



Activation of dihydrogen on supported and unsupported silver catalysts

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Received 17 July 2009, Revised 2 October 2009, Accepted 7 October 2009
Available online 14 November 2009

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 D₂ as detected by IR spectroscopy. HD is observed in temporal analysis of products (TAP) experiments when H₂ and D₂ 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 H₂ pulses on Ag/SiO₂ 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/SiO₂ shows that diffusion processes of activated hydrogen species are rate-determining at higher temperatures (≥ 373 K), when activation of D₂ on silver becomes facile. Indications of diffusion limitation are observed already at 313 K on Pt/SiO₂. TAP and DSC measurements show that H₂ is more readily activated on silver that has been treated in O₂ at 673 K followed by reduction in H₂ at 673 K. Morphological changes induced to the silver surfaces or (sub)surface oxygen species are presumed responsible for this effect

Keywords: silver catalysts, silica, hydrogen, dissociative adsorption, isotopic exchange, temporal analysis of products (TAP), differential scanning calorimetry (DSC), infrared spectroscopy (FTIR)

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/SiO₂. Comparison of the different behavior 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 catalyst, 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 H₂ with unsupported silver give a consistent picture. No measurable quantities of molecular H₂ adsorb on silver [19-21]; and only at very low temperature, can H₂ 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 H₂ molecules do not adsorb dissociatively on single crystal silver surfaces. The solubility of H₂ in silver is low [28] over a wide temperature and pressure range [29]; Kluthe et al. [30] report 10⁻¹⁴ H/Ag at 296 K. Evidence is available for the activation of H₂ on silver at elevated temperature; for example, the presence of H₂ promotes the homoexchange of ethylene on supported silver at 480 K [31]. The exchange between H₂ and D₂ 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 H₂, in comparison to other metals such as nickel, palladium, or platinum is ascribed to the filled d-band of silver [32,33].

The ability of oxide supports to interact with hydrogen is evidenced by the formation of HD from mixtures of H₂ and D₂. Silica [34], alumina [35-38], and mixed silica-alumina materials [39] all catalyze this exchange; provided they have been activated through a thermal pretreatment. Silica has been used as a catalyst in the hydrogenation of alkenes [40]. Another indicator of the activation of hydrogen on oxide surfaces is the exchange of OH to OD groups in presence of D₂, which can be monitored by IR spectroscopy [14,41,42]. This exchange occurs on both alumina [42-44] and silica [41,45] at elevated temperatures; again, thermal activation of the materials seems to be important. Carter et al. [42] 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. Addition of a metal opens up another mechanistic pathway for the exchange; in the presence of platinum the rate of D₂-induced exchange of OH groups to OD groups on alumina was increased [42].

Interaction of hydrogen with silver and support in Ag/SiO₂, Ag/Al₂O₃ and Ag/TiO₂ catalysts has been described in the literature. Reported data include H₂ chemisorption on Ag/TiO₂ [46], kinetics of H₂/D₂ exchange on Ag/Al₂O₃ [47], H₂-promoted ethene isotopic homoexchange on Ag/SiO₂ [31], hydrogenation of ethene on Ag/SiO₂, and selective hydrogenation of α,β -unsaturated aldehydes [15-17,48,49].

The affinity of silver toward oxygen is well known [50,51], and a variety of oxygen species dissolved in the bulk, in the subsurface region, and on the surface of silver have been described [51-52]. Exposure of silver to O₂ at temperatures between 800–1023 K induces massive changes in the surface morphology [51,52]; and the use of silver in oxidation reactions (of methane or methanol) can

lead to similar effects [9,11]. A pretreatment of silver catalysts in O₂ affects the adsorption [53] and conversion of CO [54,55]. A few publications indicate that a pre-treatment in O₂ affects the interaction of silver with hydrogen. Theoretical calculations predict that silver atoms in the proximity of oxygen exhibit a higher affinity toward H₂ [56,57]. Experiments show that the hydrogen adsorption capacity increases after a heat treatment in O₂ [21,58]. Moreover, oxygen impurities on the surface, which are difficult to remove [59], are believed to be responsible for the lower activation energy in the H₂-D₂-exchange reaction that is observed for granular silver in comparison to silver foil [32]. Recent investigations show that an O₂ pretreatment enhances the performance of supported silver catalysts in the hydrogenation of α,β -unsaturated aldehydes [60].

The goal of this work is to clarify whether the dissociative adsorption of H₂ 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 H₂ is compared, and the effect of an O₂ pretreatment is investigated. The temporal analysis of products (TAP) reactor, differential scanning calorimetry (DSC) and FTIR spectroscopy are used to monitor H₂-D₂ exchange, H₂ adsorption, and exchange of surface OH of the support to OD groups with D₂. The H₂-D₂ 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/SiO₂-iw and 5Ag/SiO₂-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_{BET} = 253 m²·g⁻¹; 0.2 mm < d_{particle} < 0.5 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 H₂ flow (145 cm³·min⁻¹) at 598 K for 2 h applying heating and cooling rates of 5 K·min⁻¹.

2.1.2. 10Ag/SiO₂-imp

A catalyst containing 10 wt% silver was prepared by impregnation of silica (Aerosil 200, Degussa) with an aqueous solution of AgNO₃ (Fluka). Impregnation was

