



## Activation of dihydrogen on supported and unsupported silver catalysts

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### ARTICLE INFO

#### Article history:

Received 17 July 2009

Revised 2 October 2009

Accepted 7 October 2009

Available online 14 November 2009

#### Keywords:

Silver catalysts

Silica

Dissociative adsorption

Isotopic exchange

Temporal analysis of products (TAP)

Differential scanning calorimetry (DSC)

Infrared spectroscopy (FTIR)

### ABSTRACT

The activation of dihydrogen on silica, silver, and silica-supported silver (9 wt% Ag) was investigated. Both silica and silver are individually able to dissociate dihydrogen. Silanol groups on silica undergo H → D exchange at 393 K in D<sub>2</sub> as detected by IR spectroscopy. HD is observed in temporal analysis of products (TAP) experiments when H<sub>2</sub> and D<sub>2</sub> are sequentially pulsed on silver at 673 K; even when the time delay between the isotopes is 4 s, HD is formed, indicating that long-lived surface hydrogen species are present. Differential scanning calorimetry (DSC) shows that the activation of dihydrogen is an activated process: heat signals evoked through H<sub>2</sub> pulses on Ag/SiO<sub>2</sub> grow with increasing temperature (373–523 K). Nonetheless, the presence of silver on the silica surface accelerates the Si–OH → Si–OD exchange. Investigation of the exchange kinetics on Ag/SiO<sub>2</sub> shows that diffusion processes of the activated hydrogen species are rate determining at higher temperatures (≥373 K), when the activation of D<sub>2</sub> on silver becomes facile. Indications of diffusion limitation are observed already at 313 K on Pt/SiO<sub>2</sub>. TAP and DSC measurements show that H<sub>2</sub> is more readily activated on silver that has been treated in O<sub>2</sub> at 673 K followed by reduction in H<sub>2</sub> at 673 K. Morphological changes induced to the silver surfaces or (sub)surface oxygen species are presumed responsible for this effect.

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### 1. Introduction

Silver is an active component in oxidation catalysts [1–13]; most well known is its industrial application for ethene epoxidation. However, silver can also be used as a catalyst for reduction reactions, for example, selective hydrogenation of unsaturated aldehydes such as acrolein and crotonaldehyde [14–16] or citral [17,18]. Silver catalysts favor the formation of the industrially relevant unsaturated alcohols, whereas mainly saturated aldehydes are formed on conventional hydrogenation catalysts such as Pt/SiO<sub>2</sub>. Comparison of the different behaviors of these two metals in these simple parallel reactions could give hints as to the source of selectivity and lead to an approach for the rational design of such catalysts. To evaluate the selectivity, the interaction of the catalysts with both reactants has to be considered. Here, we focus on understanding the activation of hydrogen on silver-containing materials. Because of the complexity of the cat-

alyst, its individual components, that is, silver and the silica support, will first be considered separately and then in combination.

Literature reports on the interaction of H<sub>2</sub> with unsupported silver give a consistent picture. No measurable quantities of molecular H<sub>2</sub> adsorb on silver [19–21]; and only at very low temperature, can H<sub>2</sub> be condensed onto the surface [22,23]. Dissociation of hydrogen molecules on clean silver surfaces is predicted by theoretical calculations [24–26] to be an endothermic process. Zhukov et al. [27] report that at ambient temperatures H<sub>2</sub> molecules do not adsorb dissociatively on single crystal silver surfaces. The solubility of H<sub>2</sub> in silver is low [28] over a wide temperature and pressure range [29]; Kluthe et al. [30] report 10<sup>−14</sup> H/Ag at 296 K. Evidence is available for the activation of H<sub>2</sub> on silver at elevated temperature; for example, the presence of H<sub>2</sub> promotes the homoexchange of ethylene on supported silver at 480 K [31]. The exchange between H<sub>2</sub> and D<sub>2</sub> proceeds at 603–673 K [32], and oxygen impurities seem to have a positive effect on this reaction. The general lack of affinity of silver toward H<sub>2</sub>, in comparison to other metals such as nickel, palladium, and platinum is ascribed to the filled d-band of silver [32,33]. Reactions requiring the presence of adsorbed hydrogen atoms on the surface are thus not likely on silver. Accordingly, silver alone is not used as a hydrogenation catalyst; it is, however, used in the reverse reaction, dehydrogenation,

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specifically in the oxidative dehydrogenation of methanol and ethanol to the respective aldehydes [34]. Platinum, which on the other hand is known to easily dissociate hydrogen, is used to catalyze a variety of hydrogenation and dehydrogenation reactions such as the hydrogenation of aromatics, the production of aromatics in reforming reactions, and the production of phenol from cyclohexanone and cyclohexanol [34].

