



Selective hydrogenation of benzoic acid over Au supported on CeO₂ and Ce_{0.62}Zr_{0.38}O₂: Formation of benzyl alcohol



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ABSTRACT

The gas-phase hydrogenation of benzoic acid was studied over Au supported on CeO₂ and Ce_{0.62}Zr_{0.38}O₂ (CZ). HAADF-STEM has established formation of nanoscale (mean = 1.5–2 nm) Au particles, which is consistent with CO adsorption measurements. Incorporation of Au facilitated partial support reduction during TPR to 573 K where the presence of Zr increased oxygen mobility, resulting in a greater degree of Ce⁴⁺ reduction (to Ce³⁺) in Au/CZ, as demonstrated by oxygen storage capacity and XPS measurements. Hydrogenation of an aqueous benzoic acid feed generated benzaldehyde and benzyl alcohol with a higher rate over Au/CZ that is attributed to the action of oxygen vacancies, which activate the carboxyl function for hydrogen attack. A parallel/consecutive kinetic model has been applied to quantify catalytic selectivity. A concerted (single step) conversion is proposed for Au/CeO₂ that involves bridging interaction of the benzoate with Ce cations and Au nanoparticles with hydrogen addition. A stepwise conversion on Au/CZ is achieved via a Mars and van Krevelen mechanism with benzoic acid activation at an oxygen vacancy and reaction with surface hydrogen to generate benzaldehyde as a reactive intermediate that is converted to benzyl alcohol via nucleophilic C=O attack. Switching from an aqueous to ethanolic feed increased rate due to greater oxygen vacancy availability with higher selectivity to benzaldehyde and appreciable toluene formation over Au/CZ.

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1. Introduction

Increasing sustainability demands are now placed on chemical production to improve catalytic selectivity and minimise by-product formation, circumvent separation/purification operations and avoid costly clean-up and disposal. This requires a fundamental understanding of reaction mechanisms and catalyst structure/performance relationships. Benzoic acid, the focus of this study, is an inexpensive feedstock [1] that can be hydrogenated to benzaldehyde [2] or benzyl alcohol [3,4] as important commercial products. Reaction over a range of oxide catalysts, including CeO₂ [5–8], ZrO₂ [1,7,9–11], MgO [7], ZnO [1,7,12], TiO₂ [11], HfO₂ [11] and MoO_x [13,14], in gas-phase operation (1 atm, 473–773 K) has resulted in the formation of benzaldehyde, benzyl alcohol, toluene, benzene and benzophenone (Fig. 1(A)). Infrared studies suggest dissociative adsorption to form a benzoate with coordination between the carboxylic oxygen(s) and cationic metal site(s)

[10,15–18]. In the presence of surface oxygen vacancies, hydrogenation proceeds via a redox Mars and van Krevelen (MvK) mechanism [1,7,8,11,19]. Interaction with isolated oxygen vacancies results in the removal of one oxygen from the carboxyl with the formation of benzaldehyde (step I, Fig. 1(A)) [18]. Surface hydrogen can react with this oxygen to form water, regenerating the active site [1,7]. In the presence of twin vacancies, benzoic acid adsorbs through both oxygens with reduction to produce toluene (step II) [20,21]. Toluene can also be generated on a surface that bears excess vacancies via consecutive reduction of benzaldehyde (step III) [22,23]. The steady-state concentration of oxygen vacancies controls selectivity via steps I–III [11] and is influenced by solvents/additives [1,11], but is largely determined by oxide reducibility where redox properties [22,23], metal–oxygen bond strength [11], H₂ partial pressure [22] and activation conditions [6] are crucial variables. Reducible oxides (such as Co₃O₄) exhibit a high oxygen vacancy density and promote the generation of toluene [7,11] where use of solvents or additives with an affinity for these sites (e.g. CO₂ or polar compounds such as water) favours benzaldehyde [1,11]. Adsorption on surfaces that do not bear

