Synthesis of 3-alkoxy-2,2-dimethyl-propan-1-ols by hydrogenation of 2-substituted 5,5-dimethyl-[1,3]dioxanes using copper catalysts. Part I: Investigations in the gas phase

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Abstract

The gas phase hydrogenation of 2-substituted 5,5-dimethyl-[1,3]dioxanes to 3-alkoxy-2,2-dimethyl-propan-1-ols and in particular the reduction of 5,5-dimethyl-2-phenyl-[1,3]dioxane to 3-benzyloxy-2,2-dimethyl-propan-1-ol have been investigated within the temperature range of 175 to 300°C over copper-loaded catalysts. As main catalyst system for these investigations, a Cu/H-[B]-MFI type zeolite was chosen. Other carriers for copper as silicalite-1, H-[Al]-ZSM-5 zeolite, SiO_2 and Al_2O_3 have also been tested in that hydrogenation reaction.

1. Introduction

The heterogeneous hydrogenation of 1,3-dioxanes to alcohols under ring opening has been investigated using various heterogeneous metal catalysts containing components such as Ni, Pd, Pt, Rh and Cu [1–10]. The reactions have been performed in the gas phase under normal pressure and in the liquid phase under elevated pressure. Eq. (1) illustrates the hydrogenation of 1,3-dioxanes **1** to 3-alkoxy-propan-1-ols **2**.
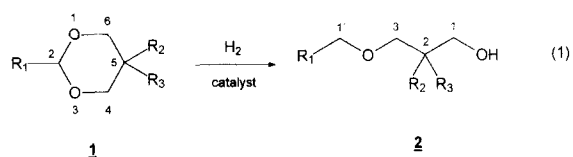

R_1 = H, alkyl, aryl, R_2, R_3 = H, alkyl

(1)

In the gas phase, the hydrogenation of 1,3-dioxanes and other 1,3-dioxacycloalkanes has been investigated extensively by Bartok et al. [7,8]. These authors have used the catalyst system Pt/thermolite at temperatures between 150°C and 300°C. Thermolite is a support of the di-

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atomaceous earth type employed in gas chromatography. It is a fire-resistant clay, consisting predominantly of calcium magnesium silicate. The metal content of the catalyst was 10 wt% Pt. The authors have investigated mainly the influences of ring size and substituents of the reactants. For example, the main reaction products obtained in the hydrogenation of 2-isopropyl-[1,3]dioxane (**1a**) are 3-isobutoxy-propan-1-ol (**2a**), 3-isobutoxy-propionaldehyde (**3a**) and isobutyric acid propyl ester (**4a**), i.e. $R_1 =$ isopropyl and $R_2 = R_3 = H$ in the formulas listed below.

2: X = CH$_2$OH
3: X = CHO

4

R$_1$ = H, alkyl, aryl, R$_2$, R$_3$ = H, alkyl
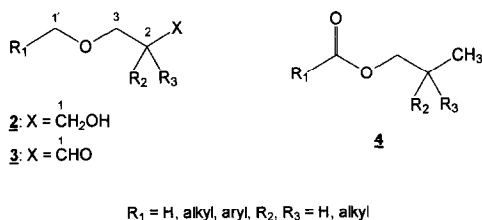
In addition to the formation of the desired 3-alkoxy-propan-1-ols **2**, 3-alkoxy-propionaldehydes **3** and esters **4** have also been identified. The aldehydes **3** as well as the esters **4** are isomerization products of the reactants **1**. The esters **4** have sometimes been the main reaction products. Bartok et al. [7,8] have discovered that the reaction path is influenced strongly by the ring size of the reactants. While the more stable five- and six-membered ring systems lead to an increased yield of esters, this reaction path has not been observed in the case of the larger and more reactive rings. Therefore, the reactants containing seven- and eight-membered rings lead to an increased total yield of the corresponding aldehydes and alcohols.

Also the substituents of the reactants affect considerably the reaction route. An increased number of substituents attached to C-2 favors the reactivity of the 1,3-dioxanes. This means that the acetals of ketones are more reactive than the acetals of aldehydes. The use of 1,3-dioxanes substituted in position 4 of the acetal

ring does not result in the formation of 3-alkoxy-propan-1-ols. The substituents in position 4 of the 1,3-dioxane rings promote the splitting of the O-3/C-4 bond and the formation of esters is increased. Investigations concerning this topic have been carried out with 4-methyl-[1,3]dioxane in the gas phase at temperatures between 180°C and 400°C [1].

