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Nanoparticles of iron and vanadium oxides supported on iron substituted LDHs: Synthesis, textural characterization and their catalytic behavior in ethylbenzene dehydrogenation

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ABSTRACT

Nanostructured catalysts derived from nanoparticles of iron or vanadium oxides supported on the matrices of iron substituted hydrotalcite-like anionic clays (layered double hydroxides, LDHs) have been obtained and tested in the process of ethylbenzene dehydrogenation to styrene. A simple synthesis method based on the LDHs "memory effect" has been used to prepare the new oxides-anionic clay structures. TEM analysis shows that on the typical FeLDH particles (average size equal to 75 nm) smaller nanoparticles are supported; their average size is equal to 7 and 11 nm for Fe/FeLDH and V/FeLDH respectively. XPS analysis indicates the presence of Fe_2O_3 and V_2O_3 on the surface of the supported LDHs. N_2 adsorption at 77 K reveals that the supported anionic clays have less accentuated mesoporous properties in comparison to the parent FeLDH matrix. The catalytic behavior of the samples is a function of the nature of the supported nanoparticles.

1. Introduction

There has been a strong incentive in nowadays research for developing new nanostructured catalysts [1]. Within nanorange, a catalyst undergoes a transition from atomic to bulk form; this gives rise to the specific properties that can be different from those corresponding to the bulk material. The specific properties of the nanostructures are able to create very unique catalytically active sites [2]. Nanostructures formed by the nanoparticles of metals or metal oxides supported on the porous matrices can be used to design complex catalyst formulations that are able to merge the redox properties of the metal or metal oxides nanoparticles with the specific properties of the matrix used for supporting them [3]. Moreover, the matrix could bring into the catalytic process not only its specific textural features (e.g. porosity, high surface area) but also its own acid–base–redox characteristics.

Layered double hydroxides (LDHs) are a class of anionic clays represented by the empirical formula $[M(II)_{1-x}\ M(III)_x\ (OH)_2]^{x+}$ $(A^{n-})\ mH_2O$; they have a lamellar structure containing different M(II) and M(III) metal cations in their brucite-like sheets and various A^{n-} charge-compensating anions in their interlayer space. The incorporation of cations with redox properties in the LDHs network creates the possibility to design them as a bifunctional matrix that displays not only a unique combination of base–redox properties, but also interesting textural features (e.g. mesoporous properties, tailored size, shape and architecture of the clay particles [4,5]. The calcination of LDHs destroys the layered structure of the clay and thus mixtures of mixed oxides are formed [4]. Based on an interesting property of LDHs, the so-called "memory effect", the clay-layered structure can be reformed when the calcined clay is exposed to an aqueous solutions of anions; the used anions can be different from those of the original LDHs [6,7]. LDH-type anionic clays have already been applied as supported matrices for the nanoparticles of different metals [8].

Styrene, an important basic chemical used as a raw material for polymers, is commercially produced by the dehydrogenation of ethylbenzene (EB) using a typical Fe–K–Cr oxide-based catalyst in the presence of a large quantity of steam [9]. The commercial catalyst shows high activity and selectivity, although it also presents some important disadvantages such as: low surface area, easy deactivation of iron based catalytically active sites, high toxicity and environmental pollution due to the chromium compounds. In this context, the search for new catalytic systems is of high interest in today's research in catalysis. The addition of CO_2 as a co-feed gas can influence the performances of the catalytic system [10–12]. Iron and vanadium substituted LDHs have been

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already reported as catalysts precursors for the process of ethylbenzene dehydrogenation [13,14]. Joining this information we have used iron substituted hydrotalcite-like anionic clays (FeLDH) as mesoporous matrix to support nanoparticles of iron or vanadium oxides. After the calcination the studied samples were tested as new catalysts in the process of ethylbenzene dehydrogenation. A simple synthesis method, based on the anionic clay "memory effect", has been developed for obtaining oxides-FeLDHs, nanostructured materials. This work presents the structural, surface and textural properties of the new nanostructures and the preliminary results of the derived catalysts in the process of EB dehydrogenation. The effect of the addition of CO_2 in the stream, as a co-feed gas, on the performance of the tested catalytic samples is also reported.

2. Experimental

2.1. Samples synthesis

2.1.1. Iron containing LDHs and the derived calcined samples

FeLDH: Iron containing layered double hydroxide was synthesized by the coprecipitation method following the procedure by Reichle [15]; 400 ml of the aqueous solutions of the metal salts used as precursors ($Mg(NO_3)_2 \cdot 6H_2O/FeSO_4 \cdot 7H2O/Al(NO_3)_3 \cdot 9H_2O$–molar ratio: 2/0.5/0.5) and the aqueous solutions (1 M) of the precipitants $NaOH/Na_2CO_3$ were added dropwise together at 310 K, under a constant flow of nitrogen in the reaction medium [4] at the constant pH of 8.9 ± 0.2. The specific effect of SO_4^{2-} for the synthesis medium of iron containing LDH it was recently reported [30]. The orange precipitate was aged at 340 K for 2 h, separated by centrifugation, washed extensively with warm double deionized water until sodium free and dried under vacuum overnight. The obtained iron containing clay was calcined in air at 723 K for 7 h with a heating rate of 8 K min^{-1}.