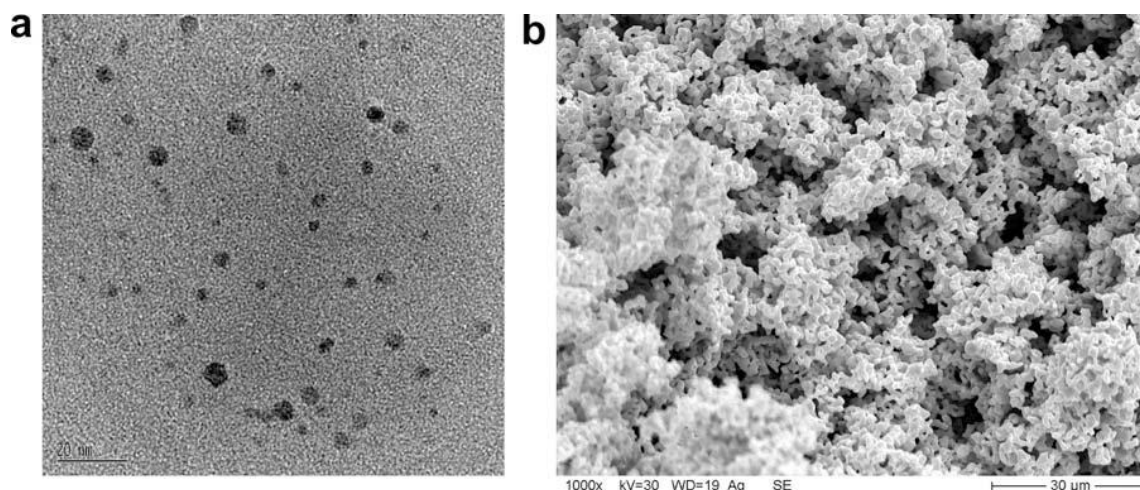


Fig. 1: (a) TEM image of 9Ag/SiO₂-iw. (b) SEM image of silver obtained through the reduction of Ag₂O at 673 K.

followed by drying (373 K, 12 h), calcination in flowing air (448 K), and reduction in flowing H₂ at 523 K for 3 h.

2.1.3. SiO₂ (lactic acid)

A reference sample, SiO₂ (l.a.), was prepared in an identical manner to 9Ag/SiO₂-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 Ag₂O was reduced in a H₂ flow (30 cm³min⁻¹) at 673 K for 20 min; a heating rate of 10 K·min⁻¹ was applied. Finally the reactor was evacuated again at 673 K before the start of the experiment. Fig. 1 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. [61]) with particle diameters of a few μm, which probably can be rather compared to the granular silver in the work of Mikovsky et al. [32] than the silver foil.

2.1.5. 6Pt/SiO₂-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_{BET} = 253 m²·g⁻¹; 0.2 mm < d_{particle} < 0.5 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 N₂ flow. The resulting material was calcined

in air flow at 523 K for 4 h (1 K·min⁻¹). Reduction was carried out in H₂ flow (167 cm³·min⁻¹) at 598 K for 4 h applying heating and cooling rates of 5 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 [62,63]. 68 mg of Ag₂O were placed within two layers of quartz particles (250–30 μm) in the isothermal zone of the TAP-reactor and were reduced as described above. Two gas mixtures of H₂/Ne=1/1 and D₂/Xe=1/1 composition were then sequentially pulsed onto the silver at 673 K. The time delay between the mixtures was varied from 0 s (simultaneous pulsing) to 4.0 s to gather information about the average lifetime of possible adsorbed H-containing species. The pulse size of Ne and Xe was in the range of 10¹⁴–10¹⁵ molecules (Knudsen diffusion regime). Transient responses were monitored at mass charge ratios (m/Q) related to reactants, reaction products, and inert gases at the reactor outlet using a quadruple mass spectrometer (Hiden Analytical HAL RC 301). The following mass charge ratios were recorded: 2 (H₂), 3 (HD), 4 (D₂), 20 (Ne) and 132 (Xe). The H₂/Ne=1/1 and D₂/Xe=1/1 pulses were repeated 10 times for each m/Q and the corresponding signals were averaged to improve the signal to noise ratio. A blank measurement was performed on quartz particles.

After the described pulse experiments, the silver was treated by O₂ pulses (ca. 144 nmol of O₂ in total) at 673 K. After a subsequent reducing step in flowing H₂ at 673 K for 0.2 h, no water was observed when H₂ was pulsed. The H₂-D₂ sequential pulse experiments were then repeated.

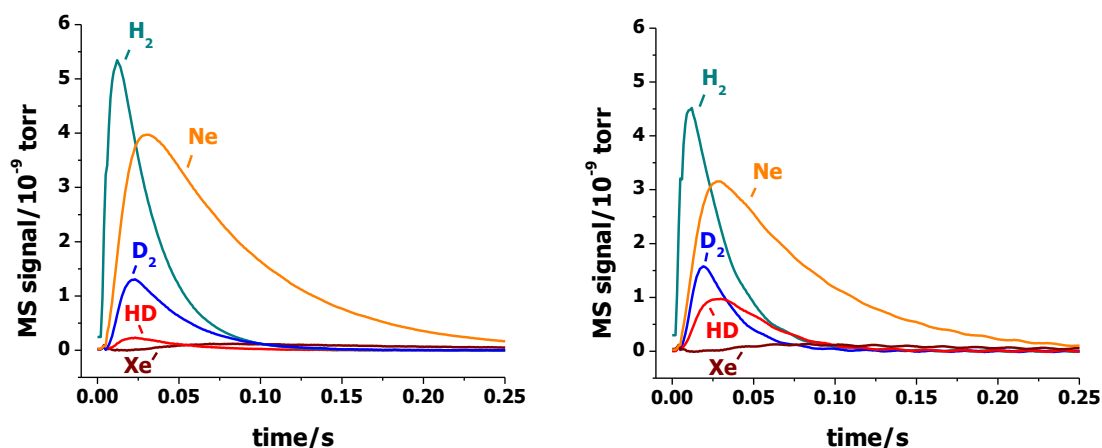


Fig. 2: Transient responses of Ne, Xe, D₂, HD, and H₂ upon simultaneous pulsing of H₂ (H₂/Ne=1) and D₂ (D₂/Xe=1) at 673 K on (a) quartz and (b) support-free silver.

