



Decomposition of formic acid over silica encapsulated and amine functionalised gold nanoparticles



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ABSTRACT

Formic acid has recently attracted considerable attention as a safe and convenient source of hydrogen for sustainable chemical synthesis and renewable energy storage. Here, we show that silica encapsulated and amine functionalised gold nanoparticles are highly active catalysts for the production of hydrogen by vapour phase decomposition of formic acid. The core-shell catalysts are prepared in a reverse micelle system that makes it possible to control the size of the Au nanoparticles and the thickness of the SiO₂ shells, which has a large impact on the catalytic activity. The smallest gold nanoparticles are 2.2 ± 0.3 nm in diameter and have a turnover frequency (TOF) of up to 958 h⁻¹ at a temperature of 130 °C. Based on detailed *in situ* ATR-FTIR studies and results from kinetic isotope labelling experiments we propose that the active site is a low-coordinated and amine functionalised Au atom, while H-assisted formate decomposition into CO₂ and H₂ is the rate limiting step.

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1. Introduction

Hydrogen produced from renewable resources holds great promise for sustainable production of chemicals and clean energy. Unfortunately, the physical properties of hydrogen gas make transportation, handling and refuelling difficult. Formic acid (HCOOH) has great potential as a hydrogen storage material and as a means to utilise CO₂ [1]. Furthermore, formic acid may be produced directly from biomass, for instance by the catalytic oxidation of cellulose using heteropoly acids [2]. In general, the decomposition of formic acid may occur via dehydrogenation (1) or dehydration (2)



The two reactions pathways are linked by the well-known water-gas shift reaction



From the perspective of energy storage, the production of pure H₂ remains an important challenge because even small amount of CO severely deactivates the platinum in fuel cell catalysts. Alternatively, the efficient activation of formic acid may be exploited for transfer hydrogenations in organic synthesis [3].

Supported gold nanoparticles have recently attracted much attention because of their surprisingly high catalytic activity for a number of reactions [4–6], in particular CO oxidation [7]. Although the intimate mechanistic details are still not fully understood, it is generally accepted that several factors contribute to the high activity [8]. In particular, the gold nanoparticles must typically be less than 10 nm in diameter so that under-coordinated, reactive gold atoms exist in large numbers at the edges and corners of the particles [9]. Supported gold nanoparticles have also previously been used to decompose formic acid in both liquid [10,11] and vapour phases [12–15]. Ojeda and Iglesia [12] showed that highly dispersed gold catalysts decomposed formic acid with higher metal-time yields than similar Pt catalysts in vapour phase. The authors suggested that the high catalytic activity was caused by dispersed Au species (undetectable by TEM) and not from visible metal nanoparticles (3–4 nm), which were active for CO oxidation and remained stable during thermal treatment. The decomposition of formic acid has also been investigated by means of periodic density functional theory calculations [16,17]. In particular, Yoo et al. [17] studied the reaction on Ag, Cu, Pd and Pt. The study was extended to other transition metals by scaling the adsorption energies of the involved reaction species with two independent descriptors, namely the CO and OH adsorption energies. Small Au clusters of 0.8 nm in diameter (13 Au atoms) were found to bind CO and OH more strongly than bulk gold, which brought the activity of Au very close to the top of the volcano plot. The small Au clusters were

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even found to be more active and selective than Pt, which is in good agreement with the results reported by Ojeda and Iglesias [12].

Here, we demonstrate that gold nanoparticles encapsulated in silica are highly effective catalysts for the vapour phase decomposition of formic acid under mild conditions. The catalysts are prepared by means of the reverse micelle methodology recently reported by Zhang et al. [18]. In this approach, the gold precursor is first precipitated with an aqueous solution of ammonia and then subjected to a controlled silica coating in a reverse micelle system comprised of a commercial surfactant (Brij-10) in cyclohexane. Furthermore, the method takes advantage of the strong interactions between gold and (3-aminopropyl)trimethoxysilane (APTMS), which gives a good control over the size and encapsulation of the Au nanoparticles. The smallest and most active gold nanoparticles were 2.2 ± 0.3 nm in diameter and decomposed formic acid with a turnover frequency (TOF) of up to 958 h^{-1} at a temperature of 130°C . To the best of our knowledge, these are the first detailed studies of the decomposition of pure formic acid over silica encapsulated Au nanoparticles in vapour phase, although Yadav et al. previously reported good results for the decomposition of sodium formate and formic acid mixtures in liquid phase using a similar catalyst design [11]. Based on *in situ* ATR-FTIR spectroscopy and results from kinetic isotope labelling experiments we propose that the active site is a low-coordinated and amine functionalised Au atom, while H-assisted formate decomposition into CO_2 and H_2 is the rate limiting step.

