



Research Paper

Ni nanoparticles supported on microwave-synthesised saponite for the hydrogenation of styrene oxide

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ABSTRACT

Several saponites were synthesised under microwaves, at different preparation conditions, to be used as supports of nickel nanoparticles for the catalytic hydrogenation of styrene oxide to 2-phenylethanol. Ni/saponites obtained by impregnation with the highest nickel content (20 wt.%) or by using saponites synthesised at lower pH (pH = 7) resulted in high activity, high selectivity to 2-phenylethanol, and high resistance to deactivation catalysts. Catalytic results were related to the different NiO-saponite interactions observed by TPR.

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1. Introduction

Saponite $M_x[Mg_6Al_xSi_{8-x}O_{20}(OH)_4]$ ($M=Na, Li, NH_4$) is a trioctahedral 2:1 smectite where some substitution of Si(IV) by Al(III) in the tetrahedral (Td) sheet causes the negative charge of layers. This charge is compensated by interlayer exchangeable cations. When these cations are exchanged by transition metal cations (Ni^{2+} , Pd^{2+} , Cu^{2+}), metallic nanoparticles can be obtained, after reduction, in the interlayer space. Aluminium can also substitute magnesium in octahedral (Oh) positions, in a ratio $3Mg^{2+}=2Al^{3+}$ without creation of positive charge, or as suggested by Suquet et al. (1981), in a ratio $1Mg^{2+}=1Al^{3+}$, creating positive charge, which compensates the negative charge of the tetrahedral sheet. Additionally, Al^{3+} and Mg^{2+} can be also present as interlayer cations.

Nowadays, interest in smectites is increasing due to their important technological applications such as for nanocomposites preparation (Liu and Breen, 2005; Xue and Pinnavaia, 2008) or as heterogeneous catalysts due to their acidity and thermal stability (Casagrande et al., 2005; Varma, 2002). Large availability and low price are major advantages for using raw saponite. However, to obtain a reproducible composition, saponite must be synthesised.

Saponite synthesising procedures often involve hydrothermal treatments in autoclaves at water autogenous pressure (5–17 MPa), and at 423–723 K for long times, from hours to days (Jaber and Miéhe-Brendlé, 2005, 2008; Klopogge et al., 1994; Vogels et al., 1997, 2005;

Zhang et al., 2010; Zhou, 2010). There is an increasing interest in using microwaves to synthesise and to modify microporous and mesoporous materials (Bergadà et al., 2007a; González et al., 2009; Newalkar et al., 2001; Vicente et al., 2009). Some studies on the use of microwaves for saponite preparation have been published (Rico et al., 2008; Trujillano et al., 2010; Vicente et al., 2010; Yao et al., 2005; Zhang et al., 2010). However, residual amounts of amorphous silica were observed for all samples when using softer preparation conditions.

2-phenylethanol (2-PEA), the main component of rose oils, is widely used as a component in all chemical perfumes and as an additive in foods. Catalytic hydrogenation of styrene oxide to selectively obtain 2-phenylethanol is a cleaner alternative to the economical, environmental and purification problems shown by classical industrial production methods (Bauer et al., 2001; Wilson, 1991). Bulk nickel, palladium, and platinum catalysts have shown to be good catalysts for this reaction (Gibson and Theiling, 1977; Mitsui et al., 1973). The use of basic solids as catalytic supports considerably improved conversion and selectivity to 2-phenylethanol, as well as catalyst life (Bergadà et al., 2007b, 2008). Nevertheless, there is no information about the behaviour of metal catalysts in the presence of acid sites for this reaction.

Other transformation reactions of styrene oxide can take place in the presence of acid sites: isomerisation to phenylacetaldehyde (PA) catalysed by Brønsted acid sites, ring-opening reaction to 2-ethoxy-2-phenylethanol (2-EPE), catalysed by Lewis and Brønsted acid sites with medium strength, and condensation reactions, which are responsible for catalyst deactivation and are catalysed by strong Brønsted acid sites in the presence of Lewis acid sites (Bergadà et al., 2009; González et al., 2009; Salla et al., 2005).

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The aim of this work was to study the catalytic behaviour of several saponite-supported nickel catalysts for the hydrogenation of styrene oxide to 2-phenylethanol. The influence of residual amorphous silica in saponites on the catalytic activity was also evaluated. Ni/saponite catalysts were obtained by impregnation with different nickel contents or by cation exchange. Saponites were synthesised under microwaves at different preparation conditions. Samples were characterised by XRD, XRF, TPR, TEM, FTIR, C.E.C. determination, N_2 adsorption, and ^{27}Al NMR techniques.

2. Experimental

2.1. Synthesis of saponites

Magnesium acetate (Aldrich 98% min. pur.), lithium hydroxide (Scharlau, 99% min. pur.), and fumed SiO_2 (Aldrich, 99.8% pur., BET area $227\text{ m}^2/\text{g}$, particle size 11 nm) were used as reagents for all samples. Nevertheless, different Al reagents were employed to achieve different pH values in the initial slurry: aluminium basic acetate (Sigma-Aldrich, 14.8% min. Al content) to obtain pH 8, and aluminium isopropoxide (Aldrich, 98% min. pur.) to obtain pH 7.

