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Carbon dioxide hydrogenation over supported Au nanoparticles: Effect of the support

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ABSTRACT

The present work aims to explore the impact of the support (M_xO_y: Al_2O_3, TiO_2, Fe_2O_3, CeO_2, ZnO) on the CO_2 hydrogenation activity of supported gold nanoparticles (Au/M_xO_y) at atmospheric pressure. The textural, redox and surface properties of Au/M_xO_y catalysts were evaluated by various characterisation methods, namely N_2 adsorption-desorption at −196 °C, temperature-programmed reduction in H_2, high resolution transmission electron microscopy and X-ray photoelectron spectroscopy. The results revealed a strong influence of the support both on CO_2 conversion and on products distribution. Gold nanoparticles supported on ZnO and CeO_2 were highly selective towards methanol. TiO_2- and Fe_2O_3-based samples demonstrated high CO_2 conversion, leading, however, almost exclusively to CO and/or CH_4. Au/Al_2O_3 was practically inactive in the investigated temperature range (200–350 °C). The following activity order, in terms of methanol formation rate, was obtained: Au/CeO_2 > Au/ZnO > Au/Fe_2O_3 > Au/TiO_2 > Au/Al_2O_3. Au/CeO_2 exhibited a methanol formation rate of 4.1×10^{-6} mol s^{-1} $g_{Au}{}^{-1}$ at 250 °C, which is amongst the highest reported at ambient pressure, in spite of the chemical inertness of bare ceria. In view of the characterisation results, the superiority of the Au/CeO_2 sample could be mainly ascribed to a synergistic effect linked to the Au-ceria interactions.

1. Introduction

The global energy demand has greatly increased since the industrial revolution and especially in the late 20th century, with more than 85% still being supplied by fossil fuels [1,2]. The dependence on fossil resources is not expected to decrease significantly over the next two decades, while the total energy demand is predicted to increase by ca. 35% by 2030 [1,2]. As a result of the extensive use of fossil fuels, atmospheric pollution has been increasing dramatically with important environmental consequences [3]. In particular, the concentration of CO_2 in the atmosphere increased from ~280 ppm in pre-industrial times to ~400 ppm nowadays, and it is predicted to reach ~570 ppm by the end of the century, unless appropriate mitigation actions will be implemented [3–5].

Therefore, it is crucial to decrease, or at least stabilize, the CO_2 concentration in the atmosphere. There are three possible strategies to achieve this target: i) reduce the rate of CO_2 emissions, ii) capture and store anthropogenic CO_2 and iii) utilize atmospheric or industrial CO_2 to produce useful chemicals and fuels [3,4,6]. The first requires improvements in the energy efficiency and a significant decrease in the use of fossil fuels, by switching to carbon free energy vectors, such as solar and other renewable energy sources [3,7]. The second option, carbon capture and sequestration (CCS), is still an uncertain solution in terms of both storage locations and long-term stability of the storage facilities [4,8,9].

The hydrogenation of CO_2 into high added-value chemicals, especially when it is combined with a renewable hydrogen source, is a promising approach for the simultaneous chemical storage of excess intermittent renewable power and the reduction of atmospheric CO_2 concentration [10,11]. From such a process, a variety of chemicals can

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be generated, with the major products being methanol (Reaction (1)), methane (Reaction (2)) and carbon monoxide (Reaction (3)):

$$CO_2(g) + 3H_2(g) \leftrightarrow CH_3OH(g) + H_2O(g), \Delta H_{298} = -49.6\ kJ/mol \quad (1)$$

$$CO_2(g) + 4H_2(g) \leftrightarrow CH_4(g) + 2H_2O(g), \Delta H_{298} = -165.0\ kJ/mol \quad (2)$$

$$CO_2(g) + H_2(g) \leftrightarrow CO(g) + H_2O(g), \Delta H_{298} = 41.2\ kJ/mol \quad (3)$$

Methanol formation through reaction (1) is an exothermic process, accompanied by a gas volume decrease. Thus, methanol synthesis is thermodynamically favoured at low temperatures and high pressures. Nowadays, methanol is produced from syngas through the so called "low pressure process", at 35–55 bar, over Cu-based catalysts and in various reactor configurations [12].

In fact, the catalytic hydrogenation of CO_2 to methanol is considered as one of the greatest challenges in the field of heterogeneous catalysis. A successful outcome in this direction will have significant environmental and economical benefits, taking into account the negative impact of CO_2 on the global climate change, but also the role that methanol can have as a possible energy storage medium in a future "methanol economy" [13].

So far, many catalyst formulations have been studied for the CO_2 hydrogenation reaction to methanol, with Cu-based materials being amongst the most efficient, but still without sufficient activity and selectivity at mild conditions. Hence, research efforts have lately been focused on the fine tuning of Cu catalysts through the use of different preparation techniques, supports and/or structural/surface promoters. In this regard, it has been recently shown that the high dispersion of Cu, combined with a high surface concentration of reduced Cu species (Cu^+/Cu^0), can significantly enhance the yield towards methanol synthesis by CO_2 hydrogenation [14,15].

