytic performance due to its balanced acidity and larger pore size. Citric acid modification further optimized the pore structure and acidity distribution of HUSY, with HUSY-0.5M showing the highest catalytic efficiency, achieving a phenol conversion of 80.4% and alkylation product selectivity of 99.6%. The variation in performance across HUSY-*x* samples was primarily associated with secondary alkylation. Furthermore, HUSY-0.5M exhibited excellent catalytic activity for different lignin derivatives (*p*-cresol, anisole, guaiacol). Overall, this study provides a feasible catalytic strategy for the preparation of high-density aviation fuel precursors using lignin-derived phenolic compounds, offering valuable insights for the sustainable utilization of biomass resources.

## Declaration of Competing Interest

The authors declare no conflict of interest.

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## 柠檬酸改性 HUSY 分子筛催化木质素衍生酚类与环己醇烷基化研究

华灿豪<sup>1</sup>, 吴靖风<sup>1</sup>, 朱玲君<sup>1,\*</sup>, 许光文<sup>2</sup>, 王树荣<sup>1,2,\*</sup>

(1. 浙江大学 能源高效清洁利用全国重点实验室, 浙江 杭州 310027;

2. 沈阳化工大学 资源化工与材料教育部重点实验室, 辽宁 沈阳 110142)

**摘要:** 通过烷基化以及后续的加氢反应, 木质素解聚生成的衍生酚类和芳醚等含氧芳烃可用于制取高密度或高热沉的航油组分。本工作以苯酚和环己醇为模化物, 考察了不同分子筛对烷基化反应活性的影响。实验结果表明, 相比于 H $\beta$ 、HZSM-5、MCM-41, HUSY 具有更好的反应活性, 这是因为 HUSY 分子筛拥有适中的孔径和酸性位点, 为烷基化反应提供产物扩散空间和活性位点。为了进一步优化分子筛孔道结构和酸性位点分布, 使用不同浓度柠檬酸对 HUSY 分子筛进行改性处理, 并与 NaOH、草酸处理的分子筛比较。结果表明, 柠檬酸处理在保持分子筛结晶度的同时调控了分子筛的酸性分布和孔道结构。分子筛对苯酚与环己醇烷基化的催化作用在不同浓度柠檬酸改性后均得到提升, 具有最高强酸/总酸比例的改性分子筛(HUSY-0.5M)显示出较优的催化性能, 苯酚转化率 80.4%, 烷基化产物选择性 99.6%。将其用于多种木质素衍生物的烷基化反应, 催化剂均显示出较高的催化活性。该工作为木质素衍生酚类烷基化制备高值动力燃料提供了新途径。

**关键词:** 柠檬酸; HUSY; 酚类烷基化; 航空燃料

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### 作者简介:



朱玲君(1977), 博士, 研究员, 研究方向为碳基材料和生物质热化学转化、能源催化, lingjun\_zhu@zju.edu.cn。



王树荣(1972), 男, 博士, 教授, 研究方向为生物质和城市固废的高效热转化、零碳燃料的合成制取及应用、先进能源转化/储能用功能材料的制备及二氧化碳的转化利用, srwang@zju.edu.cn。