

Short Communication

Acid properties of solid acid from petroleum coke by chemical activation and sulfonation



Danlin Zeng*, Shenglan Liu, Wanjun Gong, Guanghui Wang, Jianghua Qiu, Yongsheng Tian

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

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ABSTRACT

A novel solid acid was prepared from petroleum coke by KOH chemical activation and concentrated H_2SO_4 sulfonation. The solid acid was characterized by XRD, FT-IR and solid-state NMR. The characterization results show that the chemical activation and sulfonation lead to three functional Brønsted acid sites: $-\text{OH}$, $-\text{COOH}$ and $-\text{SO}_3\text{H}$ on the solid acid. The probe molecules experimental reveal that the acid strength of the solid acid is stronger than that of $\text{SO}_4^{2-}/\text{ZrO}_2$, but slightly weaker than that of 100% H_2SO_4 . The catalytic performance was evaluated by the esterification of oleic acid with methanol. The results indicate that this solid acid catalyst is very active, corresponding to high conversion (72%) of esterification reaction. In addition, the spent solid acid can be recovered by simple regeneration process.

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1. Introduction

Petroleum cokes are one of the vast by-products of petroleum industry. Most of the waste coke powder is currently stockpiled on-site, whereas small quantities of the coke are burnt as fuel. The emission of sulphur oxides, nitrogen oxides and other impurities seriously limits its use as fuel. Because of the large quantities of material available and the consistent accumulation of the waste coke, it is of great value for petroleum coke utilization.

A number of carbon precursors such as coal, petroleum coke and oil sands coke have been tested to produce porous carbons by physical activation or chemical activation, separately [1–6], however, few work has been performed to prepare solid acid using the waste petroleum coke [7]. Though it was reported that the surface oxygen groups such as $\text{C}-\text{OH}$, $\text{C}-\text{O}-\text{H}$ and some alkyl groups play an important role in activation, the nature of these acidic surface functional groups is still poorly known [7]. For its high carbon content (about 90%) and low volatile and ash content petroleum coke is the good raw materials for preparation of solid acid. In this paper, a typical Chinese waste petroleum coke was used to prepare high active solid acid by chemical activation and sulfonation. The solid acid catalyst was also characterized by XRD, FT-IR and solid-state NMR.

2. Experimental

2.1. Sample preparation

The petroleum coke (the purity is 99%) from Sinopec Wuhan Branch was used as raw material. It was ground and sieved to the particle size range of 150–180 mm. Particle size analysis was performed by dry sieving with Taylor standard sieves. The elemental analysis of the petroleum coke is listed in Table 1.

The original petroleum coke powder was physically mixed with KOH (99%) at a mass ratio of 1:3. The mixtures were loaded into a nickel crucible closed by a nickel cover, and then heat-treated in a nitrogen stream with a horizontal cylindrical furnace from room temperature to 673 K at a heating rate of 10 K min^{-1} , and held at 673 K for 1 h, then a heating rate of 6 K min^{-1} was applied up to the final activation temperature 1073 K, which was maintained for 1 h. The crucible was then allowed to cool down to room temperature under nitrogen flow. After that, the activated carbon was washed first with 0.1 M HNO_3 aqueous solution, then with distilled water until the pH of the filtrate remains at 6. Then the activated coke powder was dried in an oven for 5 h at 393 K, and then followed by grinding and sulfonation with concentrated H_2SO_4 (98 wt%), at 473 K under a N_2 flow for 10 h at the ratio of solid to liquid of 1 g: 100 mL. At last, the mixture was diluted

Table 1
Element analysis of petroleum coke (wt%).

Sample	C	H	O	N	S
petroleum coke	92.15	3.20	1.55	2.84	0.26

* Corresponding author. Tel./fax: +86 27 6886 2181.

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

with deionized water, filtered, washed thoroughly, and dried at 393 K for 12 h to obtain the solid acid catalyst.

Recycling experiments were performed to determine the catalytic stability of the solid acid catalysts. At the end of each esterification cycle, the catalyst was centrifuged, washed with acetone and dried before reuse. The spent solid acid was obtained after 5 recycle times using. Then the spent solid acid washed with acetone, dried at 120 °C under the vacuum, impregnated in 1 M H₂SO₄ for 5 h, washed with deionized water and dried at 120 °C to obtain the regenerated solid acid. Pore structure and total acid density of petroleum coke, petroleum coke after activation and solid acid from petroleum coke (fresh, spent and regenerated) are listed in Table 2.

2.2. Sample characterization

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.

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. Prior to the adsorption-desorption measurements, all the samples were degassed at 150 °C in N₂ flow for 12 h.

