Effect of Au nanoparticles on the activity of TiO_2 for ethanol upgrading reactions

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ABSTRACT

This article analyses the role of gold nanoparticles supported on TiO_2 for the gas-phase ethanol condensation. Previously, the original P25 surface was modified for increasing the Au-Ti interaction, in order to minimize the thermal deactivation. Catalysts were tested both in absence and presence of hydrogen (523–673 K, WHSV = 7.9 h^{-1}; y_{EtOH} = 0.32; y_{H2} = 0-0.1; 0.1 MPa). Parent TiO_2 is mainly selective for dehydration reactions yielding diethyl ether (favoured at low temperatures) and ethylene (favoured at higher temperatures). The presence of Au in the catalyst promotes dehydrogenation pathways, yielding acetaldehyde, as well as condensation products (mainly butanol, with selectivities close to 10%). According to DRIFT spectroscopy results, the strong ethanol adsorption on the TiO_2 surface justifies the low yields and the high relevance of side-reactions produced by inter- or intra- molecular dehydration routes (diethyl ether, and ethylene formation). The gold addition minimizes this adsorption and enhances the main route by a double role: an improvement in the dehydrogenation rate (yielding more acetaldehyde) and an enhancement in the hydrogenation steps.

1. Introduction

Although gold was historically considered as a nonactive noble metal in heterogeneous catalysis, it shows interesting properties as catalyst or promoter when it is presented as small nanoparticles [1,2]. Indeed, gold is able to catalyse many different reactions (oxidations, decompositions, hydrodechlorination reactions, etc.) at lower temperatures or with higher selectivity than other metal catalysts [3]. Supported gold materials, also promote selective hydrogenation of olefins, being these studies a turning point for gold application in catalysis [4,5]. Based on these preliminary studies, the hydrogenation of α,βunsaturated aldehydes using gold nanoparticles supported on TiO_2 and ZrO_2 was also studied, considering acrolein and crotonaldehyde as probe molecules [6,7]. Following this approach, Au supported catalysts could be interesting for other reactions, such as the ethanol-to-butanol valorisation, where hydrogen transfer reactions are relevant steps in the reaction mechanism.

Ethanol is nowadays produced from different biomass resources in large amounts [8–10], promoting de development of different valorisation routes. The ethanol gas-phase condensation is one of the most interesting ones, since it allows obtaining different compounds, such as 1,3-butadiene, 1-butanol, larger alcohols, etc., with interesting properties as biofuels and bioplatform molecules, with main attention focused on the 1butanol [11–13]. The ethanol condensation to obtain this molecule is accomplished by the Guerbet reaction, using basic materials as catalysts [14]. Despite different mechanisms have been proposed, most of the last studies consider the four-step reaction pathway as the predominant in this complex process [15–17]. This reaction mechanism, summarized in the Scheme Scheme 1, consists of the ethanol dehydrogenation to acetaldehyde, the acetaldehyde self-aldolization to obtain crotonaldehyde and two hydrogenation steps to obtain crotyl alcohol and 1butanol (main product). The dehydration of crotyl alcohol would also produce 1,3butadiene as, also of industrial interest. Main efforts to achieve a good selectivities to these compounds have been focused on the acid-base surface properties of the catalysts (considering the aldolization step as the key path), proposing hydroxyapatites and magnesia as good materials [15,17–18]. However, results are not very conclusive because main route is also conditioned by other steps that involve hydrogen and water molecules [14].

Parallel studies suggest TiO_2 as an interesting alternative because of its good redox properties that can also be very active in aldol condensations. In such a way, it has been tested in the acetaldehyde aldol-condensation, providing better results than other typical materials used for the Guerbet reaction [19,20]. However, this material has very poor performance in reactions involving dehydrogenation steps [20], so it cannot be directly used in the ethanol gasphase condensation. This fact
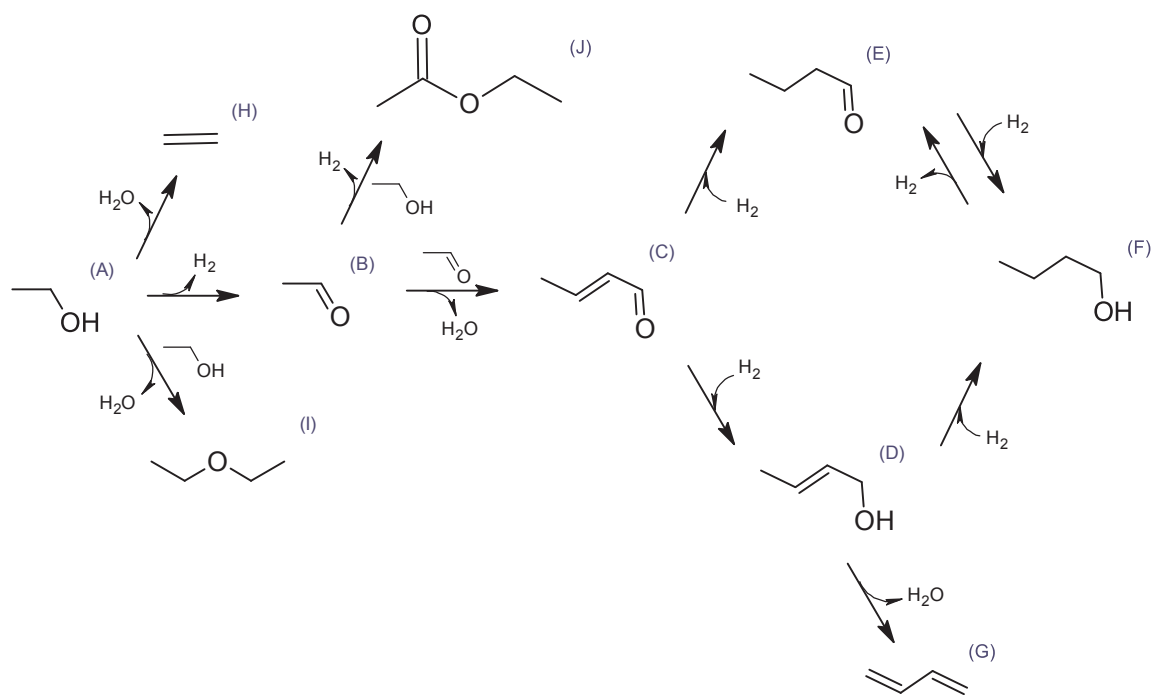
Scheme 1. Proposed ethanol condensation pathway by the four-step mechanism. Symbols: (A) ethanol; (B) acetaldehyde; (C) crotonaldehyde; (D) crotyl alcohol; (E) butanal; (F) 1-butanol; (G) 1,3-butadiene; (H) ethylene; (I) diethyl ether; (J) ethyl acetate.

