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Short Communication

Preparation of hydrocarbon dispersible HZSM-5 nanocrystals by hydrothermal crystallization of organofunctionalization seeds

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ABSTRACT

Organofunctionalization of zeolitic seeds was used to synthesize hydrocarbon dispersible HZSM-5(HDZ) nanocrystals, in which organic groups grafted on seeds not only limit the growth of nanocrystals but also change surface hydrophobicity of nanocrystals. The high dispersion of the prepared HZSM-5 nanocrystals in *n*-dodecane was observed and further confirmed by TEM. The quasi-homogeneous catalytic cracking of *n*-dodecane with HDZ showed about 30% improvement in the catalytic activity with organofunctionalization seeds, which is promising for the potential applications in some special fields.

1. Introduction

Catalytic cracking of hydrocarbons over zeolite catalysts has been widely adopted to improve the yields of light oil [1,2], and is attracting increasing attention in some new fields, for example, active cooling technology for thermal management system of hypersonic aircraft [3–5]. In this case, the hydrocarbon fuel plays dual role not only as a power source, but also as the coolant to remove waste heat from high-temperature component ascribed to the endothermic reactions, especially in the presence of zeolite catalyst. However, the application of solid zeolite in the micro channel (ca. 1 mm) of heat-exchanger is challenging due to the possible limitations of flowing and heating resistance, as well as zeolite deactivation. Recently, we proposed a quasi-homogeneous catalytic cracking of hydrocarbons using dispersible HZSM-5 nanocrystals, i.e., dispersing nanocrystals of zeolites into hydrocarbon fuels [6], which offers a promising method to obtain stable and high catalytic cracking activity in a long operation period, as both hydrocarbon fuel and dispersed catalyst are continuously fed-in and discharged.

Hydrocarbon dispersible zeolite catalyst is one of the most important concerns for this new idea. In our previous work, HDZ nanocrystals were prepared by grafting as-synthesized HZSM-5 nanocrystals (ca. 50 nm) with various alkyl groups [6,7]. The post-grafted samples displayed a stable dispersion for 24 h, and their catalytic activities were much higher than thermal cracking. However, the uncontrollable nanocrystals size and their aggregates of as-synthesized HZSM-5 were crucial problems limiting the dispersion improvement of HDZ nanocrystals in hydrocarbons. To overcome the problem, uniform-sized HZSM-5 nanocrystals with hydrophobic external surface are needed for the synthesis of HDZ nanocrystals. We noted that Serrano and co-workers proposed a novel method, i.e., organofunctionalized seed synthesis, to synthesize nanozeolites with controllable crystal size [8]. They successfully regulated the ZSM-5 crystal size to 10–20 nm with the aggregates of 200–400 nm by anchoring various kinds of and different amounts of organosilanes to the protozeolitic units during the synthesis [9–12]. Later, the method was applied by other researchers using different silanizing agents and 20–40 nm nanosized HZSM-5 crystals were also obtained, which exhibited a high activity in benzene alkylation [13], benzylation and methanol-to-gasoline reactions [14]. The organic groups grafted on the nano-seeds perturb the growth of zeolite crystals and hinder their further aggregation, thus the zeolite particles become hydrophobic and highly dispersed in the organic solvent. However, both the structure directing agent (SDA) and organosilane are removed during the calcinations, which reduces the hydrophobicity. A second grafting provides complementary surface alkyls and improves the surface hydrophobicity.

In this work, the hexyl grafted TPA-ZSM-5 nanoparticles are obtained from seeds functionalized with hexyltrimethoxysilane. After removal of the templates (calcined at 550 °C), they are regrafted to supplement the surface alkyls. Finally, the obtained HDZ nanoparticles exhibit not only improved dispersion stability due to the smaller crystal size and the grafted silane, but also significantly catalytic cracking activity using *n*-dodecane as a model fuel.

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2. Experimental

2.1. Preparation of catalyst

At the beginning, functionalized zeolite ZSM-5 nanocrystals were synthesized, based on the method published by Serrano et al. [9]. A clear solution with the molar composition: $1Al_2O_3$:$60SiO_2$:11.5TPAOH:$1500H_2O$ was hydrolyzed at room temperature (25 °C), and then precrystallized at 90 °C for 20 h. The zeolite seeds obtained were functionalized by reaction with hexyltrichlorosilane (5 mol% in regards to the silica content in the gel) at 90 °C for 6 h. Subsequently, the resulting solution was subjected to crystallization in a Teflon-lined stainless-steel autoclave at 170 °C for 5 days. After that, the autoclave was quickly cooled down. The solid products obtained were separated by centrifugation (15,000 r/min), washed three times with distilled water and finally dried overnight at 110 °C. Finally, the functionalized ZSM-5 nanocrystals were gained after calcined in the air at 550 °C for 5 h.

The calcined sample was then regrafted. Firstly the powder was dispersed in anhydrous toluene at a concentration of 50 mL toluene per gram zeolite, and then grafted with hexyltrimethoxysilane at a mass ratio of 1:1 (zeolite to hexyltrimethoxysilane) at 90 °C for 12 h under stirring. The highly dispersible zeolite was finally obtained after centrifugation (15,000 r/min), washed three times with methanol and dried overnight at 110 °C. The synthesized samples with above method were assigned as C_6-HZSM-5S, while the samples prepared following the method reported in Refs. [6,7] were assigned as C_6-HZSM-5P.