2.1.2. Nanostructures based on iron or vanadium oxides supported on the FeLDH matrix – by using the clay "memory effect"

As calcined "fresh" FeLDH powder (1.5 g) was added to the aqueous solutions (1 M) of $FeSO_4$ or $VOSO_4$, at a constant pH of 8.7 with stirring, under nitrogen atmosphere; the volumes of the aqueous solutions of the metal salts were calculated such that the ${SO_4}^{2-}$ concentration has exceeded two times the exchange capacity of the clay. The obtained samples were aged at 338 K and denoted as Fe/FeLDH and V/FeLDH respectively. The composition and the XRD structural parameters of the obtained LDHs-like samples are presented in Table 1.

2.2. Samples characterization

Elemental analyses were performed by ICP emission spectroscopy using solutions prepared by dissolving the samples in dilute H_2SO_4. X-ray powder diffraction patterns were recorded on a Shimadzu XRD 6100 diffractometer using monochromatic Cu Kα radiation ($\lambda = 0.154$ nm), operating at 40 kV and 30 mA over a 2θ range from 4 to 70°.

Table 1
Chemical composition and lattice parameters of the anionic clay-like studied samples

Sample	$Mg^{2+}:Me^{3+}$[a]	V (% mass)	Fe (% mass)	Lattice parameters (Å)	
				a	*c*
FeLDH	1.91	–	30.4	3.047	23.39
Fe/FeLDH	0.74	–	43.7	3.059	24.20
V/FeLDH	0.79	9.1	28.3	3.064	24.43

[a] Me^{3+}: Fe, V.

N_2 adsorption isotherms were measured at 77 K on a Quantachrome Autosorb-1 automated gas adsorption system. Prior to the measurements, the samples were heated for 12 h under vacuum at 383 K in order to expel the interlayer water molecules. The BET specific surface area (S_{BET}) was calculated by using the standard Brunauer, Emmett and Teller method on the basis of adsorption data. Pore size distributions were calculated from both the desorption and adsorption branches of the isotherms using the Barret, Joiyner and Halenda method [16] and the corrected Kelvin equation. X-ray photoelectron spectroscopy spectra were recorded using a Perkin–Elmer Model5500-MT spectrometer equipped with Mg Kα radiation (1253.6 eV) operating at 15 kV and 20 mA. Samples were analyzed as powders mounted onto double-sided sticky tape in an analysis chamber typically operating at 1.33×10^{-7} Pa. All binding energy (BE) values were determined using the referenced to the C 1s line (284.6 eV) of the carbon overlayer as reference. The standard deviation of the peak position was within ±0.1 eV. TEM analysis was performed on a Hitachi H-900 instrument operating at 200 kV. The samples were prepared by dispersing them in ethanol.

2.3. Catalytic tests

Catalytic tests were performed in a flowing reaction system, in the temperature range of 673–873 K, under atmospheric pressure by using "freshly" calcined samples. The sample (0.25 g) was placed between inert quartz sand layers in a fixed-bed flow reactor (a quartz glass tube with an inner diameter of 8 mm), and pretreated under N_2 from room temperature to 723 K, at a heating rate of 5 K/min. From 723 K to the reaction temperature the catalyst was maintained under a stream of N_2. The liquid ethylbenzene, held at 301.5 K in a thermostat, was then evaporated in a controlled evaporation system and fed by bubbling a gas mixture of N_2 (15 ml) and Ar or CO_2 through the evaporator; the total flow rate was 43 ml/min, (ca. 2 mmol/h of EB). The effluent from the reactor was condensed in a trap externally cooled in an ice water bath and analyzed as we reported elsewhere [13]; catalytic activity and selectivity of the tested samples were characterized by the EB conversion value (X) and the styrene selectivity (SST), calculated as it was already reported in our previous work [13].

3. Results and discussions

3.1. Characteristics of the samples

The XRD patterns of the obtained LDH-like samples are shown in Fig. 1; the characteristic reflections of LDHs with a series of ($0\ 0\ \ell$) peaks, which are sharp and symmetric at a low 2θ angle, but broad and asymmetric at a high 2θ angle [4], are observed clearly. For Fe/FeLDH and V/FeLDH the intensity of the diffraction peaks decreases from the original LDH; this may be due to a lower crystallinity and the different textural characteristics of the samples [17]. The overlapped characteristic reflections of (1 1 0) and (1 1 3) around 60° reveal that the structural disorder of the anionic clay accentuates after the reconstruction process [18]. The XRD reflections were indexed assuming a hexagonal cell with rhombohedral lattice ($R - 3$ m). The cell parameter a is a function of the metal–metal distance within the layers, while the c parameter is related to the layer to layer distance [19]. The parameter a is 3.047 Å for FeLDH though it increases to 3.055 and 3.064 Å for Fe/FeLDH and V/FeLDH, respectively. This supports the previous results regarding the elongation of the metal–oxygen bond distance of the clay matrix when a specific synthesis medium is used during the reconstruction process of the clay layered matrix [18,19]. The c parameter is equal to 23.39 Å for FeLDH though it increases to