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Effective gold catalyst supported on mesoporous silica decorated by ceria for the synthesis of high value lactobionic acid

Luis-Felipe Gutiérrez[a,b], Safia Hamoudi[a], Khaled Belkacemi[a,*]

[a] Department of Soil Sciences and Agri-Food Engineering, Université Laval, Québec, Canada G1V 0A6
[b] Department of Food Sciences and Nutrition, Université Laval, Québec, Canada G1V 0A6

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ABSTRACT

Gold supported on mesoporous SBA-15 and SBA-15-CeO_2 with Ce/Si molar ratios of 0.1, 0.2, 0.4 and 0.6 were synthesized via wet chemical process using a gold cationic complex precursor $[Au(en)_2]^{3+}$ (*en* = ethylenediamine), and investigated as catalysts for the partial oxidation of lactose to selectively synthesize lactobionic acid (LBA) for therapeutic, pharmaceutical and food grad applications.

These catalysts were characterized by N_2 physisorption, XRD, FT-IR, TEM and XPS. N_2 physisorption and XRD analysis revealed that SBA-15-CeO_2 with the investigated Ce/Si molar ratios support possess ordered hexagonal mesoporous structure, characterized with a high surface area and large pore volume, similar to SBA-15, whereas BET surface area and pore volume of catalyst were significantly decreased upon impregnation. XPS analysis revealed the coexistence of metallic and oxidized gold species (Au^0, Au^+ and Au^{3+}) in all prepared catalysts and the presence of both Ce^{3+} and Ce^{4+} oxidation states for gold supported on mesoporous SBA-15-CeO_2 catalysts.

The influence of the pH value on lactose conversion was also investigated. After 60 min of reaction, the 0.7%Au/SBA-15-CeO_2 (Ce/Si = 0.1 and 0.2) catalysts showed high catalytic activity (100% lactose conversion) and a 100% selectivity towards LBA, when they were used at a catalyst/lactose ratio of 0.2, under alkaline (pH 9.0) and mild reaction temperature (65 °C). At the optimized conditions, 0.7% Au/SBA-15-CeO_2 catalysts with Ce/Si of 0.1, 0.2 and 0.4 were more active than 0.7% Au/SBA-15 catalyst. A maximum of activity is reached at Ce/Si of 0.2. The experimental catalytic tests and characterizations show clearly the role of Ce in the enhancement in the catalyst activity was the coordination and agglomeration states of Ce atoms could have an important effect.

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1. Introduction

Since the pioneering work of Haruta et al. [1], it is now well known that the catalytic performance of heterogeneous gold catalysts strongly depends on the synthesis method, the nature of support, the gold cluster size deposited on the catalyst surface, and the thermal history of the catalyst [2]. However, the conventional wet-impregnation methods are not appropriate to obtain the required highly dispersed gold nanoparticles (Au-NPs), since they usually yield inactive large spherical particles which weakly bind to the support [3]. To avoid these problems, other methods (i.e. coprecipitation, deposition–precipitation and chemical vapor deposition) have been developed for the synthesis of gold catalysts [4–6]. Among them, the deposition–precipitation (DP) of $HAuCl_4$ aqueous solution in alkaline media (pH 6–10) has been proposed as one of the simplest techniques to obtain high dispersion of Au-NPs and highly active supported gold catalysts [3]. Nevertheless, the DP method is not appropriate for the incorporation of Au-NPs into silica materials, because under the high pH conditions required to hydrolyze the $HAuCl_4$, the weak interaction between the negatively charged silica surface and the $[Au(OH)_nCl_{4-n}]^-$ species facilitates the mobility of gold particles, which can easily sinter during the synthesis process, especially during the calcination step, yielding inactive catalysts [5]. To overcome this drawback, various alternative methods have been proposed, given that mesoporous silicas are considered very attractive catalyst supports, because of their high surface area, thermal stability, ordered structure and excellent mechanical properties. Some well documented techniques include the chemical vapor deposition using expensive organometallic gold precursors [5]; the modification of SiO_2 with organic functional groups before gold loading [7]; the one-pot synthesis by the incorporation of both gold and the coupling agent containing functional

* Corresponding author. Tel.: +1 418 656 2131x6511; fax: +1 418 656 3327.
E-mail addresses: khaled.belkacemi@sga.ulaval.ca, khaled.belkacemi@fsaa.ulaval.ca (K. Belkacemi).

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