



Short communication

# A study on the catalytic hydrogenation of aldehydes using mayenite as active support for palladium

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## ABSTRACT

Selective benzaldehyde reduction to benzyl alcohol was accomplished using a new catalyst based on Pd dispersed on mayenite ( $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ ) support. In this work, mayenite has been doped in its nanocages with  $\text{H}^-$  ions to investigate its role in the reduction of aldehydes. Benzaldehyde reduction was observed in  $\text{H}_2$  atmosphere ( $120^\circ\text{C}$ , 8 atm). Catalytic performances compared to commercial Pd/C catalyst are superior in terms of selectivity and comparable as activity.

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## 1. Introduction

The catalytic hydrogenation of aldehydes to the corresponding alcohols is an active task of research in both industrial and academic environments due to the importance of the resulting product as key intermediate for the synthesis of fine chemicals [1]. In particular, the reduction of benzaldehydes to benzylalcohols is of significant interest due to the commercial importance of benzylalcohols as solvent and as precursors in the synthesis of a wide variety of esters used in the flavor and fragrance and cosmetic industries [2].

This reaction is mainly promoted by catalytic systems based on noble metals (Pt, Pd, Ru, Rh) [3] and transition metals (Cu, Co, Ni) [4]. However, the selectivity of many systems is still low due to the tendency of benzyl alcohols to give the corresponding methyl arenes under the reaction conditions commonly used for the hydrogenation [5]. Furthermore, in the case of heterogeneous catalysts, not only the nature of the metal but also the choice of an appropriate support upon which to disperse a metal can have a relevant effect on both the activity and selectivity [6]. As a matter of fact a large variety of support have been used for palladium catalyzed hydrogenation of benzaldehyde comprising  $\text{Al}_2\text{O}_3$  [7],  $\text{SiO}_2$  [8], carbon nanotubes [9], and bentonite [10]. Moreover, recently, many Pd based catalytic systems have been developed varying the preparation strategy to obtain high reactivity catalysts in important industrial hydrogenation processes such as alkyne reduction [11].

In such scenario the study of new support for palladium based catalysts is highly desirable in order to improve the catalytic performances. For its chemical structure and its high thermal stability mayenite represents a good candidate to this purpose. Indeed, the use of mayenite as substrate for Ni catalyst was reported for biomass tar steam reforming.  $\text{O}_2^-$  and  $\text{O}_2^-$  inhibit Ni poisoning by sulfur incorporation in the cages [12]. Hosono et al. have investigated the partial oxidation of methane to CO and  $\text{H}_2$  over mayenite promoted metals such as Ni, Co, Pt, Rh and Ru [13]. Mayenite derivatives were obtained exchanging the  $\text{O}_2^-$  anions for other various ions, such as  $\text{OH}^-$  [14],  $\text{F}^-$  and  $\text{Cl}^-$  [15],  $\text{O}_2^-$  [16] and  $\text{H}^-$  [17,18]. Notably, such material, to the best of our knowledge, has not been used yet as support for noble metals in the catalytic hydrogenation. In this communication, we report on the use of mayenite hydrides as support for palladium to form a highly active and selective catalyst for the catalytic reduction of benzaldehyde. The complete characterization of the obtained catalyst by BET surface area, XRD spectra, and electronic microscopy (SEM and TEM) was also done. In addition, the selectivity in the hydrogenation of cinnamaldehyde was also investigated giving intriguing results.

## 2. Experimental part

## 2.1. Catalyst preparation

As in our previous work [19–21], mesoporous mayenite was prepared by sol–gel synthesis (see Supporting info).

Palladium loaded mayenite was prepared by reduction of  $\text{PdCl}_2$  with  $\text{NaBH}_4$  in a THF solution. 0.0895 g of  $\text{PdCl}_2$  and 4.9481 g of mayenite were added to 250 mL of distilled water. The mixture was stirred for

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4 h at room temperature than the solid was filtered and dried at 120 °C for 20 h and was added to a 0.1 M solution of NaBH<sub>4</sub> in anhydrous THF. The mixture was stirred for 5 h then the catalyst was recovered by filtration, washed with hot distilled water and dried at 250 °C for 16 h and calcined at 800 °C for 4 h. A commercial 1% Pd/C catalyst was also used for comparison. All reagents were purchased at reagent grade from Sigma Aldrich and used as received.

## 2.2. Support characterization

X-ray diffraction patterns were obtained on a Bruker D8 Advance automatic diffractometer operating with a nickel-filtered CuK $\alpha$  radiation. The BET surface area of the catalyst was determined using a Nova Quantachrome 4200e instrument using nitrogen as the probe molecule at liquid nitrogen temperature (–196 °C). The morphological and elemental analyses have been performed by a scanning electron microscope (SEM, Tescan Vega LMU) equipped with an X-ray energy dispersive microanalysis of elements having an atomic number >4, with a resolution of MnK $\alpha$  less than 123 eV (100.000 cps) (EDX, Bruker Quantax 800).

The transmission electron microscopy (TEM) images were obtained by using a Jeol Jem 1011 microscope (Jeol, Tokyo, Japan) operating at an accelerating voltage of 100 kV.

## 2.3. Hydrogen sorption test and hydride characterization

Hydrogen adsorption isotherm at 25 °C over the range 1–15 bar was obtained using a Quantachrome I-Sorb HP using ultra pure 6.0 grade H<sub>2</sub> (99.9999%V; Rivoira). Prior to the measurements, samples were degassed at 200 °C for 48 h. Analyses were conducted on 0.5 g of sample. Hydride characterization was made by <sup>1</sup>H NMR magic angle spinning nuclear magnetic resonance spectra measured with a Bruker Avance 300 spectrometer. The rotation frequency was 15 kHz. Experiment was conducted on ca. 0.1 g of powdered sample. Chemical shift scales were calibrated with the methylene absorption of the adamantane standard.

