CeO$_2$-doped nanostructured materials as a support of Pt catalysts: chemoselective hydrogenation of crotonaldehyde

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An improvement of the catalytic activity and selectivity for the selective hydrogenation of the carbonyl bond in crotonaldehyde has been observed by addition of a dopant cation (Zn$^{2+}$, Tb$^{3+}$, Ti$^{4+}$, Nb$^{5+}$) to Pt/CeO$_2$ mesostructured catalysts. A linear correlation between the yield to crotyl alcohol and the polarizability of the doping cation is reported. The formation of new catalytic active sites at the metal-support interphase favoring the polarization of the C = O bond of crotonaldehyde has been observed by FTIR spectroscopy. A correlation between the amount of these sites and the initial selectivity to crotyl alcohol is discussed.

KEY WORDS: crotonaldehyde; CeO$_2$-doped; cation polarizability; FTIR of CO adsorption.

1. Introduction

The presence of strong metal-support interaction (SMSI) effects between noble metal particles and oxidative supports under reducing conditions has become crucial in heterogeneous catalysis for many different applications [1–3]. These SMSI effects, firstly described by Tauster et al. in 1978, are characterized by a suppression of the hydrogen and CO chemisorption ability of noble metal catalysts supported on reducible oxides (TiO$_2$, CeO$_2$ and Nb$_2$O$_5$) after a reduction treatment in hydrogen at high temperature (around 773 K) [4]. Further studies by Hayek and co-workers have revealed that the SMSI effects are due either to electronic and/or geometric effects induced after different reduction treatments. Electronic effects imply charge transfer (electronic perturbations) at the interface between the metal particle and the support [5] and also the formation of noble metal-support metal intermetallic bonds with alloy formation [6]. Geometric effects imply changes in the active surface area of the metal by “wetting” of the metal particle on the support (spreading) and coalescence [7], which is favored by oxygen vacancies at the metal-support interface, or by oxide migration over the metal surface (decoration) [8].

The existence of strong metal-support interaction effects on oxide supported noble metal particles can be assessed not only by the effects described above but also using probe reactions such as those involving hydrogenation of C = O containing molecules. One example of these reactions is the chemoselective hydrogenation of $\alpha$,$\beta$-unsaturated aldehydes [9,10]. These unsaturated aldehydes contain two conjugated double bonds which are able to be hydrogenated, a C = C and a C = O.

Unfortunately, monometallic noble metal catalysts lead mainly to the production of the saturated aldehyde, which is the most stable thermodynamically and kinetically product [11]. Therefore, a promotion of the metal particle is necessary in order to modify the chemoselectivity towards the desired unsaturated alcohol. This promotion can be achieved either by the addition of a second metal (promoter) [12–14] or by the use of reducible oxide supports (CeO$_2$ [15–18], TiO$_2$ [19,20], ZnO [21] and SnO$_2$ [22]). In the case of the reducible oxides, the induction of strong metal-support interaction effects after a reduction treatment (electronic and/or geometric effects) has been proposed as responsible of the increased selectivity. In this sense, cerium based platinum catalysts have been widely used in the hydrogenation of an $\alpha$,$\beta$-unsaturated aldehyde, such as crotonaldehyde. The beneficial effect of CeO$_2$ towards the hydrogenation of the carbonyl C = O bond after a reduction treatment at high temperature (above 773 K) is still a matter of controversy and it has been attributed to the formation of defect sites (oxygen vacancies) at the metal-support interphase [17,18], the formation of CePt$_5$ alloy phases after high temperature (above 973 K) [23] or the growth of epitaxial Pt(111) on CeO$_2$ [24]. Recent studies on high surface area-nanostructured Pt/CeO$_2$-SiO$_2$ catalysts have described an important improvement in the catalytic activity, stability and selectivity towards crotylalcohol formation in comparing with the pure mesostructured Pt/CeO$_2$ catalyst and also in comparing with conventional oxide supported platinum catalysts [18]. This improvement has been attributed to the presence of highly dispersed platinum particles together with the formation of special sites “Pt-CeO$_2$$_{x}$” at the metal-support interface, as deduced from XPS and FTIR-CO adsorption experiments, which are able to polarize the carbonyl bond, thus favoring its hydrogenation.

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Considering the crucial effect of the nanosized-high surface area supports on these reactions and more specifically, the excellent behavior of the more complex mesostructured CeO$_2$-SiO$_2$ oxide in comparing with the simple CeO$_2$ counterpart, the aim of the present work is to modify the chemical and textural properties of the former mesostructured CeO$_2$ support by the incorporation of a dopant metal, i.e. di- (Zn), tri- (Tb), tetra- (Ti) or penta-valent (Nb) cation, into the bulk structure. The effect of the different doping cations on the catalytic behavior of these Pt/CeO$_2$-M catalysts will be studied on the chemoselective hydrogenation of crotonaldehyde. A correlation of the crotylalcohol yield with the nature of the doping cation will be proposed.