suggests that the introduction of a dehydrogenation/hydrogenation active metal on the catalytic surface would improve the products yields by enhancing the acetaldehyde production (reducing the αhydrogen activation energy of the adsorbed ethanol). Moreover, working under reductive conditions (hydrogen feeding) in the presence of the active metal, last hydrogenations could be also favoured [17,20].

Some authors dealt with this drawback suggesting bifunctional materials by supporting different metals that can enhance the acetaldehyde production (reducing the αhydrogen activation energy of the adsorbed feeding) [21,22]. The different reaction conditions make difficult the direct comparison among these studies. However, the comparison of FTIR peaks of ethanol adsorption when using TiO₂ or Au/TiO₂ [23], as well as the previous results reported for hydrogenation/dehydrogenation reactions [7,24], suggest that this noble metal can be a good candidate for the ethanol condensation. Deposition-precipitation methods are the most extended procedures to prepare the Au/TiO₂, highlighting the good results (small particles, good dispersion, and high impregnation efficiency) obtained when urea is used as promoting molecule (DPU process) [25,26]. These methodologies do not require any treatment at high temperature and result into very active materials for reaction at soft temperatures. However, a common disadvantage detected in these studies is the instability and sintering process suffered by the Au particles when reactions are carried out at more severe conditions [26–28]. The subsequent deactivation of these materials is justified by the increase in the atom mobility at the highest temperatures. Due to the low surface area of titania supports (around 50 m²/g for the P25) these movements produce the collapse of different particles in the same pore, and the sintering process, reaching larger metal particle sizes that are catalytically inactive. This disadvantage could be prevented by modifying the original TiO₂ structure, obtaining a support with higher surface area, or by introducing some irregularities in the surface that promotes a stronger interaction between Pt and TiO₂ surface, limiting the natural movement of gold particles.

This article presents the analysis of the results obtained in the ethanol gas-phase reactions using a catalyst based on gold nanoparticles supported on a commercial P25 material (TiO₂). The original surface was modified by adding titanium isopropoxide in order to introduce a Ti-based monolayer on the crystalline surface, enhancing the

irregularities of the original one. This procedure has been previously reported, highlighting the good improvement obtained in terms of thermal stability [29–31]. The effect of reductive conditions and the analysis of the evolution of catalytic surface by Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy highlight as the main new contributions of this study, explaining the products distribution in terms of adsorbed species and metal-support-molecules interactions.

2. Experimental methods

2.1. Catalysts preparation

The modified titanium dioxide catalyst was prepared by the homogeneous precipitation method. 3 g of TiO₂ P25 (> 99.5%, Sigma-Aldrich, BET surface area of 35 65 m² g⁻¹) were suspended in 20 mL of deionized water and after that, 6 mL of titanium(IV) isopropoxide (97%, Aldrich) were added dropwise and mixed at 363 K under soft agitation for 8 h. Isopropoxide acts as an oxide overcoating that avoids the "material gap" and "pressure gap", typical phenomena related to the coexistence of more than one crystalline phase. These phenomena justify that metal particles can experience different relative pressure because of different coordinate states, hindering the metal impregnation [32,33]. The mixture was aged at the aforementioned temperature for 48 h without stirring. Thereafter, the resulting material was dried at 373 K for 24 h, and calcined in flowing air for 2 h (5 K min¹ of temperature ramp) at 773 K to obtain the final modified TiO₂.

Regarding to the 1.5 wt % Au/TiO₂ catalyst, the metallic gold nanoparticles were synthesized by the depositionprecipitation with urea method (DPU) [25]. This method was selected considering the previous comparison among different preparation procedures reported in the literature, considering the higher activity observed when using urea instead of the traditional impregnation and photocatalytic deposition [3]. The modified TiO₂ was dried at 373 K for 12 h before its use as support for the gold deposition to clean the surface. 0.3 g of the modified TiO₂ were mixed with a mixture of 5.5 mL of an aqueous solution (4.2·10⁻³ mol L⁻¹) of the gold precursor (HAuCl₄·3H₂O, 99.9%, Aldrich) and 20 mL of a urea aqueous solution (98%, Aldrich; 4.2·10⁻¹ mol L⁻¹). The suspension was kept under stirring during all the process. The