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

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, ¹³C, ³¹P, respectively. The 90° pulse widths for ¹H, ¹³C, ³¹P were measured to be 3.7, 4.4, 3.6 μ s, respectively. The chemical shifts were referenced to tetramethylsilane (TMS) for ¹H, to hexamethylbenzene (HMB) for ¹³C, to 85% H₃PO₄ solution for ³¹P, respectively. Repetition times of 6 s for ¹H, 60 s for ³¹P single-pulse experiments were 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 CH₂Cl₂ solution containing 0.1 M TMPO in a glove box before the mixture was stirred for 3 h by an ultrasonic shaker, allowed to equilibrate for 5 h, and then evacuated under vacuum to remove CH₂Cl₂ and physisorbed TMPO completely before NMR measurements.

The various solid acids were employed as catalysts for the esterification of oleic acid with methanol. Prior to the reaction, all the catalysts were dried at 120 °C for 5 h, except for concentrated H₂SO₄. The experiments were carried out by mixing oleic acid with methanol in a flask equipped with a reflux condenser, an oil bath and a

magnetic stirrer. Once the mixture had reached the reaction temperature, the catalyst was added. The mixtures were withdrawn and centrifuged to separate the solution from the catalyst. Analysis of the reaction mixtures was carried out in a HP 6890 series gas chromatograph equipped with a flame ionization detector (FID) and a HP-5 capillary column.

3. Results and discussion

Fig. 1 illustrates the XRD patterns of the solid acid and petroleum coke. Two diffraction peaks arising at around $2\theta = 25^\circ$ and 43° in petroleum coke spectrum, corresponding to the diffraction of C (002) and C (100), respectively [7]. Compared with those of petroleum coke, the (002) peak intensity of solid acid decreased severely and the (100) peak of solid acid disappeared. According to Dahn's conclusion [8], it indicates that the solid acid consists of a single layer of polyhexagonal carbon atoms after KOH chemical activation. KOH activation process may lead to dramatic increase in the BET surface area of the solid acid.

FT-IR spectroscopy was employed to explore the changes in functional groups induced by activation and sulfonation. Observation of the spectra shows that the change between two samples is mainly due to the formation of oxygen functionalities (Fig. 2). Two bands at 1041 and 1182 cm⁻¹ in the solid acid can be assigned to the SO₂ asymmetric and symmetric stretching modes, respectively [9]. It indicates that the covalently linked sulfonic acid group was formed on the surface of the sulfonated solid acid. The band at 1738 cm⁻¹ can be attributed to the C = O stretching mode of the -COOH groups [9]. The broad band centered at 3434 cm⁻¹ was assigned to the -OH stretching mode [9]. Therefore, -COOH, -SO₃H and -OH were found as the functional groups on the solid acid.

The type and strength of acid sites are the fundamental properties of solid acid. Many methods have been developed to reveal the acid properties of solid acids. During these methods, TPD of ammonia and FTIR spectroscopy of pyridine have been commonly used for qualitative characterization on various solid acids, but the probe molecules used in these cases are normally too basic to distinguish subtle differences of acid sites, leading to simple profiles reflecting the sole presence of an averaged acid strength [10]. In the present case, a more sensitive and reliable technique [11], ³¹P MAS NMR of adsorbed trimethylphosphine (TMP) and trimethylphosphine oxide (TMPO) are used to characterize the acidity of the solid acid derived from petroleum coke. TMP is an extensively used probe molecule to discriminate Lewis acid sites and Brønsted sites in the solid acid [10]. It is well known that the formation

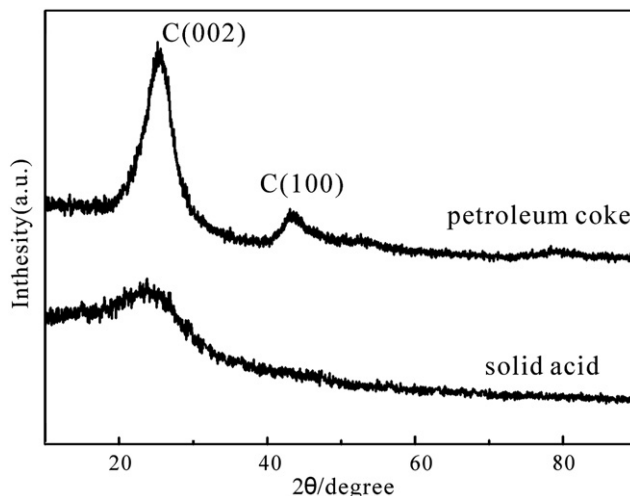


Fig. 1. XRD patterns of the solid acid and petroleum coke.

Table 2

Pore structure and total acid density of petroleum coke, petroleum coke after activation and solid acid from petroleum coke (fresh, spent and regenerated).

