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ScienceDirect

Applied Catalysis A: General 331 (2007) 19–25

APPLIED CATALYSIS A: GENERAL

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Effective catalysts, prepared from several hydrotalcites aged with and without microwaves, for the clean obtention of 2-phenylethanol

Olga Bergadà [a], Pilar Salagre [a,*], Yolanda Cesteros [a], Francisco Medina [b], Jesús E. Sueiras [b]

[a] *Facultat de Química, Universitat Rovira i Virgili, C/Marcel·lí Domingo s/n, 43007 Tarragona, Spain*
[b] *Escola Tècnica Superior d'Enginyeria Química, Universitat Rovira i Virgili, Av. Països Catalans, 26, 43007 Tarragona, Spain*

Received 10 April 2007; received in revised form 24 June 2007; accepted 15 July 2007

Abstract

Several Ni/Mg/Al hydrotalcites have been aged by different methods (conventional refluxing, conventional autoclaving, microwaves refluxing and microwaves autoclaving). The resulting catalysts have been tested in the hydrogenation of styrene oxide to obtain 2-phenylethanol, widely used in the perfumery industry. The catalysts obtained from the hydrotalcites aged under microwaves showed higher metallic areas than those obtained from the hydrotalcites aged by conventional heating. All catalysts showed total conversion and very high selectivity to 2-phenylethanol (around 95%) after 1 h of reaction. The higher metallic area and the more homogeneous distribution of low amounts of basic sites of these catalysts based on hydrotalcites when compared with other basic catalysts, as Ni-MgO systems, can explain these best catalytic results. After reusing 10 times, all catalysts showed high resistance to deactivation since they maintain high conversion and high selectivity values to 2-phenylethanol. However, some differences in their catalytic behaviour were observed that have been explained from H_2-TPD studies.

Keywords: Hydrotalcite; Microwaves; 2-Phenylethanol

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1. Introduction

2-Phenylethanol (2-PEA), the main component of rose oils, is widely used as component in all chemical perfumes, and as an additive in foods, due to its pleasant smell [1].

Catalytic hydrogenation of styrene oxide to obtain selectively 2-phenylethanol is a cleaner alternative to the economical, environmental and purification problems shown by classical industrial production methods such as the Friedel–Crafts alkylation of benzene with ethylene oxide [2,3], reacting chlorobenzene with Grignard-type reactants followed by several reaction steps [4,5], or by ring opening the epoxide with reductor agents such as hydrides or alkaline metals [6–8].

Catalytic hydrogenation of styrene oxide to obtain 2-phenylethanol (Scheme 1) has been studied from years 50 in order to solve the important problems mentioned above [9,10]. Bulk nickel, palladium and platinum catalysts have shown to be good catalysts for this reaction [11,12]. Their activity and selectivity were considerably improved with the addition of basic solutions to the reaction medium [11]. However, the basic medium could also favour condensation reactions [13]. In a previous work, we obtained high activity and high selectivity to 2-PEA when using basic Ni-MgO catalysts. The presence of magnesia, through its basicity, minimizes the ethylbenzene formation. Moreover, we found that the morphology and size of the metallic nickel particles obtained using different preparation methods also influences on the reaction products distribution [14]. Recently, from CO_2-TPD studies, we concluded that the existence of a certain interaction between the nickel and the weakest basic sites of magnesia in these Ni-MgO catalysts favour the formation of 2-phenylethanol, and minimize other side reactions like the formation of condensation products [15].

Hydrotalcite-like compounds is a class of layered materials having the general formula $[M(II)_{1-x}M(III)_x(OH)_2][A_{x/n}{}^{n-}]\cdot mH_2O$ (where M(II) and M(III) are divalent and trivalent cations and A is the interlayer anion). Structurally, layered double hydroxides (LDHs) have brucite-like ($Mg(OH)_2$) sheets where isomorphous substitution of Mg^{2+} by a trivalent cation, like Al^{3+}, occurs. The resulting positive

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[*] Corresponding author. Departamento de Quimica Fisica i Inorgànica, Universitat Rovira i Virgili, C/Marcel·lí Domingo s/n, 43007 Tarragona, Spain. Tel.: +34 977559571; fax: +34 977559563.
E-mail address: pilar.salagre@urv.net (P. Salagre).

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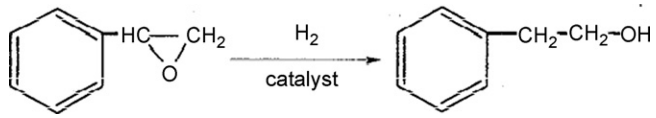
doi:10.1016/j.apcata.2007.07.017



Scheme 1. Catalytic hydrogenation of styrene oxide to obtain 2-phenylethanol.

charge excess of the layered network is compensated by anions, which occupy the interlayer space along with water molecules.

Controlled thermal decomposition of hydrotalcites gives to high-area mixed oxides, which after reduction lead to highly well dispersed metallic catalysts with basic and surface properties with numerous catalytic applications [16–19]. The acidic–basic properties of calcined hydrotalcites can be tailored by changing the calcination temperature, the nature and amount of structural cations and compensating anions, as well as, the method of synthesis of the LDH's [20,21].

