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Tuning the selectivities of Mg-Al mixed oxides for ethanol upgrading reactions through the presence of transition metals

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ABSTRACT

The effect of the presence of reduced Co and Ni (chosen as representative metals because of their good activity for dehydrogenation reactions) on the catalytic performance of basic mixed oxide (Mg-Al) for ethanol condensation is studied in this work. This effect has been studied both in absence and in presence of hydrogen, and considering the different steps of this complex reaction. Globally, best results were obtained with Co/MgAl, under reducing atmosphere, at mild temperature (below 600 K). At these conditons, 1-butanol production rates are up to eight times higher than the obtained with Mg-Al under inert atmosphere. Co has a marked activity in the dehydrogenation step, that prevails over its less relevant activity in aldolization and hydrogenation reactions. This result indicates the relevant role of this first reaction step. DRIFT spectroscopy analyses were carried out to support the experimental results and to identify the role of hydrogen and metals on the oligomerization and permanent adsorption processes, which can produce the deactivation of the catalyst.

1. Introduction

Gas-phase ethanol condensation has been intensively investigated in the last few years, because of the high potential of ethanol as bioplatform molecule [1–4]. Among the different chemicals obtained from ethanol [5–8], 1-butanol is the most valuable one, with better fuel properties than ethanol, and many uses as solvent and platform molecule. There is not agreement about the actual mechanism for 1-butanol formation. The so-called four-step mechanism (Scheme 1) is the most accepted one, although several authors also suggest the direct ethanol condensation or the acetaldehydeethanol reaction [4,9–11]. According to the four-step mechanism, acetaldehyde aldolization is usually considered as the rate-determining step since it involves two molecules, and different active sites, requiring an appropriate balance between acid and medium-strength basic sites. Different materials, mainly mixed oxides and hydroxyapatites (HPA) have been proposed as promising catalysts [4,11,12]. Despite their good activity for aldolization, experimental results indicate that the difficulty in activating the α-hydrogen of the ethoxides (previous ethanol dehydrogenation) strongly limits the final yields [13–15]. This effect was previously observed for the dehydrogenation of different alcohols, the use of transition metals in the reduced form (Co, Ni, Cu, Fe, Ir, etc.) being proposed for reducing the activation energy of the αCH bond scission [16,17]. In addition, reduced metals are supposed to alter the acid/base sites distribution in a lower extent that the metal oxides.

Under inert conditions, or in absence of any active metal for the molecular hydrogen activation, once the acetaldehyde reacts producing crotonaldehyde, the 1butanol is obtained upon two subsequent hydrogenations: terminal C=O bonds hydrogenation through the Meerwein-Ponndorf-Verley (MPV) reduction (crotonaldehyde and butanal), and hydrogenation of the unsaturated intermediates (crotonaldehyde and crotyl alcohol) by surface-mediated hydrogen transfer reaction [6,9]. Under these conditions, ethanol molecules are the hydrogen source for the former hydrogenation [18], being the hydrogen released in the dehydrogenation step [15,18,19]. HPA and mixed oxides are not very active for these reactions, so the global process is still far to be optimized.

This work is focused on the study of the effect of supporting transition metals and including hydrogen in the feed on the performance of Mg-Al mixed oxides for ethanol gas-phase condensation. It was previously suggested that the use of reducing conditions, in addition to the expected improvement in hydrogenation steps, has a positive effect on the catalyst stability, preventing the permanent deposition of unsaturated molecules [20]. Mg-Al mixed oxide was chosen as bulk material, considering the well-known behaviour of this material for this reaction [6]. The idea of using metal-modified oxides has been previously proposed by some authors, studying the effect on the upgrading of different alcohols, such as methanol or ethanol [21–23]. In this context, Co and Ni are good candidates because of their high activity for alcohol dehydrogenations [23,24]. However, most of the reported

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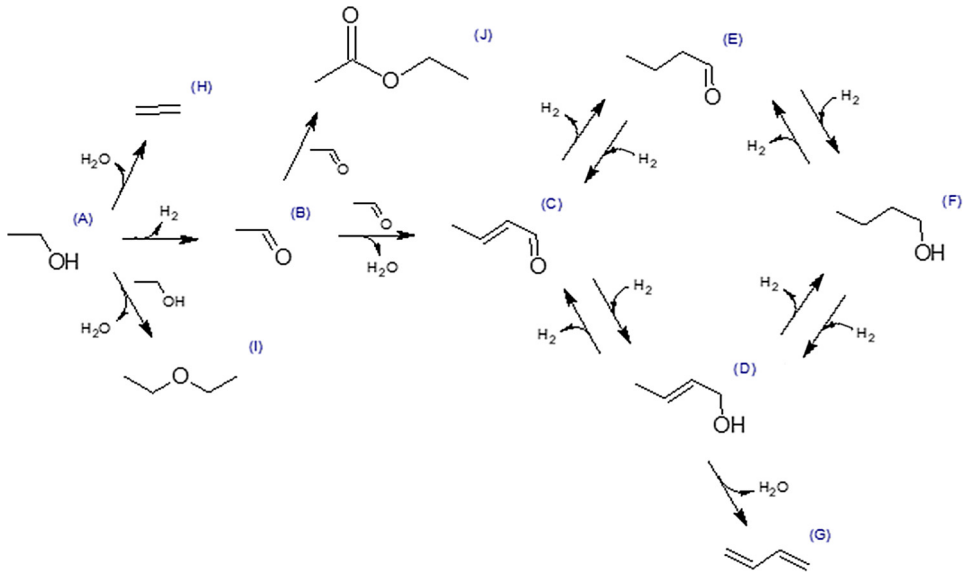

Scheme 1. Reaction mechanism for the gas phase ethanol upgrading [5–8]. Symbols: (A) ethanol; (B) acetaldehyde; (C) crotonaldehyde; (D) crotyl alcohol; (E) butanal; (F) 1-butanol; (G) 1,3-butadiene; (H) ethylene; (I) diethyl ether; (J) ethyl acetate.

studies are performed with very high metal loadings (15–20 %), masking the original acid-basic properties of the bulk material.