Three samples were prepared at initial slurry pH of 8 with different $\text{Si}^{4+}/\text{Al}^{3+}/\text{Mg}^{2+}/\text{Li}^+$ molar ratios: 11.4/2.5/12.5/8 (20% lower SiO_2 content than the stoichiometric amount), 14.3/2.5/12.5/8 (stoichiometric amount), and 26.8/2.5/12.5/8 (190% higher SiO_2 content than the stoichiometric amount). Then, they were aged by autoclaving under microwaves (Milestone Ethos Touch Control) at 453 K for 6 h (S8a, S8b and S8c, respectively). Two more samples were synthesised at the same preparation conditions than S8a and S8b but at initial slurry pH of 7 (S7a and S7b, respectively). After aging, pH was similar (around 4.5) for all samples, which were washed by centrifugation up to neutrality, and dried overnight in an oven at 353 K.

2.2. Preparation of saponites-supported nickel catalysts

Table 1 presents the preparation conditions of saponite-supported nickel catalysts. Nickel was introduced by two procedures: impregnation and cation exchange. All saponites were impregnated with nickel nitrate in the appropriate amounts to obtain 15 wt.% of Ni in the final catalysts. Samples were calcined in air at 623 K (NiOs15-S8a, NiOs15-S8b, NiOs15-S8c, NiOs15-S7a, NiOs15-S7b), and reduced under pure hydrogen at 623 K for 6 h (Nis15-S8a, Nis15-S8b, Nis15-S8c, Nis15-S7a, Nis15-S7b). Two more catalysts were obtained by impregnating S8a with nickel nitrate to result in 10 wt.%, and 20 wt.% of Ni in the final catalysts, which were obtained after calcination–reduction at the same conditions than the above samples (Nis10-S8a and Nis20-S8a, respectively).

Ni^{2+} -exchanged saponites were prepared by stirring 35 ml of Ni $(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 0.25 M with 1 g of S8a, S8b and S8c at 338 K for 2 h. Samples were calcined in air at 623 K, and reduced under pure hydrogen at 623 K for 6 h (Nie1-S8a, Nie1-S8b, Nie1-S8c) (Table 1).

Ni^{2+} -exchanged S8c was also reduced under pure hydrogen but at 673 K for 6 h (Nie2-S8c).

2.3. X-ray diffraction (XRD)

XRD measurements were made using a Siemens D5000 diffractometer (Bragg-Brentano parafocusing geometry and vertical θ – θ goniometer) fitted with a curved graphite diffracted-beam monochromator and diffracted-beam Soller slits, a 0.06° receiving slit, and scintillation counter as a detector. The angular 2θ diffraction range was between 2° and 70° . The sample was dusted on to a low background Si (510) sample holder. The data were collected with an angular step of 0.05° at 3 s per step and sample rotation. $\text{Cu}_{\text{K}\alpha}$ radiation was obtained from a copper X-ray tube operated at 40 kV and 30 mA.

The X-ray pattern was analysed using the Fundamental Parameters Approach convolution algorithm (Cheary and Coelho, 1992) as implemented in the program TOPAS 3.0 (Coelho, 2005). This approach calculates the contribution to the reflection width produced by a specific instrument configuration. The crystallite size was calculated from the net integral breadth of the reflections, β_i , (Stokes and Wilson, 1942) according to the following formula that comes from the Scherrer expression: $\beta_i = \lambda/\varepsilon \cos\theta$ where λ is the X-ray wavelength, ε is the crystallite size and θ is the Bragg angle. 060 reflection was used to calculate the crystallite size of saponites. Nickel crystallite size was calculated from 111 reflection of metallic nickel phase for supported nickel catalysts.

2.4. Infrared spectroscopy (FTIR)

Infrared spectra were recorded on a Bruker-Equinox-55 FTIR spectrometer. The spectra were acquired by accumulating 32 scans at 4 cm^{-1} resolution in the range of 400 – 4000 cm^{-1} . Samples were prepared by mixing the powdered solids with pressed KBr disks in a mass ratio of 1:250, and were dried in an oven before measurements.

2.5. X-ray fluorescence (XRF)

Elemental analyses of the samples were obtained with a Philips PW-2400 sequential XRF analyser with Phillips Super Q software. Analyses were made by triplicate for each sample.

2.6. N_2 adsorption

N_2 -adsorption–desorption isotherms were recorded at 77 K using a Micromeritics ASAP 2000 surface analyser. Prior to analysis samples were outgassed at 353 K. Specific surface areas were calculated from the BET method.

2.7. Temperature-programmed reduction

TPR experiments were carried out using a TPD/R/O 1100 (Thermo Finnigan) equipped with a programmable temperature furnace and a calibrated TCD detector. Experiments were performed with 5% H_2/Ar flowing through the sample, that was heated from 303 K to 1173 K at 10 K/min .

2.8. ^{27}Al -MAS NMR

^{27}Al -MAS NMR spectra were obtained on a Bruker AV400 spectrometer. A 4 mm BL4 MAS probe was used with the samples spun at 10 kHz at the magic angle, using pulses $< \text{PI}/12$ with a time between pulses of 1 s. Chemical shifts are given in ppm relative to $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ (0 ppm).

Table 1
Preparation conditions of the catalysts.

Catalyst	%Ni	Nickel introduction by	Reduction temperature (K)
Nis10-S8a	10	Impregnation	623
Nis15-S8a	15	Impregnation	623
Nis20-S8a	20	Impregnation	623
Nis15-S8b	15	Impregnation	623
Nis15-S8c	15	Impregnation	623
Nie1-S8a	1.2	Cation exchange	623
Nie1-S8b	1.4	Cation exchange	623
Nie1-S8c	1.6	Cation exchange	623
Nie2-S8c	1.6	Cation exchange	673
Nis15-S7a	15	Impregnation	623
Nis15-S7b	15	Impregnation	623

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