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Selective hydrogenation of crotonaldehyde on Au/HSA-CeO_2 catalysts

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Abstract

The gas-phase hydrogenation of crotonaldehyde was carried out over Au supported on high-surface area (HSA) CeO_2, previously reduced at 120 °C. The products analyzed during the initial, nonequilibrium stage showed the formation of large amounts of ethanol, which rapidly decreased with time on stream and were replaced by a combination of condensation products (mainly 2,4,6-octatrienal) under equilibrium conditions. The production of crotyl alcohol largely exceeded that of butanal at any time on stream. Under steady-state conditions, the crotyl alcohol-to-butanal ratio was equal to 1.7. When the catalyst was recalcined in air at 300 °C, just before the reduction treatment, the formation of ethanol in the initial stage and that of condensation products under steady state decreased. Besides, notable increase in the production of crotyl alcohol was observed, whereas butanal formation was unaffected. Finally, Au/HSA-CeO_2 is a highly selective catalyst for C=O bond hydrogenation when crotyl alcohol/butanal ratio is equal to 3 under a steady-state regime. These results were compared to those obtained for Au/TiO_2 [R. Zanella, C. Louis, S. Gorgio, R. Touroude, J. Catal. 223 (2004) 328]. The role of acid–base sites, as well as that of the redox centers of HSA-CeO_2, is evaluated. Even though ceria sites are engaged in the reaction, the catalytic properties of Au/HSA-CeO_2 are attributed mainly to the gold nanoparticles.

Keywords: Au/CeO_2; Ceria; Selective hydrogenation; Gold catalysts; Crotonaldehyde hydrogenation

1. Introduction

It has been demonstrated that heterogeneous gold catalysts, when prepared in an appropriate manner, are active and selective for a number of reactions. The key point is preparation of the supported gold catalysts, where the metal particles should be within the nanometer size range [1]. The most remarkable results for gold nanoparticles have been found in oxidation reactions, such as CO and VOC oxidation [2,3]. However, for hydrogenation reactions, gold has always been considered poorly reactive because of its low ability to dissociate H_2 [4].

Even if gold catalysts are not as active, they are more promising than conventional metal hydrogenation catalysts because of their higher selectivity, in, for instance, the selective hydrogenation of α,β-unsaturated aldehydes and ketones, where the challenge lies in hydrogenating the C=O bond preferentially over the C=C bond [5]. Conventional monometallic hydrogenation catalysts (Ni, Pd, and Pt), deposited on silica or alumina supports, produce saturated aldehyde as the main product [6–8]. However, using reducible oxide as a support has a significant beneficial effect on selectivity. For Pt supported on TiO_2 [9,10], ZnO [11], SnO_2 [12], or CeO_2 [13,14], 50–90% crotyl alcohol selectivity was observed (in the steady state) for crotonaldehyde hydrogenation.

Regarding the triad of group I metals, copper should be considered intrinsically unselective for the hydrogenation of α,β-unsaturated compounds [15]. Treatment with thiophene is necessary to improve the catalytic performance [16]. On the other hand, silver [17–21] and gold [22–31] catalysts lead to relatively high selectivity to the desired product, with no sophisticated catalyst preparation required, demonstrating that a particular property of gold and silver nanoparticles is their intrinsic selectivity toward hydrogenation of the conjugated C=O bond. In addition, the nature of the support has some influence on activity and selectivity.

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Focusing our attention on selective gold catalysts for the hydrogenation of α,β-unsaturated compounds, we find various explanations of how the support affects the catalytic behavior of gold. Milone et al. [26,27] concluded that the selectivity toward unsaturated alcohol is strongly influenced by the support and increases with its reducibility; they suggested that an electron transfer creates electron-enriched gold particles on which the C=O bond is activated. Regarding crotonaldehyde hydrogenation, Bailie and Hutchings [23] showed that Au/ZrO_2 and Au/ZnO are quite selective. They demonstrated that selectivity can be enhanced by pretreatment with thiophene and suggested that sites at the Au–support interface could be responsible for the carbonyl activation. The effect of thiophene was to modify these interface sites or to create new sites on the support. An increase in up to a value of 80% was found on Au/ZnO when the catalyst was reduced at high temperature (400 °C) [24]. It was proposed that this exceptionally high selectivity was due to the presence of large gold particles (up to 20 nm) on ZnO. For the same reaction, Okumura et al. [25] found selectivities to crotyl alcohol of 25% for Au/TiO_2 and 10% for Au/Al_2O_3 and Au/SiO_2, with the gold particle sizes for these different catalysts in a similar range (3–5 nm). The reaction would be slightly sensitive to the selection of the support for the product selectivity. On a Au/SiO_2 catalyst with similar particle sizes as those studied by Okumura et al., but using higher pressure and temperature, Schimpf et al. investigated the selective hydrogenation of acrolein over Au/SiO_2, Au/TiO_2, Au/ZrO_2, Au/ZnO, and Au-In/ZnO [29]. They found selectivities between 23 and 63% and concluded that the edges of single crystallites are the active sites for the preferred C=O hydrogenation. The support intervenes only to determine the morphology of the particles.

