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Efficient Production of Hydrogen from Decomposition of Formic Acid over Zeolite Incorporated Gold Nanoparticles

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Abstract: Formic acid has a great potential as a safe and convenient source of hydrogen for sustainable chemical synthesis and renewable energy storage. Here, we report a heterogeneous gold nanoparticles catalyst for efficient production of hydrogen from vapor phase decomposition of formic acid using zeolite incorporated gold nanoparticles. The catalyst is prepared by pressure assisted impregnation and reduction (PAIR), which results in a uniform distribution of small gold nanoparticles that are incorporated into zeolite silicalite-1 crystals. Consequently, the incorporated nanoparticles exhibit increased sintering stability. Based on these results, we believe that incorporation of metal nanoparticles in zeolites may find use as highly active and selective heterogeneous catalysts for the production of hydrogen in future renewable energy applications.

Hydrogen produced from renewable resources holds great promise for the sustainable production of chemicals and clean energy. Unfortunately, the physical properties of hydrogen gas make transportation, handling and refueling difficult. Formic acid (HCOOH) has recently attracted considerable attention due to its potential as a hydrogen storage material and as a way to utilize CO₂ [1]. Since formic acid can be synthesized by hydrogenation of CO₂, a possible carbon-neutral storage-and-release cycle can be envisioned, although this requires that a large amount of renewable hydrogen is readily available. Alternatively, formic acid may be produced from biomass, for instance by the catalytic oxidation of polysaccharides [2,3,4], see Figure 1.

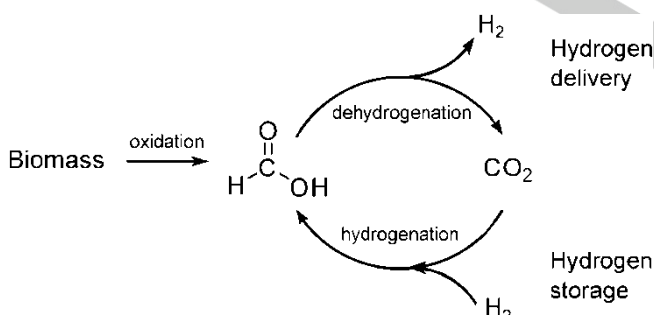
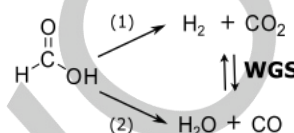


Figure 1. A possible carbon-neutral cycle for production, storage and delivery of renewable hydrogen.

The history of formic acid activation dates back to the pioneering work of Sabatier [5], who showed that its decomposition might occur via dehydrogenation (1) or

dehydration (2). The two reactions pathways are linked by the well-known water-gas shift reaction (WGS), see Figure 2.

Figure 2. Possible pathways for formic acid decomposition: dehydrogenation (1) and dehydration (2).



The first reaction is slightly exothermic, while the second is slightly endothermic. In general, the selective formation of H₂ is favored at low reaction temperatures [6].

Recently, several noble metals have attracted attention as potential catalysts for the decomposition of formic acid, including Ru, Pd and Au [7-11]. Supported Au nanoparticles have been studied as catalysts for formic acid decomposition in both liquid [12] and vapor phase [13]. In particular, Ojeda and Iglesia [14] showed that well-dispersed Au catalysts decomposed formic acid with metal-time yields higher than similar Pt catalysts under mild conditions in liquid phase. In another study, Gazsi et al. performed vapor-phase experiments to study the effect of the support and showed Au/SiO₂ to be the most active and selective catalyst with respect to the decomposition of formic acid and H₂ formation [15]. More recently, the decomposition of formic acid has also been investigated by means of periodic density functional theory calculations. In particular, Studt et al. [16] investigated the reaction over Ag, Cu, Pd and Pt. According to their calculations, small Au gold clusters of 0.8 nm in diameter are able to bind CO and OH more strongly than bulk Au, and even be more active and selective than Pt.

The encapsulation of metal nanoparticles in zeolites has recently attracted much attention [17]. In particular, the zeolite framework may introduce selectivity in terms of size- and shape selectivity [18][19] or prevent the encapsulated nanoparticles from sintering [20][21]. However, incorporating metal nanoparticles in zeolites often rely on complex synthetic procedures and expensive additives, which may prevent large-scale production and general implementation [22].

Here, we report a simple and effective method for the incorporation of gold nanoparticles in zeolite silicalite-1. The method is based on pressure assisted impregnation and reduction. In this method, the sample is first impregnated with the gold precursor solution and then reduced in an autoclave under pressure. The pressure assisted impregnation and reduction facilitates the formation of small and well-dispersed gold nanoparticles, while conventional impregnation typically results in relatively large (> 5 nm) and unreactive nanoparticles on silica [23]. Although, absence of strong metal-support interactions may result in severe redistribution of the impregnated metal during drying and reduction [24], simple impregnation is often preferred over more complicated preparative methods such as deposition-precipitation or co-

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precipitation [25]. The following results demonstrate that pressure assisted impregnation and reduction is a simple and effective method to prepare highly active catalysts comprised of zeolite incorporated gold nanoparticles. The detailed synthesis and characterization of all investigated catalysts by TEM, XRPD and nitrogen physisorption are given in the Supporting Information.

