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A Brønsted solid acid synthesized from fly ash for vapor phase dehydration of methanol

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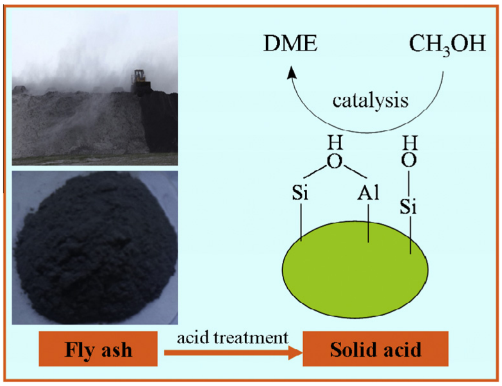
HIGHLIGHTS

- A solid acid was prepared from waste coal fly ash.
- The functional groups on the solid acid were clearly revealed.
- The solid acid exhibits excellent activity and stability for DME production.

GRAPHICAL ABSTRACT

A solid acid was prepared from the coal fly ash by acid treatment. The prepared solid acid was characterized by XRD, FT-IR, solid-state NMR and SEM. The characterization results shows that the solid acid contains two types of Brønsted acid sites: weak acidic –OH groups and strong bridging Si–O(H)–Al groups. Our results indicate that fly ash solid acid is a low cost, effective and stable catalyst that are highly suited to produce DME by dehydration reaction.



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ABSTRACT

A Brønsted solid acid was prepared from waste coal fly ash by acid treatment with concentrated H_2SO_4 at 473 K. The prepared solid acid was characterized by X-ray diffraction (XRD), Fourier-transform Infrared spectra (FT-IR), solid-state nuclear magnetic resonance (NMR) and scanning electron microscope (SEM). The characterization results show that the solid acid contains two types of Brønsted acid sites: weak acidic –OH groups and strong bridging Si–O(H)–Al groups. The acid strength of the strong acid sites is similar to that of zeolite HY (Si/Al = 3). The solid acid from fly ash exhibits excellent catalytic activity and stability in methanol dehydration reaction for dimethyl ether (DME) production. Our finding is a promising way of utilization of waste coal fly ash to prepare effective solid acid catalyst for industrial acid catalysis reactions.

1. Introduction

Coal fly ash is a porous waste by-product from coal combustion in thermal power plants. More than 800 million tons of coal fly ash are produced each year in the world [1], and the disposal of the large amount of fly ash has become a serious environmental problem. Only a small percentage (about 15%) of this waste is currently utilized as the construction materials, the adsorbents for gas and water treatment or the starting material to synthesis zeolite [2–4]. Most of the fly ash is still disposed of in landfills with the strict measures of prevention pollution at a very

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high cost. Therefore, it is necessary to pave the way for its utilization.

Possessing of enriched SiO_2, and its powder particles are predominantly spherical in shape and amorphous in nature, fly ash is an ideal raw material for the preparation of solid acid catalyst. During the last decade, some researchers have studied the utilization of coal fly ash to prepare the solid catalysts. Khatri [5] synthesized nano-crystalline activated fly ash catalyst by chemical and thermal treatment of fly ash. They suggested that surface –OH groups are responsible for the generation of surface acidity in the catalysts though no direct experimental evidence was given. In fact, the key questions in the catalysts, such as the type, structure and acid strength of the acid sites on these catalysts, are still unknown [5].

During the past few years, dimethyl ether (DME) has received global attention as a clean alternative fuel due to the increasingly stringent environmental regulations [6]. Up to now, DME is mainly produced by the catalytic dehydration of methanol, and the most solid acid catalysts used in this reaction are γ-Al_2O_3, silica–alumina, etc. [7,8]. However, those catalysts show lower efficiency due to coke formation and byproduct production during the catalysis process [9]. Thus, it would be necessary to find a more excellent catalyst to replace these solid catalysts. Herein, a typical coal fly ash was used to prepare a high active Brønsted solid acid by acid treatment using sulfuric acid. The solid acid catalyst was characterized by XRD, FT-IR, solid-state NMR and SEM. In addition, the catalytic performance was also carried out using solid acid from fly ash to investigate its catalytic activity in methanol dehydration reaction.

