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Research paper

Development of Mn or Fe sulfides in the interlayer space of raw and Alpillared bentonite



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ABSTRACT

Preparation of metal sulfide nanoclusters (Mn or Fe) confined in the interlayer space of a bentonite either with or without previous Al₂O₃-pillaring was investigated by H₂S-sulfidization of Mn²⁺- or Fe²⁺-exchanged Al₂O₃-pillared bentonite as potential strategy to control growth and mean final size of interlayered, MnS or FeS-like polynuclear nanoclusters. The materials were characterized by elemental analysis, cation exchange capacity, low-angle powder X-ray Diffraction, N₂ adsorption isotherms, simultaneous thermal analysis (DTA/TGA), diffuse reflectance UV-vis spectroscopy and high-resolution X-ray photoelectron spectroscopy. Interlayered metal sulfides were successfully obtained in pretty short time of reaction (only ~12 h). Optimal set of preparation conditions was established promoting stabilization of the interlayered metal sulfides, whereas preserving typical layered stacking of the starting clay: (i) ratio $H_2S/M_{(incorporated)}^{2+} = 50 \text{ mol/mol}$ (M = Mn²⁺ or Fe²⁺); (ii) temperature of sulfidization = 100 °C; (iii) 200 °C for final thermal treatment, irrespective the type of atmosphere used (inert-N₂ or oxidizing-air) and (iv) acid-base neutralization prior to thermal treatment did not enhance thermal stability. The most efficient Al-pillaring was achieved with 20 meq Al³⁺/g clay in terms of both higher XRD 001 basal reflection and narrower distribution of alumina-pillars. HR-XPS and DR-UV-vis analyses of the best materials with every transition metal evidenced formation of polysulfide groups and blue-shift of the absorption signal as a consequence of the modification performed on the layered aluminosilicate.

1. Introduction

Transition metal aggregates with low number of atoms have attracted great interest, as constituting a very particular kind of new state of matter with very special physicochemical properties (Galeano et al., 2011; Viswanatha et al., 2008; Wang et al., 2009; Xia et al., 2003). The preparation of metal nanoclusters is very thermodynamically unstable because of their characteristic trend of unlimited growth. Recent studies have proposed that it could be controlled by preparing them inside confined spaces of well-defined dimensions. In this sense, it has been suggested (Khaorapapong et al., 2009; Khaorapapong et al., 2008a, 2010, 2011) that the confinement of metal nanoclusters within the interlayer space of clay minerals followed by annealing might lead to a new type of expanded clay minerals with similar final structure as the conventional pillared clays (Barrault et al., 2000). Likewise, it may allow higher stability as well as control on the size of the grown metal aggregates, thanks to the tailored dimensions of the interlayer space in either raw or previously modified hosting aluminosilicate (Pillared Interlayered Clay, PILC) (Iacomi et al., 2006). Thus, the immobilization of metal sulfides within restricted spaces including those featured by clay minerals has become very attractive. Hence, incorporation of metal sulfides in silica (Hirai et al., 1999; Zhang et al., 2001), clay minerals (Stramel et al., 1986) and polymers (Antolini et al., 2005; Hirai et al., 2001) has been reported. Thin-films of metal sulfides have also been prepared by several methods for high-performance optical devices (Chavhan and Sharma, 2005; Öznülüer et al., 2006; Su and Choy, 2000). The metal sulfides at the nanoscale have been reported to display unique optical and electrical properties, as well as a variety of potential applications in electroluminescence (Lou et al., 2003) and non-linear optical devices (Chin et al., 2001). It is well-known that physical and optical properties of these metal sulfides depend in a great extent on the particle size; therefore, their successful trapping within confined spaces may indirectly control their final properties and applications (Khaorapapong et al., 2009).

