Research Paper

Catalytic activity and surface characteristics of layered Zn–Al–Si materials supported platinum

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ABSTRACT

The present work aims at the preparation and characterization of novel catalysts based on layered double hydroxide structures (LDHs) containing Zn^{2+}, Al^{3+} and Si^{4+} cations in host layers and platinum species supported over the surface of these structures. LDHs with different Zn/Al/Si ratios were prepared via a co-precipitation method. Characterization of Zn–Al–Si layered double hydroxides was carried out using energy-dispersive X-ray spectrometry, X-ray powder diffraction, infrared spectra, thermal analyses and scanning electron microscopy. Experimental results revealed the presence of only crystalline phases of layered double hydroxides containing about 20–40 mol% of aluminum and silicon. These novel materials are commonly used as supports for platinum catalysts. Layered double hydroxide supported platinum samples were characterized through nitrogen adsorption–desorption, X-ray powder diffraction, infrared spectra and thermal analyses. The activity of the prepared platinum catalysts was tested through cyclohexane dehydrogenation and n-hexane cracking using a pulse flow system. Our results suggested that the Zn–Al–Si layered double hydroxides have a positive catalytic effect towards dehydrogenation.

1. Introduction

Layered double hydroxides, also known as anionic clays or hydrotalcite (HT)-like compounds, are a class of synthetic, two-dimensional, nano-ordered layered materials whose structure can be described as brucite-like layers (Benito et al., 2010; Dávid et al., 2010; Ha and Xanthos, 2010; Hibino, 2010). In these materials, a fraction of the divalent cations octahedrally coordinated by hydroxyl groups have been replaced isomorphously by trivalent cations, giving positively charged layers with charge-balancing anions between them. Some hydrogen bonded water molecules may occupy any remaining free space in the interlayer region (Warmuth and Schollhorn, 1994; Octávio et al., 2010; Xu and Braterman, 2010; Zhang et al., 2010a). LDHs may be represented by the general formula $(M^{2+}_{1-x} M^{3+}_x (OH)_2)^{x+} (A^{n-})^{x/n} \cdot mH_2O$, where M^{2+} and M^{3+} are di- and trivalent cations, respectively, and the value of x is equal to the molar ratio of $M^{2+}/(M^{2+} + M^{3+})$ falling in the range of 0.2–0.33, and A^{n-} is an anion. As a result, a large class of isostructural materials, which can be considered complementary to aluminosilicate clays, with widely varied physicochemical properties can be obtained by changing the nature of the metal cations and the type of interlayer anions.

LDHs are promising materials for a large number of practical applications such as catalysis, adsorption, pharmaceutics, photo-chemistry, and electrochemistry (Cavani et al., 1991; Carrado and suib, 1998; Choudary et al., 2004a,b; Manivannan and Pandurangan, 2009; Wang et al., 2009; Kong et al., 2010; Stimpfling and Leroux, 2010; Tong et al., 2010a,b; Zhang et al., 2010b; Zhou, 2010). In the case of catalysis, LDHs represent an inexpensive, versatile and potentially recyclable source of widely used catalyst supports (Kapoor and Matsumura, 2004; Motokura et al., 2004), catalyst precursors (Takehira et al., 2004; Li et al., 2005; Basile et al., 2010) or actual catalysts (Costantino et al., 2003; Kirm et al., 2004; Zhan et al., 2009). A great amount of research on LDH derivatives has been devoted to the development of new catalytic materials (Rives and Ulibarri, 1999; Sels et al., 2001).

Aluminosilicate structures have many applications, and they are well-known in the literature as cationic clays, zeolites, or mesoporous materials (Tong et al., 2010a,b) however, there is no data for aluminosilicates as anionic clay. Following this line, the present work aims at the preparation and characterization of novel catalysts based on layered double hydroxide structure containing Zn^{2+}, Al^{3+} and Si^{4+} cations in host layers with different ratios of Zn/Al/Si carbonate anions as the guests as well as platinum species supported over the surface of these structures. Moreover, the catalytic activities of these catalysts for both the dehydrogenation of cyclohexane and for the cracking of n-hexane were investigated.

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2. Experimental methods

2.1. Materials

Zn–Al–Si LDHs were synthesized using a co-precipitation method at a high temperature by reacting aqueous solutions (0.07 mol) containing a mixture of zinc chloride, aluminum chloride and silicon chloride as metal precursors and urea (0.5 mol) as a precipitant and pH-controller (Saber, 2009; Saber and AlJaafari, 2009). The temperature of the mixture was adjusted to 90 °C for 24 h. The percentages of both aluminum and silicon were 10–35 mol% as shown in Table 1. For simplicity, the samples were denoted as ZA(x)S(y), where x and y are the percentages of aluminum and silicon, respectively.

2.2. Platinum loading

For platinum loading, the pretreated support was impregnated with a 0.002 M solution of $H_2PtCl_6 \cdot 6H_2O$. An appropriate volume of impregnating solution was added to the supports to obtain a 0.6 wt.% Pt in the final catalysts. The mixture was stirred for a few minutes, dried at 110 °C for 16 h and calcined at 450 °C for 2 h. Calcination before reduction was conducted to remove the water molecules that were still contained in support pores and to allow the stabilization of active sites. The Pt (IV) ions become very mobile in the presence of water at higher temperature, thereby leading to agglomeration of metallic Pt particles (Gobara, 2006; Gomaa and Gobara, 2008). The oxide samples were then reduced at 350 °C in a stream of purified dry hydrogen gas with a flow rate of 100 mL/min for 4 h.

