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Pd@Al$_2$O$_3$-Catalyzed Hydrogenation of Allylbenzene to Propylbenzene in Methanol and Aqueous Micellar Solutions

The palladium on alumina (Pd@Al$_2$O$_3$)-catalyzed hydrogenation of allylbenzene to propylbenzene was studied in methanol and aqueous micellar solutions of sodium dodecyl sulfate (SDS), decyltrimethylammonium bromide (DTAB), and t-octylphenoxypolyethoxyethanol (TX-100). Over Pd@Al$_2$O$_3$, propylbenzene was obtained via direct hydrogenation of allylbenzene and isomerization to β-methylstyrene which was hydrogenated afterwards. In aqueous micellar solutions, the reaction was faster than in pure water, but slower than in methanol due to lower hydrogen solubility. In the H$_2$O/SDS system, a higher activation energy was obtained than in methanol. For the investigated surfactants, the initial reaction rate in the micellar systems decreased in the order SDS > TX-100 > DTAB.

1   Introduction

The catalytic hydrogenation of alkenes is a reaction of great importance in organic synthesis [1]. The possibility to use heterogeneous catalysts has attracted considerable attention from an environmental point of view, due to their ease of handling, enhanced reaction rates, high selectivity, and simple work-up [2]. For the nonstereoselective hydrogenation of alkenes, Pd [3], Pt [4], Ru [5], and Rh [6] supported over Al$_2$O$_3$, activated carbon, and SiO$_2$ [7] are the most effective catalysts. They show an improved catalytic activity, high longevity, and can be easily separated from the reaction products [8]. The performance of the catalyst depends on the solvent, the size, shape and dispersion of the metal nanoparticles, and is a function of the synthesis procedure [9].

Although many reactions are developed in organic solvents, the associated high operational costs and environmental impact have sparked much research to replace the harmful solvents by aqueous reaction media. Due to the fact that many organic substrates are insoluble in water, different strategies such as aqueous-organic two-phase systems, modification of

pH, increasing of the reaction media temperature, addition of hydrophobic auxiliaries, and the use of ultrasound and microwave irradiation have been developed to overcome this problem. It has also been reported that the addition of surfactants to the reaction media to form aqueous micellar solutions or microemulsions is more efficient and useful, and from the perspective of processes more environmentally friendly. In contrast to conventional two-phase systems, the interfacial area in surfactant systems is larger and reaction can proceed also in cases where two-phase systems fail, e.g., hydroformylation of long-chain olefins [10, 11].

Many examples are presented in literature for the successful application of surfactant-based reaction media, but in the case of catalysis with noble metals, most of them are investigated with homogeneous catalyst complexes, e.g., rhodium-catalyzed hydrogenation [12] or palladium-catalyzed coupling reactions [13]. Especially the group of Prof. Lipshutz has shown that coupling or metathesis reactions can proceed with high efficiency in such media [14, 15]. Additionally, many successful examples are reported in the literature of supported noble-metal catalysts, e.g., the Pd@C-catalyzed Heck reaction [16] or the rhodium@sol-gel-catalyzed isomerization of allylarenes [17], where the surfactant solutions act as a better solvent in comparison with water. In this case, the complex surfactant-catalyst interaction stemming from surfactant adsorption needs to be considered. The literature on heterogeneously catalyzed gas/liquid reactions applying surfactants, however, is scarce [18].

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Here, Pd@Al$_2$O$_3$ was investigated as heterogeneous catalyst for the liquid-phase hydrogenation of allylbenzene (ALB) to propylbenzene (PB). ALB has an external double-bond which can isomerize, wherefore this reactant allows for the study of main reaction (hydrogenation) and side-reaction (isomerization) as a function of applied reaction conditions and catalyst. Although the hydrogenation of ALB could be carried out in the absence of any other solvent, the transfer of this reaction to an aqueous-based reaction medium was of interest. Therefore, the use of an aqueous micellar solution as "green solvent", which allows for the solubilization of ALB in water, was evaluated for three different surfactants, namely, sodium dodecyl sulfate (SDS), decyltrimethylammonium bromide (DTAB), and *t*-octylphenoxypolyethoxyethanol (TX-100), and compared to methanol as a conventional reaction medium.