## 2.4. Aldehyde reduction

Benzaldehyde hydrogenation using solely mayenite was carried out in a high-pressure reactor of 150 mL capacity equipped with a pressure gauge, safety valve, valves for gas inlet and outlet and a thermocouple for temperature sensing. 0.5 g of mayenite and 5 mL of benzaldehyde (>99%, Sigma Aldrich) were added into a glass vial equipped with a magnetic stirrer. The reactor was charged with pure hydrogen (>99%, Rivoira) at a pressure of 8 bar and maintained at 120 °C. The reaction was carried out for different times (1 to 168 h) and samples were analyzed using GC–MS instrument (Agilent 7890A) with HP-INNOWAX fused silica capillary column.

Aldehyde hydrogenation with metal loaded mayenite (Pd/mayenite 1 wt.%) was conducted at 20 and 120 °C at a hydrogen pressure of 8 bar in the range 1–24 h, using 10 mL of diethyl ether as solvent (>99.5%, Sigma Aldrich) and a substrate/metal ratio of 1000 (0.025 g catalyst and 0.25 mL benzaldehyde). For comparison reactions with Pd/C 1 wt.% were conducted using the same substrate/metal ratio and reaction conditions.

## 3. Results and discussion

### 3.1. Support characterization

The structure of mayenite has been characterized by means of X-ray diffraction. XRD studies were carried out for (A) 1 wt.% Pd/mayenite and (B) mayenite as shown in Fig. 1. Since the metal loading was very low no characteristic peak for Pd (111) was obtained at  $2\theta = 40^\circ$ . Together with the major mayenite phase, two minor phases namely

Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> and CaAl<sub>2</sub>O<sub>4</sub> were detected as shown in our previous work [21].

Palladium content in mayenite was determined by ICP-OES analysis by digesting the sample in aqua regia (37% HCl and 70% HNO<sub>3</sub> 3:1 ratio). The metal loading found out was 1.09% for Pd/mayenite.

BET surface areas of mayenite based materials and commercial Pd/C catalyst have been measured (see Supporting info). An unexpected increase in the surface area of mayenite after Pd loading was observed (from 5.4 to 16.9 m<sup>2</sup>/g). Actually, the loading of a metal on a substrate results commonly in a reduction of the surface area due to the filling of the pores by the metal particles [22]. In our case such increase is probably due to the milling of the substrate before Pd loading and during the catalyst preparation process involving continuous stirring and reaction of the support with water that causes mayenite hydrated species formation [21]. Furthermore as evidenced by the X-ray analysis (Fig. 1) the Pd loaded mayenite shows a lower degree of crystallinity with a consequent increase of the amorphous phase that we hypothesize can be related to the increase of the surface area.

SEM images in Fig. 2A show that mayenite is characterized by the presence of sheets and two types of pores can be observed: large macropores on the  $\mu\text{m}$  scale (see the left column of Fig. 2) and mesopores on the nm scale (see the right column of Fig. 2). From SEM images presented, it can be seen that the Pd/mayenite sample (Fig. 2B) still retains significant porosity, even if the sheets seem to be grown during the catalyst preparation. However, both macropores and mesopores can be still observed in Pd/mayenite sample. EDS analysis of the material shows that Pd is not uniformly distributed on mayenite (see Supporting info).

TEM micrographs were also taken to show Pd particles into the mayenite structure. Picture shows that palladium particles were in the nano-range but not well dispersed (Fig. 3).

Fig. 4 illustrates the hydrogen sorption isotherms of mayenite collected at 25 °C. The maximum amount of hydrogen sorbed as hydride results in  $2.4 \times 10^{18} \text{ cm}^{-3}$ , considering a mayenite density of  $2.85 \text{ g/cm}^3$ . This value is two orders lower than that reported by Hayashi [14] of  $2.5 \times 10^{20} \text{ cm}^{-3}$  obtained after hydrogen sorption on mayenite at 1300 °C because, as expected, temperature plays an important role on the dissociation of hydrogen molecules.

Hydride ions incorporated into the cages of mayenite after H<sub>2</sub> adsorption at 25 °C for 48 h have been characterized by <sup>1</sup>H-MAS NMR. The signal at 4.9 ppm is assigned to the H<sup>–</sup> ions in cages according to literature [23].

### 3.2. Aldehyde hydrogenation

Catalytic activity was evaluated using high-pressure reactor. Benzaldehyde was chosen as model compound for hydrogenation reactions.

Firstly, in order to assess the role of mayenite in the hydrogenation reaction we used mayenite hydride without metal impregnation under hydrogen atmosphere in the presence of benzaldehyde (120 °C, 8 bar). Notably, the conversion of benzaldehyde to benzyl alcohol was observed with good selectivity (92% benzyl alcohol) but with low activity (12% conversion after one week).

Notwithstanding this result is not significant in term of conversion this behavior reveals an important aspect referred to the reactivity of the mayenite containing H<sup>–</sup> ions. Remarkably, when benzaldehyde hydrogenation was carried out using 0.5 g of mayenite hydride (prepared through thermal treatment at 1300 °C of mayenite under hydrogen atmosphere 4 h, 8 bar H<sub>2</sub>) and 0.5 mL of benzaldehyde dissolved in 10 mL of diethyl ether at 25 °C for 3 days, without feeding hydrogen, benzyl alcohol was selectively formed with the same conversion of 12% indicating that the reduction is due to the stoichiometric reaction of hydride contained in the mayenite structure showing the non-innocent nature of such support.

Consequently, we explored the possibility to use mayenite as support for palladium in the hydrogenation reaction comparing the results

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