Sample	S_{BET} (m ² /g)	V_{tot} (cm ³ /g)	D (nm)	Total acid density (mmol/g)
Petroleum coke	39	0.023	1.28	0.02
Coke(after activation)	1266	0.756	2.12	1.02
Solid acid(fresh)	1203	0.746	2.16	5.25
Solid acid(spent)	843	0.539	2.01	2.32
Solid acid(regenerated)	1189	0.733	2.13	5.08

S_{BET} , specific surface area from BET method; V_{tot} , total pore volume; D , average pore diameter.

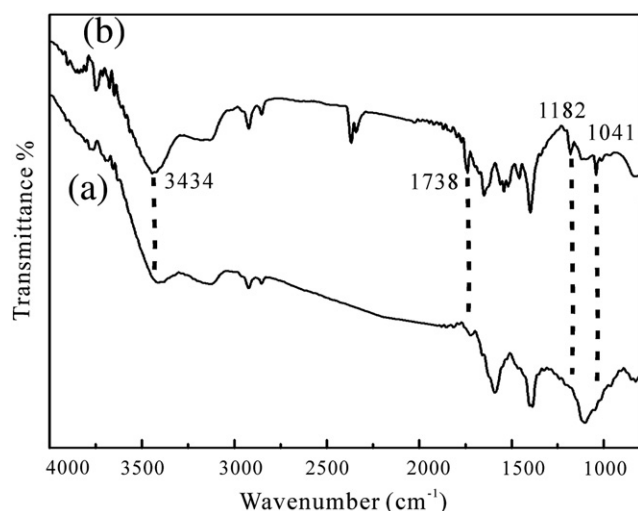


Fig. 2. FT-IR spectra of (a) the petroleum coke and (b) the solid acid.

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 spectrum obtained after adsorbing TMP onto the surface of petroleum coke and solid acid are shown in Fig. 3. Only one major peak at -60 ppm is observed in the ^{31}P MAS NMR spectrum (Fig. 3a) of TMP adsorbed on petroleum coke. According to its chemical shift, we attribute it to the physisorbed TMP on petroleum coke [10]. It indicated that neither Lewis acid site nor Brønsted acid site was detected in the original petroleum coke. While two peaks at -4 and -60 ppm are present in 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 originated from physisorbed TMP. It is obvious that negligible amount of Lewis sites exists in the solid acid as no signal appeared between -32 and -58 ppm [11]. TMPO is a useful NMR probe molecule for measuring the relative acid strengths of solid acids. The ^{31}P chemical shift of adsorbed TMPO on Brønsted acid site moved to down-field with the increase of acid strength. Since no Lewis acid sites were detected by the TMP probe molecule, the three resonances at 59, 65 and 80 ppm in the ^{31}P NMR spectrum of TMPO adsorbed on the solid acid can be all

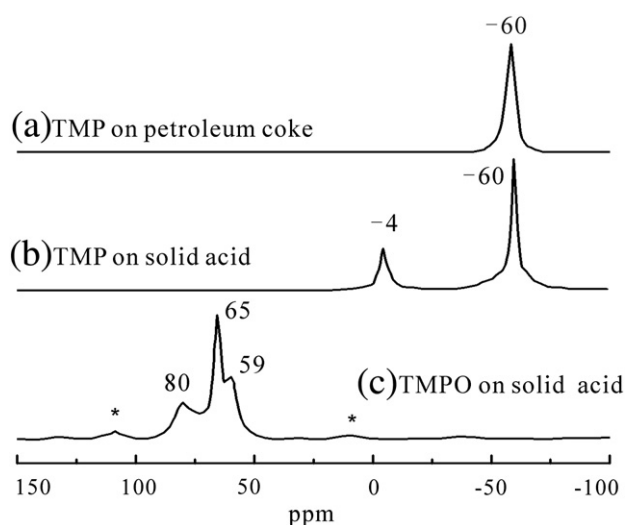


Fig. 3. ^{31}P single pulse with ^1H decoupling MAS spectra of TMP adsorbed on (a) petroleum coke and (b) solid acid, (c) TMPO adsorbed on solid acid. The asterisk denotes spinning sidebands.

attributed to Brønsted sites in the solid acid [12]. Since our FT-IR characterization has confirmed the existence of $-\text{OH}$, $-\text{COOH}$ and $-\text{SO}_3\text{H}$ functional groups, the resonance at 59 ppm is ascribed to TMPO adsorbed on the weakly acidic OH groups, while the other two signals at 65 and 80 ppm can be assigned to TMPO adsorbed on the Brønsted acid sites $-\text{COOH}$ and $-\text{SO}_3\text{H}$ groups, respectively [13]. The large chemical shift of 80 ppm indicates that the acid strength of the solid acid is stronger than that of $\text{SO}_4^{2-}/\text{ZrO}_2$ (having ^{31}P chemical shifts of 69.2 ppm) [14], but still slightly weaker than that of 100% H_2SO_4 , in which the isotropic ^{31}P shift of TMPO is 83 ppm [13].