2   Experimental

2.1   Chemicals

ALB (98 % purity), TX-100 (laboratory grade), DTAB ($\geq$ 98 % purity), and palladium on alumina (Pd@Al$_2$O$_3$, 1 wt % Pd) were obtained from Sigma-Aldrich Corp. (Germany). Sodium dodecyl sulfate (SDS, > 99.5 % purity) was from AppliChem GmbH (Germany) and methanol (MeOH, reagent grade) from VWR Chemicals (Germany). All chemicals were used without further purification.

2.2   Hydrogenation

The hydrogenation of ALB to PB was selected as model reaction to test the catalytic performance of the commercial Pd@Al$_2$O$_3$ catalyst. The reaction was carried out in methanol as reference medium and in different aqueous micellar solutions. The experimental setup for the hydrogenation of allylbenzene is illustrated in Fig. 1.

The liquid-phase hydrogenation of allylbenzene was performed in a double-walled glass reactor equipped with a mechanical gas dispersion stirrer, baffles, and a thermostat. This setup allows controlling the temperature as well as maintaining the reacting liquid saturated with hydrogen. In a typical experiment, about 1 mg palladium, 1 g ALB (8.46 mmol), and 99 mL solvent (methanol, water or aqueous micellar solution) were added to the reactor and stirred at 400 rpm under N$_2$ atmosphere at room temperature for 30 min.

Next, the stirrer speed was raised to 1200 rpm and the stirrer was immediately stopped. N$_2$ was then removed by means of a vacuum pump and replaced with H$_2$ (p = 0.11 MPa) without stirring, and the reaction was started by turning the stirrer on again at 1200 rpm. The reactions were performed in semi-batch mode with hydrogen being permanently fed to the reactor to achieve a constant pressure during the reaction. Results were
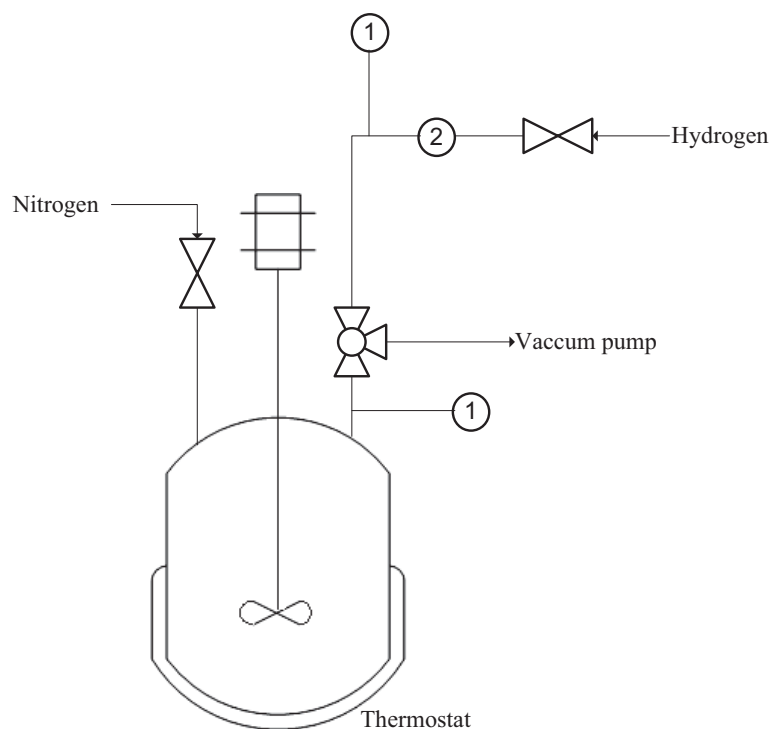

Figure 1. Experimental setup for the hydrogenation of ALB. (1) Pressure controller, (2) mass flow meter.

recorded using a Bronkhorst flow meter and pressure controller (Bronkhorst Matting GmbH, Kamen, Germany). The pressure and the hydrogen flow during the reaction were registered on a PC. At the end of reaction, a sample was taken and analyzed by gas chromatography.

