



A novel solid phosphoric acid from rice hull ash for olefinic alkylation of thiophenic sulfur in gasoline



Danlin Zeng*, Qi Zhang, Shiyuan Chen, Shenglan Liu, Yang Chen, Guanghui Wang

College of Chemical Engineering and Technology, The State Key Laboratory of Refractories and Metallurgy, Hubei Key Laboratory of Coal Conversion and New Carbon Material, Wuhan University of Science and Technology, Wuhan 430081, China

ARTICLE INFO

Article history:

Received 12 November 2014
Received in revised form 16 July 2015
Accepted 11 August 2015
Available online 13 August 2015

Keywords:

A. Surfaces
B. Chemical synthesis
C. Infrared spectroscopy
D. Catalytic properties

ABSTRACT

A novel solid phosphoric acid (SPA) was prepared from rice hull ash by impregnation with phosphoric acid and followed by calcination. The characterization results reveal that the solid phosphoric acid exhibits high surface area (335 m²/g) and acid densities (1.25 mmol/g) compared with commercial SPA catalyst. It was also clearly confirmed that silicon phosphate and silicon pyrophosphate were formed by the reaction of silica with phosphoric acid during the calcination process. The OATS catalytic performance results indicate that the solid phosphoric acid shows very good activity for thiophene alkylation reaction. This research provided a promising way to synthesis high active solid phosphoric acid for OATS desulfurization application.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Solid phosphoric acid (SPA) has been widely used in the alkylation and oligomerization reaction since the early 1930s [1]. The SPA catalyst is traditionally produced by calcination phosphoric acid with kieselguhr at high temperature. Due to their low cost, thermal stability and recyclability, this catalyst has received considerable attention mainly in the chemical industry applications.

Up to now, for the increasingly stringent environmental requirements on contamination emission during gasoline consumption, many approaches for deep desulfurization have been developed in the world [2–10]. The olefinic alkylation of thiophenic sulfur (OATS) process is one of the methods that can be operated under relatively mild conditions. Additionally, it brings a minimal loss of octane number during the desulfurization process. It would be a good alternative to the conventional catalytic hydro-desulfurization process [8]. However, it has been proved that for those competitive reactions such as aromatic alkylation and alkene oligomerization the traditional solid phosphoric acids show relatively low reaction activity in the OATS process [11,12]. Thus, to satisfy the need of large-scale industrialization of gasoline desulfurization by this technology, the catalytic activity of the solid phosphoric acid catalyst needs to be further improved.

In this paper, a novel solid phosphoric acid with high catalytic activity was prepared from rice hull ash by impregnation with phosphoric acid and followed by calcination. The solid phosphoric acid catalyst was also characterized by X-ray diffraction (XRD), Fourier-transform infrared spectra (FT-IR), solid-state nuclear magnetic resonance (NMR) and scanning electron microscope (SEM). In addition, the catalytic performance was also carried out using the solid phosphoric acid catalyst from rice hull ash to investigate its catalytic activity in olefinic alkylation of thiophenic sulfur in gasoline.

2. Experimental

2.1. Sample preparation

Rice hull was purchased from a grain depot in Wuhan, China. Rice hull was calcined at 575 °C for 10 h in air to remove the organics. Then the produced rice hull ash (RHA) was collected and sealed in a plastic bottle for the following experiment. The proximate chemical composition of the rice hull ash represented in weight percent was as follows: SiO₂ 90.25%, CaO 0.80%, Na₂O 0.71%, K₂O 0.63% and Al₂O₃ 0.24%.

The silica gels (Si-RHA) were synthesized from the rice hull ash according to the procedure reported in the literature [13,14]. To prepare the solid phosphoric acid, the silica gels (SiO₂, 99.9 wt%) were activated with 25 wt% amount of H₃PO₄ (85 wt%), at 500 °C under a N₂ flow (10 mL/min) for 12 h. At last, the mixture was diluted with deionized water, filtered, washed thoroughly, and dried at 150 °C for 12 h to obtain the solid phosphoric acid (SPA).

* Corresponding author.

E-mail address: zdanly@163.com (D. Zeng).

Table 1

Textural properties of the various samples.

Catalysts	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)	Total acid density (mmol/g)
SPA (rice hull ash)	335	0.146	1.16	1.25
SPA (commercial)	39	0.124	0.88	0.82
HY zeolite	305	0.359	1.29	0.48

catalyst. The solid phosphoric acid (commercial) was obtained from Merck. All the samples were stored in airtight plastic bottles. The textural properties of the samples are listed in Table 1.

2.2. Sample characterization

X-ray diffraction (XRD) was performed with a Philips X'PERT-Pro-MPD diffractometer, operating with CuK α radiation (40 kV, 30 mA) and Ni filter.

Particle morphology was observed with a Hitachi scanning electron microscope (SEM).

The total acid density of acid sites on the catalysts was determined by titration method [15].

Surface area and porosity properties of samples were evaluated by N₂ adsorption/desorption isotherms carried out at 77 K on a Micromeritics ASAP 2020 sorption analyzer.

The FT-IR spectra were recorded on Impact 410, Nicolet spectrometer with a resolution of 2 cm⁻¹.

All the NMR experiments were carried out at 9.4 T on a Varian Infinityplus-400 spectrometer.