2. Experimental

2.1. Sample preparation

The coal fly ash from Wuhan Qingshan thermal power plant was used as the raw material. The main components of the coal fly ash are silica, alumina, calcium and iron oxide, with small amounts of carbon, as measured by flame atomic adsorption spectrophotometry. γ-Al_2O_3 and silica–alumina (13%Al) were obtained from Merk. The chemical composition of the fly ash is listed in Table 1.

The original fly ash powder was washed with deionized water. Then the washed fly ash was activated with concentrated H_2SO_4 at 473 K under a N_2 flow for 10 h at the solid to liquid ratio of 1 g: 100 mL. At last, the mixture was diluted with deionized water, filtered, washed thoroughly, and dried at 393 K for 12 h to obtain the solid acid catalyst.

2.2. Sample characterization

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

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

The concentration of acid sites on the catalysts was determined by titration method in aqueous solution. One gram of the sample was placed in 50 ml of 0.05 M NaOH solution. The vials were sealed and shaken for 24 h and then 5 ml of the filtrate was pipetted and the excess of base was titrated with HCl. The numbers of acidic sites were calculated from the amount of NaOH that reacted with the catalyst.

Table 1
Chemical composition of fly ash (wt%).

Component	SiO_2	Al_2O_3	Fe_2O_3	CaO	C
Fly ash	60.15	23.20	1.74	1.55	1.26

Surface area and porosity properties of the samples were evaluated by N_2 adsorption/desorption isotherms at 77 K on a Micromeritics ASAP 2020 sorption analyzer. Prior to the adsorption–desorption measurements, all the samples were degassed at 150 °C in N_2 flow for 12 h.

The FT-IR spectra were recorded on Impact 410, Nicolet spectrometer with a resolution of 2 cm^{-1}. 12 mg of each sample was pressed (at 2 ton/cm^2 pressures for 15 min) into a self-supported wafer 16 mm in diameter. The wafers were heated at 200 °C in an IR cell under vacuum ($<10^{-3}$ Pa) for 4 h and then cooled to room temperature under vacuum before the IR spectra of the samples were collected.

All the NMR experiments were carried out at 9.4 T on a Varian Infinityplus-400 spectrometer with resonance frequencies of 400.12, 100.4, 161.9 MHz for ^1H, ^{13}C, ^{31}P, respectively. The 90° pulse widths for ^1H, ^{13}C, ^{31}P were measured to be 3.7, 4.4, 3.6 μs, respectively. The chemical shifts were referenced to tetramethylsilane (TMS) for ^1H, to hexamethylbenzene (HMB) for ^{13}C, to 85% H_3PO_4 solution for ^{31}P, respectively. Repetition time of 6 s for ^1H, 60 s for ^{31}P single-pulse experiments was used. The magic angle spinning rate was 5 kHz.

For the adsorption of probe molecules trimethylphosphine (TMP), samples were kept at 673 K under the vacuum less than 1×10^{-3} Pa for at least 8 h. The adsorption of TMP was performed at room temperature with a loading of *ca.* 0.1 mmol per gram catalyst. The adsorption procedure of trimethylphosphine oxide (TMPO) was different from that of TMP. About 0.5 g dehydrated sample was mixed with 3 ml CH_2Cl_2 solution containing 0.1 M TMPO in a glove box before the mixture was stirred for 3 h by an ultrasonic shaker, equilibrated for 5 h, and then evacuated under vacuum to remove CH_2Cl_2 and physisorbed TMPO before NMR measurements.

2.3. Catalytic performance

A fixed bed flow micro-reactor was used for the catalytic test of vapor phase dehydration of methanol. The catalytic performances were examined with GHSV = 40,000 h^{-1} g cat^{-1} and N_2/MeOH = 90.0/10.0 (mol%) at 0.1 MPa and 473 K. The reactant mixture was regulated by mass flow controllers. Methanol was introduced into the flow reactor by bubbling N_2 gas through a glass saturator filled with methanol. Catalyst samples were placed in the heated zone of a tubular microreactor (9 mm i.d). The outlet stream line from the reactor to a gas chromatograph was heated at 423 K to avoid condensation of reaction products. The products were analyzed by an