In the isomerization of ALB tests, samples were taken at different times and analyzed by gas chromatography. From these results, the conversion X_{ALB}[1] (%), the initial reaction rate $r_{\mathrm{ALB,0}}$ (mmol L^{-1}s^{-1}), and the PB selectivity S_{PB} (%) were calculated according to Eqs. (1), (2), and (3), respectively. The reaction rate can also be expressed by the turnover frequency (TOF) which can be calculated from Eq. (4).

$$X_{\mathrm{ALB}} = \frac{V_{\mathrm{H2,t}}}{V_{\mathrm{H2,total}}} X_{\mathrm{GC}} = \frac{V_{\mathrm{H2,t}}}{V_{\mathrm{H2,total}}}\left(100 - A_{\mathrm{ALB}}\right) \tag{1}$$

$$r_{\mathrm{ALB,0}} = c_{\mathrm{ALB,0}} \frac{\mathrm{d}X_{\mathrm{ALB,10\%}}}{\mathrm{d}t} \tag{2}$$

$$S_{\mathrm{PB}} = \frac{A_{\mathrm{PB}}}{100 - A_{\mathrm{ALB}}} \tag{3}$$

$$TOF_0 = \frac{n_{\mathrm{PB}}}{n_{\mathrm{Pd}}t} \tag{4}$$

$V_{\mathrm{H2,t}}$ is the amount of hydrogen consumed up to time t and $V_{\mathrm{H2, total}}$ is the total amount of hydrogen consumed in the reac-

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1)   List of symbols at the end of the paper.

tion. X_{GC} is the conversion of ALB obtained from the area of the ALB peak (A_{ALB}) measured by gas chromatography (see Sect. 2.3). $c_{ALB,0}$ is the initial concentration of ALB and $dX_{ALB,10\%}/dt$ is the initial slope of the plot of conversion vs. time, calculated for conversions below 10 %. A_{PB} is the area of PB peak measured by GC. n_{Pd} and n_{PB} are the moles of catalyst and produced PB, respectively.

2.3 Analysis

The variables required to calculate the conversion of ALB and the selectivity towards PB were obtained by gas chromatography using a Shimadzu GC equipped with a Carbowax 10 Column and flame ionization detector (FID). The following conditions were used for sample analysis: $T_{injector} = 220\,°C$, $T_{detector} = 270\,°C$, $T_{oven} = 110\,°C$ (isotherm), $P_{column} = 14.8\,kPa$, and nitrogen as carrier gas. The retention times obtained for the involved reactants were 7.67 min for ALB, 6.48 min for PB, 9.62 min for *cis-β*-methylstyrene, and 12.74 min for *trans-β*-methylstyrene. Before analysis, in all cases the heterogeneous catalyst was removed by filtration. Samples from methanol were measured without further treatment and aqueous samples were treated with chloroform (pure water and TX-100 solutions) or cyclohexane (SDS and DTAB). The specific surface area and the pore volume of the Pd@Al$_2$O$_3$ catalyst were obtained from nitrogen adsorption experiments using a Quantachrome instrument.

3 Results and Discussion

3.1 Kinetic Investigation of the Pd@Al$_2$O$_3$-Catalyzed Hydrogenation of Allylbenzene in Methanol

For the heterogeneously catalyzed hydrogenation reactions a commercial Pd@Al$_2$O$_3$ catalyst was applied, with a BET surface area of 170 m^{2}g^{-1}, pore size of about 20 nm, and pore volume of 1 cm^{3}g^{-1}. The size of the palladium nanoparticles was about 5 nm. Prior to the hydrogenation experiments and also between the different set of experiments, blank experiments in the absence of the catalyst were performed to check for reactor contamination. The blank value was always below 0.005 mmol L^{-1}s^{-1}, and therefore much lower as in methanol or in water as described in the discussion below. The hydrogenation of ALB to PB can proceed via two different pathways as indicated in Fig. 2.
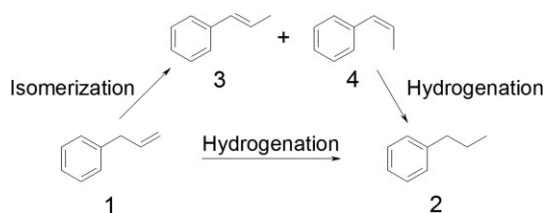

Figure 2. Scheme for the hydrogenation of ALB (1) to PB (2) via direct hydrogenation or via isomerization (intermediates *trans-β*-methyl styrene (3) and *cis-β*-methyl styrene (4)) followed by hydrogenation.