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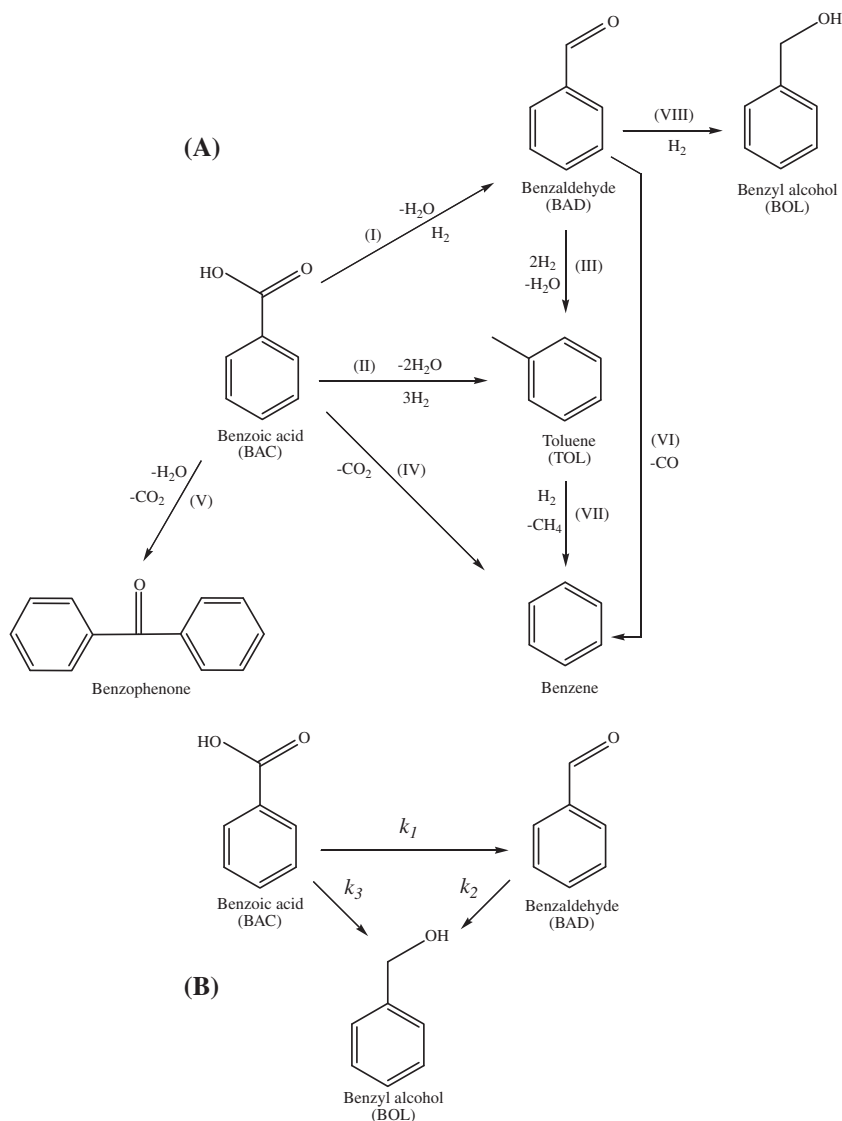


Fig. 1. (A) Reaction pathways reported in the literature for the gas-phase hydrogenation of benzoic acid over oxide catalysts. (B) Possible consecutive/parallel steps (k_1 , k_2 and k_3) associated with the conversion of benzoic acid to benzyl alcohol.

vacancies is accompanied by scission of the acidic function [9,18,21] to give benzene (step IV) and/or benzophenone (step V). Decarboxylation of benzoic acid is favoured at high temperature (>673 K) and low surface hydrogen coverage [1], but this step is slow relative to deoxygenation at vacancy sites (MvK mechanism) [22]. Benzene can also result from decarbonylation of benzaldehyde (step VI) [22] or hydrogenolysis of toluene (step VII) [18]. Hydrogenation of benzaldehyde to benzyl alcohol (step VIII) has been observed at temperatures < 630 K [7,8,12,22].

Activation of H_2 via dissociative adsorption on oxides (such as ZrO_2) has been shown to be rate determining [9]. While the incorporation of noble metals can facilitate hydrogen dissociation and influence reactivity, we could find only one report of (gas phase) benzoic acid hydrogenation over supported metals (Cu and Pt on ZrO_2) where increased H_2 uptake resulted in preferential hydrogenation (particularly in the case of Pt) of the aromatic ring with the formation of methyl-cyclohexane and cyclohexane-carboxylic acid [11]. Gold exhibits lower capacity for H_2 adsorption relative to Pt [24–26] and has been used to promote selective C=O hydrogenation in aldehydes [27–30] and ketones [31,32]. We have shown that supported Au can promote sole formation of benzyl alcohol in benzaldehyde reduction [33]. The literature dealing with benzyl

alcohol generation from benzoic acid is limited, and the possibility of a direct hydrogenation (single step) has not been investigated in any detail. The facility for oxygen vacancy formation [6,34] and the amphoteric surface properties [18] of ZrO_2 [1,7,9,10] and CeO_2 [5,6,8] can serve to promote benzoic acid \rightarrow benzaldehyde with secondary benzyl alcohol, toluene and benzene. The addition of a metal, such as Au, should favour hydrogenation (step VIII) due to increased surface hydrogen. Gold supported on CeO_2 and $\text{Ce}_{0.62}\text{Zr}_{0.38}\text{O}_2$ has exhibited activity in the hydrogenation of *p*-chloronitrobenzene [35] and crotonaldehyde [28]. In this study, we consider the catalytic action of these systems in the hydrogenation of benzoic acid directed at the selective formation of benzyl alcohol where the role of reaction temperature and solvent carrier are examined.

2. Experimental

2.1. Catalyst preparation

$\text{Au/Ce}_{0.62}\text{Zr}_{0.38}\text{O}_2$ (Au/CZ) and Au/CeO_2 were prepared by deposition–precipitation. An aqueous solution of HAuCl_4 (Alfa Aesar) served as precursor, and the oxide supports (CZ and CeO_2) were

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