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Au–TiO_2 catalysts on carbon nanofibres prepared by deposition-precipitation and from colloid solutions

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Abstract

Au catalysts have been prepared (i) on TiO_2, (ii) on carbon nanofibres (CNF) and (iii) on TiO_2 deposited onto CNF. Catalysts prepared from deposition-precipitation (DP) and from colloid solutions have been characterised using XRD, TEM, TGA and XAS and tested in the water–gas shift (WGS) reaction. DP yields large Au particles (>50 nm) on CNF-containing supports. High Au dispersion on carbon nanofibres requires preparation via other methods such as colloid formation. Au particle growth is more pronounced during the synthesis steps than during thermal treatments. This increase is not observed for the Au particles on TiO_2 but only when CNF is present, indicating that the surface properties of TiO_2 are altered by the CNF. TiO_2 XANES analyses show that distortions in the lattice symmetry of TiO_2 are introduced when the oxide is deposited on CNF. The distortion of the TiO_2 structure by the CNF may also introduce changes that promote the turnover frequencies. The WGS activity significantly improves when titania is present. This shows that coexistence of Au and TiO_2 is needed to obtain high catalytic activity in the WGS reaction, indicating that the active sites are either on the Au–TiO_2 interface or that the reaction follows a bifunctional mechanism.

Keywords: Au catalyst; TiO_2; Carbon nanofibres; Water–gas shift reaction; Deposition-precipitation; Au colloids

1. Introduction

Nanoparticles of gold supported on metal oxides have been shown to be very active catalysts for several reactions such as CO oxidation [1] and the water–gas shift (WGS) reaction [2]. The preparation of finely dispersed gold particles is believed to be a crucial step in obtaining highly active gold catalysts for the reactions. Several methods have been applied to prepare nanoparticles of Au on different supports, such as deposition-precipitation (DP) with urea or NaOH [3], aqueous impregnation [4], deposition of Au sol [5,6], flame spray pyrolysis [7] and co-precipitation [8,9]. The preparation route is critical for the Au–support interaction and for obtaining the required metal particle dispersion.

DP is the most common method for preparing highly active Au/TiO_2 catalysts, usually by deposition of $[AuO_x(OH)_{4-2x}]^{n-}$ species on the support [10]. DP is carried out by exposing the support to an aqueous solution of $HAuCl_4$. The pH is increased by addition of a base and heating leads to the formation of an oxidic precursor on the support. Moreau et al. [11] have investigated the deposition of Au on TiO_2, with the initial pH of the $HAuCl_4$ solution set at different values. They found that a pH of about 9 was optimal for obtaining high CO oxidation activity. At this pH the main species in the solution were anionic Au complexes where most of the chlorine had been removed by hydrolysis. The amount of Au deposited decreased progressively as the final pH was raised above 8. A dynamic equilibrium between the adsorbed species and the solution is established, which is shifted towards the solution side as the pH is increased. As a result, changes in the pH will influence the amount of Au deposited as well as particle sizes and hence catalytic activity. It is suggested that if the pH is kept below 6–7 during the synthesis, the support surface and/or the adsorbed complexes can still retain some chloride ions, which are promoting mobility and aggregation of the particles. Excessive particle growth can be avoided by increasing the pH.

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Deposition of highly dispersed gold on carbon is not a trivial task due to the tendency towards agglomeration of the metal particles. In addition to metal particle size, the catalyst activity and stability are also controlled by the structure and morphology of the support materials. The selection of an efficient support is thus a decisive factor to provide the desired contact between the gold particles and the substrate [12]. Controlling the Au particle size before deposition on carbon is essential. A number of different synthesis methods of Au colloids are reported in literature. The synthesis methods employ different reducing agents, which lead to various particle sizes and size distributions. The use of sodium citrate as a reducing agent is a common method for preparing Au colloids [13]. The method yields colloids fairly uniform in size with diameters in the range of 15–20 nm. The reduction of chloroauric acid with tetrakis(hydroxymethyl)phosphonium chloride (THPC) in a partially hydrolysed form gives an average particle size of about 2 nm [14]. The first reduction step of Au(III) by THPC is the generation of the active reducing agent tris(hydroxymethyl)phosphine. The formation of gold colloids is believed to proceed via gold nucleation centres with further gold atoms being attached to these centres. The reaction time required for the formation of the Au sol is depending on the adding sequence of the reagents. The use of different volumes of chloroauric acid solution and ageing time of the reducing mixture (NaOH, THPC) also has a marked impact on the outcome of the reaction [14,15].

