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Research article

Large-scale synthesis and catalysis of oleic acid-coated Fe_2O_3 for co-liquefaction of coal and petroleum vacuum residues

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ABSTRACT

Two kinds of well-dispersed oleic acid-coated Fe_2O_3 nanoparticles (NPs) were prepared using hydrothermal method as catalysts I and II in milligram- and gram-scales, respectively. According to analyses with X-ray diffraction and transmission electron microscopy, the two kinds of NPs are nearly spherical with diameters of ca. 5 and 8 nm for milligram- and gram-scale preparations, respectively. The results of co-liquefaction of coal and petroleum vacuum residue (PVR) show that catalysts I and II exhibit better activity than Fe_2O_3 and no catalyst under the same conditions carried in a 100 mL batch reactor. Specifically, the soluble portion (SP) yield is beyond 92% over Fe_2O_3, catalyst I or II, whereas the one is only 85% without catalyst. The total oil yields are 82.83% and 83.67% over catalysts I and II, respectively, whereas 74.69% and 70.35% over Fe_2O_3 and no catalyst, respectively. According to analysis with simulated distillation, diesel and gasoline yields over catalysts I and II increased compared to no catalyst.

1. Introduction

Depletion of petroleum energy requires an urgent search for other energy sources. Hence, co-processing of coal with some waste materials elicits growing interest. Co-processing of polypropylene with coal and petroleum vacuum residue (PVR) is apparently feasible to convert plastic materials and coal into liquid portion [1]. This method not only improves coal liquefaction but also reuses waste materials causing environmental disturbance [2].

Up to date, co-liquefaction of coal with PVR, plastic wastes, and biomass provides a promising prospect, and these processes have attracted a lot of attention [3–10]. In co-processing, PVR, plastic wastes, and biomass work as solvents, whereas coal acts as a catalyst carrier and/or a hydrogen shuttle [11–15]. The catalyst improves the yields of oil yield and soluble portion (SP) [16–18], as well as the quality of liquid fuels produced from co-liquefaction. Joo et al. [19] obtained higher yields of liquid fuels within the boiling range of 100–480 °C by using NiMo/Al_2O_3 as a catalyst. Fogassy et al. [20] discovered that a large portion of lignin polymers in pyrolytic oil cracked into smaller methoxyphenols during co-processing by using three zeolite-based catalysts. Besides, polar hydrocarbons in oils were converted into aromatic and saturated hydrocarbons when red mud was added during co-processing of coal and waste materials [2]. Our group recently prepared oleic acid-coated Fe_3O_4 nanoparticles (NPs) by using a method similar to that of Hyeon et al. [21]. These NPs exhibit a hydrophobic surface and demonstrate excellent catalytic performance in direct coal liquefaction owing to their high dispersion [22]. However, a detailed study on oil-soluble catalysts in co-liquefaction of coal and PVR has not yet been conducted.

Thus, in our work, milligram-scale (84 mg) oleic acid-coated Fe_2O_3 NPs were prepared using a liquid–solid–solution process [23]. The morphology of the obtained NPs was observed via transmission electron microscopy (TEM), and their phase analyses and crystal structures were investigated by X-ray diffraction (XRD). The catalytic activity of the prepared acid-coated Fe_2O_3 NPs for co-liquefaction is higher than that of Fe_2O_3, which suggests that the oleic acid-coated Fe_2O_3 NPs are promising catalysts for co-liquefaction. Thus, we prepared large-scale oleic acid-coated Fe_2O_3 NPs with properties similar to those of milligram-scale NPs. Finally, we prepared gram-scale (5.6 g) oleic acid-coated Fe_2O_3 NPs by increasing the weight ratios of ferric nitrate to mixed solvents, as well as the volumes of mixed solvents and reactors. The obtained NPs were also investigated by TEM and XRD.

2. Experimental

2.1. Samples

Xigou subbituminous coal (XSBC) was obtained from Xinjiang Autonomous Region, China. XSBC was pulverized to small particles with sizes less than 200 meshes. These particles were subsequently dried at 100 °C for 12 h. The properties of XSBC are presented in Table 1.

PVR was obtained from Karamay, Xinjiang Autonomous Region, China. The four components of PVR were determined according to Chinese Standard Analytical Method for Petroleum and Natural Gas

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Table 1
Analyses (wt.%) of XSBC.

Proximate analysis			Ultimate analysis (daf)				$S_{t,d}$	H/C	Petrographical analysis		
M_{ad}	A_d	VM_{daf}	C	H	N	O_{diff}			Vitrinite	Inertinite	Exinite
2.21	3.59	43.86	78.60	5.27	1.28	>14.45	0.39	0.8046	83.2	1.5	13.3

diff: by difference; daf: dry and ash-free base; M_{ad}: moisture (air dried base); A_d: ash (dry base, i.e., moisture free base); VM_{daf}: volatile matter (dry and ash-free base), $S_{t,d}$: total sulfur (dry base).

Table 2
Properties of PVR.

