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Microwave assisted in situ synthesis of USY-encapsulated heteropoly acid (HPW-USY) catalysts

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ABSTRACT

Under microwave irradiation, 12-tungstophosphoric acid (HPW) could be successfully synthesized in situ and encapsulated in the supercage of ultra stable Y (USY) in several minutes. But the framework of USY collapsed easily in traditional hydrothermal synthesis routine. ^{31}P MAS NMR, transmission electron microscopy (HR-TEM), N_2 adsorption, inductively coupled plasma (ICP) and X-ray diffraction (XRD) characterizations found that the formed HPW molecule located separately in the supercage of USY. Temperature-programmed desorption of NH_3 (NH_3-TPD) showed that HPW-USY exhibited stronger acidity than that of pure USY, and adsorbed pyridine infrared (Py-IR) disclosed that the concentration of Brönsted acid sites was enhanced. This hybrid solid acid exhibited higher activity in the synthesis of 4,4′-dimethyldiphenylmethane via toluene and formaldehyde and could be utilized as a solid acid catalyst in aqueous solutions.

1. Introduction

Substitution of strong liquid acids (such as HCl and sulfuric acid) by solid acids has attracted much attention in past years. In published papers, heteropoly acids with Keggin structure (abbreviated as HPA) were popularly reported for their strong acidity, ease in separation and possible utilization in recycling [1–4]. However, the high solubility of HPA in polarity solvent brings about a serious loss in reactant, which hindered the application of HPA. Many efforts have been put into avoiding the loss of HPA, such as immobilization of HPA on a support material and partial substitution of proton by Cs^+ ions [5].

As the Keggin heteropoly anions is larger (ca. 11–12 Å) than the pore diameter of zeolite Y, HPA anions cannot enter its pore channels and a severe leaching of heteropoly anions into water was observed of the supported PW catalysts, which led to their poor reusability [6–7].

Sulikowski et al. proposed that this problem could be solved by encapsulating HPA in the supercage of zeolitic matrix [8]. It is well known that ultra stable Y (abbreviated as USY) zeolite consists of almost spherical 13 Å cavities interconnected tetrahedrally through smaller apertures of 7.4 Å diameter [9]. And a Keggin structured HPA encapsulated in a supercage of USY cannot escape from its smaller apertures.

Several attempts were reported in order to encage HPW and 12-molydophosphoric acid (HPMo) in supercage of USY by a "ship in the bottle" method *via* a hydrothermal routine [10–14]. However, major drawbacks of the reported hydrothermal routine are long time (3 h), high temperature (90–95 °C) and strong acidity of the aqueous medium. The zeolitic matrix collapses easily under these conditions and amorphous SiO_2 derived from collapsed zeolite would enwrap the formed HPAs, which hindered the contact of acid sites with reactants. And the final product has a lower activity than that of pure USY [10]. It is of great practical interest to overcome the collapse of the zeolitic matrix during the preparation.

Microwave irradiation is an alternative thermal energy source to conventional heating thanks to its rapid rise in temperature and higher energy efficiency [15–20]. In a reaction irradiated with microwaves, reaction time could be reduced greatly and the procedure would be helpful to avoid the collapse of zeolitic matrix during the in situ synthesis of HPW.

In this contribution, we want to report an efficient synthesis routine of HPW encapsulated in a supercage of USY (abbreviated as HPW-USY) under microwave irradiation. The synthesized HPW-USY was characterized by ^{31}P MAS NMR, X-ray diffraction (XRD), Fourier transform infrared (FT-IR), nitrogen adsorption-desorption isotherms and inductively coupled plasma studies (ICP). And the

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location of the formed HPW was detected by transmission electron microscopy (HR-TEM), X-ray photoelectron spectroscopy (XPS), adsorbed pyridine infrared (Py-IR) spectroscopy and temperature-programmed desorption of NH_3 (NH_3-TPD). This hybrid solid acid was utilized in the synthesis of 4,4′-dimethyldiphenylmethane (abbreviated as 4,4′- DMDPM) via toluene and formaldehyde, it exhibited higher activity than pure USY.

2. Experimental

Sodium hydrogen phosphate (Na_2HPO_4), sodium tungstate ($NaWO_4{\cdot}H_2O$) and hydrochloric acid (HCl) were purchased from Shanghai Chemical Reagent Co. (China). USY zeolite was kindly supplied by Huahua Catalysis Co. (Wenzhou, China). All chemicals were used as received without further purification.

Encapsulation of HPW in zeolitic matrix was carried out via in situ synthesis under microwave irradiation. USY was first calcined at 550 °C for 3 h, and then put into an aqueous solution of well mixed Na_2HPO_4 and $NaWO_4{\cdot}H_2O$ with a controlled P/W atom ratio (1/6). A stoichiometric amount of HCl was added dropwise into the solution until pH 1.0. The flask containing the reaction mixture was placed into a microwave oven with a working frequency of 2.45 GHz (Nanjing Robot Co., LWMC-201, 650 W). Microwave irradiation was performed from 3 to 9 min. The formed HPW-USY (*x*) (where, *x* denoted the microwave irradiation time in min) was separated by filtration and washed 20 times with hot distilled water (80 °C) in order to remove the HPW anions formed on the external surface of USY completely. Finally, HPW-USY (*x*) were dried at 100 °C overnight and calcined at 250 °C for 3 h.

At the same time, a reference sample was also prepared by a hydrothermal method according to reference [12]. USY zeolite was added to a solution of Na_2HPO_4 in deionized water and the mixture was stirred for 2 h at room temperature. Then a solution containing a known amount of $NaWO_4{\cdot}H_2O$ was added dropwise. After 1.5 h of stirring, a stoichiometric amount of HCl was added dropwise at 90 °C. This suspension was stirred for 3 h at 90 °C. The synthesized sample (PW-USY (hydrothermal)) was separated and washed intensively with hot distilled water, dried at 100 °C overnight and finally calcined at 250 °C for 3 h.