It has been discovered [6] that 3-alkoxy-2,2-dimethyl-propan-1-ols **2** — after esterification with phthalic acid anhydride — can be used as softeners for polyvinyl chloride (PVC). The advantage of these softeners as compared to dioctylphthalate (DOP) is their lower tendency to diffuse out of the polymer [6]. Alcohols **2** are also important intermediates in organic chemistry. For instance, 3-benzyloxy-2,2-dimethyl-propan-1-ol (**2b**) is used for the preparation of biologically active compounds [11–14].

In theory, the hydrogenation of 2-substituted 5,5-dimethyl-[1,3]dioxanes **1** to 3-alkoxy-2,2-dimethyl-propan-1-ols **2** can proceed via reduction of 3-alkoxy-2,2-dimethyl-propionaldehydes **3** which are formed as by-products during the reaction. The isomerization reaction of acetals to the corresponding aldehydes is a well-known reaction [15–21]. It has been shown that zeolites with MFI type structure in the H form like boron pentasil zeolite H-[B]-silicalite-1 give good results in that reaction [19].

It is also known that aldehydes can be reduced to alcohols over copper catalysts. In addition, copper applied as copper chromite is an effective though polluting catalyst for the investigated reactions in the liquid phase under increased pressure [6].

For the above reasons (and also because acidic zeolites were not applied as carriers for such hydrogenation reaction before) we aimed to test the quality of the catalyst system Cu/H-[B]-silicalite-1 in the hydrogenation of 2-substituted 5,5-dimethyl-[1,3]dioxanes **1**. In particular, we studied the hydrogenation of 5,5-dimethyl-2-phenyl-[1,3]dioxane (**1b**) to 3-benzyloxy-2,2-dimethyl-propan-1-ol (**2b**). For comparison, we also checked the influence of other carriers like

silicalite-1, H-[Al]-ZSM-5 zeolite, SiO_2 and Al_2O_3. Our intention was to find catalyst systems suitable for both a gas phase hydrogenation under normal pressure and a liquid phase hydrogenation under elevated pressure. These catalysts should represent less toxic alternatives to the catalysts already known in the literature such as copper chromite and nickel oxide on silica.

2. Experimental

2.1. Preparation of 2-substituted 5,5-dimethyl-[1,3]dioxanes 1 [22]

Approximately equimolar amounts of 2,2-dimethyl-propan-1,3-diol (neopentyl glycol) and an aldehyde were placed in a flask equipped with a Dean–Stark moisture trap and a reflux condenser. 0.5 mol% p-toluene sulfonic acid and approximately 100–150 ml hexane or toluene per mol aldehyde were added. The reaction mixture was refluxed at 90–100°C until no more water was formed. After the reaction was completed, the solution was poured into 400 ml saturated sodium bicarbonate solution and washed. Next, the organic layer was washed twice with 200 ml saturated sodium bicarbonate solution and twice with 150 ml water. The organic layer was dried with sodium sulfate, the solvent removed after filtration under vacuum and the residue distilled.

2.2. 5,5-dimethyl-2-phenyl-[1,3]dioxane (1b)

B.p.: 125°C/10 mm, yield: 84% (theor.).

2.3. 5,5-dimethyl-2-isopropyl-[1,3]dioxane (1c)

B.p.: 62°C/18 mm, yield: 87% (theor.).

2.4. 5,5-dimethyl-2-propyl-[1,3]dioxane (1d)

B.p.: 71°C/19 mm, yield: 90% (theor.).

2.5. 5,5-dimethyl-2-vinyl-[1,3]dioxane (1e)

In a modification of the preparation procedure reported above, the petroleum ether fraction of a boiling point from 50°C to 70°C was used as solvent. In addition, only 10^{-4} mol% p-toluene sulfonic acid was applied as catalyst. B.p.: 44°C/10 mm, yield: 78% (theor.).

Structures 1b and 1e were confirmed by ^1H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$), whereas structures 1c and 1d were confirmed by ^1H NMR (300 MHz, $CDCl_3$) alone.

2.6. Used supports

H-[B]-silicalite-1	94.2% SiO_2, 2.3% B_2O_3
H-[Al]-ZSM-5	$SiO_2/Al_2O_3 = 54$, VAW
silicalite-1	see preparation procedure below
SiO_2	D 10-11, BASF
Al_2O_3	D 10-10, BASF

2.7. Synthesis of silicalite-1

A mixture of 200 g aqueous solution of tetrapropylammonium hydroxide (1 M) and 200 ml water was added dropwise to 78.5 g tetraethyl orthosilicate under stirring. Subsequently, after stirring for 1 h, 300 g ethanol was added. This mixture was stirred for another 2 h and then transferred into a 2.5 l stainless steel autoclave. The hydrothermal reaction was conducted under stirring (100 rpm) at 105°C for 96 h. The crystals were separated by centrifugating and washed three times with water. The material was dried at 110°C for 16 h and calcined in air at 550°C (heating rate 1°C/min) for 12 h.