As long as the presence of sulfur in fossil-based fuels is still one of the main causes of environmental pollution in many countries, the development of catalytic systems able to deplete such contents in fuels up to levels environmentally acceptable has become very important. In

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this sense, some transition metal sulfides, mainly cobalt, nickel, molybdenum and/or tungsten-based have been successfully employed as very active phases of hydrotreating catalysts (Infantes-Molina et al., 2012). It undoubtedly constitutes another field where nanosized metal sulfides might find interesting catalytic application. Likewise, Romero (Romero-Pérez et al., 2012) prepared supported RuS₂ on Al-pillared clays in order to study their performance as catalysts of the dibenzothiophene hydrodesulfurization and the influence of the added Al on the catalytic activity. So far, the preparation of several polynuclear metal sulfides on variety of supports including montmorillonites, zeolites and silicas has been developed using various experimental approaches. It is worth mentioning the solid-state reaction as reported by Khaorapapong et al. (Khaorapapong et al., 2009; Khaorapapong et al., 2008a, 2010, 2011; Khaorapapong et al., 2008b) and Kabilaphat et al. (Kabilaphat et al., 2015), who introduced the targeted metal by cation exchange on the montmorillonite as a first step, followed by hand grinding with solid sodium sulfide in agate mortar, yielding the sulfide product after four months. Meanwhile, Iacomi et al. (Iacomi et al., 2005) carried out almost the same reaction but in solid-liquid system using zeolites as supports, metal ion exchange at 23 °C and final sulfidization with dissolved Na₂S at room temperature, employing a solid to liquid ratio (s/l = 1/50) for 12 h. A little bit later, the same authors (Iacomi et al., 2006) reported formation of MnS clusters within laumontite holes by using almost the same procedure but slightly changing the sulfidization step to H_2S (40 cm³/min) at 77 °C along 12 h. This procedure was later adapted (Galeano et al., 2011) introducing polynuclear aggregates of MnS in raw calcium-rich bentonite. High metal uptake efficiency was achieved, with high specific location of the metal clusters in the clay's interlayer space and interesting performance of final solids activating catalytic wet peroxide oxidation of aqueous methyl orange with hydrogen peroxide, at room temperature and pressure.

Accordingly, this work was devoted to study the influence of the following experimental parameters on the final structure of sulfided Fe^{2+} or Mn^{2+} -exchanged bentonite, with or without previous pillaring with Keggin-like $(Al_{13})^{7+}$ ions: (i) molar ratio H_2S/M^{2+} (incorporated) ($M = Mn^{2+}$ or $Fe^{2+}_{(incorporated)}$ in the range 5–500); (ii) temperature of sulfidization (50–400 °C); (iii) temperature and atmosphere of thermal treatment (200–400 °C; N_2 or air); (iv) acid-base neutralization prior to thermal treatment; (v) different density of pillars on the starting expanded clay and (vi) use of a common ramp for H_2S streaming and final thermal treatment.

2. Experimental section

2.1. Materials

A Colombian bentonite previously refined twice by particle size ($\leq 2 \mu m$) separation, with cation exchange capacity, CEC, of 82 meq/ 100 g (dry-basis) was used as starting mineral (denoted BV-E). The elemental composition (X-ray Fluorescence, XRF, dry-basis) was determined as explained later. The material was modified using AlCl₃.6H₂O (99%, Sigma-Aldrich®), Na₂S·9H₂O (technical grade, TC Químicos), MnCl₂.4H₂O (98%, Sigma-Aldrich®), FeSO₄.7H₂O (99.5%, Panreac®), HCl (37%, Panreac®), N₂ (99.999%, Cryogas®) and synthetic air (mixture 79.0% of N₂ 99.999% and 21% of O₂ 99.6 +/- 0.5% of absolute accuracy, Cryogas®), all used as received.

2.2. Preparation of modified materials

In order to assess the effect of the pillar density, the starting mineral (BV-E) was interlayered and pillared (thermal treatment) by Al using three nominal loadings of 10 (AlP10), 20 (AlP20) or 30 (AlP30) meq Al^{3+}/g clay, mainly represented as $(Al_{13})^{7+}$ Keggin-like polycations (the intercalated materials, prior of the final heating step, were denoted as Al–I10, Al–I20 and Al–I30). The preparation of the pillared clays was carried out following a standard procedure described elsewhere

Table 1

Physicochemical properties of manganese-modified solids and starting mineral: SiO_2 normalized contents of Al_2O_3 and MnS, cationic exchange capacity, compensation of CEC and XRD-basal d-value.