In order to investigate the effect of the impregnation method on the size distribution and activity of the supported gold nanoparticles, four catalysts were prepared. The first catalyst, Au/S1_PAIR, comprised 1 wt% Au on MFI zeolite silicalite-1 (S-1) was prepared by pressure assisted impregnation and reduction (PAIR) using an aqueous solution of HAuCl₄ as metal precursor. After impregnation the catalyst was placed in the autoclave and subjected to 8 bar of H₂/N₂ and 150°C to reduce the gold precursor to nanoparticles. The second catalyst, Au/S-1_IM was obtained by simple impregnation (IM) followed by drying and reduction in H₂ flow at 350°C and atmospheric pressure. In order to investigate the sintering stability of gold nanoparticles, the two samples were additionally calcined (C) after the synthesis at 400°C for 3h in air. These samples are named Au/S-1_PAIR_C and Au/S-1_IM_C, respectively. The detailed synthetic procedures and characterization by HRTEM, XRPD and nitrogen physisorption can be found in the Supporting Information. Table 1 shows an overview of the investigated catalysts. Additionally, the two above mentioned methods were applied to produce gold nanoparticles supported on mesoporous silica. These catalysts were used as reference samples and the information about their synthesis and characterization can be found in the Supporting Information.

Table 1. Overview of the investigated catalysts.

Catalyst ^a	Average diameter ^b [nm]	Temperature of 50% conversion [°C]	STY at 120°C
Au/S-1_PAIR	2,7 ± 2,2	113	113
Au/S-1_IM	4,5 ± 3,0	122	62
Au/S-1_PAIR_C	4,0 ± 2,5	118	98
Au/S-1_IM_C	8,6 ± 3,6	131	45

[a] All catalysts were impregnated with an amount of HAuCl₄(aq) corresponding to 1wt% Au. [b] As measured from approximately 200 nanoparticles by TEM. PAIR: pressure assisted impregnation and reduction, IM: impregnation, C: additional calcination at 300°C for 3h in air.

All catalysts were characterized by TEM. For the Au/S-1_PAIR catalyst the gold nanoparticles were almost exclusively located inside the zeolite crystals. The average diameter of the Au nanoparticles were 2,7 ± 2,2 nm. For comparison, the average diameter of the nanoparticles in Au/S-1_IM were 4,5 ± 3,0 nm. The TEM image of Au/S-1_IM in Figure 3 shows that two kinds of nanoparticles are present in the sample. Small nanoparticles, which are around 2 nm located inside the crystal, and large nanoparticles, which are >5 nm in diameter and located on the external surface of the zeolite crystal. Based on the histogram of the particle size distribution presented in Figure 3, particles which are the most abundant in samples Au/S-1_PAIR and Au/S-1_IM are around 2,2 ± 0,6 nm and 1,9 ± 0,4 nm, respectively.

The TEM analysis of the calcined catalysts revealed that the Au/S-1_PAIR_C had an average particle size of 4,0 ± 2,5 nm, while Au/S-1_IM_C had an average particles of 8,6 ± 3,6 nm, see Table 1. These results clearly show that the catalyst prepared by pressure assisted impregnated and reduction were significantly more stable towards sintering than the catalyst prepared by conventional impregnation.

All catalysts were tested in vapor phase decomposition of formic acid into CO₂ and H₂. In a typical experiment, formic acid vapour was passed through a fixed-bed quartz reactor by bubbling 40 ml/min of Ar through pure formic acid at 20°C. The products were analyzed by an online non-dispersive infrared detector to quantify the amounts of formed CO and CO₂. The formation of H₂ was followed by MS.

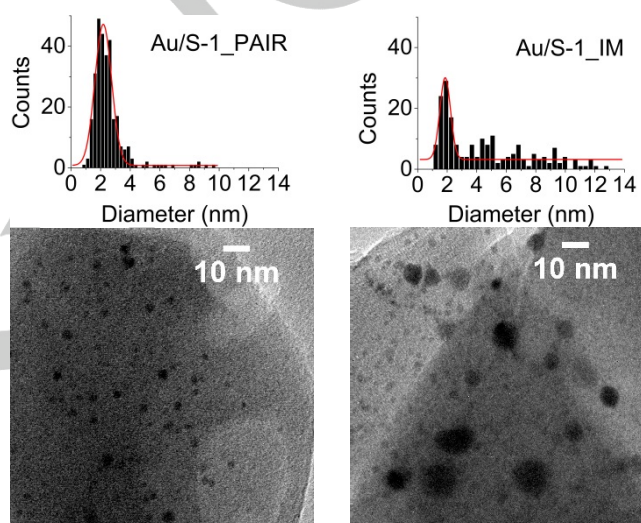


Figure 3. TEM images and nanoparticle size distribution for Au/S-1_PAIR and Au/S-1_IM catalysts.

