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Selective hydrogenation of α,β-unsaturated ketone to α,β-unsaturated alcohol on gold-supported iron oxide catalysts: Role of the support

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Abstract

The influence of the structural characteristics of the support in the liquid-phase reduction of *trans*-4-phenyl-3-buten-2-one or benzalacetone (C_6H_5–CH=CH–CO–CH_3) to the corresponding α,β-unsaturated alcohol (UA) on gold-supported iron oxide catalysts was investigated. Commercial goethite [FeO(OH)], maghemite (γFe_2O_3), and hematite (αFe_2O_3), along with an iron oxy-hydroxide prepared by precipitation, were used as supports. The catalytic behavior of Au/Fe_2O_3 reference catalyst (supplied by the World Gold Council) was also investigated. Gold-supported catalysts and the parent supports were extensively characterized by BET, X-ray diffraction, temperature-programmed reduction, and transmission electron microscopy. On all gold catalysts except the Au/Fe_2O_3 reference, the catalytic activity increased with increasing gold content. The lowest activity of reference with respect to the catalyst with a similar gold loading has been ascribed to the different sample pretreatments. Samples prepared by us were reduced under very mild conditions (in H_2 at 343 K for 1 h), whereas the Au/Fe_2O_3 reference was calcined at 773 K. From our data, no correlations can be drawn between activity and selectivity and mean gold particle size. Selectivity toward the hydrogenation of the conjugated C=O bond varied with the structural characteristics of the support, ranking in the order FeO(OH) > iron oxy-hydroxide > γFe_2O_3 > αFe_2O_3. On the most selective catalyst—gold supported on goethite—the selectivity toward the formation of UAs was 64%. A correlation between the reducibility of catalysts and selectivity was found. Selectivity toward the formation of UA increased with the reducibility of the support. In accordance with data in the literature, we propose that an electron transfer from the reduced support to the metal creates more electron-enriched gold particles on which the back-bonding with the π^* C=O orbital is favored, so that the hydrogenation of the C=O group increases over that of the C=C group. However, it cannot be ruled out that the enhancement of the selectivity is favored through a cooperative effect of special Fe(III) or Fe(II) sites, and that more negatively charged gold nanoparticles nearby present the reduced support.

Keywords: Gold catalysts; Selective hydrogenation; α,β-Unsaturated ketones; α,β-Unsaturated alcohols; Iron oxide

1. Introduction

Recent studies have widely reported that gold-supported catalysts show a remarkable selectivity toward the hydrogenation of the conjugated C=O bond in the hydrogenation of α,β-unsaturated aldehydes [1–5] and ketones [6,7]. The catalytic behavior of gold in the hydrogenation of the α,β-unsaturated ketones is of a particular relevance from both a scientific and a synthetic standpoint, due to the fact that the selective hydrogenation of these substrates by gaseous H_2 in the presence of heterogeneous catalysts is very difficult [8], although it can be easily achieved under hydrogen transfer conditions [9,10]. The reduction of lactonic enone, an intermediate in the prostaglandin synthesis, to secondary allylic alcohol occurs with high yields on Pt–Sn supported on SiO_2 catalysts, using isopropyl alcohol as a hydrogen donor [10]. Catalysts contain alloyed Pt–Sn particles covered by oxidized forms of tin at the surface, together with ionic tin on the support. It has been suggested that the high selectivity in the hydrogenation of lactonic enone is the result of decreased adsorption of C=C bond on Pt–Sn alloyed particles, activation of carbonyl on the oxidized Sn ions, and the use of hydrogen transfer agent, which favors a lower hydrogen coverage with respect to gaseous hy-

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drogen [10]. Another factor contributing to the enhanced hydrogenation rate of the conjugated C=O bond is steric hindrance at the C=C bond of the prostaglandin-type unsaturated ketone. The importance of steric hindrance at the C=C bond has been confirmed by experiments carried out with methylvinylketone, which, under similar reaction conditions, was reduced mainly to saturated ketone [10].

Recently, De Bruyn et al. [11] reported on the chemoselective reduction of complex α,β-unsaturated ketones to unsaturated alcohol (UA) over Ir-supported catalysts. A number of substrates, (steroid enones, prostaglandin intermediates, α-ionone, and β-ionone) with varying degrees of substitution on the conjugated C=C bond have been investigated. The reductions were carried out in the liquid phase at 298 K in the presence of gaseous H_2. On all of the substrates but the prostaglandin intermediates, the chemoselective reduction of enones to allylic alcohol occurs when isopropyl alcohol (secondary alcohol) or isoamyl alcohol (tertiary alcohol) are used as solvents. The use of methanol (primary alcohol) leads to the preferential hydrogenation of the C=C bond with formation of saturated ketone. Among the catalysts investigated, Ir supported on β-zeolite are more selective toward hydrogenation of the conjugated C=O bond. Ir supported on C and TiO_2 also show higher selectivity ($>45\%$) in the hydrogenation of α-ionone using isopropyl alcohol as a solvent [11]. In contrast, in earlier work, Kaspar et al. [8] found that Ir/TiO_2 catalyst showed no selectivity in the gas-phase hydrogenation of mesityl oxide (4-methyl-3-penten-2-one).

