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Influence of the support composition on the hydrogenation of acrolein over $Ag/SiO_2–Al_2O_3$ catalysts

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ABSTRACT

The gas phase hydrogenation of acrolein over supported silver catalysts has been investigated with a focus on the influence of the support acidity. Acidity has been varied by preparing silver catalysts supported on silica/alumina supports with varying SiO_2/Al_2O_3 ratio. After the catalytic experiments the Ag catalysts exhibit similar particle sizes, as revealed with TEM (transmission electron microscopy). The acidity of the samples was estimated using TPD of adsorbed ammonia which gives the total acidity of the samples, furthermore by IR of adsorbed pyridine to identify the Brønsted and Lewis acidity. No Brønsted acidity was found, and the Lewis acidity showed a clear dependence on the support composition. It is shown that a high total acidity and a high amount of strong Lewis acid sites on the catalysts cause a low conversion of acrolein and low selectivity to allyl alcohol. The interaction of silver with the support or effects of the metal–support perimeter are discussed as possible reasons for this behaviour.

1. Introduction

The production of allyl alcohol is of industrial interest because it is an important intermediate in the synthesis of allyl ethers and allyl esters as well as in the production of pharmaceutical products, fine chemicals and perfumes. Several approaches can be used to produce allyl alcohol, e.g. basic hydrolysis of allyl chloride, isomerisation of propylene oxide or saponification of allyl acetate. Furthermore, the gas phase hydrogenation of acrolein is also an option for the industrial production of allyl alcohol [1,2].

The use of typical hydrogenation catalysts like Pt, Pd, or Ni supported on non-reducible oxides leads mainly to the saturated aldehyde (reaction 1 in Fig. 1), which is understandable since thermodynamics and kinetics favour the hydrogenation of the C=C-bond over the C=O-bond [3].

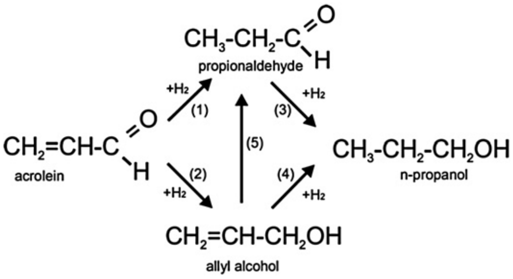

Fig. 1. Reaction network of the acrolein hydrogenation.

The usage of supported silver as a hydrogenation catalyst resulted in a lowering of this disadvantageous course of the reaction and selectivities to allyl alcohol up to 44% [4–11] have been reached. Even higher selectivities of 75% [7,8] can be obtained over AgIn/support catalysts. Despite a possible industrial application of silver catalysts for the hydrogenation of acrolein, various studies have been performed by our group to elucidate the factors which govern the selectivities in this reaction over silver. In these studies it was shown that the partial pressures of the reactants as well as the nanostructure of the catalysts have an influence on the selectivity towards the different products. For the formation of allyl alcohol a reaction pressure of at least 100 mbar is needed. Beyond this reaction pressure it is supposed that the adsorption geometry changes due to increasing coverage, leading to changes in hydrogenation selectivities. Small supported Ag particles favour the formation of allyl alcohol, which is likely related with the presence of electropositive sites like edges and kinks [4,5,10]. Defect site and subsurface oxygen have further been identified as an important factor influencing the selectivities in acrolein hydrogenation over silver [5,11,12]. These may especially be stabilised at the metal–support interface, making it possible to tune the catalytic properties by choosing an appropriate support material.

The goal of the present investigation is to determine the influence of the kind of support and the support acidity on the

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Table 1
Composition of the support and the corresponding description for the catalysts used in this study.

SiO_2 content [%]	Al_2O_3 content [%]	Description of the catalyst
100	0	20Ag/SA100-P
80	20	20Ag/SA80-P
60	40	20Ag/SA60-P
40	60	20Ag/SA40-P
20	80	20Ag/SA20-P
0	100	20Ag/SA00-P

gas phase hydrogenation of acrolein over $Ag/SiO_2–Al_2O_3$ catalysts. From inorganic chemistry oxides of non-metals like SiO_2 are referred to as “acidic” oxides and oxides of metals are defined as “basic” oxides [13]. On one hand, the properties of the support material depend on the crystal chemical features of the bulk, on the other hand it also depends on the surface properties. Mixed oxides like silica/alumina contain covalent and ionic characteristics. Additional Brønsted acid sites are generated by bridging aluminium atoms. Our strategy was therefore to study the influence of support composition and acidity of $Ag/SiO_2–Al_2O_3$ catalysts with varying silica/alumina ratio to obtain catalysts with varying acidity.

2. Experimental

2.1. Catalyst preparation

Silver catalysts with a varying silica/alumina ratio were synthesised by co-precipitation [14,15]. Different silica/alumina ratios were used to obtain a variation of support acidity. A defined amount of $Al(NO_3)_3{\cdot}9H_2O$ (99.999%, Alfa Aesar) and $AgNO_3$ ($\geqslant$99.9%, Roth) was dissolved in distilled water. The amount of $AgNO_3$ was adjusted to yield 20 wt% of Ag in the final catalyst. This mixture was added to a 25% ammonia solution under stirring. Subsequently, a defined amount of 30 wt% silica-sol (Ludox AS-30 colloidal, Aldrich Co.) was added to the reaction mixture. The solvent was then evaporated in a water bath at 60 °C until a gel was obtained. Thereafter, the gel was dried in a vacuum oven at 110 °C for at least 12 h. The resulting solid was crushed to particles $\leqslant$500 µm and calcinated at 500 °C for 2 h in flowing air.