Figure 4 shows the yield of H₂ against the temperature of the reaction. The Au/S-1_PAIR catalyst exhibited the highest catalytic activity for formic acid decomposition and reached 50% conversion at 113°C. Even after calcination at 400°C in air, the catalyst remained very active and reached 50% conversion at 118°C. The Au/S-1_IM catalyst, prepared by conventional impregnation, reached 50% conversion at 122°C, while the calcined sample only reached 50% conversion at 131°C, see Figure 4. The low activity is a direct consequence of the thermal deactivation caused by sintering. Selectivity towards H₂ and CO₂ ranged between 85-90% above 100°C. In general, this selectivity is lower than in liquid phase (up to 100%) [25,26], but significantly higher than previously reported for e.g. Au/TiO₂ in vapor phase (70%) [27]. Comparing to the performance of other noble metals in gas phase reaction, the 50% conversion was reached for Au/S-1_PAIR catalyst at slightly higher temperatures than reported in [6] for Pd/C (100°C), but much lower than reported in [11] for Ru supported on carbon nanofibers (190°C). However, it has to be noted that the materials were tested at different conditions.

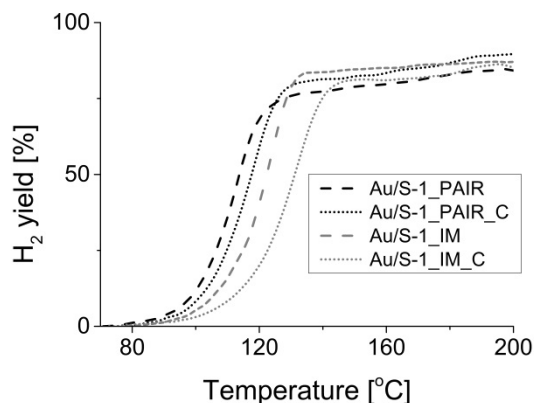


Figure 4. Yield of hydrogen as a function of temperature of the reaction temperature.

The catalyst stability tests were carried out at 120°C (around 50% conversion) of the Au/S-1_PAIR catalyst and Au/S-1_IM catalyst over the course of 28 h, see Figure 5. The catalytic tests revealed that the catalysts were stable and showed no sign of deactivation.

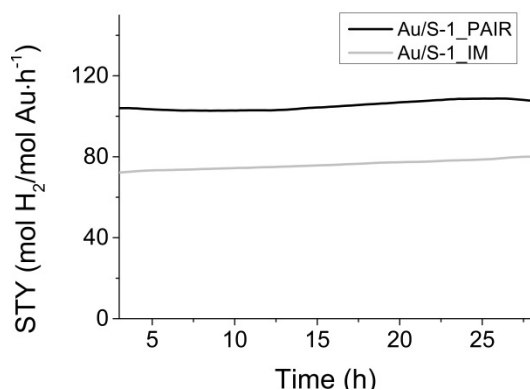


Figure 5. Catalyst stability test performed at 120°C for Au/S-1_PAIR and Au/S-1_IM for 28 h. STY is defined as mol H₂/mol Au hour⁻¹.

In conclusion, we have developed a simple and effective method to incorporate gold nanoparticles into silicalite-1 zeolite crystals using pressure assisted impregnation and reduction. The prepared catalysts contain small nanoparticles with a narrow size distribution of around 2 nm, which are readily accessible to formic acid through the inherent microporous framework. The incorporated nanoparticles were highly active for the formation of H₂ by vapor phase decomposition of formic acid, even after exposure to high temperatures. We therefore expect that pressure assisted impregnation and reduction of zeolites and zeolite like materials may become a helpful tool in the development of new materials with improved catalytic properties.

Supplementary Information provides details about synthesis and characterization of discussed catalysts using TEM, XRD,

and N₂ physisorption as well as catalytic activity of the reference catalysts in gas phase decomposition of formic acid.

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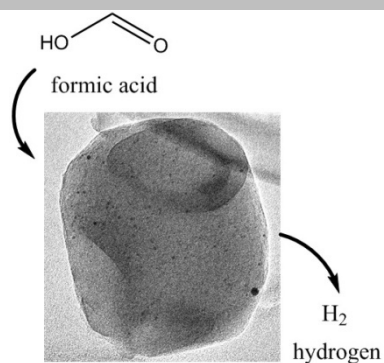
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COMMUNICATION

Pressure assisted impregnation and reduction (PAIR) is a simple and effective method to incorporate small gold nanoparticles into zeolite silicalite-1. The zeolite incorporated nanoparticles show good catalytic activity for production of H₂ from vapour phase decomposition of formic acid.



*Agata Gallas-Hulin, Jerrick Mielby, Søren Kegnæs**

Page No.1 – Page No.3

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