



# Infrared Spectroscopic Investigation of Hydrogen and Acrolein Activation on Ag/SiO<sub>2</sub> Hydrogenation Catalysts



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## Introduction

Selective hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes is one route to unsaturated alcohols with the double bond in allylic position, which are important intermediates for the production of fine chemicals, pharmaceuticals and perfumes. Supported Ag or Au are suitable catalysts, and more selective than e.g. Ru or Ni systems [1-3]. Little is known about the adsorption and activation of hydrogen and, e.g., acrolein on silver, and possible effects of the support. Here we use infrared spectroscopy to follow the interaction of the individual reactants with Ag supported on SiO<sub>2</sub>.

## Experimental

Silver (9 wt%) was deposited onto SiO<sub>2</sub> by incipient wetness impregnation or by precipitation [4]. Transmission IR spectra were recorded using a PerkinElmer S 2000 and self-supporting wafers. Adsorption of H<sub>2</sub> or D<sub>2</sub> was performed at 77 K after activation at 689 K in vacuum. Exchange reactions were conducted in a quartz cell after reduction in flowing H<sub>2</sub> at 698 K and subsequent evacuation.

Propene and acetone have been used as model substances for C=C and C=O-bond interaction with the catalyst surfaces. *In situ* DRIFTS spectra were collected during the adsorption of propene or acetone over SiO<sub>2</sub> and a support free silver catalyst in a temperature range of 323 – 523 K at ambient pressure, using a Bruker Equinox and a home made *in situ* DRIFTS cell.

## Results

IR spectra of H<sub>2</sub> adsorption at 77 K on Ag/SiO<sub>2</sub> samples show a shift of the OH stretching frequency of the silanol groups by  $\approx 35 \text{ cm}^{-1}$ , indicating adsorption of H<sub>2</sub> on

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the support. There was no evidence in the spectra for H<sub>2</sub> adsorption on Ag. Equivalent results were obtained when using D<sub>2</sub>. However, exchange of Si-OH to Si-OD groups was observed at 298 K and above. This isotopic exchange reaction and the reverse reaction of Si-OD to Si-OH require the cleavage of D<sub>2</sub> or H<sub>2</sub> molecules; hence this reaction can be considered a model reaction for one of the key steps of the hydrogenation reaction, namely the hydrogen activation. The kinetics of the forward and backward exchange were studied by following the area of the OD band as a function of time (Fig. 1).

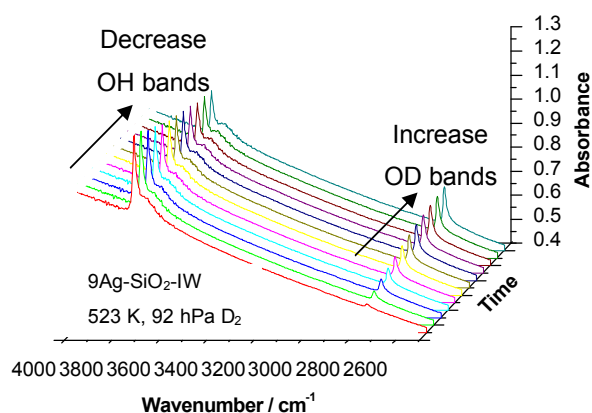


Figure 1: IR spectra of exchange of Si-OH to Si-OD groups.

The rate increased with increasing temperature and D<sub>2</sub> pressure. The presence of Ag accelerated the exchange. Rate data were analyzed by the methods of initial rates, and by fitting a 1<sup>st</sup> or 2<sup>nd</sup> order rate law. In an Arrhenius plot data points scattered considerably, and the current data situation allows only placing apparent activation energies in the range 20–45 kJ/mol.

*In situ* DRIFTS studies show an opposite temperature dependence of the adsorption of propene and acetone over the two catalyst model systems, SiO<sub>2</sub> and support-free Ag. Whereas for the support the intensity of adsorbate bands decreases with the temperature, it is vice versa for the support-free silver. Possible (unavoidable) gas phase contributions hamper the interpretation of the results for the latter sample. Experiments regarding the adsorption of acrolein, which contains both functionalities, –C=C and –C=O, as well as experiments using Ag/SiO<sub>2</sub> catalysts, are under way. The results show that both reactants, H<sub>2</sub> and aldehyde, interact with the SiO<sub>2</sub> support and with silver, and only *in situ* studies with correlation of adsorbate concentrations and catalytic performance will allow identification of relevant surface species.

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