Before the use as catalysts, the powders were extruded without binders, sieved and calcined at 550°C for 6 h. The fractions with a particle size

between 1.0 mm and 1.6 mm were used for catalytic runs in the fixed bed reactor.

2.8. Ion exchange and impregnation of the supports [19,23,24]

The loading of copper onto granulated material in a large amount was done by pumping an aqueous solution of a copper salt through the material in a vertical tube while the metal salt was used in a large excess. The loading of copper was done by using either $Cu(NO_3)_2 \cdot 3H_2O$ or $Cu(CH_3COO)_2 \cdot H_2O$ aqueous solution. Usually, the loading was carried out at temperatures of 70°C or 80°C for 24 h. Addition of a 25% solution of ammonia in water to the solution of the metal salt resulted in a pH of 10.5 for the metal loading. Using this method, more copper could be taken up by the support in a shorter period of time than without ammonia. In this case, the metal loading was done in such a manner that an exactly calculated amount of copper salt — based on the desired final copper content of the catalyst — was pumped through the support until the intense blue color of the solution vanished. Subsequently, the metal-loaded support was washed with distilled water, then dried and calcined.

The loading of copper onto powder or granulated material in a small amount was carried out at room temperature by stirring the support in a solution of the copper salt in a round bottom flask or by careful rotation of the flask. Usually, ion exchange was achieved by stirring the support two or three times in the aqueous metal salt solution for 24 h with use of a large excess of the metal salt. Finally, the material was filtered, washed, dried and calcined. Impregnations with copper were done with exactly calculated amounts of copper salt and the smallest possible amounts of the solutions were used. After the impregnation, the solvent was distilled off carefully under vacuum and the catalyst was dried and calcined.

The metal contents of the catalysts were ana-lyzed by AAS after dissolving the catalysts in an aqueous solution of HF.

2.9. Used catalysts

Cu/H-[B]-silicalite-1	0.6 wt% Cu	catalyst A_1
Cu/H-[B]-silicalite-1	1.1 wt% Cu	catalyst A_2
Cu/H-[B]-silicalite-1	3.2 wt% Cu	catalyst A_3
Cu/H-[B]-silicalite-1	5.3 wt% Cu	catalyst A_4
Cu/H-[B]-silicalite-1	11.4 wt% Cu	catalyst A_5
Cu/H-[B]-silicalite-1	4.0 wt% Cu	catalyst A_6
Cu/H-[B]-silicalite-1	5.2 wt% Cu	catalyst A_7
Cu/H-[B]-silicalite-1	4.4 wt% Cu	catalyst A_8
Cu/H-[B]-silicalite-1	5.1 wt% Cu	catalyst A_9
Cu/H-[Al]-ZSM-5	3.8 wt% Cu	catalyst B
Cu/silicalite-1	12.3 wt% Cu	catalyst C
Cu/SiO$_2$	4.4 wt% Cu	catalyst D
Cu/Al$_2$O$_3$	4.8 wt% Cu	catalyst E

2.10. Hydrogenation experiments

Catalyst screening tests under isothermal conditions and normal pressure in the gas phase were carried out in a fixed bed tube reactor (diameter: 0.6 cm, length: 90 cm in form of a coil). The reactor was thermostated by a home-made oven. Before starting the reaction, the catalyst was dried for 30 min at reaction temperature under nitrogen flow of 4.5 1/h. Afterwards, the desired hydrogen flow was adjusted and the solution of the reactant was pumped by a metric pump (Telab PTFE BF 411/30E) through the reactor. The reaction products were trapped in a cooling unit and the quantitative determination of the reactants and the products was done by gas chromatography. Mass balances of at least 95% have been achieved. The gas chromatographic results for the hydrogenation of acetal **1a** were obtained by using tridecane as standard and are given in mass%.

2.11. Identification of the products

As products, the following substances were detected: 3-benzyloxy-2,2-dimethyl-propan-1-ol

(2b), 3-benzyloxy-2,2-dimethyl-propionalde-hyde (3b), toluene, benzyl alcohol, benzal-dehyde and 2,2-dimethyl-propan-1,3-diol. Benzoic acid 2,2-dimethyl-propyl ester (4b) as a possible isomerization product of acetal 1a was not observed during our investigations. The reaction products have been identified either by transformation to derivatives and subsequent analysis or by enrichment of the reaction samples. Therefore, some of the products had to be synthesized independently.