2.3. Characterization

Powder X-ray diffraction (XRD) spectra were registered between 1.8° and 50° on a Rigaku RINT 2200 using CuKα (filtered) radiation ($\lambda = 0.154$ nm) at 40 kV and 20 mA. Thermal analyses (TG, DTG, and DTA) of nano-layered materials up to 800 °C were carried out at a heating rate of 10 °C/min in a flow of nitrogen using a Seiko SSC 5200 apparatus. DSC–TGA analyses were carried out for all supported metal oxide samples using simultaneous DSC–TGA SDTQ 600 (USA) under N_2 atmosphere, with a heating rate of 10 °C min⁻¹. FT-IR spectra (KBr disc method) were recorded on a Horiba FT-720. Scanning electron microscopy (SEM) was performed with a JEOL: JSM-6330F (15 kV/ 12 mA). The SEM/EDS measurements were carried out with a JEOL JED-2140. Nitrogen adsorption–desorption isotherms at 77 K (−196 °C) were obtained with a NOVA 3200 apparatus (USA). The

Fig. 1. X-ray diffraction patterns of Zn–Al–Si LDH with different percentages of aluminum and silicon: (a) 25%, (b) 30%, (c) 40% and (d) 70%.

samples were previously degassed under vacuum at 200 °C for 4 h. Surface areas (S_{BET}) were calculated from multi-point plots at relative pressures (P/Po) ranging from 0.05 to 0.30. Pore size distribution was calculated with the Barrett, Joyner and Halenda (BJH) method using the adsorption branch of the isotherms.

2.4. Catalytic processes

Catalytic activity of all samples was tested through n-hexane cracking and cyclohexane dehydrogenation as two model reactions using a micro catalytic pulse-flow system. The reactor effluent was passed through a chromatographic column for separation and determination of products using a flame ionization detector connected to a computerized data acquisition station. The column length was 200 cm, had an internal diameter of 0.3 cm, and contained acid washed PW Chromosorb (60–80 mesh size) loaded by 15 wt.% Squalane. The reactions were carried out under atmospheric pressure at temperatures ranging from 250 to 450 °C. The hydrogen flow rate was kept constant at 50 mL/min. Prior to catalytic activity tests, the reduced catalyst samples were activated by heating in H_2 for 2 h at 450 °C. The chromatographic column temperature was adjusted and controlled at 50 °C.

3. Results and discussion

3.1. X-ray powder diffraction

There are no XRD results reported in the literature for Zn–Al–Si LDH. However, the XRD results of ZA(15)S(10), ZA(15)S(15) and ZA(20)S (20) are similar to those of previously published for Zn–Al LDH (JCPDS
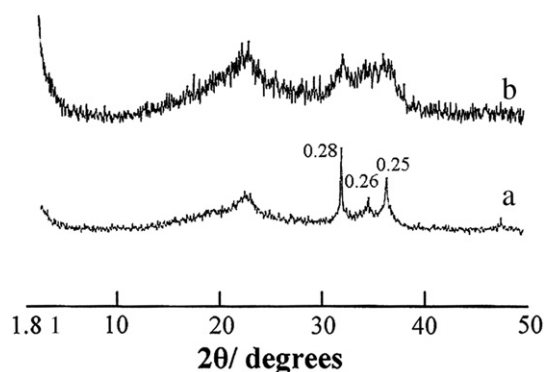
Fig. 2. X-ray diffraction patterns of Zn–Al–Si LDH after calcinations at 500 °C: (a) sample with aluminum and silicon 25%, and (b) sample with aluminum and silicon 30%.

Table 1
X-ray diffraction data for Zn–Al–Si LDHs and surface parameters for their samples supported platinum with different ratios of Zn:Al:Si.

Sample	mol%			d_{003} (nm)	C (nm)	S_{BET} (m²/g)	S_{BJH} (m²/g)	S_t (m²/g)	V_p (ml/g)	R_p (nm)
	Zn	Al	Si							
Pt/ZA(15)S(10)	70	15	10	0.776	2.328	54.4	288.6	54.4	0.224	9
Pt/ZA(15)S(15)	70	15	15	0.785	2.355	68.7	241	68.7	0.235	6.9
Pt/ZA(20)S(20)	60	20	20	0.764	2.292	123	197	123	0.308	5.0
Pt/ZA(35)S(35)	30	35	35	–	–	141	346	141	0.412	5.8

C: the thickness of the brucite-like layer and the interlayer distance, which is commonly calculated as three times the spacing for plane (003).
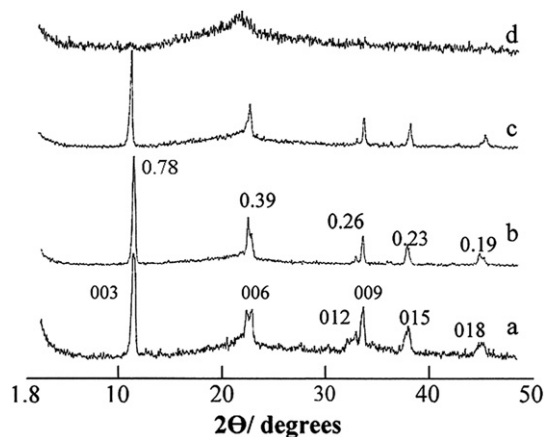S_{BET}: specific surface area according to Brunauer Emmit Taylor equation.
BJH: surface area calculated by applying Barrett–Joyner–Halenda method.
S_t: specific surface area calculated by applying t-method.
Vp: total pore volume, taken at 0.99 P/Po of the adsorption isotherm.
Rp: average pore size.