In methanol, which was used as reference solvent in these investigations, the reaction is very fast and about 85 mmol L^{-1} are converted to PB within a few minutes using only 100 mg Pd@Al$_2$O$_3$ (1 mg Pd), see Fig. 3.
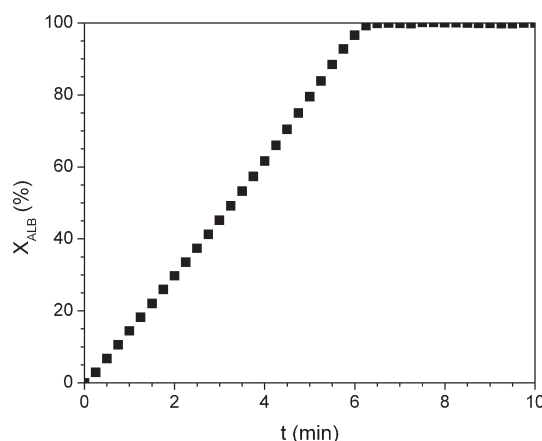

Figure 3. Conversion profile for the hydrogenation of ALB in methanol. Reaction conditions: 84.6 mmol L^{-1} ALB, 1 mg Pd, 99 mL MeOH, $P = 0.11$ MPa, $T = 25\,°C$, $n = 1200$ rpm.

However, as the fast reaction makes sampling difficult, the ALB concentration was increased to about 340 mmol L^{-1} in order to collect more data to investigate the effect of isomerization. In addition, ALB hydrogenations were performed at 6 °C and 25 °C, and ALB conversion and PB selectivity were calculated from the samples taken during the reaction, Fig. 4.

It was found that isomerization and hydrogenation of ALB take place as parallel reactions and PB selectivity is about 70–80 %. However, selectivity to PB increases with ALB conversion and would reach 100 % because no other product than PB is obtained under the applied pressure of about 0.11 MPa hydrogen. That Pd primarily catalyzes the hydrogenation was also detected by Nazarova et al. [19]. In the following experiments the effects of stirring rate (*n*), amount of catalyst (m_{Pd}), and temperature (*T*) were investigated in detail.

3.1.1 Effect of Stirring Rate

It is well-known that in gas/liquid reactions film diffusion may have a major impact on the catalytic activity; therefore, the stirring rate was varied to find a suitable value able to provide a sufficient interfacial area for the gas-to-liquid transport. According to Fig. 5, mass transfer limitations are avoided by conducting experiments at stirring speeds between 1000 and 1400 rpm. Therefore, a stirring speed of 1200 rpm (20 s^{-1}) was selected.

3.1.2 Variation of Catalyst Amount

The effect of the catalyst concentration was studied using 0.25, 0.5, 1.0, and 1.5 mg of the Pd@Al$_2$O$_3$ catalyst, while keeping all other experimental conditions constant. Fig. 6 shows the results
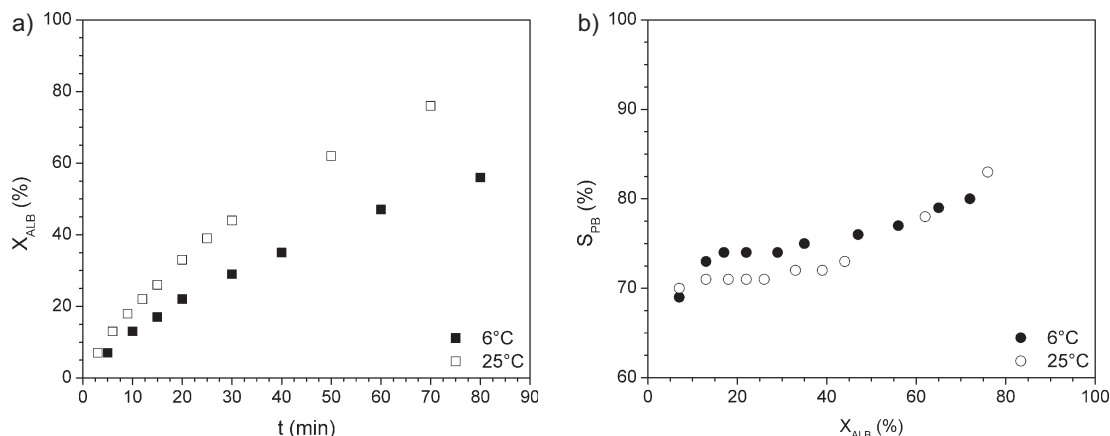
Figure 4. (a) ALB conversion (X_{ALB}) and (b) PB selectivity (S_{PB}) for the catalyzed hydrogenation of ALB (c_{ALB} = 338.5 mmol L^{-1}) over Pd@Al$_2$O$_3$ (1 mg Pd) in methanol at 6 °C and 25 °C.
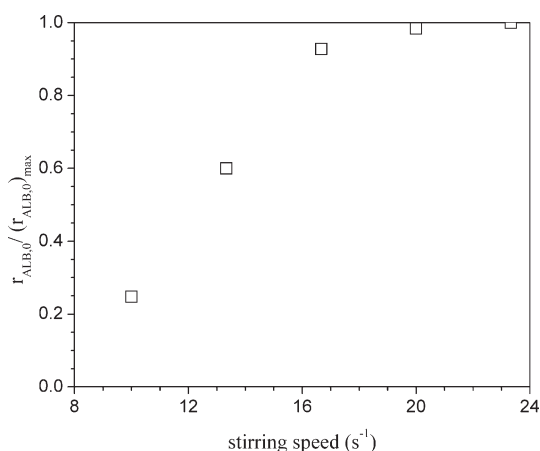