2.11.1. 3-Benzyloxy-2,2-dimethyl-propan-1-ol (2b)

For enrichment of the reaction samples, the desired alcohol 2b was synthesized by the method of Williamson [25]. 0.2 mol 2,2-di-methyl-propan-1,3-diol (neopentyl glycol) was dissolved in 500 ml toluene by stirring and heating the mixture at 105°C. Approximately 0.1 mol sodium was added in small portions. After completion, the mixture contained a voluminous white precipitate and was refluxed for 2 h. Then, 0.15 mol benzyl bromide was added dropwise and the reaction mixture was refluxed for an additional 16 h. The voluminous precipitate disappeared and a fine white precipitate developed instead. Subsequently, the reaction mixture was washed five times with 100 ml water and the organic layer was dried with sodium sulfate. After filtration of the drying agent, the solvent was removed under vacuum and the residue was distilled. B.p.: 58°C/0.1 mm Hg, yield: 76% (theor.).

2.11.2. 3-Benzyloxy-2,2-dimethyl-propionalde-hyde (3b)

The aldehyde 3b was transformed into its neopentyl glycol acetal 2-(2-benzyloxy-1,1-di-methyl-ethyl)-5,5-dimethyl-[1,3]dioxane (1f) by the procedure used to synthesize the reactants 1 and the resulting acetal 1f was investigated by NMR spectroscopy. B.p.: 110–112°C/1 mm Hg, yield: 47% (theor.).

2.11.3. Benzoic acid 2,2-dimethyl-propyl ester (4b)

The preparation of the ester 4b followed basically the same procedure as given for acetals 1. B.p.: 110°C – 113°C/7 mm Hg, yield: 50% (theor.).

Structures 2b and 3b were confirmed by ^{1}H NMR (300 MHz, CDCl$_3$) and ^{13}C NMR (75 MHz, CDCl$_3$), whereas structure 4b was confirmed by ^{1}H NMR (300 MHz, CDCl$_3$) alone.

3. Results and discussion

The optimization of hydrogenation of 1,3-dioxane 1b was carried out over catalyst Cu/H-[B]-silicalite-1 (4.0 wt% Cu, catalyst A$_6$ and 5.2 wt% Cu, catalyst A$_7$) at the following starting reaction conditions: $T = 300°C$, $p = 1$ bar, WHSV $= 1$ h^{-1}, solvent: 1,4 – dioxane (reactant:solvent $= 1.0$ g:4.3 g), $\dot{V}_{H_2} = 0.4$ l/h (H$_2$:reactant $= 2:1$), TOS $= 8$ h. For clarity, only the conversions and the selectivities for alcohol 2b and for aldehyde 3b are presented in the following figures (Figs. 1–7).

3.1. Influence of the nitrogen flow rate on the hydrogenation reaction

The addition of nitrogen to the reaction mixture with the rate within the limits between $\dot{V}_{N_2} = 0$ and 20 l/h and corresponding shortening of the contact time from 2.5 s to 0.3 s resulted in the decrease of the conversion and the selectivity for alcohol 2b (see Fig. 1).

3.2. Influence of the hydrogen flow rate on the hydrogenation reaction

However, the increase of the hydrogen flow rate up to $\dot{V}_{H_2} = 10$ l/h (H$_2$:reactant $= 50:1$) had a positive effect on the reaction in spite of a corresponding shortening of the contact time from 2.5 s to 0.6 s (see Fig. 2).
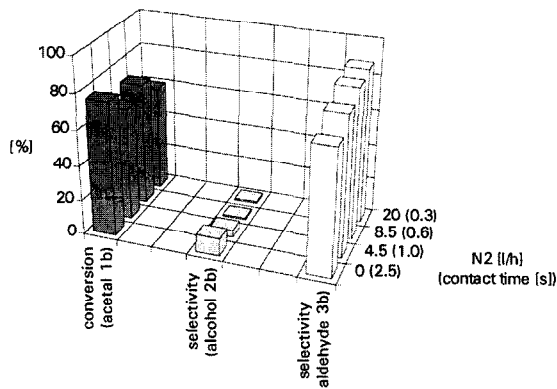
Fig. 1. Influence of the nitrogen flow rate on the hydrogenation of 5,5-dimethyl-2-phenyl-[1,3]dioxane (**1b**). Reaction conditions: T = 300°C, WHSV = 1 h^{-1}, p = 1 bar, $\dot{V}_{H_2}$ = 0.4 1/h, catalyst: Cu/H-[B]-silicalite-1 (5.2 wt% Cu, catalyst A$_7$), reactant:1,4-dioxane = 1.0 g:4.3 g, TOS = 8 h.