The ability of oxide supports to interact with hydrogen is evidenced by the formation of HD from mixtures of H<sub>2</sub> and D<sub>2</sub>. Silica [35], alumina [36–39], and mixed silica-alumina [40] materials all catalyze this exchange; provided they have been activated through a thermal pre-treatment. Silica has been used as a catalyst in the hydrogenation of alkenes [41]. Another indicator of the activation of hydrogen on oxide surfaces is the exchange of OH to OD groups in the presence of D<sub>2</sub>, which can be monitored by IR spectroscopy [14,42,43]. This exchange occurs on both alumina [43–45] and silica [42,46] at elevated temperatures; again, thermal activation of the materials seems to be important. Carter et al. [43] found a logarithmic rate law for the exchange on alumina. The formation of surface OD groups indicates that hydrogen is activated at or near surface OH groups, or can migrate. The addition of a metal opens up another mechanistic pathway for the exchange; in the presence of platinum the rate of D<sub>2</sub>-induced exchange of OH groups to OD groups on alumina was increased [43].

Interaction of hydrogen with silver and support in Ag/SiO<sub>2</sub>, Ag/Al<sub>2</sub>O<sub>3</sub>, and Ag/TiO<sub>2</sub> catalysts has been described in the literature. Reported data include H<sub>2</sub> chemisorption on Ag/TiO<sub>2</sub> [47], kinetics of H<sub>2</sub>/D<sub>2</sub> exchange on Ag/Al<sub>2</sub>O<sub>3</sub> [48], H<sub>2</sub>-promoted ethene isotopic homoexchange on Ag/SiO<sub>2</sub> [31], hydrogenation of ethene on Ag/SiO<sub>2</sub>, and selective hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes [15–17,49,50].

The affinity of silver toward oxygen is well known [51,52], and a variety of oxygen species dissolved in the bulk, in the subsurface region, and on the surface of silver have been described [51–53]. Exposure of silver to O<sub>2</sub> at temperatures between 800 and 1023 K induces significant changes in the surface morphology [52,53]; and the use of silver in oxidation reactions (of methane or methanol) can lead to similar effects [9,11]. A pre-treatment of silver catalysts in O<sub>2</sub> affects the adsorption [54] and conversion of CO [55,56]. A few publications indicate that a pre-treatment in O<sub>2</sub> affects the interaction of silver with hydrogen. Theoretical calculations predict that silver atoms in the proximity of oxygen exhibit a higher affinity toward H<sub>2</sub> [57,58]. Experiments show that the hydrogen adsorption capacity increases after a heat treatment in O<sub>2</sub> [21,59]. Moreover, oxygen impurities on the surface, which are difficult to remove [60], are believed to be responsible for the lower activation energy in the H<sub>2</sub>-D<sub>2</sub>-exchange reaction that is observed for granular silver in comparison to silver foil [32]. Recent investigations show that an O<sub>2</sub> pre-treatment enhances the performance of supported silver catalysts in the hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes [61].

The goal of this work is to clarify whether the dissociative adsorption of H<sub>2</sub> on silver is endo- or exothermic and to evaluate whether a significant coverage of activated hydrogen is to be expected on the silver and perhaps also on the support under typical hydrogenation conditions. The activity of silver, silica, and silica-supported silver in the activation of H<sub>2</sub> is compared, and the effect of an O<sub>2</sub> pre-treatment is investigated. The temporal analysis of products (TAP) reactor, differential scanning calorimetry (DSC), and FTIR spectroscopy are used to monitor H<sub>2</sub>-D<sub>2</sub> exchange, H<sub>2</sub> adsorption, and exchange of surface OH of the support to OD groups with D<sub>2</sub>. The H<sub>2</sub>-D<sub>2</sub> exchange and the isotopic exchange reaction of Si-OH to Si-OD groups require the activation and cleavage of dihydrogen molecules. The factors influencing this key step are identified and the implications for selective hydrogenations are discussed.