Organic matter content (wt.%)				Metal content (μg/g)				Boiling range (°C)	Acid value (mg KOH/g)	Carbon residue (%)
Saturate	Aromatics	Resin	Asphaltene	Ni	V	Fe	Ca			
25.95	24.62	49.32	0.10	31.80	0.75	56.60	588.20	>520	2.78	13.14

Table 3
The conditions for preparing catalysts I and II.

Catalyst	Reactor (mL)	$Fe(NO_3)_3 \cdot 9H_2O$ (mmol)	Sodium oleate (mmol)	Distilled water (mL)	Ethanol (mL)	Hexane (mL)
I	100	1	3	10	20	30
II	1000	70	210	100	200	300

Industry (SY/T 5119–2008) which is commonly used in China for geochemical samples. The properties of PVR are listed in Table 2.

2.2. Preparation of Fe_2O_3 NPs

The hydrothermal synthesis reactor (100 mL) was used for catalyst I. Typically, $Fe(NO_3)_3 \cdot 9H_2O$ (1 mmol) and sodium oleate (3 mmol) were combined with distilled water (10 mL), absolute ethyl alcohol (20 mL), and n-hexane (30 mL) in a three-necked flask. The weight ratio of ferric nitrate to mixed solvents was 0.004 under this condition. The solution was kept and stirred at 70 °C under reflux for 1 h. After cooling the reactor to room temperature, the resulting solution was placed in a hydrothermal synthesis reactor, and reacted at 200 °C for 3 h. Subsequently, the reactor naturally cooled down to room temperature. Afterward, the resultant liquid was placed in a separating funnel and left to stand for 1 h. The substrate and upper organic layer containing the oleic acid-coated Fe_2O_3 NPs were then separated. The NPs were washed and precipitated with absolute ethyl alcohol and n-hexane in turns, followed by centrifugation at 4000 rpm. In addition, the procedure for catalyst II was similar to that of catalyst I. The only differences were the amounts of reagents and the volume of the reactor. The weight ratio of ferric nitrate to mixed solvents also increased from 0.004 to 0.03. The differences of preparation conditions between catalyst I and II were summarized in Table 3.

2.3. Characterization of catalysts

XRD crystallographic information was recorded using a Rigaku D/max-ga X-ray diffractometer with a scanning speed of 2° min^{-1}, ranging from 20° to 80° with Cu Kα radiation (λ = 1.5418 Å). TEM images were generated using Hitachi H-600 at an accelerated voltage of 100 kV. Fourier transform infrared (FTIR) spectra were obtained with a Bruker EQUINOX55 spectrophotometer within the wavenumber interval of 4000–1000 cm^{-1}.

2.4. Co-liquefaction of XSBC and PVR

Co-liquefaction experiments (Fig. 1) were performed in a 100 mL autoclave reactor. Up to 7.0 g of dry and ash-free (daf) XSBC, 7.0 g of PVR loaded with 2 wt.% catalysts (catalyst I, catalyst II, or Fe_2O_3), and 7.0 g of tetralin were charged into the reactor. Air in the autoclave was replaced by twice with hydrogen, which was pressurized to an initial pressure of 7.0 MPa at room temperature. The reactor was maintained at 400 °C for 1 h. Subsequently, the gaseous product was collected in a gas bag and analyzed by a gas chromatograph. The resulting mixtures were separated by Soxhlet solvent extraction sequentially with hexane and tetrahydrofuran (THF) into hexane-soluble portion (oil), hexane-insoluble but THF-soluble portion (HITSP) as asphaltene and preasphaltene (A + PA), and THF-insoluble portion (THFISP) as residue. The yield of each portion was calculated on daf XSBC and PVR. The liquid products were determined using a gas simulated distillation method in accordance with the Chinese Standard Analytical Method for Petrochemical Industry (SH/T0558-1993). This method was commonly used for distillation in China. Liquid products were cut into five parts from initial boiling point (IBP), which are gasoline (IBP-180 °C), diesel (180–350 °C), kerosene (140–240 °C), distillates (350–500 °C), and heavy oil portion (>500 °C).

3. Results and discussion

3.1. Morphology and crystal structure analysis of catalysts

XRD was employed to obtain the crystallographic information and the patterns of Fe_2O_3, catalysts I and II (Fig. 2). Notably, these catalysts

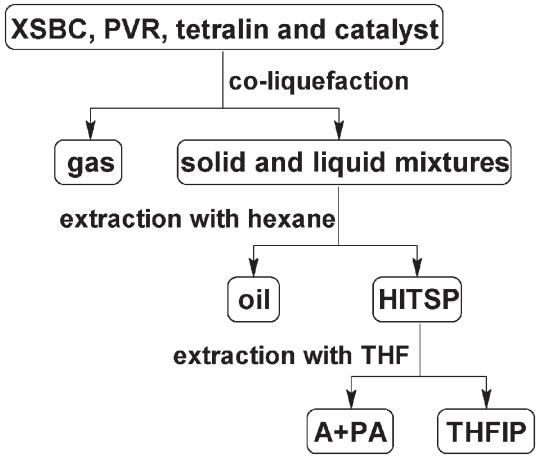

Fig. 1. Diagram of co-liquefaction and product separation.