

Synthesis of 3-benzyloxy-2,2-dimethyl-propan-1-ol by hydrogenation of 5,5-dimethyl-2-phenyl-[1,3]dioxane using copper catalysts. Part II: investigations in the liquid phase

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Abstract

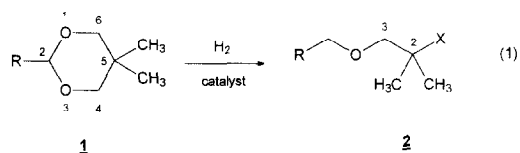
The hydrogenation of 5,5-dimethyl-2-phenyl-[1,3]dioxane to 3-benzyloxy-2,2-dimethyl-propan-1-ol has been investigated within the temperature range from 150°C to 220°C over copper-loaded catalysts. Under elevated pressure in a continuous flow reactor, good results have been obtained using the catalyst system Cu/H-[B]-silicalite-1. The results have been compared to those obtained over two catalyst systems known in the literature, i.e. nickel oxide on silica and copper chromite.

Keywords: 3-benzyloxy-2,2-dimethyl-propan-1-ol; 5,5-dimethyl-2-phenyl-[1,3]dioxane; Copper catalysts; Hydrogenation; Liquid phase

1. Introduction

The heterogeneous hydrogenation of 1,3-dioxanes to alcohols under ring opening has been investigated over catalysts containing various metals such as Ni, Pd, Pt, Rh and Cu [1–10]. The often used copper catalysts have favorably been applied in particular as copper chromite which is, however, a strongly polluting species due to the presence of chromium. The nickel containing catalysts are also environmentally not benign. The hydrogenations have been carried out in the gas phase under normal pressure and in the liquid phase under elevated pressure

as well. The preparation of 3-alkoxy-2,2-dimethyl-propan-1-ols **2** out of 2-substituted 5,5-dimethyl-[1,3]dioxanes **1** in the liquid phase according to Eq. (1) has been described by Otte et al. using copper chromite or nickel oxide and nickel oxide on inert carriers like silica [6].



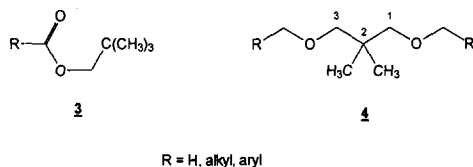
R = H, alkyl, aryl, X = CH₂OH

(1)

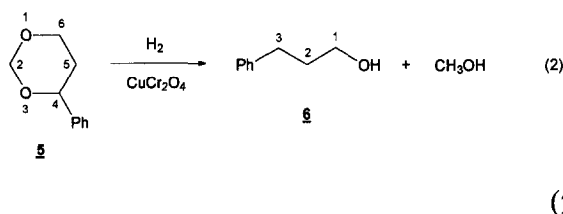
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The reactions have typically been performed at temperatures between 180°C and 220°C and

pressures from 200 bar to 300 bar. In comparison with the results obtained by Bartok et al. [7–10] who used platinum doped catalysts in gas phase reactions, carboxylic acid 2,2-dimethyl-propyl esters **3** are not formed by isomerization of the starting material. Instead, 1,3-dialkoxy-2,2-dimethyl-propanes **4** (diethers of neopentyl glycol) were detected as by-products.



Under conditions comparable to those used by Otte et al., substituents in position 4 of acetals **5** direct the hydrogenation towards the formation of primary alcohols **6** according to Eq. (2). Simultaneously, methanol is generated as well [3–5].



It has been discovered [6] that 3-alkoxy-2,2-dimethyl-propan-1-ols **2** — after esterification with phthalic anhydride — can be used as softeners for polyvinyl chloride (PVC). The advantage of these softeners as compared to dioctyl phthalate (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 (**2a**) has been used for the preparation of biologically active compounds [11–14].

In previously performed investigations in the gas phase, we found that the use of Cu/H-[B]-silicalite-1 as catalyst leads to promising results concerning the hydrogenation of 5,5-dimethyl-2-phenyl-[1,3]dioxane (**1a**) to 3-benzyloxy-2,2-

dimethyl-propan-1-ol (**2a**) [15]. Therefore, this catalyst system has been chosen to study this reaction in the liquid phase under elevated pressure. A number of other catalysts have also been investigated regarding their influence on the examined reaction. The most promising catalyst has been compared with the literature-known catalysts copper chromite and nickel oxide on silica. Moreover, the intention of our work was to find an alternative and less toxic catalyst system.

2. Experimental

2.1. Preliminary remarks

The preparation of the reactants and the characterization of the products obtained in gas phase hydrogenations as well as the ion exchange and impregnation procedures have been described elsewhere [15]. The spectroscopic data of the by-products formed in liquid phase hydrogenations are given in Table 1.

Cu, Cu₂O and CuO were commercial grade materials purchased from Merck KGaA and Aldrich-Chemie GmbH and Co. KG.

Before the use as catalysts in the fixed bed reactor, 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 catalysis.

2.2. Hydrogenation experiments

The hydrogenations of cyclic acetal **1a** were studied under elevated pressure. They were carried out in a batch as well as in a continuous flow reactor.