The OATS experiments were carried out in a fixed-bed flow reactor (9 mm id \times 300 mm length). After activation at 300 °C, the catalyst was cooled down to room temperature, and then the model gasoline (thiophene:1-hexene:benzene:*n*-octane ratio is 1.25:4.71:12.2:81.84 wt%) was fed into the reactor. The liquid products were analyzed by a HP6890 gas chromatograph equipped with HP-5 column. The OATS reactions were carried out under the following conditions: reaction temperature is 90 °C, catalyst weight is 3.0 g and WHSV is 3.0 h⁻¹.

3. Results and discussion

Fig. 1 illustrates the XRD patterns of (a) the rice hull ash (RHA), (b) silica from rice hull ash (Si-RHA) and (c) the solid phosphoric acid (SPA). The broad diffraction peak at $2\theta = 22.5$ in rice hull ash is corresponded to the diffraction of amorphous silica [16] (Fig. 1a). The peaks ($2\theta = 29.3, 32.0, 39.2, 42.6$ and 48.1) are due to crystalline silica in the XRD pattern of silica from the rice hull ash (Fig. 1b),

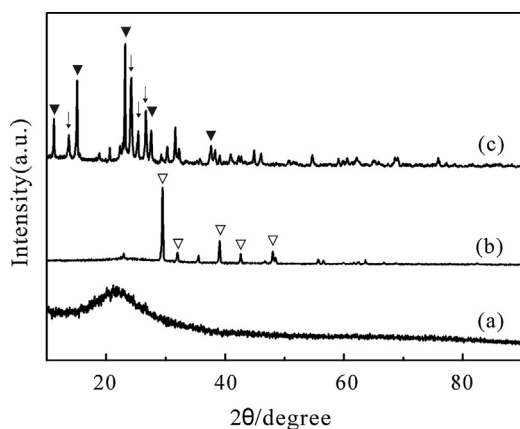


Fig. 1. XRD patterns of (a) rice hull ash (RHA), (b) silica from rice hull ash (Si-RHA) and (c) solid phosphoric acid from rice hull ash (SPA). ↓, ▲, ▽ denote peaks of silicon pyrophosphate, silicon phosphate and silica, respectively.

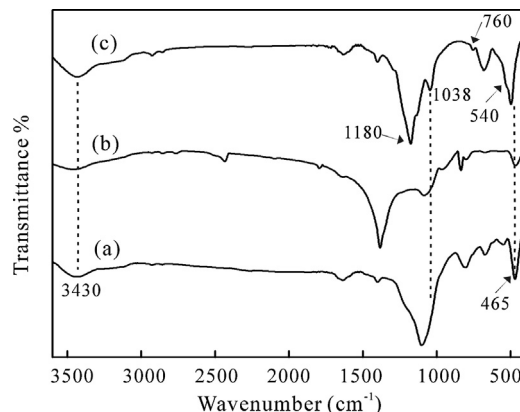


Fig. 2. FT-IR spectra of (a) RHA, (b) Si-RHA and (c) SPA samples.

which indicates that crystalline silica is obtained from the rice hull ash by calcination [17]. While in the XRD pattern of the solid phosphoric acid, the peaks at 11.2, 15.0, 23.2, 27.5 and 37.6 arising from silicon phosphate can be clearly observed (Fig. 1c). In addition, silicon pyrophosphate (due to the peaks at 13.6, 24.1, 25.2 and 26.6) is also generated in the catalyst [18]. Therefore, it can be concluded that silicon phosphate and silicon pyrophosphate are formed from the reaction of silica and phosphoric acid by calcination.

FT-IR spectroscopy was employed to characterize (a) RHA, (b) Si-RHA and (c) SPA samples (Fig. 2). The band at 462 cm⁻¹ can be attributed to Si–O–Si stretching mode [19] (Fig. 2), indicating that SiO₂ exists in all the three samples. While the bands assigned to P₂O₇⁴⁻ stretching mode at 1180 and 760 cm⁻¹ can also be clearly observed in the spectra (Fig. 2c) [18]. Furthermore, two bands at 1038 and 540 cm⁻¹ in the samples can be assigned to the PO₄³⁻ asymmetric and symmetric stretching modes, respectively [20]. Obviously, the appearance of P₂O₇⁴⁻ and PO₄³⁻ groups is the key difference between the SPA and RHA samples. The band at

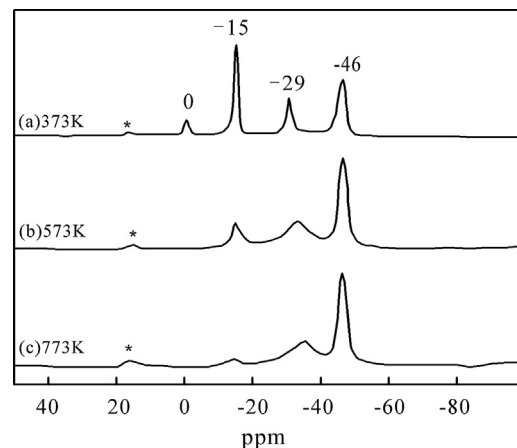


Fig. 3. ³¹P single pulse with ¹H decoupling MAS spectra of SPA samples calcined at the different temperature of (a) 373 K, (b) 573 K and (c) 773 K. The asterisk denotes spinning sidebands.

Download English Version:

<https://daneshyari.com/en/article/1487544>

Download Persian Version:

<https://daneshyari.com/article/1487544>

[Daneshyari.com](https://daneshyari.com)