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Short communication

Highly efficient catalysts for the synthesis of adipic acid from *cis*,*cis*-muconic acid

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ABSTRACT

Performing catalysts have been synthetized through incipient wet impregnation and tested for *cis*,*cis*-muconic acid hydrogenation to adipic acid. The activity of Pt-based catalysts has been compared with an Ni-based catalyst at a gentle condition. A supported 14.2 wt% Ni on γ-alumina converted 100% of muconic acid, yielding 99.4 mol% of adipic acid.

1. Introduction

cis,*cis*-Muconic acid (CCMA) is a diunsaturated dicarboxylic acid with six carbon atoms that is currently gaining interest because it represents a potential precursor for adipic acid (AA) production. In fact, CCMA can be hydrogenated into AA in a reductive atmosphere in the presence of heterogeneous catalysts [1,2]. AA is currently one of the most important chemicals, and the 2.6×10^6 tons annually produced are mainly used for the manufacturing of nylon 66 [3]. AA is also used for the production of gelatines, jams, polyamides, polyurethanes and lubricants [4].

Over the last few years, attempts to obtain CCMA by means of microbial approaches have been reported. One of the most promising of these attempts concerns the batch fermentation of D-glucose, through which CCMA has been obtained with a 22% molar yield after culturing modified *Escherichia coli* for 48 h [2]. With this process, a considerable amount of CCMA was obtained by fermenting a solution of one of the most very widespread existing material, the D-glucose. In fact, D-glucose can be obtained by depolymerizing cellulose or hemicellulose, and thus it could be easily from several kind of biomaterial, such as herbaceous biomass, softwood, hardwood, or crop residues. Another way of obtaining CCMA is to produce CCMA from toluene, using a mutant strain of Pseudomonas putida, without CCMA degrading enzymes. The mutant strain has been shown to accumulate 5 g/l of the product after 3 h of activity [5]. Other substrates have also been investigated: the production of CCMA from benzoic acid, using a mutant strain of Corynebacterium glutamicum or *Pseudomonas*, has been reported [6–8]. In the former case, the productivity and yield of CCMA were rather low, while in the latter, an almost 100% of yield was reached. Furthermore, two studies have been conducted on the production of CCMA from catechol, even though this substrate is very toxic and much more expensive than the other listed ones [9,10]. CCMA can also be obtained from biorefinery process intermediates and from the selective conversion of lignin, in which unsaturated oxygenated compounds, such as quinones, are converted into CCMA [11]. Recently, Vardon et al. [12] attempted the route of lignin biological transformation into CCMA and subsequent hydrogenation to AA by employing high selective Pd-based catalyst. The authors underlined the importance of lignin valorization for the biorefinery viability and sustainability; in fact, nowadays the lignin, that is the second most widespread biopolymer after cellulose, is normally undervalued and only used for heat and energy production in actual biorefinery plants [12].

Also in the past, similar pathways were carried out by employing supported noble metal catalysts in water or ethanol [2,13,14]. Draths et al. and then Niu et al. investigated CCMA hydrogenation under Pt, supported on active carbon catalysts, and achieved notable results; in these cases, the metal load was 10 wt% and, after some hours of reaction, a 90 to 97% molar yield of AA was achieved. Moreover, severe operative conditions, characterized by 34 bar of H_2 pressure, were adopted. J. M. Thomas et al., also obtained the quantitative hydrogenation of CCMA to AA using an high H_2 pressure (30 bar); even in this case, the active phase was essentially represented by noble metal, and some Ru-based bimetallic nanocatalysts, supported on mesoporous silica, were successfully tested. Nowadays, the efforts made to design new sustainable processes for the conversion of biobased chemicals to valuable ones should

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be focused on the use of alternative, less expensive, active phase and milder operative conditions.

Over the last few years, Nickel has become a valid alternative to noble metals for organic compound hydrogenation. The choice of Nickel was essentially due to its great interaction with hydrogen molecules and to its lower cost: in fact, Ni is nowadays >10 times cheaper than Pt (7.6 $/lb against the 90.0 $/lb of Pt) [15,16]. Several works have reported how olefins, such as toluene, naphthalene and benzene, can be hydrogenated successfully into their corresponding alkanes using Nickel based catalysts supported on alumina [17–19]. It is well known how the preparation and pretreatment of supported Nickel can affect the activity of the catalyst. Generally, the sol-gel technique has been indicated, even in the case of Ni, as the best method to obtain a high metal dispersion on the catalysts [20]. Nevertheless, metal organic precursors, such as nickel acetylacetonate, have to be employed with these techniques and a low metal content is normally obtained [18,21].

The aim of the present study was to demonstrate how a well dispersed Ni on a γ-alumina catalyst, obtained through incipient wet impregnation method, with a nickel (II) nitrate solution, could efficiently convert CCMA into AA in gentle operative conditions in an aqueous medium.