Sample	Content (wt%) ^a		CEC ^b	CC ^c (%)	d_{001}^{d}
	Al ₂ O ₃	MnS	(ineq/ 100 g)		(IIII)
BV-E	31.82	0.04	82	_	1.56
AlP10	39.75	0.08	52	37	D
AlP20	41.35	0.12	37	55	1.83
AlP30	47.42	0.13	8	90	1.72
AlP20-Mn	40.75	7.28	45	45	1.63
AlP20-Mn(5)S100	-	-	15	66	1.53
AlP20-Mn(50)S100	-	-	7	84	1.60
AlP20-Mn(500)S100	-	-	29	35	D
AlP20-Mn(5)S100-350	-	-	37	18	1.52
N ₂					
AlP20-Mn(50)S100-350	-	-	9	80	-
N ₂					
AlP20-Mn(500)S100-	-	-	4	91	D
350 N ₂					
AlP20-MnS50-200 N2	40.70	3.63	9	80	1.49
AlP20-MnS100-200 N ₂	41.09	2.70	8	90	1.59
AlP20-MnS-150-200 N ₂	37.78	3.78	10	88	1.57
AlP20-MnS400	41.17	3.58	17	79	D
AlP20-MnS100-200Air	44.71	3.03	7	91	1.61
AlP20-MnS100-400 N2	38.86	2.89	14	82	D
AlP20-MnS100-400Air	44.27	3.29	15	82	D
AlP20-MnS100-n-200 N2	38.58	3.80	13	84	D
AlP10-MnS100-200 N2	44.44	2.55	54	34	D
AlP30-MnS100-200 N2	50.38	2.31	68	17	1.58
BV-Mn	30.17	4.92	29	64	D
BV-MnS100-200 N2	28.63	3.91	60	27	D

^a All contents are normalized to the SiO₂ content in the starting clay BV-E in order to rule-out dilution effect produced by incorporation of either Al, S and Mn upon modification. Determined by atomic absorption spectroscopy (AAS), dry basis.

^b CEC: Cationic Exchange Capacity (dry-basis).

^c CC: Compensation of CEC.

^d Obtained from oriented specimens. D: Delaminated material.

(Galeano et al., 2010). First of all, the intercalating agent was prepared by hydrolysis of 0.2 mol/dm³ AlCl₃.6H₂O at 70 °C under gentle stirring with 0.2 mol/dm³ NaOH poured dropwise to get a final ratio OH⁻/Al³⁺ = 2.4. The mixture was then further aged under stirring at the same temperature for 2 h. Afterwards, the solution was dropped on 2.0% w/v dispersion of BV-E bentonite previously swollen in distilled water under stirring for 2 h at room temperature. The resulting interlayered material was washed in dialysis tubing cellulose membrane (average flat width 43 mm, Sigma[®]) until the conductivity of the washing water decreased below 35 µS/cm, dried at 60 °C and finally heated at 500 °C for 2 h.

The starting clay as well as the three pillared clays were then employed as supports to grow and immobilize either the Mn (yielding AlPD-MnSX-Tatm series of materials, where D = pillar density; X = temperature of sulfidization; T = temperature of final thermal treatment; atm = atmosphere used in final thermal treatment) or the Fe sulfide clusters (yielding AlPD-FeSX-Tatm series of materials) (see Tables 1 and 2, respectively). In the case of Mn-series, an extra group of samples was first prepared in order to determine the optimal molar ratio $H_2S/(Mn^{2+} \text{ or Fe}^{2+})_{(incorporated)}$; for instance, sample AlP20-Mn (5)S100-350 N₂ was prepared from AlP20-pillared bentonite, sulfidized at 100 °C under $H_2S/(Mn^{2+})_{(incorporated)}$ molar ratio = 5.0 and finally thermally treated at 350 °C under nitrogen as inert atmosphere.

The Mn^{2+} and Fe^{2+} ions were introduced in the minerals (either, starting or pillared) by cation exchange. The procedure was adapted from the one originally reported by Iacomi et al. (Iacomi et al., 2005) to develop clusters trapped inside zeolite structures. It began with cation exchange of every solid with aqueous 0.5 mol/dm³ MnCl₂.4H₂O or FeSO₄.7H₂O (5.0 cm³ solution/g clay) throughout 8 h under constant stirring at room temperature. In this research, the starting

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