2. Experimental section

A high surface area, thermally stable, nanostructured CeO$_2$ was prepared by self-assembly of individual CeO$_2$ nanoparticles in a liquid crystal phase [25]. More specifically, a water, acid colloidal dispersion of CeO$_2$ nanoparticles (~4 nm) was poured into an aqueous solution of poly (alkylene oxide) triblock copolymer designated EO$_{20}$PO$_{70}$EO$_{20}$. The resulting suspension solution of poly (alkylene oxide) triblock copolymer nanoparticles was aged at 318 K for 16 h until a precipitate was formed. The resulting solid was recovered, washed with distilled water and air-dried at 353 K. Then, the copolymer template was removed by slowly increasing the calcination temperature from 293 to 773 K, staying at this temperature for 6 h. The BET area of the resulting mesostructured CeO$_2$ after calcination was 166 m$^2$ g$^{-1}$.

A series of CeO$_2$ doped nanostructured materials with di- (Zn$^{2+}$), tri- (Tb$^{3+}$), tetra- (Ti$^{4+}$) and penta-valent (Nb$^{5+}$) cations were prepared by wet impregnation of the preformed mesostructured CeO$_2$. More specifically, an aqueous solution of the corresponding dissolved salts (ex. Tb(NO$_3$)$_3$) was placed together with the aforementioned CeO$_2$. The resulting solid was dried overnight at RT and calcined at 673 K during 6 h (1 K min$^{-1}$). This impregnation, drying and calcination procedure was repeated in a second cycle under identical conditions [25]. Nitrogen adsorption-desorption isotherms and TEM confirmed that the doped materials maintain the nanostructure of the original CeO$_2$ [26]. The BET surface area of the resulting CeO$_2$-doped materials after calcination ranges from 140–150 m$^2$ g$^{-1}$.

Pt/CeO$_2$ and doped Pt/CeO$_2$-M catalysts (1 wt% Pt) were prepared by wet impregnation of the support with an aqueous solution of [Pt(NH$_3$)$_4$(NO$_3$)$_2$ (Aldrich). Afterwards, the catalysts were dried at 353 K and calcined in air at 673 K for 4 h.

Kinetic measurements on vapor-phase chemoselective hydrogenation of crotonaldehyde (Fluka, > 99.5%) were carried out in a fixed-bed stainless steel tubular reactor (12 mm internal diameter, 340 mm length) equipped with a coaxial thermocouple for temperature measurement. Before the catalytic run, the catalyst (100 mg, 0.2–0.6 mm particle size diluted with 0.4 g of SiC) was reduced under flowing hydrogen (50 cm$^3$ min$^{-1}$) at low (473 K) and high (773 K) temperature for 1 h (5 K min$^{-1}$). After the reduction treatment, the catalyst was cooled in flowing H$_2$ down to the desired reaction temperature (303 K and 353 K). Then, the catalyst was contacted with the reaction mixture (H$_2$/CROALD ratio of 60) formed by passing a hydrogen flow through a thermostabilized saturator (278 K) containing the unsaturated aldehyde. The reaction products were analyzed by on-line gas chromatography with a Rt-x-WAX 30 m semicapillary column.

Fourier transform infrared (FTIR) experiments were recorded on a Bio-Rad FTS-40A spectrophotometer in the transmission mode by using a quartz infrared cell fitted with KRS-5 windows and an external furnace. The spectra were recorded using a MCT detector and the spectral resolution was 4 cm$^{-1}$. Watts of catalyst samples (10 mg cm$^{-2}$) were reduced in situ with a H$_2$ flow at 773 K for 1 h. After reduction, the samples were evacuated for another hour at the same temperature and cooled down to 298 K. CO was introduced at 298 K with calibrated volumes (1.55 cm$^3$). The CO pressure was varied from 30 to 100 mbar.

3. Results and discussion

Small angle X-ray scattering (SAXS) of the nanostructured CeO$_2$ material exhibits a single low angle peak centered at 11 nm [18]. The 2D X-ray diffraction pattern of a selected area in the material shows a hexagonal structure which is in accordance with the regular hexagonal array of nanoparticles (~4 nm) observed with TEM. Wide-angle X-ray diffraction studies confirm the crystalline nature of the CeO$_2$ with the characteristic diffractogram of the fluorite structure showing peaks at 27.3°, 31.8°, 46.0° and 54.8°. Interestingly, the XRD pattern of the nanometric doped CeO$_2$ particles is slightly shifted in comparing with the original CeO$_2$, which indicates the formation of well crystallized Ce$_{1-x}$M$_x$O$_2$ ($x = 0–0.2$) solid solutions in which the dopant has entered the nanoparticle and is uniformly distributed through it (see ref. [26]).

3.1. Pt/CeO$_2$ catalyst

The un-doped mesostructured Pt/CeO$_2$ catalyst has been already studied and discussed in a previous paper [18]. Briefly, FTIR studies of CO adsorbed on the in situ reduced (773 K) Pt/CeO$_2$ catalyst shows the presence of characteristic IR bands of linear adsorbed CO (2063 cm$^{-1}$), Pt-dicarbonyl species (1984 cm$^{-1}$) and bridge CO species (1908 cm$^{-1}$), together with the development of new carbonate bands in the 1600–1700 cm$^{-1}$ region.