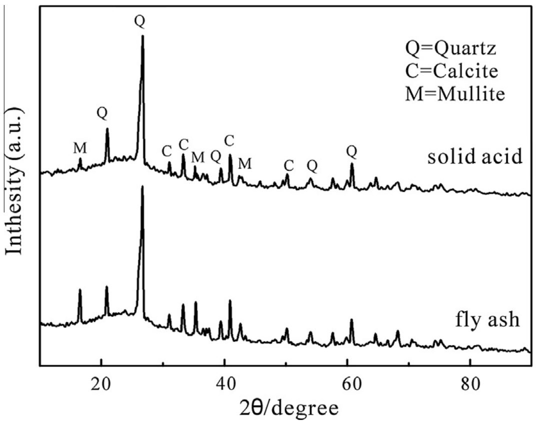

Fig. 1. XRD patterns of the solid acid and fly ash.

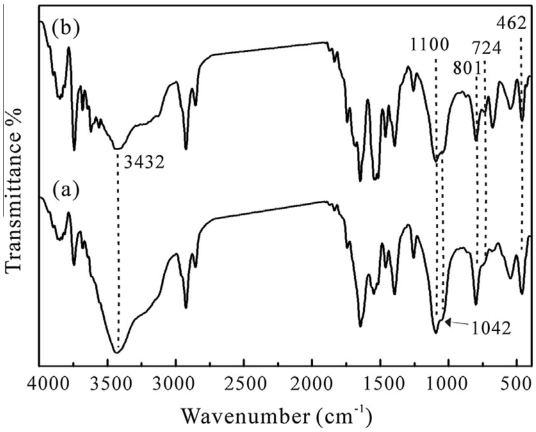

Fig. 2. FT-IR spectra of (a) the solid acid and (b) fly ash.

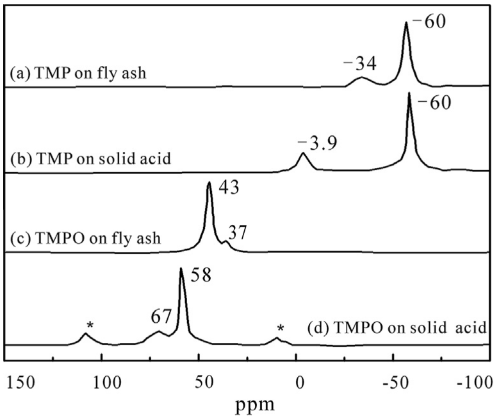

Fig. 3. ^{31}P single pulse with ^{1}H decoupling MAS spectra of TMP adsorbed on (a) fly ash and (b) the solid acid; TMPO adsorbed on (c) fly ash and (d) the solid acid. The asterisk denotes spinning sidebands.

online gas chromatograph using Porapak N ($\varnothing 3 \times 200$ mm) and Unibeads ($\varnothing 2 \times 200$ mm) C columns and a flame ionization detector (FID). The reaction performance results including methanol conversion (X_{MeOH}), DME selectivity (S_{DME}) and yield (Y_{DME}) were subsequently calculated.

3. Results and discussion

Fig. 1 illustrates the XRD patterns of the solid acid and fly ash. The XRD characterization results show that quartz (SiO_2), mullite ($2SiO_2{\cdot}3Al_2O_3$) and calcite ($CaSO_4$) are the main crystalline phase in the two samples [5]. By comparing the diffraction peaks in the corresponding samples, we can find that the intensity of diffraction peaks for mullite decreases while the intensity of diffraction peaks for quartz and calcite are almost unchanged, indicating that some mullite has been dissolved by H_2SO_4 solution during the acid activation process.

FT-IR spectroscopy was employed to characterize the fly ash and the solid acid (Fig. 2). Two bands at 1100 and 801 cm^{-1} in the samples can be assigned to the Si–O– antisymmetric and symmetric stretching modes, respectively [10]. The band at 462 cm^{-1} can be attributed to Si–O–Si stretching mode [10]. In addition, the small band at 724 cm^{-1} is due to Al–O– stretching modes [10]. The band assigned to Si–O–Al stretching mode at 1042 cm^{-1} can also be clearly observed in the spectra [11]. We can find that the intensity of the band at 3432 cm^{-1} related to the hydroxyl groups (–OH) in the solid acid is stronger than that in the fly ash, indicating that more –OH groups are introduced in the solid acid by acid activation.

