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Characterization of Al, Cr-pillared clays and CO oxidation

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ABSTRACT

Bentonite from Turkey was used in pillared clay synthesis by use of single and mixed oxide pillars of aluminium and chromium. X-ray photoelectron spectroscopy (XPS) confirmed that chromium was in two different oxidation forms, while energy dispersive spectroscopy (EDS) indicated the dispersion of chromium on the surface of the pillars and the clay mineral layers. The basal spacing of montmorillonite, and as a result, the specific surface area values were increased by pillaring. The microsurface area and micropore volume values occupied a considerable part of the total values. Nitrogen adsorption/desorption studies and scanning electron microscopy (SEM) images confirmed that the micropore and mesopore size distributions were not affected by synthesis conditions. Fourier transform infrared spectroscopy (FTIR) showed the presence of Brønsted and Lewis acid sites. The maximum conversion of carbon monoxide was observed with the use of a pillaring solution having a Cr/Al ratio of 0.33.

1. Introduction

Due to their molecular sieve properties, high surface area and physical/chemical adsorption sites, pillared clays (PILCs) found many applications as adsorbents, catalysts and catalyst supports (González and Moronta, 2004; Salerno et al., 2004; Manohar et al., 2006). Generally, smectites are used due to their swelling properties and high cation exchange capacity (Figueras, 1988; Bergaya et al., 2006). Although attention is usually focused on pillaring with monometalic pillars, there are some advantages of PILCs composed of mixed polycations. First, the thermal, hydrothermal and catalytic properties of the PILCs can be increased by the use of mixed metal pillaring agents. While one of the pillars' components provides structural and thermal stability with the desired pore structure, the catalytic/adsorbing sites result from the correct choice of a second pillaring source. The structural and acidic properties of Al-PILC are improved by use of second pillaring agents derived from transition metals such as Fe, Cr, Si, Ti, Zr etc. (Kloprogge, 1998; Gil et al., 2000). Chromium is interesting for catalytic applications because of the different oxidation states (Mata et al., 2007). The literature shows that Al-PILCs have high thermal stability (Ding et al., 2001). Whereas Cr-PILCs are stable only to about 200 °C especially after calcination in air 200 °C (Sychev et al., 1997a; Roulia, 2005; Mata et al., 2007). Thermal stability of PILCs containing chromium was enhanced by the addition of aluminium pillars (Gil et al., 2000; Ding et al., 2001).

The catalytic activities of PILCs containing chromium and/or aluminium have been tested in reactions such as the toluene disproportionation (Auer and Hofmann, 1993), deep oxidation of methylene chloride (Storaro et al., 1997), tiophene hydrodesulfurization (Sychev et al., 1997b), 2-propanol and methanol dehydration (Mishra and Parida, 1998), hydrocracking of heavy liquid fuels (Gyftopoulou et al., 2005), carbon monoxide oxidation (Carriazo et al., 2007a, 2007b; Pérez et al., 2008). Beside the catalytic activity, adsorption properties of PILCs containing aluminium and/or chromium are reported in the literature (Karamanis and Assimakopoulos, 2007; Bouchenafa-Saïb et al., 2007; Arfaoui et al., 2008; Guerra et al., 2008). Adsorption of copper and zinc ions from aqueous solutions were was tested by the activated clays from Middle Anatolian (Noyan et al., 2006, 2007; Veli and Alyüz, 2007).

In the present study, Al-, Cr- and Cr/Al-mixed PILCs syntheses were carried out and the effects of the synthesis conditions on their physicochemical and structural properties were analyzed by XRF, EDS, XPS, XRD, N_2-sorption, SEM and FTIR techniques. Oxidation of carbon monoxide is required for air cleaning, purifying of reformer gases for fuel cell application (Gulari et al., 1999). In the present study, the effectiveness of the some samples in a simple CO oxidation reaction was tested.

2. Experimental

Bentonite from the Hancili region (Central Anatolia, Turkey), called Hancili Green Bentonite (HGB), was used as the starting material for the PILC synthesis. Some physicochemical and mineralogical

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characteristics of HGB were previously reported (Tomul and Balci, 2008). A bentonite sample was mixed with 1 M $CaCl_2$ solution (1/11 g/cm^3) for 24 h. The Ca-saturated bentonite was washed with deionized water until excess chloride ions were removed (silver nitrate test), and dried at room temperature (Tomul and Balci, 2008).

2.1. PILCs synthesis

As described by Zhao et al. (1995), the Al-pillaring solution was prepared by slow addition (0.5 $cm^3 cm^3 min^{-1}$) of 0.4 M NaOH solution to 0.4 M $AlCl_3 \times 6H_2O$ solution under vigorous stirring until the molar ratio of OH^-/Al^{3+} reached 2.4, followed by aging for 14 days at room temperature. The Cr-pillaring solution was prepared by adding 0.4 M Na_2CO_3 dropwise (0.5 $cm^3 min^{-1}$) to 0.4 M $CrCl_3 \times 6H_2O$ solution under vigorous stirring until a pH of 4.10 was reached. The solution was aged 7 days at room temperature and then aged at 120 °C for 4 h before use. The Cr/Al-pillaring solutions were prepared by adding the Cr-pillaring solution to the Al-pillaring solution to obtain Cr/Al ratios of 0.33, 1.0 and 3.0, and stirring for 2 h at room temperature. The mixed metal pillaring solutions were aged in the same way like the Cr-pillaring solution.