The conversion stayed almost at the same level, whereas the selectivity for alcohol **2b** increased. Therefore, all subsequent experiments were done without addition of nitrogen, but with hydrogen at the high flow rate of $\dot{V}_{H_2}$ = 10 1/h.

3.3. Influence of the reaction temperature on the hydrogenation reaction

The so far attained selectivity for alcohol **2b** with values around 40% at conversion of approximately 75% is not satisfying yet. Therefore
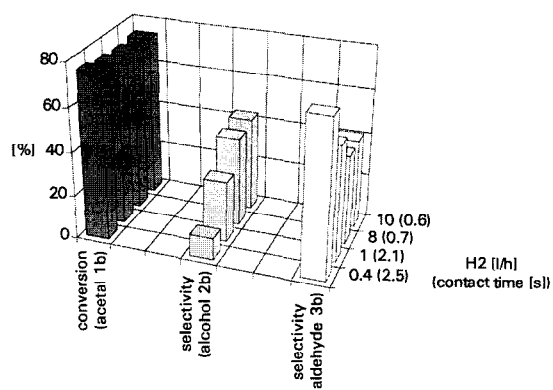

Fig. 2. Influence of the hydrogen flow rate on the hydrogenation of 5,5-dimethyl-2-phenyl-[1,3]dioxane (**1b**). Reaction conditions: T = 300°C, WHSV = 1 h$-^1$, p = 1 bar, catalyst: Cu/H-[B]-silicalite-1 (5.2 wt% Cu, catalyst A$_7$), reactant:1,4-dioxane = 1.0 g:4.3 g, TOS = 8 h.
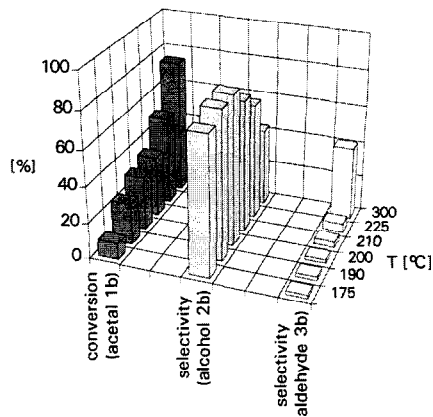

Fig. 3. Influence of the reaction temperature on the hydrogenation of 5,5-dimethyl-2-phenyl-[1,3]dioxane (**1b**). Reaction conditions: WHSV = 1 h^{-1}, p = 1 bar, $\dot{V}_{H_2}$ = 10 1/h, catalyst: Cu/H-[B]-silicalite-1 (5.2 wt% Cu, catalyst A$_7$), reactant:1,4-dioxane = 1.0 g:4.3 g, TOS = 8 h, τ = 0.6–0.7 s.

the reaction temperature was changed (see Fig. 3).

Indeed, within the temperature range from 190°C to 200°C, much higher selectivities for alcohol **2b** of about 80% were achieved but the conversion is lowered to 20–30%. One can also see that the selectivities for aldehyde **3b** are higher at increased temperatures. This is similar to the findings by Bartok et al. [8] who investigated the hydrogenation reaction of different dioxacycloalkanes using the catalyst system Pt/thermolite. The authors explain this observation by a higher activation energy for the hydrogenation to the alcohols than for the isomerization to the corresponding aldehydes.

3.4. Influence of the weight hourly space velocity on the hydrogenation reaction

Through variation of the weight hourly space velocity (WHSV), it was checked whether the low conversion at 190°C could be increased at constant selectivity for alcohol **2b**. Therefore, the concentration of the reactant in the solvent was changed. The WHSV was varied within the limits from 0.3 h^{-1} to 2.3 h^{-1} (see Fig. 4).

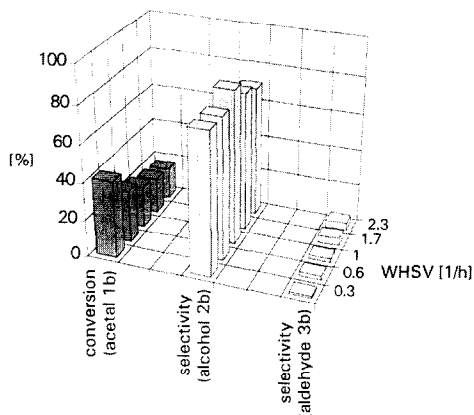As expected, the conversion decreases with higher WHSV. The selectivity for alcohol **2b**,