The type and strength of acid sites are the fundamental properties of solid acid catalysts. As a basic molecule, trimethylphosphine (TMP) has been successfully used to probe acid type (Brønsted or Lewis acid sites) in the solid acid [12]. It is well known that the formation of $TMPH^+$ due to the interaction of TMP with Brønsted acid sites will give rise to a ^{31}P resonance at about -2 to -4 ppm, while TMP molecules bound to Lewis acid sites will result in ^{31}P resonances in the range from -32 to -58 ppm. The ^{31}P single pulse spectra obtained after adsorbing TMP onto the surface of fly ash and solid acid are shown in Fig. 3. One major peak at -60 ppm is observed in the ^{31}P MAS NMR spectrum (Fig. 3a) of TMP adsorbed on fly ash. According to its chemical shift, we attribute it to the physisorbed TMP on the fly ash [12]. The other small peak at -34 ppm can be assigned to TMP adsorbed on the Lewis acid sites in the fly ash. While two peaks at -3.9 and -60 ppm are present in

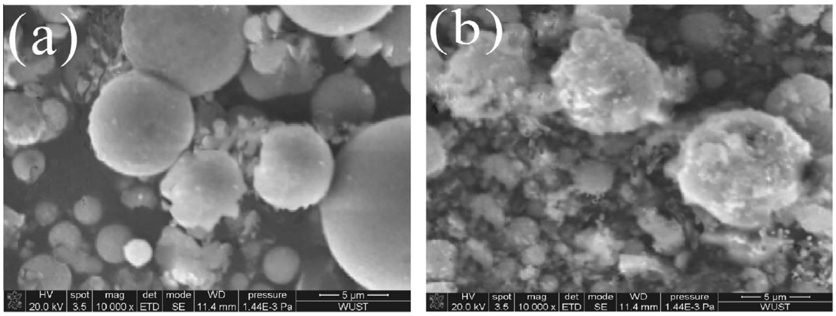

Fig. 4. SEM images of (a) fly ash and (b) the solid acid.

Table 2
Textural properties and the catalytic performance of the various catalysts.

Catalysts	S_{BET} (m^2/g)	V_{tot} (cm^3/g)	D (nm)	Total acid density (mmol/g)	X_{MeOH} (%)	S_{DME} (%)	Y_{DME} (%)
Solid acid	203	0.116	2.16	3.25	94	96	90
Silica–alumina	289	0.124	0.58	0.82	86	95	82
γ-Al_2O_3	210	0.059	0.29	0.48	73	90	66

S_{BET}, specific surface area from BET method; V_{tot}, total pore volume; D, average pore diameter.
Reaction condition: 473 K, 0.1 MPa and GHSV = 40,000 h^{-1} g cat^{-1}.

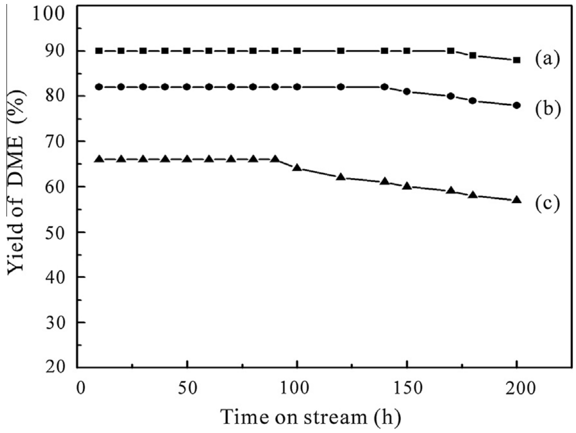

Fig. 5. Variation of yield of DME (Y_{DME}) of (a) the solid acid from fly ash, (b) silica-alumina and (c) γ-Al_2O_3 catalyst as a function of time on stream, T = 473 K, 0.1 MPa and GHSV = 40,000 h^{-1} g cat^{-1}.