Figure 5. Normalized reaction rate as a function of the stirring speed. Reaction conditions: 84.6 mmol L^{-1} ALB, 1 mg Pd, 99 mL methanol, P = 0.11 MPa, T = 25 °C.

of the variation of the mass of Pd@Al$_2$O$_3$ catalyst. An increase in the reaction rate as the catalyst concentration increases can be noted. The initial reaction rate was observed to be a linear function of catalyst weight in the range of 0.25–1.5 mg Pd. The initial reaction rate for standard conditions of 1 mg Pd, 84.6 mmol L^{-1} ALB, and 0.1 MPa pressure is about 0.12 mmol L^{-1}s^{-1}. Taking into account an initial selectivity towards PB of 70 %, this corresponds to a TOF value of 50 h^{-1}.

This fact suggests that the mass transfer of hydrogen from the gas to the liquid phase and the diffusion of dissolved hydrogen to the catalyst occur rapidly and do not limit the overall process. From the plot of ln $r_{ALB,0}$ vs. ln m_{Pd} (not shown), a reaction order of 1 is obtained for the reaction.

3.1.3 Effect of Reaction Temperature

To assess whether the reaction is controlled by the reaction kinetics or by transport phenomena, ln k was plotted vs. 1/T (Fig. 7), with k calculated from Eq. (4).

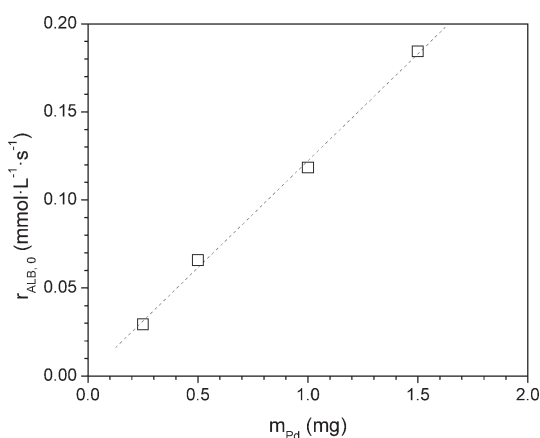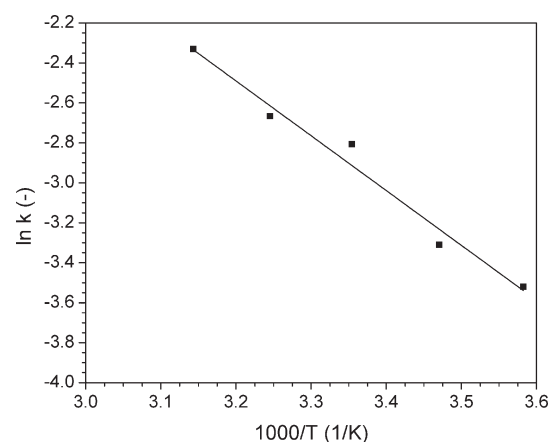**Figure 6.** Initial reaction rate as a function of the Pd@Al$_2$O$_3$ amount. Reaction conditions: 84.6 mmol L^{-1} ALB, 99 mL methanol, P = 0.11 MPa, T = 25 °C.

