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Effect of mass-transfer control on HY zeolites for dimethoxymethane carbonylation to methyl methoxyacetate

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ABSTRACT

A series of hierarchical HY zeolites were prepared by using sequential acid (H_4EDTA) and alkaline (NaOH and NH_4OH) solution treatments. The nitrogen adsorption-desorption analysis proved that the mesoporous structure was definitely formed with the pore diameter at about 3.5 and 17.5 nm, and the external surface area and mesopore volume significantly increased. The XRD, XRF, and NH_3-TPD characterization results disclosed that the relative crystallinity, crystalline sizes, and acidity of as-treated HY zeolites decreased as compared with parent HY although their Si/Al ratios were higher. The zeolites were conducted in vapor phase carbonylation of dimethoxymethane (DMM) to methoxyacetate (MMAc) at 5.0 MPa and different temperatures. As compared with reference HY, the DMM conversion and MMAc selectivity obviously increased from 50.41% to 90.91% and from 34.79% to 84.57% at 383 K, respectively. The DMM conversion were closely related to the medium-strong acid amount and greater amount of medium-strong acid sites resulted in higher DMM conversion. The catalytic stability of HY-DAl$_{0.11}$-DSi$_{\mathrm{NaOH}0.05}$ was carried out at 393 K and 5.0 MPa for 100 h. The DMM conversion (about 97%) and products selectivity (MMAc: 84%) kept unchanged during the whole carbonylation process, exhibiting excellent catalytic stability, which was also supported by the TG-DTA analysis that the carbon deposition was effectively suppressed. In a word, as-treated HY zeolites with larger external surface area and mesopore volume that contributed to promoting the mass transfer efficiency exhibited much higher DMM conversion, MMAc selectivity and excellent catalytic stability than parent HY.

1. Introduction

Over the past decade, hierarchical zeolites, which have unique pore sizes [1] with micro/mesoporous structure [2,3], received much attention because of its enhanced performance in some catalytic reactions with space and diffusion limitations problems [4]. For example, the conversion and selectivity of benzene alkylation are obviously promoted with hierarchical catalysts instead of micropore zeolites because of enhanced accessibility [5] and diffusion [6,7]. Hierarchical zeolites used in Fischer-Tropsch synthesis can obviously improve the mass transport and increase the selectivities of C_5–C_{11} hydrocarbons [8]. Besides, the catalytic stability of hierarchical HZSM-5 for methanol to gasoline reaction [9] is significantly improved.

Methyl methoxyacetate (MMAc) is a kind of high value-added and important fine chemical. Recently, MMAc is mainly used in manufacture of protectants and pharmaceuticals [10]. Nevertheless, only a few literatures or patents reported the synthesis routes of MMAc, as below: reaction of methyl chloroacetate with sodium methoxide [11], couple of formaldehyde derivatives with methyl formate [12,13], and carbonylation of dimethoxymethane (DMM) [14,15].

In former work [15], the DMM conversion reached about 100% with high MMAc selectivity (74.32%) via the D-009B catalyst and sulfolane as a solvent under 383 K and 5 MPa for 6 h. D-009B, a kind of sulfonic acid resin catalyst, has strong acidity and is beneficial for DMM carbonylation to produce MMAc. However, the sulfonic acid group in the as-used catalyst was continuously taken off by the reactants and products in a long-time reaction process. A.T. Bell reported the vapor phase cabonylation of DMM to MMAc with 79% selectivity by using H-FAU zeolite [14]. After that, lots of efforts had been made in studying the effect of different topological structures and Si/Al ratios of zeolites on DMM carbonylation. FAU had a very high selectivity to MMAc as compared with MFI, MOR and BEA [16–18]. It was proposed [16,17]

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that the low rate of MMAc formation observed at low Si/Al ratios was due to the repulsive interactions between adsorbed species located within the same supercage or channel intersection.

We consider that the diffusion and mass transfer efficiency of MMAc is limited in FAU micropore channels due to its small pore opening (0.74 nm) and large molecular weight (104.1 g/mol). More importantly, a low mass transfer rate of MMAc could result in the deactivation of as-used zeolites because the heavy products remaining on the acid centers in the channel are beneficial for the formation of carbon deposition, that readily covers the active sites. Hence, the hierarchical FAU with large external surface area and mesoporous will significantly contribute to the mass transfer efficiency of MMAc, leading to the increase of MMAc selectivity and catalytic stability.

Currently, bottom-up [19–21] and top-down [22–25] methods are usually applied to synthesize hierarchically structured zeolites. For bottom-up approaches, the mesopore introduced with the usage of templates and the microporous are one-step synthesized [26,27] simultaneously. However, bottom-up methods are difficult for industrial manufacture because mesopore-inducing agents are highly expensive and non-readily available [27]. For top-down methods, the micropore zeolites are used as starting materials and the mesoporous are introduced by post-synthetic treatments [28]. In fact, post-synthetic treatments like desilication [28–31] and dealumination [31–33] processes are easily-operated and economical.

In this paper, HY with Si/Al = 2.70 was applied as the reference and initial precursor. The hierarchical HY zeolites were pretreated by using sequential acid (H_4EDTA) and alkaline (NaOH and NH_4OH) solution treatments. The dealumination process should be carried out before desilication because the framework Si is difficult to be removed to form a hierarchical structure in high Al content of the zeolites [28,34]. Although the acid amount, acid strength, and crystallinity of the as-treated hierarchical HY zeolite decreased, the DMM conversion, MMAc selectivity, and catalytic stability were significantly enhanced because of its larger external surface area, mesopore structure, and the promoted mass transfer ability.