In Table 1 the nominal contents of silica and alumina of the different supports and the corresponding description of the catalysts are summarised.

2.2. Catalytic experiments

Catalytic experiments were performed in a computer-controlled tubular gas phase micro-reactor system, which has been described in detail elsewhere [16]. Directly before the catalytic measurement the catalysts were activated by in situ-reduction with hydrogen for 2 h at 325 °C. In this study the following reaction conditions were used: temperature $T = 250\,^{\circ}\mathrm{C}$, total pressure $p_{\text{total}} = 1$ MPa, molar ratio hydrogen/acrolein = 20, $W/F_{\text{AC},0} = 15.3\ \mathrm{g\,h\,mol^{-1}}$, with W as the weight of the catalyst and $F_{\text{AC},0}$ as the molar flow of acrolein. In the course of the study the $W/F_{\text{AC},0}$ ratio was varied, as specifically indicated in the text.

The effluent from the reactor is composed of acrolein and the reaction products shown in Fig. 1 as well as byproducts (lower hydrocarbons, oligomers) and was analysed on-line every 15 min by a gas chromatograph (HP 5890 series II) which was equipped with a flame ionisation detector and a 30 m J&W DB-WAX (polyethylene glycol: polar) capillary column. The reaction was carried out until steady state was reached and all selectivities reported in this publication are steady state values.

2.3. Catalyst characterisation

The catalysts were characterised by transmission electron microscopy (TEM) and BET surface area measurements. Analysis of the particle size distribution was performed by TEM using a JEM-3010, JOEL operating at 300 kV. Recording of the micrographs was done under the Scherzer focus condition. Subsequently, the software Digital Micrograph by GATAN was used to evaluate the particle size distribution from the TEM images and to calculate the average Ag particle size by sizing at least 300 particles.

The BET surface area was determined with a QUANTACHROME Adsorb-3B using nitrogen as probe gas.

Additionally, the acidity of the catalysts samples was investigated via temperature programmed desorption of adsorbed ammonia (“NH_3-TPD”) and infrared spectroscopic investigation of the adsorption and desorption of pyridine (“pyridine-IR”). To measure the desorption spectra of the samples an AMI-1 (Altamira/Zeton) system was used. The NH_3 desorption experiments were conducted in flowing helium and desorbed NH_3 was detected with a thermal conductivity detector. The desorbed ammonia was absorbed in 0.05 N sulphuric acid and subsequently titrated with 0.05 N NaOH. “Tashiro-indicator,” consisting of a solution of methyl red and methylene blue in ethanol with a transition at pH 5.4 was used for the titration.

Pyridine-IR was used to determine the different acid sites on the catalyst surface due to the fact that differently bonded pyridine gives specific absorption bands. Pyridine adsorbed at Lewis (L-Py) and Brønsted (PyH^+) acid sites exhibits bands at around 1445–1460 and 1540–1548 cm^{-1}, respectively. The bands of hydrogen-bonded pyridine (hb-Py) are in similar ranges of 1440–1447 and 1590–1600 cm^{-1} [13,17,18].

The spectra were recorded using a Bruker IFS 66 spectrometer equipped with a heatable and evacuable IR cell with CaF_2 windows, connected to a gas dosing-evacuating system. The powdered samples were pressed into self-supporting wafers with a diameter of 20 mm and a weight of 50 mg. Prior to pyridine adsorption, the samples were pretreated in flowing 5% H_2/Ar at 350 °C for 1 h followed by cooling to ambient temperature. Then, pyridine was adsorbed at this temperature for 1 h by bubbling an Ar stream through a pyridine-containing saturator. The physisorbed pyridine was removed by evacuating during 5 min at ambient temperature. The desorption of pyridine was followed by heating under vacuum up to 350 °C. The infrared spectra were recorded in transmission mode with 2 cm^{-1} resolution and 100 scans.

3. Results

3.1. Catalyst characterisation by TEM

Figs. 2 and 3 display post-mortem (i.e. after use in the catalytic reaction) TEM images and the particle size distributions of the samples 20Ag/SA100-P (Fig. 2) and 20Ag/SA80-P (Fig. 3). It can be seen, that the silver particles are well dispersed over the support material. From Fig. 3, left, we speculate, that the silver particles are in very close contact with the support and that it is partly encapsulated by the support. The same phenomenon was observed in a pronounced occurrence for Ag/TiO_2 catalyst systems [19,20]. However, at this point of research we can not provide further evidence for this speculation.

The particle size distribution in Fig. 2 of sample 20 Ag/SA100-P is very narrow in comparison to the sample 20 Ag/SA80-P which has a wider distribution in the range between 2 to 8 nm.

The average silver particle sizes of the various catalysts before and after the pre-treatment as well as after the catalytic experiments are summarised in Table 2.