2.2. Characterization

X-ray diffraction (XRD) data in the 2θ range of 5° to 40° were collected on a Rigaku D-max 2500V/PC X-ray diffractometer (Rigaku Corporation) using Cu Kα radiation source (40 kV, 200 mA). Thermogravimetric and differential thermal analyses (TG–DTA) were obtained by using RIGAKU standard-type spectrometer (Rigaku Corporation). The samples were put into platinum pans, which were hung in the heating furnace at a heating rate of 10 °C/min. Transmission electron microscopy (TEM) images were obtained at room temperature on a Tecnai G2F20 field-emission transmitting electron microscope (Philips). Prior to the observation, the samples were dispersed in ethanol under ultrasonic and finally deposited over a carbon-coated copper grid.

2.3. Catalytic tests

Catalytic activity of HDZ nanocrystals was examined by a model reaction, i.e., catalytic cracking of *n*-dodecane, on an electrically heat tube reactor (300 × 3 × 0.5 mm) as show in our previous work [15,16]. 0.08 g HDZ nanocrystals were dispersed into 40 g of *n*-dodecane under ultrasonic for 10 min, and then introduced into the reactor after preheated to 450 °C. As a reference, the HZSM-5 coatings (ca. 3 μm thickness) were prepared by classic washcoating methods to examine the heterogeneous catalytic cracking activity. Catalytic cracking reaction was performed under the following conditions: 10 mL/min, 550 °C and 4 MPa. Finally, the cracked fuel was cooled and then flowed into a gas–liquid separator. The gaseous and liquid products were analyzed using the previous method [15,16], and the reaction rate was indexed by the mole of *n*-dodecane converted per gram zeolite in 1 s.

3. Results and discussion

3.1. Crystal structure and porosity

Fig. 1 illustrates the XRD diffractograms of ZSM-5 nanocrystals with and without seed organofunctionalization, calcinations and regrafting treatment. All the samples are highly crystalline and show the typical

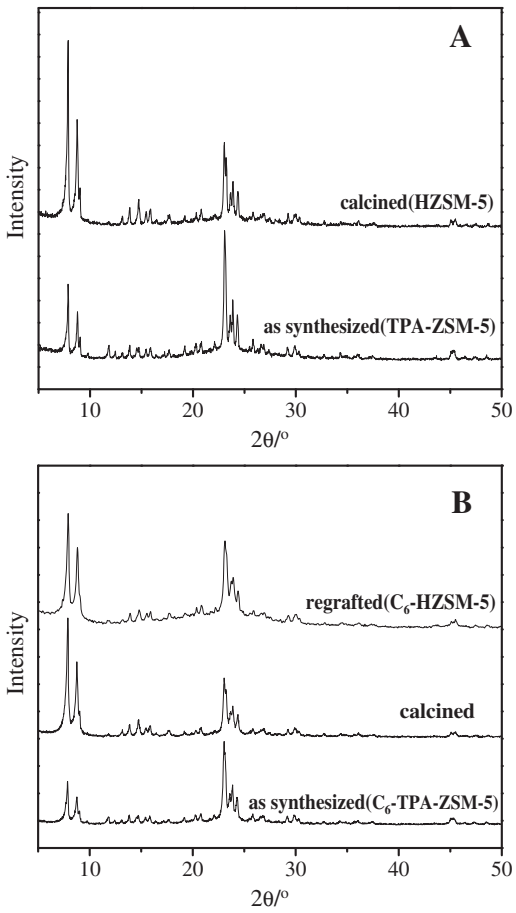

Fig. 1. XRD patterns of (A) TPA-ZSM-5 and (B) C_6-TPA-ZSM-5 after seed passivating synthesis, calcinations and regrafting treatments.

patterns of the MFI zeolitic structure after different treatments, indicating that ZSM-5 nanocrystals can be synthesized using seed silanization method, and the calcination and regrafting processing did not provoke substantial changes in the crystalline structure. When compared with ZSM-5, there is a clear broadening and lower intensities of all the peaks for the C_6-HZSM-5, regardless of calcined or not, which is attributed to smaller crystals. The nitrogen adsorption–desorption isotherms of the C_6-HZSM-5 zeolite and the reference material are shown in Fig. S1 (of the Supporting Information), and the textural properties of the samples are summarized in Table S1 (of the Supporting Information).

3.2. Grafting ratio of hexyl groups

To obtain the information on the removal of TPA^+ species during calcinations, TG–DTA analyses on the TPA-ZSM-5 and C_6-TPA-ZSM-5 are given in Fig. 2. A high weight loss is observed in both the TPA-ZSM-5 and C_6-TPA-ZSM-5 samples between 350 °C and 500 °C with a strong exothermic peak at 390 °C and a relatively weak one at 470 °C corresponding to the removal of the TPA^+ species strongly held inside the zeolite micropores. In the 200–350 °C region, there is another weight loss in the C_6-TPA-ZSM-5 sample (none in the TPA-ZSM-5 sample), can be ascribed to the removal of surface hexyl groups. This result suggests that the stabilization temperature of the TPA^+ species is much higher than that of grafted hexyl groups. Thus the latter doesn't exist after calcinations. Therefore, regrafting with organosilane is indeed necessary to supplement the surface alkyls.

The regrafted hexyl groups on the surface of HZSM-5 nanocrystal are further characterized by TG–DTA analyses, as shown in Fig. 2C. The TG–DTA curves present a high weight loss in the range of 250–550 °C with two strong exothermic peaks at 280 °C and 350 °C respectively, owing