Thus, the aim of this work is to study the role of Co and Ni as reduced nanoparticles in the promotion of the steps catalyzed by these metals, but affecting, as little as possible, the acid-basic properties of the original bulk material (Mg-Al). We propose catalysts with only 1 wt. % of metal, prepared by surface deposition. This procedure is typically used with noble metals, but not so often for transition ones. In fact, in most of the works reported, the metal is introduced into the bulk structure, modifying the original coordination lattice by substituting the original cations [25,26]. The second modification proposed in this work is to feed controlled amounts of hydrogen, in order to both, keep reduced these nanoparticles, and to improve their performance in hydrogenation steps. This idea is supported by our previous studies with Au/TiO_2 for this reaction, obtaining an improvement of 74% in the conversion and almost 10% in the 1-butanol selectivity when working in presence of H_2 [27].

2. Experimental methods

2.1. Catalysts preparation

Mg-Al mixed oxide (Mg/Al = 3) was obtained by the calcination of the corresponding hydrotalcite, prepared by coprecipitation of the Mg and Al nitrates (Aldrich magnesium nitrate hexahydrate, and Aldrich aluminium nitrate nonahydrate) at low super-saturation and under sonication. The detailed procedure is reported in the literature [6]. The gel was precipitated by increasing the pH to 10 with a NaOH solution (10 wt.%) and it was aged at 353 K for 24 h. The solid phase was centrifuged, washed with deionized water to pH 7 and dried at 383 K for 24 h, yielding the hydrotalcite (HT). Finally, the mixed oxide was obtained by calcining the HT in flowing air, from 293 to 973 K with a temperature rate of 5 K min^{-1}, holding this setpoint for 5 h.

The Ni/Mg-Al and Co/Mg-Al materials (1 wt.% of metal) were synthesized by incipient wetness impregnation, using nickel (II) nitrate 6-hydrate (Panreac), and cobalt (II) nitrate 6-hydrate (Panreac). After the impregnation, the catalysts were treated under airflow from 293 to 973 K with a temperature ramp of 5 K min^{-1}, holding this temperature for 5 h, in order to remove the precursor salts. The reduced metals were obtained by treating the materials in flowing H_2Ar mixture (10 vol. % of H_2; 20 mL min^{-1}) at 823 K for 6 h, according to the results observed during the characterization of the calcined precursors. In order to avoid further metal re-oxidation, the reduction was performed in-situ before each experiment.

2.2. Catalysts characterization

Temperature-programmed reduction analyses (TPR) were carried out in a Micromeritics 2900 TPD/TPR instrument, in order to define the reduction temperature of the catalysts precursors. In good agreement with the typical procedure, 10 mg of calcined catalytic precursors were treated under H_2 flow (10 vol.% H_2/Ar) from 298 to 973 K, with a temperature rate of 2.5 K min^{-1}. Once the final catalysts were obtained, morphologic properties were determined by N_2 physisorption at 77 K in a Micromeritics ASAP 2020 using the Brunauer-EmmettTeller (BET) method to analyse the surface area, and the Barret-Joyner-Halenda (BJH) method to calculate the pore volume and diameter. Surface basicity and acidity were analysed by temperature programmed desorption (TPD) using a Micromeritics 2900 TPD/TPR. 10 mg were pretreated in He flow and saturated with CO_2 or NH_3 to determine the basicity or acidity, respectively. The evolution of CO_2 and NH_3 signals were followed in a Pfeiffer Vacuum Omnistar Prisma mass spectrometer, as well as the temperature was increased at 2.5 K min^{-1} between 298 and 973 K.

The crystallographic structure of the catalysts was determined by X-ray diffraction (XRD) using a Philips PW 1710 diffractometer with a CuKα line (1.54 Å) in the 2θ range within 5 and 80° at 2° min^{-1} of scanning rate. High-resolution transmission electron microscopy (HRTEM) analyses of the fresh materials were carried out to determine the nanoparticle size and distribution, as well as the metal dispersion, in a JEOL JEM2100 instrument. H_2 chemisorption was also performed in order to determine the metal dispersion and the crystallite size of the fresh and used catalysts, using the same instrument as for the morphological study (Micromeritics ASAP 2020).

2.3. Catalytic studies

Activity experiments were carried out from 523 to 723 K (with steps of 50 K) in a 0.4 cm i.d. U-shaped fixed bed quartz reactor located inside a controlled electric furnace. The catalyst (150 mg; 250–355 μm) was placed above a quartz wool plug. The sample was pre-treated at 473 K for 1 h in flowing He before each experiment. Absolute ethanol was supplied with a syringe pump in the He or H_2-He (10 vol.% of H_2) flow, causing the in situ vaporization, obtaining a 32 vol.% of ethanol, fed to