In order to evaluate the activity of the solid acid in the reaction, a comparative study was made between the solid acid prepared from petroleum coke, concentrated H_2SO_4 and other two typical solid acid catalysts sulfated zirconia and HZSM-5 ($\text{Si}/\text{Al} = 38$). The reaction used was the esterification of oleic acid (20 mmol) with methanol (100 mmol) at 80°C . The same amount (0.015 g) of all the catalysts was used in the reactions. As can be seen in Table 3, the solid acid from petroleum coke shows higher esterification activity than other two typical solid acid catalysts, but still lower activity than that of concentrated H_2SO_4 . Compared with the liquid acid, the lower activity of the solid acid is maybe due to its lower proton density and resolvability in the reaction.

The catalytic stability of the solid acid from petroleum coke was evaluated by running the esterification reaction five times with the same catalyst. As shown in Fig. 4, the conversion of oleic acid gradually decreased from 72% to 60% in the five cycles. By compared the data of the fresh and the spent (after used by five cycles) solid acid in Table 2, the total acid density was reduced from 5.25 mmol/g to 2.32 mmol/g. While by regeneration process, the acid density was recovered to 5.08 mmol/g. The remaining active sites are approximately 96% of that in the fresh solid acid. Being still attached to the carbon surface after five reaction cycles, those acid sites were able to reuse in the catalytic reaction. Therefore, it can be inferred that leaching of polycyclic aromatic hydrocarbons bearing SO_3H groups is unlikely the main reason for catalyst deactivation. The catalytic activity loss was probably attributed to some active acid sites of the catalyst being covered by the resultant. These covered acid sites can be reactivated by simple regeneration process. Since our coke solid acid is relatively non-toxic, easy separation and can be recycled for reusing. Thus, it would be a promising green solid acid catalyst for industrial application.

4. Conclusions

In summary, a novel solid acid was prepared from petroleum coke by KOH chemical activation and concentrated H_2SO_4 sulfonation. Our characterization results shows that the solid acid contains functional groups such as $-\text{OH}$, $-\text{COOH}$ and $-\text{SO}_3\text{H}$ and its acid strength is stronger than that of $\text{SO}_4^{2-}/\text{ZrO}_2$, but slightly weaker than that of 100% H_2SO_4 . The catalytic performance was evaluated by the esterification of oleic acid with methanol. The results indicated that the conversion reached 72% using the solid acid from petroleum coke when the

Table 3
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)	Yield (%)	TOF (h^{-1})
Solid acid	1203	0.746	2.16	5.25	72	46
$\text{SO}_4^{2-}/\text{ZrO}_2$	153	0.230	5.20	4.43	68	36
HZSM-5	370	0.124	0.58	1.12	50	28
H_2SO_4 (98%)	—	—	—	20.40	88	130

S_{BET} , specific surface area from BET method; V_{tot} , total pore volume; D , average pore diameter.

TOF (Turn over frequency) was evaluated on the basis of the mol of converted reactant, the mol of acid sites and reaction equilibrium time.

Reaction condition: 20 mmol oleic acid; 100 mmol methanol; 0.015 g catalyst; 80°C .

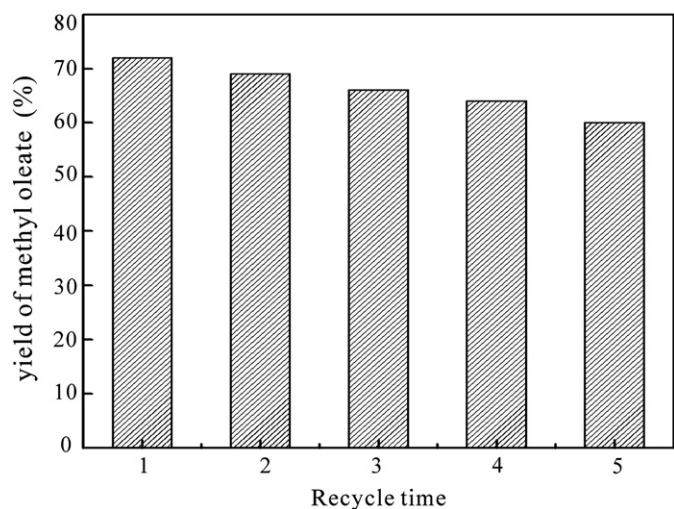


Fig. 4. The recycling of the solid acid from petroleum coke for the esterification of oleic acid with methanol. Reaction condition: 20 mmol oleic acid; 100 mmol methanol; 0.015 g catalyst; 80 °C.

reaction was carried out at 80 °C with a catalyst amount of 0.015 g and the reactant amount of 20 mmol oleic acid and 100 mmol methanol. In addition, the spent solid acid from petroleum coke can be recovered by simple regeneration process. It is possible that this green solid acid can be widely used in the acid catalyzed reaction.

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