Fig. 4. Influence of the weight hourly space velocity (WHSV) on the hydrogenation reaction of 5,5-dimethyl-2-phenyl-[1,3]dioxane (**1b**). Reaction conditions: $T = 190°C$, $p = 1$ bar, $\dot{V}_{H_2} = 10$ l/h, catalyst: Cu/H-[B]-silicalite-1 (4.0 wt% Cu, catalyst A_6), reactant:1,4-dioxane = 1.0 g:20.2–1.0 g:1.7 g, TOS = 8 h, $\tau = 0.6$ s.

however, does not remain constant. There is a slight maximum at WHSV $= 1$ h^{-1} with a selectivity of about 80%. The selectivity decreases at smaller and at higher values of WHSV. It is supposed that this is due to two contrary effects which are connected to an increased WHSV. On the one hand, the hydrogen:reactant ratio decreases, i.e. the selectivity for alcohol **2b** declines as has been demonstrated above by changing the hydrogen flow rate (see Fig. 2). On the other hand, the conversion decreases simultaneously and this means that consecutive reactions can take place to a smaller extent. Consequently, an increase in the selectivity for alcohol **2b** is observed.

3.5. Influence of the copper content of the catalyst on the hydrogenation reaction

Another important factor concerning the hydrogenation results is the metal content of the catalyst. The results obtained by variation of the metal content between 0.6 wt% Cu (catalyst A_1) and 11.4 wt% Cu (catalyst A_5) are demonstrated in Fig. 5.

The conversion remains almost the same. The selectivity for alcohol **2b** increases with copper content while the selectivity for aldehyde **3b** decreases. This indicates that this part of alde-

hyde **3b** which is reduced to alcohol **2b** is getting higher with increasing copper content of the catalysts.

3.6. Influence of pre-reductions of the catalyst on the hydrogenation reaction

Pre-reduction of Cu/H-[B]-silicalite-1 (4.0 wt% Cu, catalyst A_6) was carried out under 100% hydrogen overnight at a hydrogen flow rate of $\dot{V}_{H_2} = 10$ l/h. Temperatures of the pre-reductions were 250°C, 300°C, 350°C and 400°C. The hydrogenation of 1,3-dioxane **1b** was carried out immediately after the pre-reduction and was done under the reaction conditions resulting in the highest selectivity for alcohol **2b** (reaction conditions: $T = 190°C$, $p = 1$ bar, WHSV $= 1$ h^{-1}, $\dot{V}_{H_2} = 10$ l/h, reactant:1,4-dioxane $= 1.0$ g:4.3 g, TOS $= 8$ h, $\tau = 0.7$ s). The changes in the conversion due to various pre-reductions were not significant. Moreover, the selectivity for alcohol **2b** could not be improved.

3.7. Influence of different carriers for copper on the hydrogenation reaction

Additional to the carrier H-[B]-silicalite-1 (4.0 wt% Cu, catalyst A_6), also H-[Al]-ZSM-5 (3.8
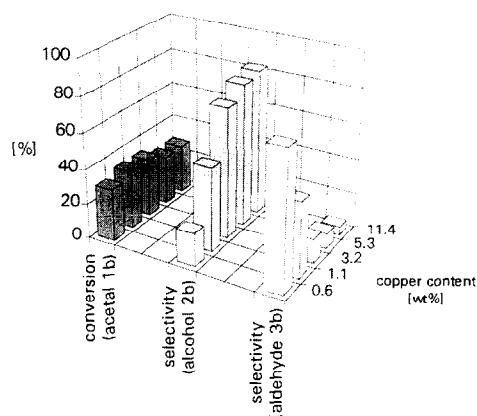

Fig. 5. Influence of the copper content of Cu/H-[B]-silicalite-1 (catalysts A_1 to A_5) on the hydrogenation of 5,5-dimethyl-2-phenyl-[1,3]dioxane (**1b**). Reaction conditions: $T = 190°C$, WHSV $= 1$ h^{-1}, $p = 1$ bar, $\dot{V}_{H_2} = 10$ l/h, reactant:1,4-dioxane $= 1.0$ g:4.3 g, TOS $= 8$ h, $\tau = 0.7$ s.
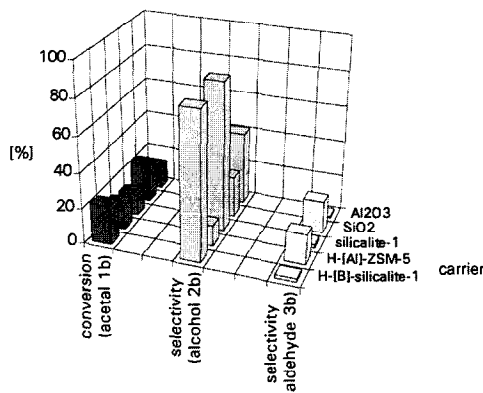
Fig. 6. Influence of copper carriers on the hydrogenation of 5,5-dimethyl-2-phenyl-[1,3]dioxane (**1b**). Reaction conditions: T = 190°C, WHSV = 1 h^{-1}, p = 1 bar, $\dot{V}_{H_2}$ = 10 l/h, reactant:1,4-dioxane = 1.0 g:4.3 g, TOS = 8 h, τ = 0.7 s.