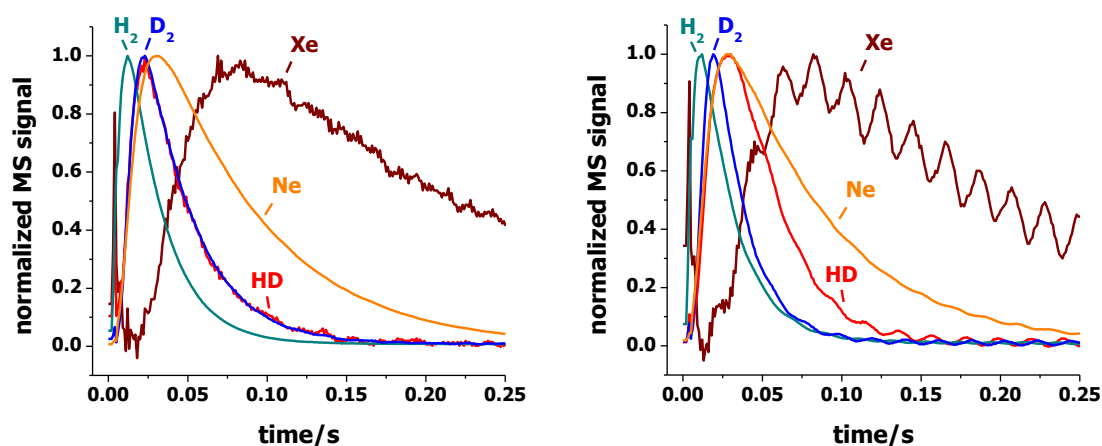


Fig. 3: Height-normalized transient responses of Ne, Xe, D₂, HD, and H₂ upon simultaneous pulsing of H₂ (H₂/Ne=1) and D₂ (D₂/Xe=1) at 673 K on (a) quartz and (b) support-free silver.

2.2.2. Differential scanning calorimetry (DSC)

Hydrogen adsorption calorimetry was performed with a Setaram DSC111 differential scanning calorimeter. The carrier gas (argon 99.999%) was further purified by a BTS cartridge to remove trace amounts of O₂ and by a molecular sieve cartridge to remove water. The apparatus allows dosing small amounts of hydrogen, typically 10⁻⁷ mol H₂, into the carrier gas. Approximately 80 mg of catalyst was filled in a quartz reactor tube, which was placed in the calorimetric block and purged with the carrier gas.

Standard pre-treatment (“PT1”) of the catalysts consisted of reduction in a flow of H₂ (48 cm³·min⁻¹) at 598 K for 2 h followed by a purge in flowing argon for 2 h at 598 K. Finally the catalyst was cooled to a selected temperature in the range 373–598 K. Heating and cooling rates were 10 K·min⁻¹ during the pre-treatment.

To determine the effect of treatment in O₂, the standard reducing pre-treatment was modified and a third pre-treatment including exposure to O₂ was applied. During the modified reducing pre-treatment (“PT2”) the catalysts were heated to 578 K at a rate of 10 K·min⁻¹ in an argon flow and remained under these conditions for 100 min. Hereafter the reduction was carried out in a flow of H₂ for 150 min followed by a purge in argon for 130 min before starting the experiment. The corresponding pre-treatment including exposure to O₂ (“PT3”) was similar to PT2, but the initial period of 100 min in argon at 578 K was replaced by the following sequence: 15 min in argon, 75 min in O₂, and 10 min in argon.

The DSC reactor effluent stream was analyzed by a Pfeiffer QMS 422 mass spectrometer.

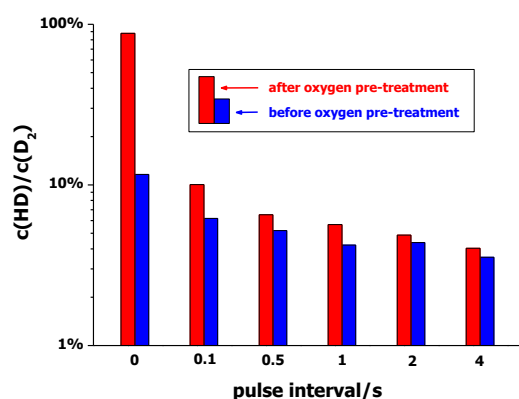


Fig. 4: The ratio of outlet concentrations of HD and D₂ in the D₂ pulse upon sequential pulsing of H₂/Ne=1/1 and D₂/Xe=1/1 with different time delays (Δt) on non-pretreated (blue bars) and O₂-pretreated (red bars) unsupported silver at 673 K.

2.2.3. IR spectroscopy

Transmission infrared measurements were carried out with a Perkin Elmer S 2000 FTIR spectrometer with an integrated *in situ* quartz cell sealed by CaF₂ windows. The powder samples were pressed to self-supporting wafers with an approximate area weight of 10 mg·cm⁻². Pre-treatment was identical for all of the samples: evacuation at room temperature, followed by reduction in H₂ (1 bar) at 598 K for 2 h (a heating rate of 10 K·min⁻¹ was applied). Evacuation to 1·10⁻⁶ mbar at 598 K for another 2 h was performed to remove formed water before cooling (10 K·min⁻¹) to the desired temperature in the range 313–393 K. A final pressure of 110 mbar of D₂ was introduced to the cell. During the exchange process spectra were continuously recorded and related to the background spectrum taken of the empty cell immediately before dosing deuterium into the cell. Each spectrum (16 scans) was recorded in the wavenumber range of 5500–900 cm⁻¹. Spectra were converted from transmittance to absorbance, and the OH and OD band areas were determined through integration in the ranges 3800 to 3200 cm⁻¹ and 2800–2450 cm⁻¹, respectively (as indicated in Fig. 6b).