On the other hand, bulk Au is not an active catalyst for most reactions, due to its high molecular stability and its low adsorption energy [16]. While the ability of gold to act as a hydrogenation catalyst was early observed [17], for a long time this feature was rarely used. However, gold in the form of nanoparticles has been reported as highly active for many catalytic reactions, involving, CO oxidation, water-gas shift (WGS) and CO_2 hydrogenation, among others [18–24]. Significant experimental [19,25] and theoretical [26–28] work has been conducted over the past years in order to understand this peculiar behaviour of gold. The important effect of several preparation parameters on the catalytic activity of gold nanoparticles (Au NPs) revealed their high structure sensitivity [22]. Two main reasons for the high activity of Au NPs can be accounted: (1) the high population of low-coordinated sites on the surface of NPs [27], and (2) the quantum size effects [25].

Besides the nanoparticle size, the activity of gold catalysts also depends strongly on the support. Various oxides have been tested as carriers (*e.g.*, TiO_2, Fe_2O_3, ZnO, ZrO_2, CeO_2) [21,23,24,29–31]. It has been reported that gold is, in general, more active, when combined with highly reducible oxides [21,30,32]. For example, in the case of the WGS reaction, the improved redox behaviour of Au/Fe_2O_3 catalysts has been considered responsible for the enhanced activity [32,33]. A further crucial role of the support is the modification of Au NPs local surface structure through strong metal-support interactions (SMSI), of either electronic (*e.g.*, charge transfer between metal and support) or geometric (*e.g.*, modification of Au NPs morphology) nature [18,22,34–37]. For instance, it was reported that Au NPs supported on TiO_2 presented a more spherical shape, while those supported on ZnO showed a polyhedral morphology [20]. In a comprehensive review by Liu et al. [37] on the role of the support in catalysis by gold, it was made clear that many factors, involving the size and shape of Au and the morphology of the support, could affect the interfacial contact between Au NPs and reducible metal oxides (RMOs), and in turn the catalytic activity. On the other hand, the performance of Au catalysts supported on irreducible metal oxides (IMOs) can be mainly attributed to the abundance of low coordinated sites on their surface.

Regarding the role of the support in CO_2 hydrogenation reaction over Au NPs, Hartadi et al. [23] recently showed that the nature of the support (Al_2O_3, TiO_2, ZnO and ZrO_2) can notably affect the activity and selectivity of the catalysts. Au/ZnO was found to be the most selective catalyst towards methanol formation, followed by $TiO_2 > ZrO_2 > Al_2O_3$. In a similar manner, by comparing Au/TiO_2, Au/ZrO_2 and Au/ZnO, Sakurai et al. [38] concluded that the use of more acidic supports can lead to higher CO_2 conversions, accompanied, however, by a lower selectivity towards methanol.

Despite the intense interest in the field, no definitive conclusions in relation to the influence of the support on Au-catalysed CO_2 hydrogenation have been obtained. Moreover, no special attention was given so far to the use of CeO_2 and Fe_2O_3 oxides as supporting carriers of Au nanoparticles for the CO_2 hydrogenation reaction, despite their excellent redox properties and extensive use as supports [5,39]. In this regard, the present work aims to shed more light on the role of support on the CO_2 hydrogenation activity of supported Au NPs, by systemically investigating various oxides of different textural/redox properties (Al_2O_3, TiO_2, CeO_2, Fe_2O_3, ZnO) as supporting carriers.

2. Experimental

2.1. Catalysts preparation

Au (1.0 wt.%) was loaded on the commercial oxide supports (Al_2O_3 from Aldrich, CeO_2 from Fluka, Fe_2O_3 from Sigma Aldrich, TiO_2 P25 and ZnO AdNano VP 20 from Evonik Degussa) by the Deposition-Precipitation (DP) method, described in detail elsewhere [21,40]. In brief, the pH of a $HAuCl_4$ solution was adjusted to 9 by adding NaOH solution (0.1 M). Then the oxide carrier was added, and the obtained solution was aged at room temperature for 12 h. The precipitate was finally filtered, washed and dried at 110 °C for 12 h. Gold loading was determined by atomic absorption spectrometry (AAS) using an AAS UNICAM spectrophotometer. Samples were previously treated with aqua regia for 2 h. A loading of 1.0 ± 0.3 wt.% Au was determined for all samples.

2.2. Characterisation studies

The as-prepared Au/M_xO_y samples were characterized by various techniques in order to explore the influence of support nature on their textural, morphological, redox and surface properties. In particular, the textural properties were determined by N_2 isotherms at −196 °C by employing the Brunauer–Emmett–Teller (BET) equation [41]. To assess the reducibility of the samples, Temperature Programmed Reduction (TPR) experiments were carried out under H_2 atmosphere. The oxidation state of Au species was determined by X-ray photoelectron spectroscopy (XPS) analyses. Finally, high resolution transmission electron microscopy (HR-TEM) was used to examine the Au nanoparticles size and distribution. The experimental procedure followed in characterization studies along with the employed apparatus are described in detail in previous publications [21,42].

2.3. Catalytic evaluation studies

The CO_2 hydrogenation performance of the prepared catalysts was examined in a U-shaped fixed-bed reactor using 0.4 g of sample. High purity (> 99.99%, Air Liquide Hellas) CO_2 and H_2 gases were fed to the reactor through mass-flow controllers (Brooks 5850E). The inlet partial pressure of CO_2 was kept constant at 10 kPa, whereas that of H_2 varied between 10 and 90 kPa, in order to reveal the impact of the reactants composition on the activity and selectivity performance. The total flow rate was 100 $cm^3\ min^{-1}$, corresponding to a GHSV of around 20,000 h^{-1}.

The composition of reactant and product streams was analysed by