wt% Cu, catalyst B) and silicalite-1 (12.3 wt% Cu, catalyst C) as well as SiO$_2$ (4.4 wt% Cu, catalyst D) and Al$_2$O$_3$ (4.8 wt% Cu, catalyst E) were tested (see Fig. 6).

When comparing the catalysts with similar copper loading, the catalyst system Cu/H-[B]-silicalite-1 showed the best hydrogenation result. All other catalyst carriers were less suitable. In the case of Cu/H-[Al]-ZSM-5, Cu/SiO$_2$ and Cu/Al$_2$O$_3$, it could be assumed that pre-reduction of the catalysts improves the selectivity for alcohol **2b**. This was checked with Cu/H-[Al]-ZSM-5. After a pre-reduction, even worse hydrogenation results were obtained. Therefore, it is more likely that other reasons are responsible for such effects. On the one hand, the catalysts Cu/H-[Al]-ZSM-5, Cu/SiO$_2$ and CuAl$_2$O$_3$ could possess bad isomerization properties. This assumption is supported by results shown in Fig. 6. It indicates that the sum of the selectivities for alcohol **2b** and aldehyde **3b** as the possible intermediate for the alcohol formation is clearly lower in the case of the ineffective catalysts than the selectivity for alcohol **2b** in the case of the effective catalysts. On the other hand, the catalysts that lead to unsatisfactory selectivities for alcohol **2b** could possess insufficient hydrogenation properties. Fig. 6 shows that the catalysts Cu/H-[Al]-

ZSM-5 and Cu/SiO$_2$ produce the largest amounts of aldehyde **3b**.

Whether shape selectivity could be involved, i.e. whether the reaction is taking place on the outer surface only or also inside the microporous system, can only be determined by choosing substrates with bulkier groups. Such experiments are in preparation. Not even with molecular modelling can it be proven whether the substrate used in this work can reach the inner zeolite surface or not.

Copper-impregnated silicalite-1 having the highest copper content (12.3 wt% Cu) shows a similar selectivity for alcohol **2b** and a lower conversion of the reactant **1b** in comparison to Cu/H-[B]-silicalite-1 with 4.0 wt% Cu (see Fig. 6). The same holds for Cu/H-[B]-silicalite-1 with a copper loading of 11.4 wt% Cu (see Fig. 5) which is similar to the copper content of Cu/silicalite-1 (12.3 wt% Cu).

3.8. Influence of the time of stream on the hydrogenation reaction

The obtained changes of catalytic results with time on stream (TOS) are most distinct at the beginning of the hydrogenation reactions (see Fig. 7).

Usually, the conversion decreases slightly whereas the selectivity for alcohol **2b** increases.
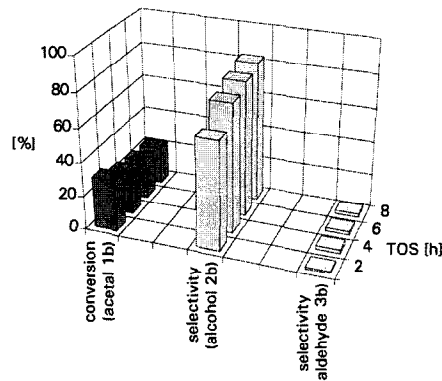

Fig. 7. Influence of the TOS on the hydrogenation of 5,5-dimethyl-2-phenyl-[1,3]dioxane (**1b**). Reaction conditions: T = 190°C, WHSV = 1 h^{-1}, p = 1 bar, $\dot{V}_{H_2}$ = 10 l/h, catalyst: Cu/H-[B]-silicalite-1 (4.0 wt% Cu, catalyst A$_6$), reactant:1,4-dioxane = 1.0 g:4.3 g, τ = 0.7 s.

This is due to a coking of the catalyst. At the beginning of the reaction, the catalyst is most active and produces the highest amount of by-products. The coking reduces both the activity and the conversion of the catalyst. Thereby, the formation of by-products decreases and thus the selectivity for alcohol 2b increases.