2. Experimental section

2.1. General synthesis

The Au@SiO₂ core-shell catalysts were prepared according to a modified literature procedure [18]. In a typical synthesis, 4.25 g of Brij C10 was dissolved in 7.5 ml of cyclohexane at 50°C . Then, 0.5 ml of HAuCl₄ (0.25 M) was added dropwise under stirring, followed by 0.8 ml of aqueous NH₃ (25%), 150 μl APTMS and 2 ml of tetraethyl orthosilicate (TEOS), which were added in order with intervals of 2 min. The hydrolysis and condensation of TEOS were allowed to proceed for 2 h at 50°C followed by stirring overnight with no heating. The product was collected by centrifugation, washed with ethanol, dried at 80°C and then reduced under hydrogen gas (10% H₂ in N₂) for 2 h at 200°C using a heating ramp of $5^\circ\text{C}/\text{min}$. In order to investigate the effect of the size of the Au nanoparticles and the thickness of the SiO₂ shells, we prepared three other catalysts by increasing the amount of cyclohexane (15 ml), decreasing the concentration of HAuCl₄ (0.125 M) and increasing the amount of TEOS (4 ml), respectively. Furthermore, we prepared one catalysts comprised of pure SiO₂.

2.2. Catalytic tests

The vapour phase decomposition of HCOOH was performed at atmospheric pressure in a 3 mm quartz fixed-bed reactor. The formic acid was introduced to the reactor by bubbling Ar (40 ml/min) through pure formic acid kept in a thermostatic bath at 20°C , which resulted in gas composition of around 7% formic acid. The reaction gas was preheated to the reaction temperature and then passed through the reactor, which contained the fractionated catalyst (180–355 μm). The amount of catalyst (50–100 mg) was adjusted to the Au loading in order to have a constant weight hourly space velocity (WHSV) of around 138 g formic acid/g Au h⁻¹. The reaction products, which were either CO₂ and H₂ or CO and H₂O, were quantified with an online Rosemount BINOS 100 non-dispersive infrared (NDIR) detector that followed the for-

mation of CO and CO₂ as function of the reaction temperature as measured inside the reactor. The formation of other important products (in particular H₂) was followed by an online Pfeiffer Vacuum ThermoStar mass spectrometer (MS). All catalysts were tested under the same reaction condition using a preprogrammed heating profile going from 20 to 200°C and then back to 20°C by $2^\circ\text{C}/\text{min}$. All kinetic data were collected after the temperature had reached 200°C . The kinetic isotope effect was investigated by replacing HCOOH with HCOOD, DCOOH and DCOOD, respectively.

2.3. In situ ATR-FTIR spectroscopy

The reaction mechanism was investigated using a Thermo Fisher iS50 Fourier transformation infrared (FTIR) instrument with a Specac high-temperature Golden Gate diamond attenuated total reflectance (ATR) accessory, which could heat the sample area up to 300°C . A custom build flow cell allowed the catalyst to be studied under reaction conditions by *in situ* ATR-FTIR. The catalyst was gently pressed into a wafer and mounted in the ATR flow cell using an inner piston, which pressed the catalyst against the ATR-diamond to ensure intimate contact, while the formic acid vapour was passed over it. A schematic drawing of the setup is given in the supporting information (Fig. S10). Further details, descriptions and drawings of the environmental ATR-FTIR device and the concept behind it can be found elsewhere [19].

All *in situ* ATR-FTIR experiments were performed at 120°C . Before exposure to formic acid, the catalyst was first dried in a flow of dry nitrogen (25 ml/min) for around 1 h at the same temperature.

The procedure for the *in situ* experiments with DCOOD was similar to the experiments described above. However, to exchange mobile protons on the amine species, and thus make the interpretation more straightforward, the catalyst was first stirred in D₂O for 48 h at 100°C . The D₂O treated catalyst was then dried in an oven prior to the preparation for ATR-FTIR analysis. The enrichment procedure did, however, not result in a complete exchange of the mobile protons.

2.4. Computational methods

Assignments of vibrational modes were carefully performed in a combination of density functional theory (DFT) calculations and reference experiments with deuterated formic acid. The DFT calculations were performed using the BP86 functional with the TZVP basis set in Gaussian 09. No scaling factor was applied for the calculated spectra. Silica surface was simulated with a small H₃Si₄O₆-OH unit, which despite its simplicity, is known to give good results for studies of vibrational modes [20]. Silica grafted propyl amine was simulated using the analogous H₃Si₄O₆-(CH₂)₃NH₂. Screenshots of the structures and selected vibrational modes are shown in the supporting information Fig. S11. An overview of relevant spectral assignments and approximate modes is also given in supporting information Scheme S1.

3. Results and discussion

3.1. Characterisation

Fig. 1 shows a representative TEM image of the Au@SiO₂ core-shell catalyst as prepared by the general synthesis described in Section 2.1. The image shows how the individual Au nanoparticles were uniformly encapsulated in small spheres of SiO₂ with a shell thickness of 8–12 nm. TEM images of all the prepared catalysts are shown in the supporting information.

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