Solid-state ^{31}P MAS-NMR spectra were obtained at room temperature with a 300 MHz spectrometer (Avance 300, BRUKER). For ^{31}P spectra, 90° pulse (2 μs) and 60 s delay were used to acquire about 200–300 transients of 2k complex data.

XPS analyses of the fresh PW-USY (7) and in situ Ar ionic sputtered PW-USY (7) were conducted on a PHI 5600 spectrometer (Physical Electronics) under 10^{-10} Torr, Al-Kα source (1486.6 eV). The analyzed area was 8000 Å in diameter and the binding energies were calibrated by contaminated carbon (C_{1s} at 285.0 eV). Ar ionic sputtering was performed with a beam energy of 4 keV and a sputtering rate of 25 Å min^{-1} for 4 minutes.

In situ pyridine adsorption was carried out by FT-IR spectroscopy (Nikolet 560, USA). The sample was first degassed (10^{-3} mbar, 200 °C for 4 h) in an IR cell and then the spectra of adsorbed pyridine were recorded.

The textural structure of HPW-USY was measured by nitrogen adsorption at −196 °C using an OMNISORP 100CX system (COULTER Co., USA). All samples were pretreated at 250 °C in vacuum, and the pore structure was calculated from adsorption isotherms. The micropore diameter in a range of 5.5–18 Å was calculated by the Horvath–Kavazoe (HK) method and a mesopore size in a range of 30–1000 Å was calculated by Barrett–Joyner–Halenda (BJH) method.

The element contents were measured using ICP in IRIS Intrepid II XSP (Thermo Fisher Scientific, USA) after leaching the metal ions with HF and diluting with distilled water (for aluminum, phosphorus and tungsten) or very dilute aqueous NaOH solution (for silicon) to specific volumes.

HR-TEM images were obtained using an accelerating voltage of 200 kV in JEM 2010HR (JEOL Ltd., Japan). Samples were first ground to powder, suspended in tetrachloromethane under supersonic shaking and finally dispersed on a copper grid. Energy dispersive X-ray analysis (EDX) was performed with an INCA Energy 300 (Oxford, UK).

XRD patterns were obtained on an D8 ADVANCE (BRUKER, Germany) instrument using nickel-filtered Cu Kα radiation at 40 kV and 40 mA. Diffraction data were recorded with a rate of 0.01° s^{-1}.

The acidity of synthesized HPW-USY catalysts was performed via NH_3-TPD. Each sample was first treated at 300 °C in Ar flow of 30 ml min^{-1} for 1 h, and then cooled to room temperature, exposed to 20% NH_3/Ar for 30 min, and purged by Ar at 100 °C for 5 h in order to eliminate the physical adsorbed ammonia. Temperature programmed desorption was conducted by ramping to 750 °C at 10 °C min^{-1} and NH_3 ($m/e = 16$) in effluent was detected and recorded as a function of temperature by a quadrupole mass spectrometer (OmniStarTM, GSD301, Switzerland).

Condensation between toluene and formaldehyde over these HPW-USY catalysts was carried out in a custom-designed 150 cm^3 stainless autoclave (Lanzhou, China). A mixture of toluene (450 mmol), paraformaldehyde (30 mmol of HCHO) and nitrobenzene (20 mmol, internal standard) was poured into the catalyst. The suspension was vigorously stirred with a magnetic stirrer at 140 °C (4 h). After the reaction, the reactor was cooled to room temperature, solid catalyst was separated by centrifuging, and organic reactant solution was diluted with ethanol and analyzed using an FID gas chromatography–mass spectrometer equipped with a 25 m capillary column of a cross-linked 5% phenylmethylsilicone (HP5988A, USA).

3. Results and discussion

The detected ^{31}P MAS NMR spectrum of PW-USY (7) is a broader (ca. 20.0 ppm) peak with a chemical shift at −15.0 ppm from H_3PO_4 (Fig. 1); this profile was wider than that of bulk HPW (a sharp signal at −15.3 ppm with a width of ca. 1 ppm) [8,21]. This broader spectrum could be due to the fact that the encapsulated Keggin unit located separately in the supercage of USY and its electronic environment would be disturbed by the surrounding Si, Al and O of the zeolitic matrix.

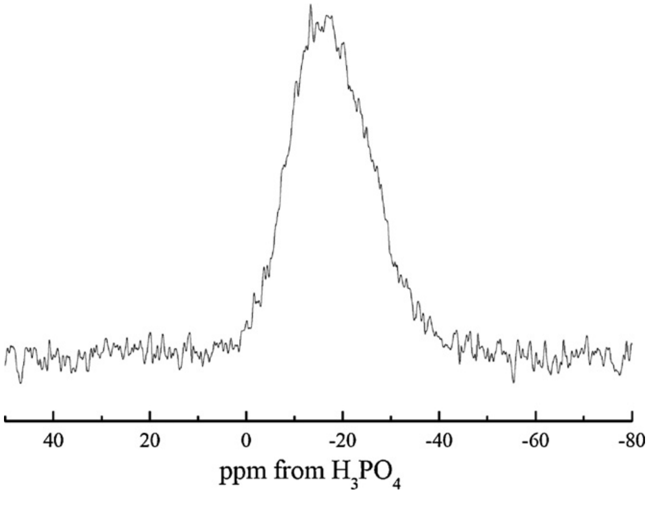

Fig. 1. Solid-state ^{31}P MAS NMR spectra of HPW-USY (7).