



Selective production of furfuryl alcohol from furfural by catalytic transfer hydrogenation over commercial aluminas

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ABSTRACT

Three commercial aluminas (γ -Al₂O₃) have been evaluated as inexpensive catalysts in the Meerwein-Ponndorf-Verley (MPV) reaction to reduce furfural (FUR) to furfuryl alcohol (FOL), using isopropanol (i-Pr-OH), 2-butanol (2-bu-OH) and cyclohexanol (CH-OH) as sacrificing alcohol under mild conditions. All γ -Al₂O₃ have been characterized by XRD, ²⁷Al NMR and FT-IR spectroscopies, NH₃-TPD and XPS. The aluminas are active catalysts, giving rise to FOL as main product, with a yield higher than 90% after 6 h at 150 °C. The catalytic data also reveal that linear alcohols, such as isopropanol and 2-butanol, lead to higher FUR conversion values in comparison to cyclohexanol. However, the presence of H₂O in the reaction medium has an adverse effect in FUR conversion by the transformation of active Lewis acid sites into Brønsted ones, which are inactive in the MPV reaction.

1. Introduction

Biomass is the unique alternative to replace traditional fossil resources from which energy, fuels and chemicals can be obtained [1]. Lignocellulosic biomass, composed by cellulose (40–50%), lignin (15–25%) and hemicellulose (20–35%), is a suitable and available carbon source for chemical synthesis without competing with the food chain [2–6]. Furfural (FUR) is one of the main products which can be derived from the lignocellulosic biomass, with a high industrial importance associated to its large spectrum of applications. The presence of an aldehyde group and an aromatic ring makes FUR an interesting platform molecule. In addition, these features are responsible of its high reactivity, which have prompted the establishment of several chemical routes to convert FUR in other high value-added products [2,4]. Among these chemical pathways, FUR hydrogenation is one of the most widely used reactions for FUR valorization, yielding several products, such as furfuryl alcohol (FOL), methylfuran, methyltetrahydrofuran, furan, tetrahydrofuran, cyclopentanone or olefins. FUR hydrogenation can proceed through liquid or gas phase, having been proposed a wide range of transition metals such as Cu [7–10], Ni [11,12], Co [13], Pd [14,15], Pt [16,17] or Ru [18] as active phase, to replace the industrial copper chromite hydrogenation catalyst [19,20], because of the high toxicity of chromium species. The largest FUR production takes place in

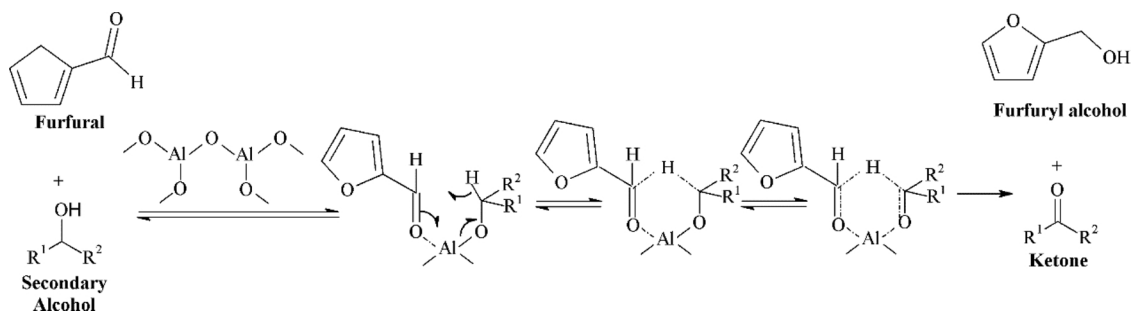
China, counting about 70% of the global world production, followed by Dominican Republic and South Africa, all of three countries responsible of the 90% of total production (280 kTn per year) [5].

Nevertheless, an efficient alternative to the classical catalytic hydrogenation, in which hydrogen is the reducing agent, could be the catalytic transfer hydrogenation (CTH), already proposed to transform ketones or aldehydes in alcohols, since, in this way, the use of high hydrogen pressures is avoided. In this sense, in the mid of 1920s, Meerwein, Ponndorf and Verley (MPV) reported that aldehydes and ketones can be reduced by secondary alcohols in the presence of a Lewis acid or basic catalyst [21–25]. Lewis acid sites were able to activate the C=O bond of aldehydes or ketones, while the alcohol suffers deprotonation. Moreover, the formation of a six-membered intermediate was postulated, with the participation of the hydrogen in the position C_α, being both aldehyde/ketone and the deprotonated alcohol directly activated on the Lewis acid sites [26,27].

The MPV process is easy, with low requirements for reactants purity and high chemoselectivity, due to reactivity of the carbonyl group of both aldehydes and ketones, while double and triple bonds are unreactive. Traditionally, the MPV reaction takes place using aluminum (Scheme 1) [28–30] zirconium [30] and magnesium [31] complexes or alkoxides, as homogenous catalysts; however, these catalysts display several drawbacks, such as expensive separation and purification of

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Scheme 1. Mechanism of the MPV reaction using furfural and a secondary alcohol as starting molecules.

products, and moisture sensitivity. In this context, heterogeneous catalysts have emerged as alternative for MPV processes, due to their easier separation and ability to be reused. These include metal oxides [32–35], hydrotalcites [36,37] and zeolites [38–43]. Among them, alumina (Al_2O_3) is an attractive catalyst due to its high availability, low cost, environmentally benignity and relatively low toxicity. Moreover, the synergy between acid and basic sites has been highlighted to explain the higher catalytic activity of hydrotalcites in comparison to the pure basic oxides, and it could be also applied to the case of alumina, but this has been scarcely evaluated in this catalytic process [30].