2. Experimental section

2.1. Catalyst preparation

HY zeolite (Nankai University Catalyst Co, bulk Si/Al = 2.70, H-form as a reference). **Dealumination:** HY (13.40 g) was first added into 200 mL H_4EDTA solution and stirred at 338 K for 6 h, followed by filtration and washing with deionized water for three times. The desired sample was dried at 393 K for 8 h, followed by calcination at 823 K for another 4 h in air to obtain the precursor, noted as HY-DAl_n. **Desilication:** HY-DAl_n (1.70 g) was poured into 50 mL NaOH or NH_4OH solution and stirred at 338 K or at room temperature for 30 min, followed by filtration and washing with deionized water for three times. The desired sample was dried at 393 K for 8 h, followed by calcination at 823 K for another 4 h in air to obtain the precursor. Alkaline treatment using NaOH treatments was labeled as "DSi_{NaOHn}", and NH_4OH treatments was noted as "DSi_{NH4OHn}" (DSi: desilication). In all cases, the suffix "*n*" represents the concentration of the solution. After dealumination and desilication pretreatments, 10 g precursor was converted into its NH_4^+ form by exchanging with 100 mL NH_4NO_3 (1 mol/L) aqueous solution at 338 K for 2 h, followed by filtration and washing with deionized water. The desired sample was dried at 393 K for 8 h, followed by calcination at 823 K for another 6 h in air to obtain HY-DAl_n-DSi_n.

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) patterns were acquired with a Bruker D8 advance diffractometer using Cu K α (λ = 0.15406 nm) radiation. Data was recorded in the 2 θ range from 5 to 45° with a step size of 0.05° at 40 kV and 40 mA. The HY zeolite crystallite average size as calculated by the Scherrer formula. Besides, the variation in zeolite crystallinity resulting from post-synthetic modifications was derived from the relative intensity of the reflection (533) at 2θ of 23.58°, assuming that the reference crystallinity is 100% [28].

A Bruker S4 pioneer advanced X-ray fluorescence (XRF) spectrometer was used to determine the chemical composition with different Si/Al ratios.

N_2 isotherms were measured in a Quantachrome (Autosorb iQ Statio) instrument at 77 K after the treatment of samples at 573 K in vacuum for 3 h. The surface area was determined by using a Brunauer-Emmett-Teller (BET) method. Barrett-Joyner-Halenda (BJH) and Horváth-Kawazoe (HK) methods were applied to calculate the pore size distribution in the mesopore and micropore region, respectively.

The NH_3-TPD experiments were carried out on a Builder PCA-1200. The sample (ca. 200 mg) was pretreated at 573 K in a flow of 30 mL/min He for 1 h. After the pretreatment, the sample was cooled to 353 K and exposed to NH_3 for 10 min. Then, the physically adsorbed NH_3 should be removed by He at the same temperature until the baseline was stable. Thereafter, NH_3-TPD was conducted in a constant flow of He (30 mL/min) from 373 to 973 K at a heating rate of 10 K/min. The amount of desorbed NH_3 was detected by a thermal conductivity detector.

TG-DTA analysis proceeded in the thermal analysis equipment (STA 449C Jupiter, NETZSCH). 2 mg precursor was performed in a flow of 80 mL/min air with the temperature increasing from 313 to 1073 K at a heating rate of 10 K/min.

2.3. Catalytic reaction

The vapor phase carbonylation of dimethoxymethane (DMM) was performed using 1 g catalyst at 5.0 MPa CO in a continuous flow fixed-bed stainless steel reactor with an 8.5 mm inner diameter. 20 mL/min CO bubbled through a stainless-steel saturator filled with DMM (98%, Aladdin) maintained at room temperature and 80 mL/min pure CO were mixed together and introduced into the reactor. All the reaction products were analyzed online by a gas chromatograph (GC-2014C) equipped with a HP-FFAP capillary column connected to a flame ionization detector. The conversion of DMM and the products selectivities were calculated on the basis of weight, as follows [17]: DMM Conv. = $(DMM_{in} - DMM_{left})/DMM_{in}$; MMAc selectivity was calculated on the basis of weight, MMAc Sel. = $MMAc_{formation}$/the mass of all products.

3. Results and discussion

3.1. XRD and XRF analysis of the as-treated hierarchical HY zeolites

The X-ray diffraction (XRD) patterns of HY, HY-$DAl_{0.11}$ (pretreated by 0.11 M H_4EDTA solution for dealumination), HY-$DAl_{0.15}$ (by 0.15 M H_4EDTA) and HY-$DAl_{0.15}$-$DSi_{NH4OH0.05}$ (by 0.15 M H_4EDTA and further pretreated by 0.05 M NH_4OH for desilication) are displayed in Fig. 1(A). The crystalline sizes of HY, HY-$DAl_{0.11}$, HY-$DAl_{0.15}$, and HY-$DAl_{0.15}$-$DSi_{NH4OH0.05}$, which were derived from the strongest intensity of the reflection (331) at 2θ of 16.25° and calculated by the Scherrer formula, were 36.60, 33.50, 29.20, and 20.20 nm, respectively. The crystallinity of as-treated HY catalysts calculated by comparing the relative intensity divided by the reference at 2θ of 23.58° were 58.39%, 22.93%, and 18.68%, assuming that the crystallinity of reference HY was 100%. Above mentioned results evidently demonstrated that with increasing the concentration of H_4EDTA, the relative crystallinity gradually decreased and the crystalline sizes also slowly reduced. After dealumination by H_4EDTA solution, further desilication by NH_4OH resulted in much more serious collapse of crystal structure. As known, H_4EDTA was a kind of chelating agent that could remove the Al atoms from the framework of zeolite [28]. Therefore, more Al atoms were extracted