



Research paper

Synthesis and characterization of 12-tungstophosphoric acid intercalated layered double hydroxides and their application as esterification catalysts for deacidification of crude oil



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ABSTRACT

12-tungstophosphoric acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$, HPW) intercalated layered double hydroxides (LDH) ($\text{M}^{2+}/\text{Al}^{3+} = 2$, $\text{M}^{2+} = \text{Mg}^{2+}, \text{Zn}^{2+}, \text{Ni}^{2+}$) were prepared by an ion-exchange method. The as-prepared LDH show a strong reflection around 8.4° corresponding to a basal spacing of 1.05 nm, which is considered as heteropolyacid salts or polytungstate intercalated LDH in almost all literature. Further systemic experiments and characterizations demonstrated that such reflection can be attributed to the intercalation of HPW, in which HPW may graft with the vacancies in the layer and orient in the interlayer with the C_2 axis perpendicular to the layers. HPW intercalated LDH show higher catalytic activity than nitrate LDH for the esterification between ethylene glycol and naphthenic acids in crude oil. It is found that the total amount of acidic sites dominates the esterification activity. Due to the immobilized HPW active sites and the enlarged interlayer space, HPW intercalated LDH may act as an interlayer catalytic reactor to improve the esterification activity.

1. Introduction

Polyoxometalates (POMs) are a class of molecular anionic metal-oxide clusters (Pope, 1983), which can be divided into two main categories, isopolyacids (IPAs) and heteropolyacids (HPAs). IPAs contain only transition metal ions and oxide ions, whereas HPAs incorporate one or more heteroatoms such as P^{5+} , Si^{4+} and As^{5+} (Pope, 1983). HPAs systems are very attractive due to the variety and selectivity of their properties and structures (Song and Barteau, 2004). One of the most important properties of HPAs is the strong acidity (Borrás-Almenar et al., 2003). In particular, the Keggin-type 12-tungstophosphoric acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$, HPW), which is made up of a central PO_4 tetrahedron surrounded by four trimetallic groups of three edge-sharing WO_6 octahedra, is considered to be the most stable and acidic HPAs and is widely used in acid catalysis (Brahmkhatri and Patel, 2011; Baroi and Dalai, 2014).

Naphthenic acids constituted by five- or six-membered rings and one carboxyl are the dominant acids in crude oil (Barrow et al., 2009). The crude oil with total acid number (TAN) above $1.0 \text{ mg KOH}\cdot\text{g}^{-1}$ is regarded as high acid crude oil, which leads to the serious corrosion on refinery equipment. Among various deacidification methods, catalytic esterification between alcohol and naphthenic acids has been proved to

be an efficient technique, due to its low-cost, environmental pollution-free and mild reaction conditions. Development of effective esterification catalysts for deacidification of crude oil has become of great interest to researchers.

Layered double hydroxides (LDH), also known as hydrotalcite-like compounds, are a group of anionic layered materials, which can be represented by the general formula $[\text{M}_2^+ \text{M}_x^{3+}(\text{OH})_2]^{x+}(\text{A}^{n-})_x/n\cdot\text{mH}_2\text{O}$, where M^{2+} and M^{3+} are di- and trivalent metal cations in the host layer, respectively, A^{n-} is interlayer exchangeable guest anions (Cavani et al., 1991). Due to the acid-base properties, LDH can be used as esterification catalysts for deacidification of crude oil. Zhu's group (Huang et al., 2011; Li et al., 2013) used MgAl and ZnAl LDH as esterification catalysts to remove acids from VGO and crude oil. They found the layered structure of LDH was beneficial to the esterification activity. Our group (Wu et al., 2011; Wang et al., 2015) also found MgAl and NiAl LDH were active for esterification between naphthenic acids and ethylene glycol (EG). However, the activity of LDH catalysts needs to be further improved.

