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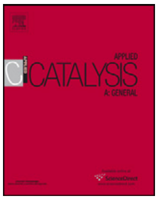

Selective hydrogenolysis of glycerol over copper catalysts both in liquid and vapour phase: Correlation between the copper surface area and the catalyst's activity

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Dedicated to Prof. Dr. H. Knözinger on the occasion of his 75th birthday.

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ABSTRACT

The hydrogenolysis of glycerol was performed both in liquid and in vapour phase by the use of different copper catalysts. The reactions in liquid phase were carried out using copper catalysts which differ in their copper content (36–89 wt.%) and, thus, in their composition while for the hydrogenolysis of glycerol in the vapour phase a set of different silica supported copper catalysts (Cu/SiO_2, low copper loading) was prepared either by incipient wetness (IW) or by ion exchange technique (IE).

Concerning the reactions in the vapour phase complete conversion of glycerol and a selectivity to 1,2-propanediol of 87% was achieved over a Cu/SiO_2_IE catalyst under optimised reaction conditions (255 °C, 15 bar, 300 ml/min H_2). In liquid phase hydrogenation, 1,2-propanediol was nearly the sole product (selectivity = 98%), and conversions up to 52% were obtained according to a space–time–yield of 5.9 $g_{1,2\text{-propanediol}}/(g_{Cu}\ h)$.

N_2O chemisorption was carried out in order to determine the specific copper surface area of the catalysts. For both the reaction in liquid phase and in vapour phase there is a linear relationship between the specific copper surface area and the catalytic activity not only for glycerol hydrogenolysis, but also for glycerol dehydration to acetol and the subsequent hydrogenation of the latter to 1,2-propanediol.

1. Introduction

As the byproduct of biodiesel production from vegetable oils glycerol is one of the promising platform molecules for the production of chemicals which are derived from fossile raw materials nowadays. Possible routes to convert glycerol to molecules with practical applications include the oxidation to dihydroxyacetone, the generation of hydrogen or the hydrogenolysis to 1,2-propanediol [1]. The latter reaction can be carried out both in liquid and in gas phase. Concerning the liquid phase the most commonly applied heterogeneous catalysts are based on Ru [2–6] and Cu [7–12]. In contrast to Ru based catalysts which suffer from rather low selectivities to 1,2-propanediol copper catalysts combine high conversions of glycerol with high selectivities to the desired product 1,2-propanediol.

Recently, the role of the copper particle size of the catalyst regarding its catalytic activity was highlighted in literature. Balaraju et al. suggested that a relationship between the Cu dispersion and glycerol conversion exists [8]. Moreover, Huang et al. [11] reported that the conversion of glycerol tends to increase with increasing amount of copper surface area, whereas this effect was superimposed by a dependence on the contents of sodium correlated with the preparation of the catalysts. Wang and Liu [7] investigated the effect of the crystallite sizes of spent catalysts on the glycerol conversion and the selectivity to 1,2-propanediol on a Cu/ZnO catalyst. However, the Cu and ZnO crystallite size was varied by the choice of different initial pH values of the reaction mixture showing that smaller ZnO and Cu crystallite sizes lead to a higher glycerol conversion and selectivity towards 1,2-propanediol, respectively. In the case of methanol synthesis over copper based catalysts a dependence of the activity on the specific copper surface area could be proved, whereas a distinction was made between binary and ternary catalysts [13].

Several publications deal with the hydrogenolysis of glycerol in the gas phase either to produce 1,3-propanediol [14] or 1,2-propanediol. Concerning the latter one different supported Pd, Ni and Cu catalysts [15–19] were applied. Like for the reaction in liquid phase over copper based catalysts high selectivities to 1,2-propanediol and acetol along with high conversions of glycerol are achieved [15–19]. In order to evaporate glycerol at rather moderate temperatures either the pressure in the reactor was decreased [17] or high H_2/glycerol molar ratios were applied [16]. However, in both cases considerable amounts of acetol are formed although the selectivity to 1,2-propanediol can be enhanced by the increase

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Table 1
Copper surface areas, S_{Cu}, of different Cu/SiO_2 catalysts in dependence of their preparation method determined by N_2O chemisorption (IW – incipient wetness, IE – ion exchange).

Catalyst	Reduction temperature [°C]	S_{Cu} [m^2/g]
$5Cu/SiO_2$_IW	400	1.1
$10Cu/SiO_2$_IW	400	1.5
$20Cu/SiO_2$_IW	400	1.4
$20Cu/SiO_2$_IW	600	1.0
Cu/SiO_2_IE_0.015	600	2.5
Cu/SiO_2_IE_0.05	600	3.9
Cu/SiO_2_IE_0.2	600	3.5

of the H_2 stream velocity [16] or by carrying out the hydrogenolysis of glycerol at elevated pressures [16]. Moreover, the appliance of a temperature gradient over the catalyst bed leads to an increased selectivity to 1,2-propanediol as the hydrogenation of acetol is thermodynamically favoured at lower temperatures [18,19].

In the present study the hydrogenolysis of glycerol is conducted (a) in the liquid phase over a series of copper catalysts which differ in their copper content, i.e., with high copper loading, and (b) in the vapour phase over a set of self-prepared Cu/SiO_2 catalysts exhibiting a low content of copper. In both cases the influence of the copper surface area on the observed catalytic activity was examined.