3. Results

3.1. TAP

To probe the activity of silver for activation of dihydrogen, H₂/Ne=1/1 and D₂/Xe=1/1 mixtures were sequentially pulsed at 673 K with time delays of 0–4 s between the pulses. The non-normalized transient responses of Ne, Xe, H₂, HD, and D₂ recorded in the experiments with a time delay of 0 s are shown in Fig. 2a+b. Only minute amounts of HD are detected in the pulse that passed through a quartz bed, whereas metallic silver produces significant amounts of HD. The formation of HD on silver

is corroborated by analysis of the shapes of the height-normalized transients of H₂, HD, and D₂ in Fig. 3a+b. According to the laws of diffusion, a HD impurity in H₂ or D₂ would evolve between H₂ and D₂. If HD is a reaction product, its transient should appear after that of D₂. Fig. 3a illustrates that the transients of HD and D₂ recorded in the experiment with the quartz particles are congruent and offset from the H₂ curve. These data indicate that the HD signal is an artifact caused by the limited resolution of the MS. A small signal at m/Q=3 is recorded during analysis of D₂, making impossible the detection of low amounts of HD in excess of D₂. The formation of HD on silver is evidenced by the fact that the HD response is significantly delayed compared to the D₂ response. This delay in response is even observed when applying a spacing of 4.0 s between the H₂ and D₂ pulses (not shown), whereby the offset between the HD- and D₂-transients diminishes with increasing time delays. To quantify the effect of the time delay on the HD formation and thus on the lifetime of hydrogen species on the surface, the ratios of the HD and D₂ concentrations were calculated for each time delay (Fig. 4). The highest ratio is observed when H₂ and D₂ are simultaneously pulsed. The ratio decreases with increasing time delay indicating that surface hydrogen species desorb as gas-phase H₂ or become non-reactive.

The H/D isotopic exchange experiments were repeated after the silver had been treated by O₂ pulses at 673 K followed by reduction in H₂ at the same temperature for 0.2 h. No water was detected when H₂ was pulsed over the material after the reducing treatment; hence no oxygen species are present on or near the surface, or they are strongly bound, or not electrophile. Water formation from dihydrogen requires a redox reaction on the surface, whereas the exchange reaction does not. As in the experiments without oxidative treatment, HD is formed. The ratios of the HD and D₂ concentrations obtained after the two different activation procedures are compared in Fig. 4 and show that the ability of silver to catalyze the H/D exchange is promoted through the intermittent O₂ treatment.

3.2. DSC

Interaction of supported silver catalysts with H₂ was investigated by DSC measurements. Fig. 5a shows calorimetric responses during dosing of H₂ pulses into the carrier gas. Very little heat evolves during H₂ pulses at 373 K; however, at higher temperatures the heat signals become more pronounced. Although hard to discern, the positive signals are followed by negative heat signals from desorption, which are broader and are tailing more than the sharp adsorption signals. Except for the first few pulses, the adsorption signals are equally sized and the areas of the desorption signal are only slightly smaller than those of the adsorption signals. This behavior indicates that adsorption is largely reversible. The first signals are higher than the subsequent signals, indicating that some irreversible ad-

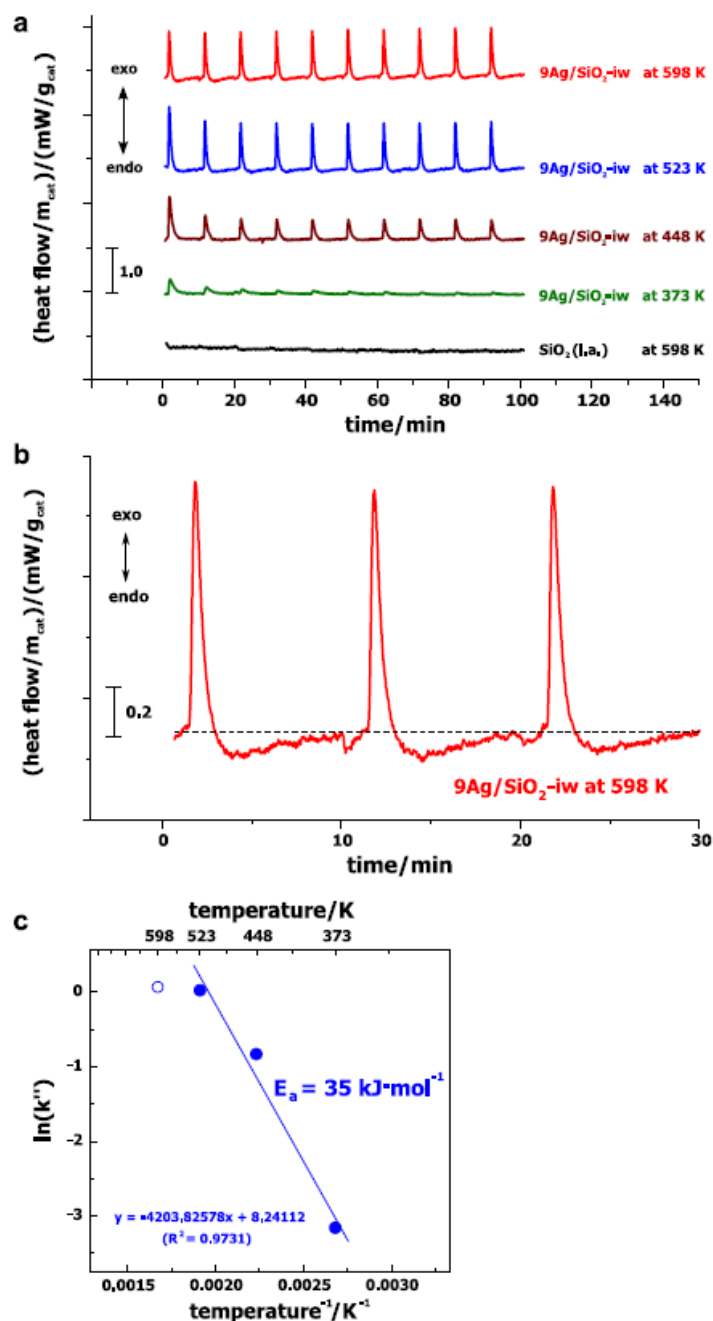


Fig. 5: (a) Heat flow during temperature dependent calorimetric experiments of hydrogen adsorption on 9Ag/SiO₂-iw (standard pre-treatment). Hydrogen pulses of 8×10^{-8} mol H₂/pulse were applied periodically (every 10 min) at 373 K, 448 K, 523 K and 598 K. (b) Enlarged section of (a). (c) Arrhenius plot obtained from DSC data.

sorption occurs initially, particularly at low temperature. However, only minute amounts of hydrogen remain irreversibly adsorbed on the supported silver catalyst even during the initial pulses, and it is impossible to determine hydrogen adsorption enthalpies.