## 2. Experimental section

### 2.1. Catalyst preparation

#### 2.1.1. 9Ag/SiO<sub>2</sub>-iw

Catalysts containing 9 wt% silver supported on silica were prepared by the incipient wetness technique. Silica (Alfa – Johnson Matthey; “silica gel, large pore”;  $S_{\text{BET}} = 253 \text{ m}^2 \text{ g}^{-1}$ ;  $0.2 \text{ mm} < d_{\text{particle}} < 0.5 \text{ mm}$ ) was dried in vacuum at 373 K for 16 h. An aqueous solution of silver lactate was slowly added and the resulting material was dried in an extractor hood for 48 h at room temperature and for another 2 h at 333 K under vacuum. Reduction was carried out in a H<sub>2</sub> flow ( $145 \text{ cm}^3 \text{ min}^{-1}$ ) at 598 K for 2 h applying heating and cooling rates of  $5 \text{ K min}^{-1}$ . C–H vibrations in the IR spectra indicated that traces of lactate decomposition products remained on the surface. Fig. 1a shows a TEM image of this catalyst, obtained with a JEOL JEM-3010 equipped with a LaB<sub>6</sub> cathode at 300 kV acceleration voltage. The silver particles are 2–5 nm in size, with straight, often equally long edges and frequent right angles, suggesting a cube-like morphology. A detailed microscopic characterization of 9Ag/SiO<sub>2</sub>-iw can be found elsewhere [16,62,63].

#### 2.1.2. 10Ag/SiO<sub>2</sub>-imp

A catalyst containing 10 wt% silver was prepared by the impregnation of silica (Aerosil 200, Degussa) with an aqueous solution of AgNO<sub>3</sub> (Fluka). Impregnation was followed by drying (373 K, 12 h), calcination in flowing air (448 K), and reduction in flowing H<sub>2</sub> at 523 K for 3 h. Completeness of decomposition and desorption of nitrate has been examined by IR spectroscopy.

#### 2.1.3. SiO<sub>2</sub> (lactic acid)

A reference sample, SiO<sub>2</sub> (l.a.), was prepared in an identical manner to 9Ag/SiO<sub>2</sub>-iw, only the silver lactate solution was replaced by a solution of lactic acid in water.

#### 2.1.4. Silver

Unsupported silver was obtained by an *in situ* reduction of silver(I) oxide (Johnson Matthey) in the TAP reactor. After evacuation the Ag<sub>2</sub>O was reduced in a H<sub>2</sub> flow ( $30 \text{ cm}^3 \text{ min}^{-1}$ ) at 673 K for 20 min; a heating rate of  $10 \text{ K min}^{-1}$  was applied. Finally the reactor was evacuated again at 673 K before the start of the experiment. Fig. 1b shows a scanning electron microscopy image (ZEISS DSM 962, operated at 30 keV) of an analogously prepared sample. The preparation yields silver in a sponge-like morphology (cf. [64]) with particle diameters of a few micrometers, which probably can be rather compared to the granular silver in the work of Mikovsky et al. [32] than to silver foil.

#### 2.1.5. 6Pt/SiO<sub>2</sub>-iw

A catalyst containing 6 wt% platinum on silica was prepared by the incipient wetness technique. Silica (Alfa – Johnson Matthey; “silica gel, large pore”;  $S_{\text{BET}} = 253 \text{ m}^2 \text{ g}^{-1}$ ;  $0.2 \text{ mm} < d_{\text{particle}} < 0.5 \text{ mm}$ ) was dried in vacuum at 393 K for 3 h. An aqueous solution of tetramine-platinum(II) nitrate (Alfa Aesar) was slowly added and the resulting material was dried in a desiccator for 48 h and for another 2 h at 363 K in N<sub>2</sub> flow. The resulting material was calcined in air flow at 523 K for 4 h ( $1 \text{ K min}^{-1}$ ). Reduction was carried out in H<sub>2</sub> flow ( $167 \text{ cm}^3 \text{ min}^{-1}$ ) at 598 K for 4 h applying heating and cooling rates of  $5 \text{ K min}^{-1}$ .

### 2.2. Analytical methods

#### 2.2.1. Temporal analysis of products (TAP)

Heterogeneous H/D isotopic exchange on silver was investigated in a TAP-2 reactor, which is described in detail elsewhere

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