the ^{31}P MAS NMR spectrum (Fig. 3b) of TMP adsorbed on the solid acid. The former can be unambiguously assigned to TMP adsorbed on the Brønsted acid sites and the latter is due to the physisorbed TMP. Compared with the fly ash, it is obvious that negligible amount of Lewis sites exists in the solid acid since no signal appeared between −32 and −58 ppm [13]. It can be concluded that the Lewis acid sites in fly ash have been induced into Brønsted acid sites in solid acid during acid activation process. Trimethylphosphine oxide (TMPO) has been shown to be more sensitive in revealing the strengths of acid sites in various solid acid catalysts [14]. The ^{31}P chemical shift of adsorbed TMPO on Brønsted acid sites moved to down-field with the increase of acid strength. As shown in Fig. 3c, two signals (at 43 and 37 ppm) are observed in the ^{31}P NMR spectrum of TMPO adsorbed on the fly ash [15]. The former signal (43 ppm) originates from the physisorbed TMPO, while the latter (37 ppm) is ascribed to TMPO adsorbed on the Lewis acid sites in fly ash, which is consistent with TMP characterization. Since no Lewis acid sites were detected on the solid acid by the TMP probe molecule, the two resonances at 67 and 58 ppm in the ^{31}P NMR spectrum of TMPO adsorbed on the solid acid can be both attributed to Brønsted sites in the solid acid [15]. Our FT-IR characterization has confirmed the existence of –OH functional groups, thus, the resonance at 58 ppm is ascribed to TMPO adsorbed on the weak acidic OH groups [16]. Sheng et al. [17] reported that bridging Si–O(H)–Al group is responsible for the Brønsted acid site on the SiO_2/Al_2O_3 catalyst. Based on the FT-IR characterization, Si–O–Al groups are present on the solid acid, therefore, the signal at 67 ppm can be assigned to TMPO adsorbed on the Brønsted acid sites bridging Si–O(H)–Al groups in the solid acid. The chemical shift of 67 ppm indicates that the acid strength of the solid acid is similar to that of zeolite HY (Si/Al = 3), on which the isotropic ^{31}P shift of TMPO is 65 ppm [14].

Scanning Electron Microscopy (SEM) was used to determine the morphology and particle size of the raw material fly ash and the solid acid from the fly ash. Fig. 4a shows the spherical particles of the original fly ash with a diameter ranging from 1 to 10 μm and their surface is smooth. After the acid activation, the particle morphology of solid acid becomes irregular and the surface is rougher than that of the raw material (Fig. 4b), indicating that some components in the fly ash were dissolved by sulfuric acid during the acid activation process.

Table 2 shows the catalytic performance for methanol dehydration over γ-Al_2O_3, silica–alumina and the prepared catalysts under the steady-state conditions. As reported in Table 2, compared with pure γ-alumina catalyst, the silica–alumina catalyst shows higher methanol conversion and DME selectivity. Meanwhile, the solid acid from fly ash exhibited highest activity for DME formation among all the samples. Previous studies have shown that the acid sites in the catalyst are responsible for the methanol to DME reaction [18–20], which is consistent with our experimental results. Since the amount of acidic sites over solid acid from fly ash is about 3.25 mmol/g, whereas for silica–alumina sample is about 0.82 mmol/g and for γ-Al_2O_3 is 0.48 mmol/g, therefore, this solid acid is more active than the other two typical catalysts under the same reaction condition.

Fig. 5 illustrates the long-term stability of the pure γ-Al_2O_3, silica–alumina and the solid acid catalyst, respectively. As it can be seen, the solid acid from fly ash shows excellent stability for dehydration reaction.

Based on the above discussion, it can be concluded that the solid acid from fly ash with the highest amount of acid sites exhibit best catalytic performance and stability under the test conditions. Finally, this kind of low cost catalyst appears to be the best alternative for dehydration reaction.

4. Conclusions

In summary, a Brønsted solid acid was prepared from coal fly ash by acid activation. The prepared solid acid was characterized by XRD, FT-IR, solid-state NMR and SEM. Our characterization results show that the solid acid contains two types of Brønsted acid sites: weak acidic –OH groups and strong bridging Si–O(H)–Al groups. The acid strength of the strong acid sites is similar to that of zeolite HY (Si/Al = 3). Our catalytic performance results indicate that the fly ash-based solid acid is a low cost, effective and stable catalyst that is highly suited to the production of DME by dehydration reaction. In addition, it is possible that this solid acid catalyst from waste fly ash can serve as an alternative for solid acid catalyst in the future.

Acknowledgments

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