The highest point in the heat evolution signals was taken as a measure of the adsorption rate. It is assumed that the maximum rate is reached before depletion of H₂ in the pulse can have an effect on the rate. An Arrhenius plot can then be assembled, which is shown in Fig. 5b. The measurement at the highest temperature of 598 K did not fall in

line with the others; most likely it is outside of the regime that is controlled by adsorption kinetics. An activation energy of about 35 kJ/mol resulted from the analysis of the slope.

In a comparable experiment with Pt/SiO₂ no H₂ reaches the MS at the reactor outlet, consistent with irreversible adsorption; only at higher pulse numbers than in this experiment does H₂ become detectable in the effluent. Compared to conventional hydrogenation catalysts such as Pt/SiO₂ the interaction of hydrogen with silver catalysts is

thus very weak. Blank measurements with SiO₂ (l.a.) reveal no interaction at all, even at 598 K.

To confirm the effect of an O₂ pretreatment that was observed for unsupported silver in the TAP experiments, a similar pretreatment was carried out before the DSC measurements. 10Ag/SiO₂-imp was activated in two different ways: by conventional pretreatment (PT2), or by a sequence including O₂ exposure before the final reduction step at 578 K (PT3). Average peak areas were obtained through integration of 70 pulses during a periodic pulse experiment. The heat that evolved during interaction of silver (after normal pre-treatment) with a H₂ pulse was approximately 2.4 mJ, after the pre-treatment in O₂ it was about 3.6 mJ. The higher integral heat could indicate a higher heat per adsorbed hydrogen or a higher number of adsorbed hydrogen species. The catalyst was reduced after the O₂ exposure as in the conventional pretreatment, and hence additional contributions from reduction enthalpy are not expected to contribute to the result. During the pulse experiment the formation of water was not detected by MS.

3.3. FTIR spectroscopy

The H→D exchange of the support's silanol groups through reaction with D₂ was monitored by infrared spectroscopy. During this process the ν(OH) band at 3740 cm⁻¹ is diminishing, while the intensity of the ν(OD) band at 2760 cm⁻¹ is increasing, as shown in Fig. 6a. Band areas were determined by integration as exemplified in Fig. 6b. Development of the area of the ν(OD) band for several catalysts and two different temperatures is presented in Fig. 6c. Repeat measurements of the exchange were compared without further analysis and after normalization to the wafer area weight, but in both cases the obtained curves of the band area as a function of time were not congruent. However, normalization of the band area values to their saturation value shows that the shape of the curves is very well reproducible.

Exchange on silica proceeds rapidly in the beginning and then slows down. The curves obtained for the metal-containing catalysts are characterized by an even steeper beginning than that of the silica, consistent with a very fast initial rate, and a slow approach to a final value. The presence of metals on the support influence the exchange rates, and the initial rates increase in the following order: SiO₂ < Ag/SiO₂ << Pt/SiO₂. As expected, increasing exchange rates are observed with increasing temperatures.

The kinetics of the exchange reaction were analyzed in two ways. First, the method of initial rates was applied. The OD band area grows linearly with time for the first few minutes and the slope during this period was taken as a measure of the rate. Assuming that variations of the D₂ partial pressure and the surface concentration of OH groups are negligible during this short time span, the rate becomes proportional to the rate constant and an Arrhenius plot can be derived. An example is given in Fig. 6d. The results of

this method were found to depend significantly on the selection of points. The obtained plots were always characterized by two slopes. The higher slope (at lower temperatures) was used to derive the activation energy for the isotopic exchange reaction on Ag/SiO₂. The mode of the obtained distribution was about 26 kJ/mol.

Because of the uncertainty resulting from the analysis of initial rates, the whole curves were also analyzed and were found to be well described by the following function:

$$area(OD) = b \cdot \frac{(K \cdot t)^c}{1 + (K \cdot t)^c} \quad (1)$$

The parameter *c* approaches a value of 0.5 for 9Ag/SiO₂-iw at temperatures above 353 K and for Pt/SiO₂ at 313 K, whereas for SiO₂ a value close to one was obtained for *c* at a temperature of 393 K. The parameter *b* represents the final value of the OD band area (after infinitely long reaction time). Table 1 shows the fit results; a maximum of 900 min was analyzed. The ratio of the final OD band area to the disappeared OH band area varied between about 0.63 and 0.73, indicating a lower molar absorption coefficient of the OD relative to the OH vibration. The bands of the OH groups never disappear entirely; the highest observed conversion was 68% after reacting silica with D₂ for 48 h at 393 K.

Table 1: Fit results of OD band area evolution with time applying Eq. (1). Parameters obtained from fitting of the non-normalized experimental data up to 900 min.

Catalyst	T/K	OD _{end} /cm ⁻¹	<i>c</i>	K/min ⁻¹	R ²
6Pt/SiO ₂ -iw	313	47	0.50	0.03893	0.99894
9Ag/SiO ₂ -iw	393	49	0.50	0.01032	0.99932
9Ag/SiO ₂ -iw	393	58	0.53	0.00863	0.99934
9Ag/SiO ₂ -iw	373	48	0.50	0.0074	0.99861
9Ag/SiO ₂ -iw	373	44	0.53	0.00893	0.99867
9Ag/SiO ₂ -iw	353	61	0.57	0.00558	0.99886
9Ag/SiO ₂ -iw	353	51	0.51	0.00792	0.99827
9Ag/SiO ₂ -iw	333	45	0.57	0.00629	0.99759
9Ag/SiO ₂ -iw	333	39	0.55	0.00536	0.99843
9Ag/SiO ₂ -iw	313	39	0.73	0.00492	0.99892
9Ag/SiO ₂ -iw	313	43	0.75	0.00474	0.99907
SiO ₂ (l.a.)	393	73	1.00	0.01163	0.99992