Highly dispersed gold is regarded as a potentially useful material for various industrial and environmental applications [16]. A wide range of oxide support materials have been investigated for the WGS reaction, including TiO_2 [17–19], ZnO [20], ZrO_2 [21], CeO_2 [2,22,23] and Fe_2O_3 [24,25]. The stability of Au supported on Fe_2O_3 in particular is limited due to the tendency of agglomeration of gold particles. This is probably related to a reduction in total surface area by transforming γ-Fe_2O_3 to α-Fe_2O_3 and Fe_3O_4 [24]. Gold supported on CeO_2 doped with La or Ga [2,26,27] and promoted with various elements [28] have been studied for the water–gas shift (WGS) reaction in order to improve the activity and stability of the catalysts.

The WGS reaction is a key step in fuel processing to generate pure H_2 for fuel cell applications. In such applications a successful catalyst needs to possess high activity as well as good structural stability at pertinent conditions. Andreeva et al. [29] reported that Au enhances the catalytic activity of iron oxide for the WGS reaction and that the activity is comparable with that of a conventional copper based catalyst. Sakurai et al. [17] have reported catalytic activity for Au/TiO_2 where the turnover frequency was four times higher at 100 °C than for a commercial Cu/ZnO/Al_2O_3 catalyst. Comparable CO conversion rates to commercial catalysts were obtained with Au loadings in the range of 5–10 at.%. Fu et al. [30] have reported that the activity is higher for Au/CeO_2 compared to Au/TiO_2. Sakurai et al. [31] have also studied the same reaction in a stream of CO, CO_2, H_2O, H_2 and He. Au/CeO_2 had a much higher activity than Au/TiO_2, Pt/CeO_2 and a commercial Cu/ZnO/Al_2O_3 at temperatures below 250 °C where the CO conversion was close to equilibrium. The Au/CeO_2 catalysts maintained 100% selectivity to CO_2 up to 350 °C.

Carbon nanofibres (CNF) have been used in the present work to disperse and stabilise the TiO_2 support and hence the Au particles. The use of CNF as support material in heterogeneous catalysis has attracted growing interest due to their specific characteristics. The CNF are resistant to acid/base media and the precious metals can easily be recovered by burning off the support [32]. The size and morphology of the CNF provide high surface areas while maintaining macroscopic pore sizes and hence good transport properties in the reactor, and reduced risk of micropore-induced diffusion limitations. Bulushev et al. [33] showed that gold nanoparticles of 2–5 nm supported on woven fabrics of activated carbon fibres were effective for CO oxidation at room temperature. Gold catalysts on carbon supports are so far most commonly used for liquid reactions, such as oxidation of alcohols and sugar [34].

The scope of the present work is to examine how the physical and chemical properties of the Au particles are influenced by the choice of support material and synthesis methods. The catalysts have been studied by various characterisation techniques and tested in the WGS reaction. The changes in the structure of Au and TiO_2 for different pretreatments have been investigated by X-ray absorption spectroscopy (XAS). The Au catalysts have been prepared by DP with urea and deposition of Au from colloid solutions on different supports. The supports used are TiO_2, CNF, and TiO_2 deposited on CNF. The results show that the properties obtained from the synthesis methods are highly dependent on the choice of support material.

2. Experimental

2.1. Catalyst preparation

CNF were synthesized in a fixed-bed reactor at 600 °C using a Ni–hydrotalcite derived catalyst. The catalyst was reduced at 600 °C for 4 h in H_2/N_2 (25/75 ml/min) before reaction. CH_4/H_2 (160/40 ml/min) was used as the reaction gas mixture [35].

Before deposition of the metals, the CNF were treated in acid to remove the Ni catalyst from the preparation. This method also introduces surface functional groups, which act as anchoring sites for the catalyst precursors. CNF were refluxed in concentrated nitric acid for 1 h followed by filtration, washing in distilled water until stable pH (close to 6) and dried in an oven at 100 °C for 12 h. The acid treatment was performed twice.

The catalysts supported on CNF have been prepared in two steps; first deposition of the TiO_2 onto the CNF followed by deposition of gold. The amount of titania deposited is 10 wt.% of the total catalyst. For both preparation methods, the amount of gold in the solution corresponds to a gold loading of 2 wt.% of the total catalyst. The supports were weighed before any treatment. Since the treatments may lead to weight-loss in the materials, loadings of more than 2 wt.% were measured for some of the catalysts.