It was demonstrated that HPW intercalated LDH catalysts show greater advantages over LDH or HPW alone, for example, the acidity of LDH can be effectively enhanced (Kagunya et al., 1996; Das and Parida, 2007) and the stability of HPW can be improved (Omwoma et al.,

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2014). Therefore, plenty of literature exists on the preparation of HPW intercalated LDH and their application as catalysts for Knoevenagel condensation (Jia et al., 2015), dyes degradation (Jia et al., 2015), oxidative desulfurization (Yu and Wang, 2013), epoxidation of allylic alcohol (Liu et al., 2009), NO reduction (Wongkerd et al., 2008), esterification of acetic acid (Das and Parida, 2007), oxidative bromination of phenol (Parida et al., 2006), etc. However, to date, there is no report on HPW intercalated LDH as esterification catalysts for deacidification of crude oil.

In this work, HPW intercalated MgAl, ZnAl and NiAl LDH with M^{2+}/Al^{3+} molar ratio of 2 were prepared and used as esterification catalysts for deacidification of crude oil. A characteristic XRD reflection at 8.4° corresponding to a basal spacing of 1.05 nm was observed in the as-prepared HPW intercalated LDH, which is quite different to that reported in almost all literature in which such reflection was attributed to HPA salts or polytungstate intercalated LDH. Additional experiments and characterizations were performed and the results demonstrated that this reflection should be ascribed to HPW intercalated LDH. In addition, the relationship between the esterification activity and acidity of HPW intercalated LDH was studied.

2. Experimental section

2.1. Sample preparation

Nitrate LDH precursors (LDH- NO_3) with M^{2+}/Al^{3+} ($M^{2+} = Mg^{2+}$, Zn^{2+} , Ni^{2+}) molar ratio of 2 were prepared by the co-precipitation method. A mixed solution containing $M(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ (1 M in total, $M^{2+}/Al^{3+} = 2$) was placed in a 500 ml three-neck flask. Then, a NaOH solution (2 M) was added dropwise to the flask at $40^\circ C$ under vigorous stirring. The resulting slurry was transferred into a Teflon-lined autoclave and aged at $100^\circ C$ for 12 h. The suspension was filtered, washed several times with water and finally dried at $80^\circ C$ for 6 h. The products were denoted as Mg_2Al-NO_3 , Zn_2Al-NO_3 and Ni_2Al-NO_3 , respectively.

HPW intercalated LDH (LDH-PW) were prepared by an ion-exchange method. 1.0 g LDH- NO_3 was dispersed in 50 ml water at $60^\circ C$ for 6 h. Subsequently, 50 ml HPW solution (0.02 M) with pH of 4.5, which was pre-adjusted by 0.1 M NaOH, was added to the above slurry under vigorous stirring. The pH of the mixture was kept at 4.5 by addition of 0.2 M HNO_3 . After that, the mixture was refluxed at $60^\circ C$ for 24 h under vigorous stirring. The resulting suspension was filtered, washed several times with water, and dried at $80^\circ C$ for 6 h under vacuum. The products were named as Mg_2Al-PW , Zn_2Al-PW and Ni_2Al-PW , respectively. All the water used in the synthesis process is CO_2 -free and deionized.

2.2. Characterization

X-ray diffraction (XRD) patterns were obtained on an X'PERT PRO diffractometer (Panalytical, Netherlands) equipped with an X'Celerator detector, using Cu $K\alpha$ and operating at 40 kV and 40 mA. The data were recorded in the range of 2θ from 5° to 70° with a 0.02° per step and counting time 12 s each step.

Fourier transform infrared spectra (FT-IR) were recorded on a WQ520 spectrophotometer (Beifen, China) in the range of 4400 to 400 cm^{-1} with a resolution of 2 cm^{-1} .

Raman spectra were recorded on a Raman micro IM-52 spectrometer (Oceanoptics, USA) with a He-Ne laser operating at 785 nm and power of 11 mW.

Solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) spectrum for ^{31}P was recorded on an AV III-500 spectrometer (Bruker, Switzerland) equipped with a 4 mm MAS probe.