The Ca-saturated bentonite (HGB) was dispersed in demineralized water (0.3% w/w), and the pH of the bentonite suspension was adjusted to 7.10 by the dropwise addition of HCl or NaOH solutions (0.01 mol dm^{-3}) and then allowed to rest for 14 days to maximize swelling. The pillaring solutions were slowly added to the bentonite suspension under stirring at room temperature, maintaining a ratio of 3 mmol of total metal per gram of bentonite, and stirred for 2 h at room temperature and another 2 h at 70 °C. The suspension was left overnight at room temperature. The ion-exchanged bentonite samples were vacuum filtered, washed with deionized water until excess chloride ions were removed (as confirmed by the silver nitrate test), and dried at room temperature before calcination at 300 and 500 °C for 2 h.

2.2. Characterizations

The chemical compositions of the bentonite were determined by Philips X' Cem X-ray fluorescence spectroscopy (XRF) and the pillared clays by JEOL JSM-6400 energy dispersive spectroscopy (EDS) and SPECS X-ray photoelectron spectroscopy (XPS). X-ray diffraction (XRD) patterns were obtained with a Phillips PW 3710 diffractometer using Cu-Kα radiation. Semi-quantitative percentages of the clay were calculated by means of mineral intensity factors suggested by Yalçın and Bozkaya (2002) based on the external standard method of Brindley (1980). The textural properties of samples degassed at 300 °C for 5 h were studied by N_2-sorption measurements at 77 K within P/P_0 values of 10^{-5}–0.999 in a Quantachrome Autosorp 1C. The total pore volume (V_t) was estimated from the desorption data at P/P_0 values of ~0.99. The specific BET surface area was calculated in the range P/P_0 of 0.05 to 0.30. The mesopore surface area (S_{BJH}), mesopore size distribution and mesopore volume ($V_{m,\ BJH}$) were estimated by the Barrett–Joyner–Halenda (BJH) method from desorption data within P/P_0 of 0.96–0.20. The micropore size distribution and micropore volume ($V_{\mu,SF}$) were estimated by the Saito–Foley (SF) method (Rauquerol et al., 1999). The total (from the slope of the first linear segment, S_t) and external surface area (from the slope of the second linear segment, S_{ext}) and micropore volume (from the intercept of the second linear segment, V_μ) values were determined from the *t*-plot using de Boer thickness. The micropore surface area (S_μ) was found from the difference between specific BET surface area and the external surface area (Rauquerol et al., 1999). The scanning electron microscopy (SEM) microphotographs were obtained in a Philips XL-30S FEG using powder samples without coating. FTIR spectrums spectra of both bentonite and PILC samples with and without 1-week of pyridine sorption (at room temperature under the vacuum) were taken in the range of 400–4000 cm^{-1} with an Ati Unicam Mattson 1000 FTIR spectrometer using the KBr pellet technique. The FTIR spectrum of all the samples were was taken on the same day under the identical conditions.

Table 2
Al 2p and Cr 2p binding energies and Cr and Al atom % values of Al-PILC, Cr/Al-PILC (0.33) and Cr-PILC

	Binding energies (eV)			Atom % (EDS)		Atom % (XPS)	
	Al 2p	Cr 2p		Al	Cr	Al	Cr
Al-PILC	75.3	–	–	9.61	–	10.2	–
Cr/Al-PILC(0.33)	74.4	579.0	577.2	8.75	3.00	8.2	1.3
Cr-PILC	75.3	579.0	577.2	6.52	4.43	7.3	2.0

2.3. Catalytic application

CO oxidation of calcined Al-, Cr-, and Cr/Al-PILCs at 300 °C was performed in a fixed bed tubular reactor (Güldür and Balıkçı, 2003). A typical gas mixture (1% CO, 21% O_2 and 78% He) was passed through the bed, which was composed of 50 mg of catalyst packed between two quartz wool plugs, at a total flow rate of 25 cm^3 min^{-1} (SV=45 000 h^{-1}). CO oxidation was studied at 100 °C–550 °C with a heating rate of 15 °C min^{-1} and with 30 min dwell time at the selected reaction temperature. Composition of the products was determined using a Clarus 500 Perkin Elmer Gas Chromatography with thermal conductivity detector.

3. Results and discussion

3.1. Physicochemical properties of bentonite and pillared bentonite

The chemical analysis (determined by XRF and EDS) results of HGB and PILCs are presented in Table 1. The mild greenish color of the bentonite came from the high iron content. The high Na_2O content (2.81%) and the basal spacing value at room temperature (1.24 nm, 2θ 2θ=7.12°) indicated that the bentonite was in the Na^+ form. The high SiO_2 content (66.95%) with reflections around 2θ=26.6°, and 2θ=28° indicated the presence of quartz (appr. 11%), feldspar (appr. 14%)

Table 1
Chemical properties of bentonite and PILCs

Sample	Cr/Al in pillaring solution	Metal oxides %								
		SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	Cr_2O_3	SiO_2/Al_2O_3 (Cr free basis)
HGB	Host	66.95	18.38	6.11	2.75	1.80	2.81	1.19	–	3.64
Al-PILC	–	63.31	23.65	8.47	1.71	0.80	1.09	0.97	–	2.68
Cr/Al-PILC (0.33)	0.33	59.36	20.93	6.06	1.93	0.00	0.00	1.01	10.72	2.84
Cr/Al-PILC (1.0)	1.0	57.22	15.82	6.58	1.68	0,54	1.50	0.97	15.69	3.62
Cr/Al-PILC(3.0)	3.0	60.24	15.48	5.78	1.54	0.84	1.67	1.21	13.25	3.89
Cr-PILC	–	58.09	15.35	5.44	1.24	0.44	3.06	0.82	15.57	3.78