Figure 7. Arrhenius plot for the hydrogenation of ALB to PB in methanol. Reaction conditions: 84.6 mmol L^{-1} ALB, 1 mg Pd, 99 mL methanol, P = 0.11 MPa.

The rate constant k was calculated from the initial reaction rate $r_{ALB,0}$ and the hydrogen concentration in methanol c_{H2} at different temperatures. A linear relationship between 6 °C and 45 °C was found and the corresponding value of the activation energy was about 23 kJ mol^{-1}, indicating the absence of mass transfer limitations in the heterogeneous reaction.

$$k = \frac{r_{ALB,0}}{c_{H2}} \tag{5}$$

There is no reference value for the activation energy for ALB hydrogenation in literature. Meille et al. [20] studied the hydrogenation of α-methyl styrene (AMS), which has a similar structure to ALB, and for the kinetically controlled reaction the activation energy is about 40 kJ mol^{-1}. Our lower E_A value for ALB hydrogenation could be due to pore diffusion limitations. The influence of the particle size on the reaction rate to exclude such limitations was not studied, because a sieving of the commercial catalyst will affect the distribution of the active compound.

3.1.4 Effect of Allylbenze Concentration and Hydrogen Pressure

The ALB concentration was varied, but there was no significant influence on the reaction rate so that a zero-order reaction can be assumed. A zero-order reaction is often reported in literature for the hydrogenation of olefins with supported metal catalysts, e.g., in the Pd/Al$_2$O$_3$-catalyzed hydrogenation of AMS [20]. Because of the glass reactor used for the hydrogenation experiments, a detailed investigation of the hydrogen dependency was not possible. However, from a few data points measured between 0.08 and 0.13 MPa, a reaction order of about 1.7 was calculated. A reaction order of 1 is reported for the Pd/Al$_2$O$_3$-catalyzed hydrogenation of AMS [20]. Because of the fact that ALB partially isomerizes, a reaction order >1 is expected, then hydrogen is also consumed in the hydrogenation of the intermediates.
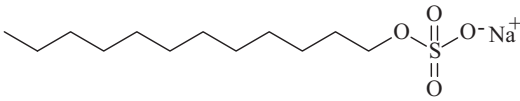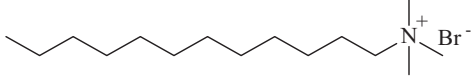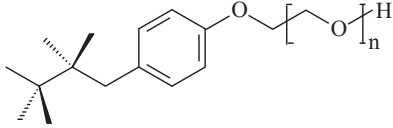
3.1.5 Catalyst Recycling

The advantage using a heterogeneous catalyst is its easy recyclability by, e.g., sedimentation or filtration. The Pd@Al$_2$O$_3$ catalyst used in this investigation was recovered by filtration at the end of the reaction and thoroughly washed with water between the runs to remove adsorbed reactants; its activity was checked to determine the recyclability of the catalysts. The catalysts was recycled two times and the experimental results showed that the reaction rate was 0.0155, 0.0140, and 0.0123 mol L^{-1}min^{-1}, in the first reaction and the first and second recycled, respectively, which is probably related with loss of mass of the catalyst in the filtration process leading to a slightly lower activity; however, it is within handling losses expected during the workup.

3.2 Kinetic Investigation of the Pd@Al$_2$O$_3$-Catalyzed Hydrogenation of Allylbenzene in Aqueous Micellar Solutions

After testing the hydrogenation of ALB in methanol, the reaction medium was changed to water and aqueous micellar solutions of SDS as anionic surfactant, TX-100 as nonionic surfactant, and DTAB as cationic surfactant. The structure and critical micellar concentration (cmc) surfactant properties [21] are given in Tab. 1.

The initial reaction rate in water is about four to five times lower, i.e., 0.023 mmol L^{-1}s^{-1}, than in methanol under similar reaction conditions. The main reasons for the lower activity are a) the low hydrogen solubility in water (three to four times less in comparison to methanol), and b) that hydrogenation is carried out in a liquid/liquid two-phase system, because ALB is water-insoluble. The hydrogen solubility was calculated from the total pressure and the thermodynamic properties of the solution [22]. After adding the surfactant, the reaction rate rises with increasing surfactant concentration until reaching a plateau as indicated in Fig. 8; at a total surfactant concentration of 4 wt %, the initial reaction rate increased by a factor of 3 and 2.2 for SDS and TX-100, respectively.