The FUR conversion through MPV reaction has been reported using zeolites [40,42,44] or mesoporous silica modified with heteroatoms to generate Lewis acidity [39,45]. The FUR hydrogenation leads to furfuryl alcohol, which can react with the secondary alcohol to produce furfuryl ethers. In addition, the process can go forward the formation of other products, such as levulinic acid or γ -valerolactone, due to the coexistence of Lewis and Brønsted acid sites [44]. In any case, all of them are high value-added chemicals. Thus, furfuryl alcohol is largely employed for resins because of its interesting thermal, mechanical and chemical properties, and high resistance against corrosion [2], while furfuryl ethers can be used as blending components of gasoline [46] or as flavors [47].

The aim of this work was the evaluation of a series of commercial aluminas in the FUR hydrogenation by the MPV reaction, by considering the different surface properties of aluminas to establish structure-activity relationships. In addition, several key experimental variables, such as the reaction temperature, the alcohol:furfural molar ratio and the nature of the secondary alcohol, were optimized to attain the highest conversion and selectivity to a particular hydrogenated product. Finally, the reutilization of the solid catalysts was also studied.

2. Materials and methods

2.1. Reagents

Commercial aluminas were supplied by Alfa-Aesar (Brockmann Grade I, 58 Å). These aluminas were denoted as acid, neutral and basic alumina, being labeled as A- Al_2O_3 , N- Al_2O_3 and B- Al_2O_3 , respectively, and they were employed as received.

The reagents used in the hydrogen transfer reaction of furfural to furfuryl alcohol were furfural (Sigma-Aldrich, 99%), isopropanol (VWR, HPLC grade, 99.9%), 2-butanol (Sigma-Aldrich, 99.5%) and cyclohexanol (Sigma-Aldrich, 99%), as sacrificing alcohols, and *o*-xylene (Sigma-Aldrich, 99.9%) as internal standard.

Gases used were He (Air Liquide, 99.999%), H_2 (Air Liquide, 99.9999%), N_2 (Air Liquide, 99.99999%) and NH_3 (Air Liquide, 99.9%).

2.2. Catalysts characterization

The identification of crystalline phases in aluminas was carried out by X-ray diffraction (XRD), using a PANalytical automated diffractometer (EMPYREAN model) and $\text{Cu-K}\alpha$ (1.5406 Å) radiation, with

a last generation PIXcel detector. The average crystallite size and the lattice strain were estimated by the Williamson-Hall method, using the equation $B \cos \theta = (K \lambda / D) + (2 \varepsilon \sin \theta)$, where θ is the Bragg angle, B is the full width at half maximum (FWHM) of the XRD peak, K is the Scherrer constant, λ is the wavelength of the X-ray and ε the lattice strain [48].

Textural parameters (S_{BET} , V_p and D_p) were evaluated from N_2 adsorption-desorption isotherms at -196°C , determined by using an automatic ASAP 2020 system from Micromeritics. Prior to adsorption, samples were outgassed at 200°C and 10^{-4} mbar, overnight. Surface areas were determined by using the Brunauer-Emmett-Teller (BET) equation assuming a cross section of 16.2 \AA^2 for the nitrogen molecule [49]. The pore size distribution was calculated by the density functional theory model (DFT) [50], whereas total pore volume was obtained from N_2 adsorbed at $P/P_0 = 0.996$.

The amount of acid sites was determined by temperature-programmed desorption of ammonia (NH_3 -TPD). 0.08 g of catalyst was previously evacuated in a He flow (40 mL min^{-1}) from room temperature to 550°C , with a rate of $10^\circ\text{C min}^{-1}$, and cooled under the same conditions until 100°C . After that, the catalyst was saturated with NH_3 for 5 min. Then, a He flow (40 mL min^{-1}) was passed to eliminate the physisorbed ammonia. Finally, temperature-programmed desorption was carried out by heating the samples from 100 to 550°C , at a heating rate of $10^\circ\text{C min}^{-1}$. The desorbed ammonia was quantified by a thermal conductivity detector (TCD).

FTIR spectra after pyridine adsorption were recorded on a Shimadzu 8300 FTIR spectrometer at a resolution of 4 cm^{-1} . Each spectrum was average over 128 scans. Self-supporting wafers of samples, with a weight/surface ratio of about 12 mg cm^{-2} , were placed in a vacuum cell with greaseless stopcocks and CaF_2 windows. Samples were evacuated at 350°C and 10^{-4} Torr overnight, exposed to pyridine vapors for 15 min at room temperature, and then outgassed at different temperatures. The net FTIR spectra of adsorbed pyridine were obtained after subtracting the background spectrum of the solid.

X-ray photoelectron spectra were collected using a Physical Electronics PHI5700 spectrometer with non-monochromatic $\text{Mg K}\alpha$ radiation (300 W, 15 kV and 1253.6 eV) with a multichannel detector. Spectra of samples were recorded in the constant pass energy mode at 29.35 eV using a 720 μm diameter analysis area. Charge referencing was measured against adventitious carbon (C 1s at 284.8 eV). A PHI ACCESS ESCA-V6.0F software package was used for acquisition and data analysis. A Shirley-type background was subtracted from the signals. Recorded spectra were always fitted using Gaussian-Lorentzian curves in order to determine the binding energies of the different element core levels more accurately.

The TG-DSC data were recorded with a Mettler-Toledo (TGA/DSC-1) instrument equipped with a MX5 microbalance. The temperature was varied from RT to 900°C at a heating rate of 5°C min^{-1} . The measurements were performed with samples in open platinum crucibles under an air flow.

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