The chemical composition (Mg, Zn, Ni, Al, W and P) of LDH was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on an Optima 7300 V spectrometer (PerkinElmer,

USA).

Thermogravimetric and differential scanning calorimetry (TG-DSC) were carried out on a STA-449F3 thermal analyzer (Netzsch, Germany). About 10 mg sample was loaded in an alumina crucible and heated at a rate of $10^\circ C \cdot \text{min}^{-1}$ from 40 to $750^\circ C$ under an air flow of $60\text{ ml} \cdot \text{min}^{-1}$.

Scanning electronic micrograph (SEM) images were obtained on an EVO MA15 instrument (Carl Zeiss, Germany). Before testing, samples were dispersed in cyclohexane by sonication and then a drop of suspension was deposited on a brass holder and sputtered with gold.

The strength and amount of acid sites of LDH were determined by Hammett indicator and n-butylamine titration technique. Crystal violet ($pK_a = 0.8$), bromophenol blue ($pK_a = 3.86$), methyl red ($pK_a = 4.8$) and bromthymol blue ($pK_a = 7.2$) were used as indicators. Samples were ground into fine powder and sieved to pass through a 100 mesh sieve. Before measurement, the samples were heated at $120^\circ C$ for 2 h under vacuum.

2.3. Catalytic activity

Crude oil was provided by Suizhong oilfield, whose TAN, density and water content is $2.38\text{ mg KOH} \cdot \text{g}^{-1}$, $0.97\text{ g} \cdot \text{cm}^{-3}$ at $20^\circ C$ and 0.28 wt%, respectively. For the catalytic esterification reactions, 20 g crude oil, 0.2 g catalyst and 1 ml EG were placed into a 250 ml three-neck flask equipped with an electric motor stirrer, a thermometer and a condenser connected with a water separator. Then, the mixture was heated to $180^\circ C$ and kept at this temperature for 2 h. After reaction, the catalyst was recovered by filtration and washing with xylene several times to remove the residual crude oil. The TAN of oil was measured according to ASTM D664.

The kinetic experiment of esterification between crude oil and EG was performed under the condition of 50 g oil, 0.5 g catalyst, 2.5 ml EG and $180^\circ C$. The oil sample was periodically withdrawn at the interval of 20 min and then its TAN was measured. Before the kinetic experiment, a series of preliminary experiments were performed to reduce the mass transfer limitation. It is found that the stirring speed above 300 rpm and the particle size of catalyst below 40 mesh can eliminate the external and internal diffusion influences and ensure the reaction under kinetics-controlled regime. Therefore, the kinetic experiment was carried out at the stirring speed of 400 rpm and the catalyst was ground to 40–60 mesh. The concentration of naphthenic acids (C_A) was calculated by the TAN and density of crude oil (Huang et al., 2011). According to the reference (Li et al., 2013), when EG is far excess of stoichiometric amount, the kinetics of esterification between naphthenic acids and EG can be described as follows, wherein k and n represent the rate constant and reaction order, respectively.

$$r_A = -\frac{dC_A}{dt} = kC_A^n \quad (1)$$

3. Results and discussion

3.1. XRD

The XRD patterns of LDH- NO_3 and LDH-PW are shown in Fig. 1. All LDH- NO_3 samples exhibit the typical patterns of layered structure with strong reflections at the lower 2θ range. The value of basal spacing of the (003) plane (d_{003}) is 0.89 nm, in agreement with that reported in the literature (Yang et al., 2003). Compared with LDH- NO_3 , the (003) reflections of LDH-PW (Fig. 1b) shift to lower angles around 8.4° corresponding to the d_{003} value around 1.05 nm.

It's worth noting that the shortest van der Waals diameter for a Keggin ion is around 0.99 nm (Pope, 1983), taking account into that the layer thickness of LDH is 0.48 nm (Cavani et al., 1991), the d_{003} value for LDH intercalated with Keggin ions should be around 1.47 nm, as reported by most researchers (Liu et al., 2009; Liu et al., 2007; Narita

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