Hydrotalcites are conventionally prepared by coprecipitation, wherein metal nitrates and precipitants are added slowly and simultaneously at a fixed pH under stirring. The main disadvantage of this method is the time required to crystallize the hydrotalcite (about 1 day) [16]. Interestingly, hydrotalcites obtained by microwave irradiation present smaller particles sizes and higher specific surface areas than conventional samples reducing considerably the aging time [22–27]. However, some authors reported the presence of surface-defective sites in the resulting Mg/Al mixed oxides when the hydrotalcite was aged by microwave irradiation [28]. In a previous work, we related the appearance of surface-defective sites in Ni/Mg/Al hydrotalcites aged by microwaves at 453 K at longer times (2 h) to the higher basicity observed for these samples by CO_2-TPD [29].

Taking into account the good results found by using basic Ni-MgO catalysts, as commented above, we believe that Ni/Mg/Al hydrotalcites can be good candidates to be used as catalytic precursors for the hydrogenation of styrene oxide in order to obtain selectively 2-phenylethanol since, after calcination-reduction, they can lead to well-dispersed metallic nickel interacting with basic particles. In this work, we prepared several Ni/Mg/Al hydrotalcites with low amounts of Mg and Al in order to avoid higher basicity that could be responsible for undesirable reactions. The hydrotalcites were aged using different methods (conventional refluxing, conventional autoclaving, microwaves refluxing and microwaves autoclaving) and different aging conditions (temperature and time). The corresponding catalysts have been tested in the hydrogenation of styrene oxide in the liquid phase in order to study the influence of the hydrotalcites aging step on their surface properties and, consequently, on the catalytic behaviour of the resulting catalysts.

2. Experimental

2.1. Catalysts preparation

Hydrotalcites were synthesized by traditional coprecipitation method at room temperature at constant pH (pH 8 ± 0.1), using aqueous solutions containing in appropriate amounts $Ni(NO_3)_2\cdot 6H_2O$, $Mg(NO_3)_2\cdot 6H_2O$ and $Al(NO_3)_3\cdot 9H_2O$ with a 1 M NaOH titrating solution which was simultaneously added to an aqueous solution of 0.05 M $Na_2CO_3\cdot 10H_2O$. The ratio M^{2+}/Al^{3+} was 4:1 and the ratio Ni^{2+}/Mg^{2+} was 6:1. Dropwise addition was performed under vigorous magnetic stirring. After complete precipitation, the gels were aged at different conditions.

Two samples were aged without microwaves, one by refluxing the gel under stirring for 18 h at 343 K (sample R), and the other by autoclaving the gel in an oven at 403 K for 6 h (sample A). Three more samples were aged by using a laboratory microwave oven (Milestone ETHOS-TOUCH CONTROL). One was prepared by refluxing the gel under microwave irradiation at 343 K for 2 h (sample RMW), and the other two were aged in an autoclave reactor under microwaves at soft conditions (403 K for 15 min) (sample AMW1), and at harder conditions (453 K for 2 h) (sample AMW2), respectively. Finally, all samples were filtered and washed several times with deionised water and the solids were dried in an oven at 393 K overnight.

Hydrotalcites were calcined at 623 K in a nitrogen flow (1.5 mL/s) for 2 h (samples R_C, A_C, RMW_C, $AMW1_C$ and $AMW2_C$). These calcined hydrotalcites were reduced under pure hydrogen at 623 K for 6 h. The corresponding catalysts are named as R_R, A_R, RMW_R, $AMW1_R$ and $AMW2_R$.

2.2. Air-free sampling

The catalysts were always handled under air-free conditions after the reduction step. The catalysts were transferred in degassed cyclohexane and under a hydrogen atmosphere at room temperature. The cyclohexane surface-impregnated samples were further isolated from the air with sticky tape for XRD monitoring where a glove box was used for mounting. Catalytic activity was measured in situ, in the same reactor after reduction, where gas purges, positive gas pressures and Schlenk techniques were used when necessary.

2.3. X-ray diffraction (XRD)

Powder X-ray diffraction patterns of the different samples were obtained with a Siemens D5000 diffractometer using nickel-filtered Cu Kα radiation. Samples were dusted on double-sided sticky tape and mounted on glass microscope slides. The patterns were recorded over a range of 2θ angles from 10° to 90° and crystalline phases were identified using the Joint Committee on Powder Diffraction Standards (JCPDS) files: 089-0460-hydrotalcite, 04-0850-Nickel, *syn*-Ni; 04-0835-Bunsenite, *syn*-NiO.

2.4. Nitrogen physisorption

BET areas were calculated from the nitrogen adsorption isotherms at 77 K using a Micromeritics ASAP 2000 surface analyzer and a value of 0.164 nm^2 for the cross-section of the nitrogen molecule. Brunauer, Emmet and Teller (B.E.T.) theory were applied to calculate the total surface area of the samples.