A peculiarity of gold is its intrinsic selectivity toward hydrogenation of the conjugated C=O bond using gaseous H_2 as a reductant. We have previously verified that during the liquid-phase hydrogenation of several substrates, including *trans*-4-phenyl-3-buten-2-one (benzalacetone), 4-methyl-3-penten-2-one, and 3-penten-2-one, the reduction occurs by means of molecular H_2, and the mechanism of hydrogen transfer from the alcohol to the substrate does not occur [7].

In the liquid-phase hydrogenation of benzalacetone on gold supported on Al_2O_3, the selectivity toward the formation of UA approaches 10%; a strongly enhanced selectivity ($>60\%$) has been obtained on gold supported on iron oxide catalysts [7]. Moreover, it has been pointed out that iron oxide by itself is not sufficient to enhance the hydrogenation rate of C=O with respect to the C=C bond in hydrogenation of the α,β-unsaturated ketones—both gold and iron oxides are necessary. Indeed, when the hydrogenation of benzalacetone was carried out on catalysts prepared by dispersing colloids of metallic ruthenium on the same iron oxide support used to disperse gold, the selectivity of UA was $<2\%$ [7]. This indicates that the catalytic behavior arises from a synergetic effect between the two constituents.

It has been argued that the intrinsic selectivity of gold can be due to the adsorption mode of the conjugated systems on this metal. Some have proposed that among the different adsorption modes of the conjugated systems [12,13], gold is likely a metal on which the 1,2-C=O adsorption mode is preferred over the 1,4-C=C–C=O mode. The scarcity of the 1,4-C=C–C=O species on gold catalysts, which are responsible for the formation of saturated aldehydes or ketones [12,13], is in accordance with the higher intrinsic selectivity of gold catalysts toward the formation of UA.

In the hydrogenation of benzalacetone, selectivity to UA is strongly influenced by the microstructural characteristics of the iron oxide support. Gold supported on amorphous oxy-hydroxides or on a partially crystallized mixture of goethite [FeO(OH)], ferrihydrite, and hematite (αFe_2O_3) is more selective than gold supported on well-crystallized hematite [7].

The aim of the present work is to gain a deeper insight into the role of the support in the catalytic behavior of gold catalysts in the hydrogenation of benzalacetone. Consequently, we investigated the catalytic activity of gold catalysts supported on single-phase iron oxides, including goethite, maghemite (γFe_2O_3), and hematite, and also of gold supported on a mixture of goethite, ferrihydrite, and hematite. We performed a detailed characterization of the catalysts to clarify the nature of the active sites.

2. Experimental

2.1. Sample preparation

Au-supported catalysts were prepared by deposition-precipitation in accordance with Haruta's procedure [14]. The deposition-precipitation of gold onto the supports was done by adding the support to an aqueous solution of $HAuCl_4$ previously adjusted at pH 7–8 with NaOH. The slurry was maintained at 343 K, under vigorous stirring, for 2 h. Then the samples were filtered, washed with deionized water until chloride was eliminated, and dried under vacuum at 353 K for 1 day.

Goethite, maghemite, and hematite used as supports were commercial products purchased from Aldrich. An iron oxy-hydroxide support was prepared by precipitation of iron hydroxide from a solution of $Fe(NO_3)_3 \cdot 9H_2O$ (Fluka) as starting materials. The precursor was poured into an aqueous solution of Na_2CO_3, 1 M (pH = 11.9) and maintained at 353 K under vigorous stirring. The solid was digested overnight at room temperature, washed with water until free of chloride ions ($AgNO_3$ test), then dried under vacuum at 353 K for 1 day.

The gold content was determined by measuring the absorbance of gold solutions at $\lambda = 400$ nm [15]. The solutions were prepared by dissolving the catalysts in HCl–HNO_3 (3:1 by volume), then adding a solution of tin(II) chloride in hydrochloric acid.

2.2. Sample characterization

Surface area measurements were made using the BET nitrogen adsorption method in a conventional volumetric apparatus, after outgassing (10^{-4} mbar) the sample at 353 K for 2 h. X-ray diffraction (XRD) studies were carried out with an Ital-Structures diffractometer using nickel-filtered Cu-K_α radiation by mounting the powder samples on Plexiglas holders. Diffraction peaks were compared with those reported in the JCPDS Data File.