4. Discussion

4.1. Activation of dihydrogen

The TAP data provide evidence that HD is not formed in measurable amounts when a mixture of H₂ and D₂ is brought into contact with silica for less than a second at temperatures up to 673 K. There are two possible routes for the formation of HD on silica, one is through activation

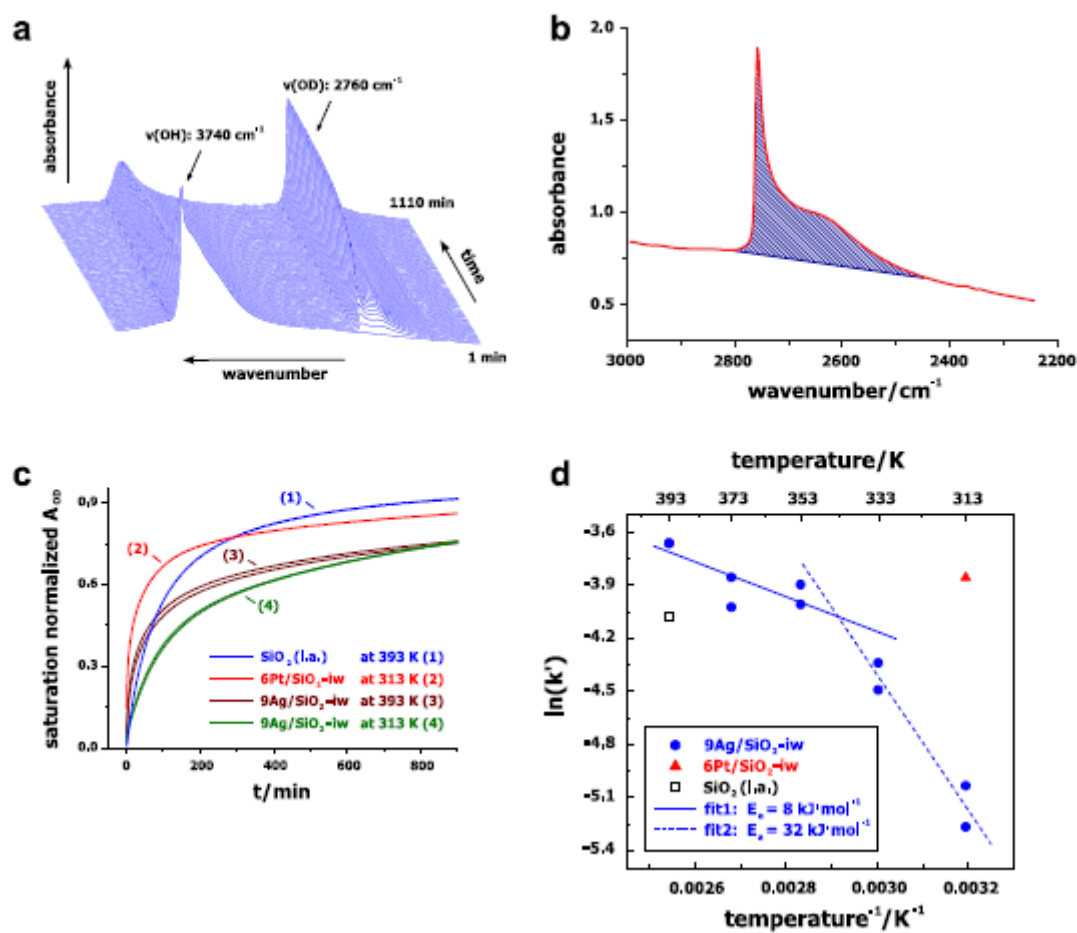


Fig. 6: a) IR spectra of silica during HD-exchange with 106 hPa D₂ at 393 K; b) Integration range; c) Development of the v(OD) band at 2760 cm⁻¹ with time for SiO₂, Ag/SiO₂, and Pt/SiO₂ at various temperatures. D₂ pressure 110 hPa (static atmosphere). d) Arrhenius plot obtained from analysis of initial rates of OD band growth.

of H₂ and of D₂ and subsequent interaction of the activated species; the other is through an exchange reaction of D₂ with surface Si–OH groups. Neither of these two pathways proceeds with a high enough rate to yield detectable amounts of HD in the TAP experiments. This result is not necessarily in contradiction with the report of Bittner et al. [34], who did observe HD in a pulse experiment with several minute long pulses. Indeed, the IR data show that at prolonged reaction times, Si–OD groups are formed on the surface. Theoretically, this reaction could occur without the formation of HD, if two OH groups reacted with D₂ to give two OD groups and H₂. The gas phase was not analyzed for HD in the IR experiments.

The observed kinetics for the exchange of Si–OH to Si–OD groups can be interpreted after reformulating Eq. 1. The ratio θ of the area of the forming OD-band to its final value b corresponds to the fraction of exchanged OH groups to exchangeable OH groups. It is assumed that the fraction of non-exchangeable OH groups is not accessible. This fraction has been reported to vary depending on the type and treatment of silica [64]. The reacted fraction θ is then obtained as follows:

$$\Theta = \frac{(Kt)^c}{1 + (Kt)^c} \quad (2)$$

The exchange rate is obtained through differentiation:

$$\frac{d\Theta}{dt} = cK^c \frac{t^{c-1}}{(1 + (Kt)^c)^2} \quad (3)$$

For silica, c was close to 1. For $c=1$ Eq. (3) simplifies to

$$\frac{d\Theta}{dt} = \frac{K}{(1 + Kt)^2} \quad (4)$$

Solving Eq. 2 for t (with $c=1$) and substituting the result into Eq. 4, results in Eq. 5:

$$\frac{d\Theta}{dt} = K(1 - \Theta)^2 \quad (5)$$

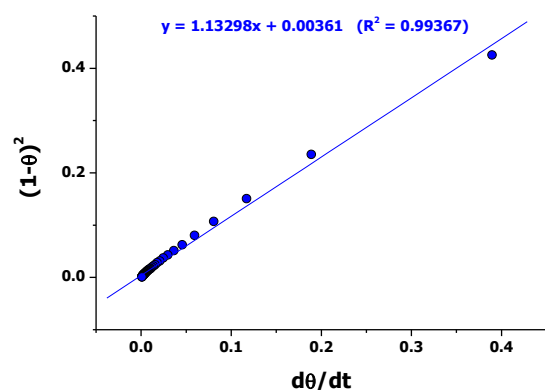


Fig. 7: Plot showing the relation between $(1-\theta)^2$ and $d\theta/dt$. Data from SiO_2 at 393 K and 105 hPa D_2 . $(1-\theta)^2$ calculated from OD band area normalized to the final value b as obtained by fit; derivative $d\theta/dt$ calculated from fitted curve (Eq. 1) to reduce noise.