3.9. Influence of different reactants on the hydrogenation reaction

Finally, the hydrogenation in the gas phase was investigated over Cu/H-[B]-silicalite-1 using various 5,5-dimethyl-[1,3]dioxanes 1 differently substituted in position 2 of the acetal ring (reaction conditions: $T = 300°C$, WHSV = 1 h^{-1}, $p = 1$ bar, $\dot{V}_{H_2} = 10$ l/h, catalysts: Cu/H-[B]-silicalite-1 (4.4 wt% Cu, catalyst A_8 and 5.1 wt% Cu, catalyst A_9 (indicated by '*'), reactant:toluene = 1.0 g:4.3 g, TOS = 8 h, $\tau = 0.8$ s). As substituents R_1, phenyl, propyl, isopropyl and vinyl were employed. The yield of alcohol 2 decreased in the following order of substituents R_1:

phenyl $\geq$ isopropyl $\gg$ propyl = vinyl *

5,5-dimethyl-2-isopropyl-[1,3]dioxane (1c) gave results comparable to those obtained with phenyl-substituted 1,3-dioxane 1b (conversion of acetals 1b, 1c: 75–85%, selectivity for alcohols 2: 45%). Under the applied reaction conditions at 300°C the other two acetals 1d, 1e were decomposed completely into low boiling substances which were not investigated (conversion of acetals 1d, 1e: 100%, selectivity for the alcohols 2: 0%). These acetals 1d, 1e had to be reduced at much lower temperature but no optimization has been performed so far. Interestingly, this sequence is not valid for the isomerization of the investigated compounds to 3-alkoxy-2,2-dimethyl-propionaldehydes over H-[B]-silicalite-1 using nitrogen instead of hydrogen as carrier gas. In this case, we found the following order for the yield of aldehydes 3 after TOS = 6 h:

vinyl > phenyl $\gg$ isopropyl = propyl

In the case of the isomerization reaction over H-[B]-silicalite-1, the shown sequence is not valid for the conversion of acetals 1 and the selectivity for aldehydes 3. At approximately the same conversion — except for more stable isopropyl-substituted 1,3-dioxane 1c — the selectivity for aldehydes 3 decreases in the following order of substituents R_1: phenyl $\approx$ vinyl > isopropyl > propyl.

The different results for the hydrogenation and the isomerization of acetals 1 seem to indicate parallel processes for these two reactions. However, it has to be considered that hydrogen could influence the original product composition due to its nature as a reaction gas. In contrast to an inert carrier gas as nitrogen, hydrogen could possibly take part in consecutive reactions, e.g. in the hydrogenation of alcohols 2 to alkanes and 2,2-dimethyl-propan-1,3-diol.

4. Conclusions

In the gas phase, the hydrogenation of 5,5-dimethyl-2-phenyl-[1,3]dioxane (1b) to 3-benzyloxy-2,2-dimethyl-propan-1-ol (2b) has been investigated under normal pressure in a continuous flow reactor using copper-loaded catalysts. H-[B]-silicalite-1, silicalite-1, H-[Al]-ZSM-5, SiO_2 and Al_2O_3 have been applied as carriers for copper and the best results have been obtained with the catalyst system Cu/H-[B]-silicalite-1. At a low temperature of 190°C, selectivity for alcohol 2b of 80% at conversions of 20% to 30% has been achieved. Enhancement of temperature to 300°C has resulted in an increase of the conversion. However, the selectivity for alcohol 2b decreased due to an increase of the selectivity for 3-benzyloxy-2,2-dimethyl-propionaldehyde (3b) which is a formal oxidation product of alcohol 2b. In contrast to the results of Bartok et al. [7–10] who used platinum catalysts in the hydrogenation of other dioxacycloalkanes than acetal 1b, no ester formation by isomerization of the reactant 1b has

been observed. Finally, the influence of various substituents R_1 in position 2 of 5,5-dimethyl-[1,3]dioxanes **1** on the hydrogenation reaction was checked with R_1 = phenyl, propyl, isopropyl and vinyl. Under the applied reaction conditions at 300°C over Cu/H-[B]-silicalite-1, only isopropyl-substituted acetal **1c** led to results comparable to those obtained with phenyl-substituted 1,3-dioxane **1b**. The other two acetals **1d, 1e** were decomposed completely into low boiling substances.

On the basis of the above results, the catalyst system Cu/H-[B]-silicalite-1 has also been tested in the hydrogenation of 5,5-dimethyl-2-phenyl-[1,3]dioxane (**1b**) to 3-benzyloxy-2,2-dimethyl-propan-1-ol (**2b**) under elevated pressure in the liquid phase [26].

Acknowledgements

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