2. Experimental

2.1. Preparation of the catalysts

Cu/SiO_2 catalysts (Table 1) were prepared using two different preparation methods, incipient wetness and ion exchange technique. For the preparation of the catalysts by incipient wetness silica (Degussa, Aerolyst 3041) was impregnated with the required volume (0.9 ml/g) of an aqueous solution of $Cu(NO_3)_2 \cdot 2{,}5H_2O$. After being dried all catalysts were calcinated at 500 °C for 2 h in pure oxygen and, finally, reduced in a stream of hydrogen for 2 h at either 400 °C or 600 °C. The catalysts prepared by incipient wetness are assigned to $5Cu/SiO_2$_IW, where the number is related to the theoretical copper content in the reduced catalyst.

For the preparation of the Cu/SiO_2 catalysts by ion exchange technique, $Cu(NO_3)_2 \cdot 2{,}5H_2O$ (0.814 g, 3.5 mmol) was solved in 70 ml deionized water ($c_{Cu} = 0.05$ mol/l) followed by the addition of ammonium hydroxide until a pH value of 11 was achieved. Afterwards 2 g silica was added to the solution and the mixture was stirred for 30 min. Throughout this time the pH was adjusted to a value of 11 by the use of ammonium hydroxide. The suspension was filtered and washed with deionized water. Finally the catalyst was dried over night at 60 °C, calcined at 500 °C for 2 h in pure oxygen and reduced in a stream of hydrogen for 2 h at 600 °C. Henceforth, the catalysts prepared by ion exchange will be denoted as Cu/SiO_2_IE_0.05 while the number describes the copper concentration in the copper nitrate solution during the preparation.

Commercial catalysts (Table 2) were provided by KataLeuna GmbH Catalysts/CRI.

Table 2
Copper surface areas, S_{Cu}, of various commercial copper catalysts determined by N_2O chemisorption.

Catalyst	Composition [wt.%]	S_{Cu} [m^2/g]
1	CuO [60], ZnO [40]	16.2
2	CuO [47], Cr_2O_3 [46], BaO [7]	12.0
3	CuO [40], ZnO [40], Al_2O_3 [20]	4.7
4	CuO [70], SiO_2 [30]	8.5
5	CuO [89], SiO_2 [9], CaO [2]	5.1
6	CuO [36], ZnO [48], Al_2O_3 [16]	11.9

2.2. Hydrogenolysis of glycerol in liquid phase

The hydrogenolysis of glycerol in liquid phase was conducted in a teflon-lined 300 ml stainless steel autoclave (Parr) at a stirring speed of 1000 rpm. Initially, the reactor was filled with 177 g of pure glycerol along with 3 g catalyst and pressurized with hydrogen to a pressure of 2.5 MPa. After the reactor was heated to a temperature of 200 °C the pressure was adjusted to 5.0 MPa. During the course of hydrogenolysis, samples were taken periodically and analysed with a HPLC device with an Aminex HP X 87 column equipped with a refractive index and ultraviolet detector.

2.3. Hydrogenolysis of glycerol in gas phase

For the hydrogenolysis of glycerol in gas phase a fixed-bed reactor (length 15 cm and inner diameter 1 cm) was used at a temperature of 245 °C and a pressure between 0.1 MPa and 1.5 MPa. Hydrogen and an aqueous solution of glycerol were introduced into the reactor through a heated evaporator. Experiments starting with acetol instead of glycerol were also carried out. The liquid products were collected in a condenser in order to be analysed every 30 min by HPLC. The gas phase was analysed by a GC equipped with a micro-thermal conductivity detector. The selectivity to the products was calculated as the ratio between the amount of carbon atoms in the particular product and the quantity of carbon atoms in the converted glycerol.

2.4. Characterisation of the catalysts

N_2O chemisorption was carried out by the means of a Porotec TPD/R/O 1100 device. Prior to N_2O chemisorption the catalyst was reduced in a stream of 4.95% hydrogen in argon (20 ml/min) at a heating rate of 5 °C/min and a temperature of 270 °C. Afterwards the sample was cooled down to room temperature and a stream of 1% N_2O in helium (12 ml/min) was passed over the catalyst. Finally, the amount of produced Cu_2O was determined by a second TPR at the conditions described previously. The copper surface area was calculated assuming a ratio of copper atoms at the surface and adsorbed oxygen (Cu_s/O_{ads}) of two and a value of 1.46×10^{19} Cu_s atoms m^{-2}.

3. Results and discussion

3.1. N_2O chemisorption

Several Cu/SiO_2 catalysts which differ in their preparation method, copper content and reduction temperature were characterized by N_2O chemisorption to determine their copper surface areas (Table 1). However, by the variation of the reduction temperature and the copper content of the catalysts prepared by incipient wetness the copper surface area was only slightly varied. In contrast, the choice of the preparation method has a larger influence on the copper surface area as it was strongly increased in the case of the catalysts prepared by ion exchange technique. Thus, the copper surface areas of the Cu/SiO_2 catalysts vary from 1 m^2/g to 3.9 m^2/g, respectively.

Besides the Cu/SiO_2 catalysts commercial ones were characterized by N_2O chemisorption (Table 2). Like for the catalysts used in the gas phase the commercial catalysts differ in their copper surface area over a wide range, as to say from 4.7 m^2/g to 16.2 m^2/g. However, there is no clear correlation between the copper surface area and the copper content of the catalysts. Therefore, other reasons like the influence of the support material or maybe different preparation methods must account for the differences in the copper surface areas.