Such a rate law is consistent with dissociative Langmuir adsorption kinetics, that is, when two free sites are needed in order to adsorb two fragments of a molecule after dissociation. A plot of $d\theta/dt$ vs. $(1-\theta)^2$ is shown for pure silica in Fig. 7. The correlation is close but not perfect as is expected because the fit of the entire data set yielded a value of $c=0.9$. A value of $c=1$ is obtained when only the first 900 min (Table 1) are considered. The rate of exchange observed for pure silica thus closely approaches Langmuir kinetics for dissociative adsorption. Carter et al. [42] also observed that OH/OD exchange kinetics (on alumina) follow the laws of chemisorption kinetics. The sites for activation of the D_2 could be the support OH groups themselves or neighboring sites. It was shown by IR spectroscopy that H_2 and D_2 interact directly with the Si-OH groups of silica, at least at liquid N_2 temperature [14]. The interaction is rather weak as indicated by a red-shift of the OH frequency of only 15–18 cm^{-1} , and this type of adsorbate may not be the precursor for the isotopic exchange reaction. In conclusion, a mechanism in which a D_2 molecule directly interacts with a single OH-group does not seem likely; rather, the observed rate law suggests that two sites are necessary for the activation of dihydrogen on a silica surface.

The TAP data indicate that activation and dissociative adsorption of H_2 and D_2 takes place on silver at 673 K. The presence of a support is not required, as suspected previously [14,16]. Following the argument that the filled d-band of silver prevents interaction with H_2 [32,33,65], one may in turn suspect that silver that interacts with dihydrogen is characterized by structural defects at the surface or impurities that alter the electronic situation. The activated species from H_2 and D_2 on the silver surface must have opportunity to react with each other, which may arise because they are retained on the surface long enough while having sufficient mobility, or because the coverage is significant. When H_2 and D_2 were sequentially pulsed over unsupported silver with various time delays (from 0 to 4 s),

HD was observed during the D_2 pulse. The amount of HD formed decreased with increasing pulse intervals. It follows that, albeit the high temperature of 673 K, activated hydrogen species on silver have a lifetime in the second range. This conclusion is corroborated by the DSC data, which show desorption of H_2 to be much slower than adsorption over a temperature range from 373 to 523 K.

Given the fact that activated hydrogen is retained by silver for several seconds, spillover onto the support, followed by migration and reaction has to be considered. Acrolein is known to interact with silanol groups [66,67] and if active hydrogen became available, the hydrogenation reaction could also occur on the support. The rate of HD exchange of OH groups of the silica support in the presence of silver in comparison to the exchange of the pure support is an indicator for the availability of activated hydrogen on the entire support surface. The rate of the exchange reaction may be determined by activation of D_2 on the silver surface, by spillover, or by migration; of course there is a contribution from reaction of D_2 with the silica surface but this reaction is slow. The results of the fits in Table 1 show that at sufficiently high temperatures, c in Eq. 2 assumes a value of 0.5. In this case, the following differential equation results for θ :

$$\frac{d\theta}{dt} = \frac{1}{2} K \frac{(1-\theta)^3}{\theta} = \frac{1}{2} K \left(\frac{1}{\theta} - 3 + 3\theta - \theta^2 \right) \quad (6)$$

At small values of θ , the first term in the parentheses is dominant. A rate inversely proportional to the degree of conversion (here the degree of exchange) is known from reactions limited by one-dimensional diffusion, in which one of the reactants has to diffuse through an increasing distance of already reacted material. Dissociation of D_2 on platinum proceeds easily, and the TAP and DSC results indicate that D_2 dissociates on silver at elevated temperatures. If one envisions rapid activation of D_2 on a metal particle and migration of an activated deuterium species across the surface to un-exchanged OH groups, diffusion indeed may become rate-limiting. This interpretation is in line with a switch to a diffusion limited D-H exchange reaction of various oxides in supported rhodium catalysts at temperatures above 353 K [68]. The reaction front should progress radially from the silver center and the rate law of two-dimensional diffusion, with the rate being proportional to $-1/(\ln(1-\theta))$, should be applicable [69]. However, for very small values of θ (< 0.05) these two rate laws are not distinguishable because the radial spread is insignificant as long as the reaction front is close to the metal particle. For higher exchange degrees, Eq. (6) is not so easily interpretable. It is conceivable that at a high degree of exchange the role of the metal becomes insignificant and a rate law similar to that observed for pure silica should apply. Consistent with this consideration is the fact that the highest order term is θ^2