Table 1. Structure and critical micellar concentration of investigated surfactants.

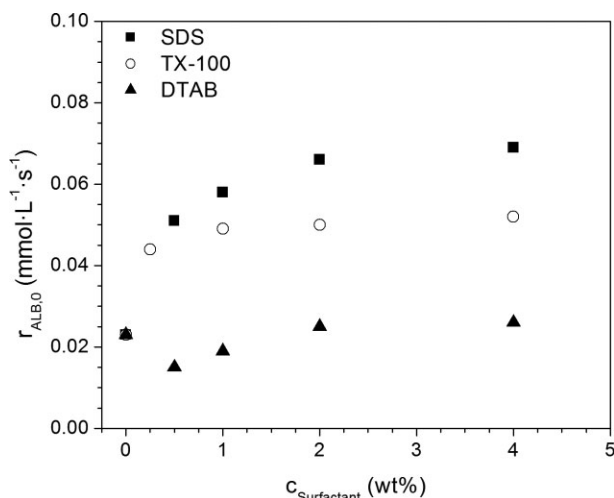| Surfactant	Structure	Type	cmc [g L^{-1}]
SDS		Anionic	2.25
DTAB		Cationic	5.57
Triton X-100		Nonionic	0.325

Figure 8. Hydrogenation of ALB in aqueous micellar solutions of SDS, TX-100, and DTAB at different surfactant concentrations. Reaction conditions: 84.6 mmol L^{-1} ALB, 1 mg Pd, water, $P = 0.11$ MPa, $T = 25\,°C$, $V = 100$ mL.

While for the nonionic surfactant TX-100, which has the lowest cmc, micelles are already present at surfactant concentrations above 0.03 wt %, for the anionic surfactant SDS and the cationic surfactant DTAB, micellization starts at higher surfactant concentrations of about 0.2 and 0.6 wt %, respectively. However, for the hydrogenation experiments carried out at surfactant concentrations of 1 wt % and above, the formation of micelles can be ensured. To discuss the observed reaction rates, it can be assumed that ALB is first solubilized by the micelles and then transferred to a surfactant layer which is adsorbed on the surface of Pd@Al$_2$O$_3$, where the reaction takes place. This mechanism is also proposed by Shinde et al. [23] for the aqueous micellar-catalyzed Heck reaction with a heterogeneous Pd/C catalyst.

From earlier hydrogenation experiments with dibutylitaconate, a substrate which has a similar hydrophobic character as ALB, it is known that the size of the micelles increases by a factor of 5 to 10 %. With higher surfactant concentration more ALB is solubilized and its increased concentration leads to a higher reaction rate. An enhanced reaction rate with increasing surfactant concentration is also reported by Shinde and Bhagwat over Pd/C-catalyzed Sonogashira reactions [24]. Interestingly, at the same surfactant concentration there is no positive effect for DTAB and the rate is the same than in water. The reason for the low activity in the case of DTAB is currently unclear and, because of the very complex nature of the reaction system, needs further investigation.

From another set of experiments with surfactants from the Marlophen series (NP5 to NP9), it was found that the reaction rate increases with the hydrophilicity of the surfactant, because solubilization of ALB is supported. Taking into account the hydrophilic-lipophilic balance (HLB) values of the surfactants, the reaction rate should be higher in H$_2$O/SDS (HLB = 40) followed by H$_2$O/DTAB (HLB = 24.3) and H$_2$O/TX-100 (HLB = 13.5). However, the reaction in DTAB was the slowest and so it can be assumed that the interaction between the sur-

factant and the support has to be considered. In the case that the size of the micelles is the major reason for the activity, ALB hydrogenation should be lower in H$_2$O/TX-100, because TX-100 forms the largest micelles which might not be able to reach the Pd nanoparticles which are inside of the pores. So the only possible assumption for the observed difference in the activity is the dissimilar adsorption behavior of the surfactants on solid surfaces.

For the nonionic surfactant TX-100, adsorption is only possible due to hydrophilic/hydrophobic interactions. In the case of the ionic surfactants SDS and DTAB, adsorption is also possible due to different charges involved. Considering the positive ξ-potential of Pd/Al$_2$O$_3$ [25], the different behavior can be explained by a repulsion of the cationic micelles with the substrate. In contrast, SDS will be attracted, leading to a better transfer of the substrate to the catalyst.