For Au/TiO_2, Zannella et al. [30] studied the affects of the preparation method, gold particle size, and reaction temperature in the 80–160 °C range, as well as the concentration of oxygen vacancies at the gold–titania interface, on the hydrogenation of crotonaldehyde. They found that the reaction rate was sensitive to particle size, whereas the selectivity was independent of reaction temperature, preparation method, and reduction pretreatment, demonstrating that oxygen vacancies are not involved in the reaction.

The logical approach for the further investigation of this peculiar behavior of gold catalysts in the selective hydrogenation of α,β-unsaturated carbonyl compounds is to compare gold catalysts deposited on different supports. Consequently, here we report the results obtained for crotonaldehyde hydrogenation over gold supported on high-surface area ceria (Au/HSA-CeO_2). The reaction was performed under the same experimental conditions as for Au/TiO_2 [30]. To the best of our knowledge, this is first time that Au/HSA-CeO_2 has been used in the hydrogenation of crotonaldehyde. Previously, Au/CeO_2 was used mainly in the water–gas shift reaction [32] and the combustion of volatile compounds [33], where ceria plays an active role by supplying oxygen.

In this work, attention was focused on the influence of the gold–support interaction on the selectivity to different products, as well as the role of Lewis acid and basic sites and redox properties of the ceria in the reaction.

2. Experimental

2.1. Catalyst preparation

Ceria from Rhône Poulenc (Acalys HSA 5) with a surface area of 240 $m^2\,g^{-1}$ and a pore volume of 0.2 $ml\,g^{-1}$ was used as a support, and $HAuCl_4{\cdot}xH_2O$ (Alfa Aesar) was used as a gold precursor. Before preparation, CeO_2 was dried in air at 500 °C for 1 h.

The catalyst was prepared by the deposition–precipitation method with sodium bicarbonate. The support was mixed at 70 °C with aqueous solution containing the desired amount of gold. The pH of the solution was adjusted to 8 by adding dropwise 0.1 M Na_2CO_3 solution under vigorous stirring. The suspension was filtered, and the catalyst precursor was washed with ammonia solution (4 $mol\,L^{-1}$) to eliminate Cl^- and then with hot water (80 °C) to wash off the Na^+ ions. The catalyst was then dried at 100 °C for 12 h and calcined under air at 300 °C (1 °C/min) for 4 h before being stored in a sealed vessel.

2.2. Characterization

The concentrations of Au and Ce were determined by atomic absorption spectroscopy (AAS) at CNRS, Vernaison, France. X-ray diffraction (XRD) analysis of Au/HSA-CeO_2, reduced at 120, 300, and 500 °C, was done using a Siemens D 5000 polycrystalline diffractometer with Cu$K\alpha$ radiation.

X-ray photoelectron spectroscopy (XPS) measurements were carried out with a VG ESCA III spectrometer with an Mg anode source ($K\alpha = 1253.6$ eV) without a monochromator. Before analysis, two different pretreatments were performed in situ in the preparation chamber attached directly to the analysis chamber: calcination at 300 °C and calcination at the same temperature followed by reduction at 120 °C. Charging corrections were carried out using the binding energy (BE) of Ce^{4+} ($3d_{3/2}$ $4f^0$) at 916.6 eV according to [34], because this peak is very well defined. In this case, the C (1s) peaks could not be used for a BE reference, because the line shape showed a superposition of several components.

The reducibility of the catalysts was followed by temperature-programmed reduction (TPR) in a conventional flow system. Samples were previously calcined at 300 °C and then purged with Ar at the same temperature. Afterward, the catalyst was cooled in Ar, then switched to a H_2/Ar (5%) mixture. The temperature was linearly increased up to 730 °C, and hydrogen consumption was measured with a thermal conductivity detector.

2.3. Catalytic test

The reaction was performed in a glass flow reactor operating at atmospheric pressure, as described elsewhere [35]. Before running the catalytic test, samples were submitted to one of two in situ pretreatments: (a) reduction at 120 °C for 1 h in H_2 or (b) calcination at 300 °C for 1 h with 25 $cm^3\,min^{-1}$ of air, cooling to room temperature, followed by reduction for 1 h at 120 °C. Between treatment switches, the reactor was exhaustively evac-