The following picture on the dihydrogen activation and further reaction on silica-supported silver catalysts evolves from the TAP, DSC, and IR results. The adsorption

of dihydrogen on silver is activated, as is typical for many dissociative adsorptions, and proceeds with measurable rates only at elevated temperatures. The apparent activation energy for H₂ is estimated to be about 35 kJ/mol. The DSC data indicate that most of the hydrogen is adsorbed reversibly and desorbs within minutes once the H₂ partial pressure decreases after the pulse passes. The lifetime on the surface of silver is long enough to allow the activated hydrogen species to react with a 4 s delayed D₂ pulse in the TAP experiments. Initial rate data on the exchange of Si-OH to Si-OD groups, which were found to vary greatly depending on the analysis, gave an activation energy of about 26 kJ/mol for the reaction of D₂ with Ag/SiO₂. One could speculate that the highest barrier may be the dissociation of D₂ on silver; and the activation energy for the dissociation of D₂ on silver would be expected to be higher than that of H₂ because its zero point energy is 7.6 kJ/mol lower than that of H₂ [70]. However, analysis of the OD band growth kinetics indicates that at high temperatures on Ag/SiO₂ or in the presence of a metal that is highly active for dihydrogen dissociation, such as platinum, the reaction becomes quickly limited by diffusion of the active hydrogen species across the surface. Perhaps this is the reason why the activation energy that was obtained from the initial rates is lower than that obtained for H₂ activation. Exchange of D₂ with the OH groups on silica also occurs in the absence of a metal. This mechanism requires two sites on the surface and is very slow at low temperatures. It may contribute to the isotopic exchange of OH groups on silica-supported silver catalysts on patches of surface that are remote from any metal particle.

4.2. Effect of a pre-treatment in O₂

A pre-treatment of silver catalysts in O₂ was found to affect the activation of D₂ and H₂ by TAP and DSC measurements. Significantly more HD is formed after an O₂ pre-treatment and a greater amount of heat is evolving during hydrogen adsorption. Catalytic results evidence a faster hydrogenation of acrolein after a pre-treatment in O₂-containing atmosphere [60]. In light of the TAP and DSC results this effect can be explained by the facilitated activation of dihydrogen on the pretreated silver surface.

Treatment of silver in O₂ at elevated temperatures can lead to the formation of surface, bulk, and subsurface oxygen species [50,51], which influence the state of adjacent silver atoms. According to theoretical calculations [24-26,71], the dissociation of dihydrogen on clean, oxygen-free silver surfaces is an endothermic process. This is seemingly in contradiction to the observed heat evolution during the DSC experiments; however an absolutely oxygen free surface may be difficult to obtain in practice [59]. Taking the effect of adjacent oxygen atoms in silver in account, dissociation of hydrogen becomes exothermic [56]. In two recent DFT investigations Rösch and coworkers demonstrate how oxygen in different forms on the silver surface lowers the activation barrier for the dissociative adsorption

of H₂ and can even make it strongly exothermic through formation of very stable products [57,71]. Water and OH groups can be formed in the reaction of an oxygen-containing silver surface with H₂ but active hydrogen species are also generated [57].

Treatment of silver in O₂ does not only increase the conversion rate of the reactant (acrolein) but also affects the selectivity. In general, metals and alloys that interact weakly with H₂ seem to have a higher selectivity towards the unsaturated alcohol in the hydrogenation of α,β -unsaturated aldehydes. For example, supported gold catalysts interact weakly with H₂ [72,73] compared to conventional hydrogenation catalysts such platinum or palladium and exhibit high selectivities towards allylic alcohols [74-76]. Modification of Rh/SiO₂ by tin decreases the heat of H₂ adsorption compared to the monometallic Rh/SiO₂ catalyst [77-79] whereas the intramolecular selectivity to trans-crotyl alcohol in the gas phase hydrogenation of crotonaldehyde strongly increases with the Sn/(Rh+Sn) ratio (up to $x = 0.6$). It is thus somewhat surprising that the second effect of the pre-treatment in O₂, which enhances the interaction of silver with H₂, is a higher selectivity toward allyl alcohol. There are two possible explanations for this phenomenon, namely the nature of the active hydrogen species in the presence and absence of oxygen on the surface differs, with the species in the presence of oxygen favoring C=O bond hydrogenation. Alternatively, the adsorption geometry of the second reactant, acrolein, could be affected through the pretreatment in O₂. Oxygen species on the silver surface can affect the nature of the acrolein adsorbate; simple changes in the silver surface morphology such as faceting that occur through contact with O₂ at elevated temperatures [51,52] can also lead to sites with an altered geometry and hence an altered acrolein adsorbate structure. Oxygen is in principle also amply available during the hydrogenation catalysis, as it is present in the reactants and products.

5. Summary and conclusions

1. Dissociation of H₂ (D₂) occurs on unsupported silver catalysts (TAP) as well as on the metal-free support (FTIR spectroscopy).
2. Adsorption of H₂ on silver is activated (DSC).
3. Silica-supported silver catalysts exhibit a very weak interaction with hydrogen compared to similar platinum catalysts.
4. The presence of a metal leads to an increase of the H→D-exchange rates of the supports silanol groups (SiO₂ < Ag/SiO₂ << Pt/SiO₂). At low temperatures, the dissociation of dihydrogen on the silver is rate-determining, at high temperatures or on platinum, the diffusion of activated hydrogen on the support becomes rate-limiting (DSC, FTIR spectroscopy).
5. A pre-treatment with O₂ leads to an increased interaction with hydrogen (DSC, TAP) and thus presumably

a higher coverage, which leads to faster hydrogenation of acrolein (catalysis).

In light of the results, the conditions of acrolein hydrogenation on silver (523-598 K, 10-50 bar) can be understood in that a minimum temperature is required to activate hydrogen, while high hydrogen pressure is beneficial for the hydrogen coverage on silver. However, there is more than one effect of pressure. The total pressure needs to be 100 hPa or higher to produce allylic alcohol [14,15,80,81], which is caused by variations in the mode of acrolein adsorption as the surface becomes more populated (by acrolein or other adsorbates). The improvement of catalytic performance through a treatment in O₂ is explained by residual oxygen in silver, which facilitates the dihydrogen activation, presumably through withdrawing electron density from the d-band states. H₂ can be activated on unsupported silver, but the support affects the particle size and

the performance [14,81,82]. Excellent results with Ag/ZnO [14,81] suggest that the oxygen content of silver may be increased on reducible supports, which would be favorable for H₂ activation.

Acknowledgements

The authors thank M. Klimczak for providing the electron microscopy images of unsupported silver. Financial support by DFG priority program 1091, grants CL168/1-5 and JE 267/3-1, is gratefully acknowledged.

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