Besides the surfactant concentration, also the temperature was varied to determine the activation energy for the aqueous micellar solution with SDS as surfactant. The Arrhenius plot is given in Fig. 9; the solubility of hydrogen in water was also considered for the calculation of the rate constant.
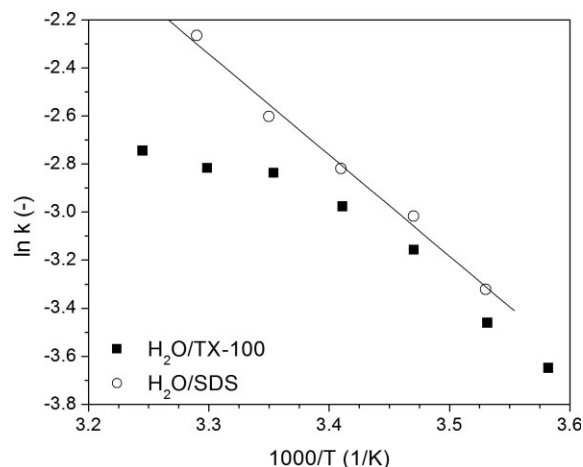

Figure 9. Arrhenius plot for the hydrogenation of ALB to PB in H$_2$O/TX-100 and H$_2$O/SDS (1 wt %). Reaction conditions: 84.6 mmol L^{-1} ALB, 1 mg Pd, water, $P = 0.11$ MPa.

From the slope of the kinetically controlled regime, the activation energy is 34.8 kJ mol^{-1}, a value slightly higher than in methanol. In addition, the temperature dependency for aqueous micellar solutions of TX-100 was studied and the activation energy was 30.4 kJ mol^{-1}. The higher activation energy also indicates a decrease in mass transport limitations, because an adsorbed SDS layer on the Pd/Al$_2$O$_3$ surface can support the ALB transport.

4 Conclusions

A palladium supported on alumina (Pd@Al$_2$O$_3$) catalyst was evaluated in the hydrogenation of ALB in methanol. A stirring speed of 1200 s^{-1} was sufficient to avoid gas/liquid mass transport limitations; additionally, between 0.25 and 1.5 mg Pd, the

reaction rate was directly proportional to the mass of the catalyst and increased with reaction temperature. To transfer the reaction from an organic to more environmentally friendly solvents, water was used as reaction medium; however, the catalytic activity in terms of ALB conversion was higher in methanol than in water, due to the improved solubility of ALB and hydrogen in organic solvents. The addition of anionic, cationic, and nonionic surfactants to water indicated that neutral and anionic surfactants have a positive effect on the reaction rate, while no effect is observed for the cationic surfactants. These results clearly show that the transfer of ALB hydrogenation from organic solvent- to aqueous-based reaction media is possible, but surfactant selection to dissolve ALB into water has to be done carefully.

Acknowledgment

The authors have declared no conflict of interest.

Symbols used

A	[–]	area of the peak
C	[mol L^{-1}]	concentration
dX/dt	[% min^{-1}]	initial slope of the plot of conversion vs. time
k	[s^{-1}]	rate constant
m	[g]	mass of catalyst
n	[s^{-1}]	stirring rate
P	[kPa]	pressure
r	[mmol L^{-1}s^{-1}]	reaction rate
S	[%]	selectivity
T	[°C]	temperature
V	[mL]	volume of hydrogen consumed
X	[%]	conversion

Subscripts

ALB	allylbenzene
H2,t	up to time t
H2, total	in the reaction
PB	propylbenzene
10%	calculated for conversions below 10 %
0	initial

Abbreviations

ALB	allylbenzene
AMS	α-methyl styrene
BET	Brunauer-Emmett-Teller
cmc	critical micellar concentration
DTAB	decyltrimethylammonium bromide
FID	flame ionization detector
GC	gas chromatography
HLB	hydrophilic-lipophilic balance
PB	propylbenzene
Pd@Al$_2$O$_3$	palladium on alumina
SDS	sodium dodecyl sulfate
TOF	turnover frequency
TX-10	t-octylphenoxypolyethoxyethanol

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