2. Experimental

2.1. Catalysts preparation and activity test

In order to prepare the catalysts, supports were dried for 2 h at 473 K to remove moisture from the pores; impregnation was then carried out by slowly dropping precursor under stirring at 313 K. The precursors and supports were stirred for 2 h; the ratio between precursor solution volume (V_{prec}) and mass of the support employed (m_{supp}) was tailored for each support. In particular, considering the higher surface area and pore volume of active charcoal, for the carbonaceous support a V_{prec}/m_{supp} of about 3.4 was used, while for the metal oxides, characterized by a lower porosity grade, a V_{prec}/m_{supp} ratio of about 1.7 was adopted. After impregnation, the mixture was dried overnight at 393 K and calcined at 773 K for 3 h under an N_2 flow. The weight loss regarding the activated charcoal-based catalysts preparation was quantified as 6.6 wt% of the initial catalysts weight. Finally, the catalysts were pretreated under an H_2 flow (5 vol% in Ar) for 3 h at 573 K. Impregnations were performed using H_2PtCl_6 on titania, alumina and active carbons, for the Pt-based catalysts, in order to obtain an amount of metal of between 5 and 10 wt% [22,23]. Pt/C 10 wt% (9.3%Pt/C) was therefore prepared to compare the present results with those of previous published works. About 5 wt% of platinum was loaded onto γ-alumina (5.2%Pt/Al_2O_3), active carbon (5.3% Pt/C) and titania (5.0%Pt/TiO_2) to explore the effect of the metallic loading reduction and the influence of the different supports on the hydrogenation. A 15 wt% Ni on γ-alumina (14.2%Ni/Al_2O_3) catalyst was synthetized through the incipient wet impregnation method. In a typical experiment, about 300 mg of catalyst was added to 50 ml of 1 wt% CCMA solution and a pressure of pure H_2 equal to 10 bars was established inside the reactor chamber. When the reactor was sealed, before pressuring with H_2, the headspace was purged three times using N_2; after that, the H_2 was flowed inside the reactor. All the experiments were carried out until the selected temperature set point and the reaction time were reached, after which the reactor chamber was cooled down with a fast quenching.

2.2. Characterization of liquid products and catalysts

The amount of metal was measured by means of inductively coupled plasma mass spectrometry (ICP-MS), while the phase structure of the prepared catalysts was evaluated by performing X-ray diffraction (XRD, Panalytical X'Pert Pro, 2θ range 20–90, step 0.02, time per step 240 s). Surface areas (S_{BET}), micropore and mesopore surface area (S_{micro}, S_{meso}), micropore and mesopore pore volume (V_{micro}, V_{meso}) and total pore volume (V_{pores}) of all the catalysts were determined using a surface area and porosity analyser, in agreement with N_2 adsorption/desorption at 77 K [24,25]. Before the physisorption of N_2, all the catalysts were degassed for 2 h at 473 K (for all the isotherms obtained, see from Figs. S1 to S5 of the Electronic supporting information, ESI). The Brunauer-Emmet-Teller (BET) method was used to determine the surface area of the catalysts in the 0.05–0.20 relative pressure range, while the mesoporous surface area and volume of samples and mean pore diameter were obtained with the Barret, Joyner & Halenda (BJH) adsorption method. The microporous surface area and volume were determined by using t-plot adsorption method. The mean particle diameter of the metals (d_p), active site surface area (S_{met}) and the metal dispersion degree (D) were evaluated by means of CO chemisorption techniques [24,26,27]. In order to analyse metal dispersion, metal particle diameter and metal surface area, which were calculated by means of CO pulse chemisorption techniques, the samples were first pretreated under a 40 ml/min O_2 flow, starting from room temperature until 573 K was reached and were then left under this O_2 flow for 1 h. A 40 ml/min flow of 5 vol% H_2 in Ar was then introduced to reduce the metal on the catalysts using a temperature ramp of 20 K/min until 673 K; this condition was maintained for 3 h. After 2 h of He purging, from 673 K till room temperature, 15 CO pulses, using helium as the carrier (20 ml/min), and a loop volume of 0.308 ml were introduced.

Liquid products were determined by high performance liquid chromatography; *trans*-β-hydromuconic acid (tβhMA), which results from the incomplete CCMA hydrogenation, and the CCMA isomerization product, *trans-trans*-muconic acid (ttMA), were among the CCMA by-products. Analyses of the liquid products were carried out using a Rezex ROA organic acid H^+ column (300 × 7.8 mm, Phenomenex) at 333 K and a mobile phase flow equal to 0.6 ml/min. Five millimeters of an aqueous sulfuric acid solution was selected as the mobile phase to elute the samples. The whole analysis lasted 40 min. The organic acid concentrations were quantified by means of a refraction index detector (RID), using an external standard calibration method.

Table 1
Morphology, metal dispersion and loading of the investigated catalyst.

Catalyst	S_{BET}[a] (m^2/g)	S_{micro}[b] (m^2/g)	S_{meso}[c] (m^2/g)	V_{pores}[d] (cm^3/g)	V_{micro}[b] (cm^3/g)	V_{meso}[c] (cm^3/g)	d_p[c] (Å)	S_{met}[e] (m^2/g)	D[e] (%)	Metal loading[f] (wt%)
9.3%Pt/C	587.5	248.7	338.8	0.56	0.12	0.38	59.2	5.2	20.3	9.3
5.3%Pt/C	768.6	389.5	379.1	0.61	0.19	0.42	58.4	3.0	21.3	5.3
6.2Pt/Al_2O_3	97.4	0.0	97.4	0.23	0.00	0.23	79.9	1.8	10.7	6.2
5.0%Pt/TiO_2	79.1	0.0	79.1	0.29	0.00	0.29	130.5	2.9	21.5	5.0
14.2%Ni/Al_2O_3	135.2	0.0	135.2	0.20	0.00	0.20	47.6	8.6	8.6	14.2

[a] BET surface area is obtained from N_2 adsorption isotherm in the relative pressure range. 0.05–0.20.
[b] Surface area of micropore and volume of micropore are obtained from the t-plot adsorption method.
[c] Surface area and volume of mesopore and mean pore diameter are estimated from the BJH adsorption plot method.
[d] Pore total volume ($V_{meso} + V_{micro}$).
[e] Calculated with CO pulse chemisorption techniques.
[f] Determined with ICP-MS analysis.