Autoclaves of 75 ml volume were used for batchwise screening tests of catalyst in liquid phase at elevated pressure. These autoclaves could be employed to a pressure of maximum 100 bar and temperature of maximum 300°C in a temperature-controlled oil bath. They con-

tained a glass inlet and a teflon-coated stirrer. The dried solutions of the reactants in 1,4-dioxane were kept under nitrogen. The powder catalyst was dried at 300°C in air for 30 min and then added to the reactants. After evacuation and refilling the autoclave with nitrogen three times, the suspension of the reaction mixture was filled by means of a syringe under nitrogen into the glass inlet. Finally, hydrogen was introduced until the desired pressure was reached and the reaction temperature was set. The reaction took place under stirring. After the reaction, the catalyst was separated by centrifugation and the product mixture was examined by gas chromatography (GC).

Catalyst screening tests in a continuous flow reactor under elevated pressure in liquid phase were performed in a fixed bed tube reactor (diameter: 0.9 cm, length: 30 cm). The reactor could be employed at pressure of maximum 100 bar and heated up to 450°C with a heating tape. After placing the catalyst in the reactor, hydrogen was introduced. The pressure could be regulated by a pressure-relief valve at the outlet of the apparatus. When the desired pressure was achieved, the reactor was heated up to 250°C and the catalyst was pre-reduced for 1 h. Subsequently, the reaction temperature was set and

the reactants were pumped by a metric pump (Latek P400) into the reactor. The products were trapped by a cooling system and analyzed by GC.

Mass balances of at least 95% have been achieved. The gas chromatographic results were obtained by using tridecane as standard and are given in mass%.

2.3. Identification of the products

The following substances were detected as products: 3-benzyloxy-2,2-dimethyl-propan-1-ol (**2a**), 3-benzyloxy-2,2-dimethyl-propionaldehyde (see Eq. (1), X = CHO), 1,3-dibenzyloxy-2,2-dimethyl-propane (**4a**), toluene, benzyl alcohol, benzaldehyde and 2,2-dimethyl-propan-1,3-diol. In some cases, also saturated reactant 5,5-dimethyl-2-cyclohexyl-[1,3]dioxane (**1b**) and saturated product 3-cyclohexylmethoxy-2,2-dimethyl-propan-1-ol (**2b**) could be observed. Benzoic acid 2,2-dimethyl-propyl ester (**3a**) as a possible isomerization product of acetal **1a** was not observed during our investigations.

The spectroscopic data of the diether **4a** and the saturated compounds **1b** and **2b** are given in the following section. 1,3-dibenzyloxy-2,2-di-

Table 1

| Used supports | | |
|-----------------------------------|---|----------------|
| H-[B]-silicalite-1 | 94.2% SiO ₂ , 2.3% B ₂ O ₃ | BASF AG |
| H-[Al]-ZSM-5 | SiO ₂ /Al ₂ O ₃ = 54 | VAW GmbH |
| silicalite-1 | as described in [15] | |
| SiO ₂ | D 10-11 | BASF AG |
| Al ₂ O ₃ | D 10-10 | BASF AG |
| NaY | SiO ₂ /Al ₂ O ₃ = 6 (IR) | Grace GmbH |
| HY | SiO ₂ /Al ₂ O ₃ = 16 (IR) | PQ Corporation |
| Used catalysts | | |
| CuCr ₂ O ₄ | 33 wt% Cu, 27 wt% Cr, 11 wt% Ba | Süd-Chemie AG |
| NiO/SiO ₂ | 50 wt% Ni, 4.4 wt% Cu, < 0.4 wt% Al ₂ O ₃ , < 0.2 wt% Fe ₂ O ₃ , < 0.1 wt% Na, < 0.05 wt% S | Süd-Chemie AG |
| Cu/H-[B]-silicalite-1 | 4.0 wt% Cu | catalyst A |
| 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 |
| Cu/NaY | 5.4 wt% Cu | catalyst F |

methyl-propane (**4a**) was distilled from the reaction mixture and investigated by NMR spectroscopy. The saturated compounds **1b** and **2b** were identified by GC/MS and GC/IR spectroscopy. The identification procedures and spectroscopic data of the other identified reaction products are given in Ref. [15].

2.4. 1,3-dibenzyloxy-2,2-dimethyl-propane (**4a**)

b.p.: 100°C–105°C/0.1 mm Hg.

The structure of product **4a** was confirmed by ^1H NMR (300 MHz, CDCl_3) and ^{13}C NMR (75 MHz, CDCl_3).

2.5. 5,5-dimethyl-2-cyclohexyl-[1,3]dioxane (**1b**)

GC/IR: $\nu = 2940$ (s), 2857 (m), 1463 (w), 1396 (w), 1129 (m), 1110 (m), 1032 (w), 998 (w) cm^{-1} .

GC/MS (70 eV): m/z (%) = 197 ($\text{M}^+ - 1$, 1.7), 115 (100), 95 (13), 83 (22), 69 (63), 56 (32), 55 (23), 45 (24), 41 (50), 39 (10), 29 (18).

2.6. 3-cyclohexylmethoxy-2,2-dimethyl-propan-1-ol (**2b**)

GC/IR: $\nu = 3667$ (w), 3582 (w), 2937 (s), 2867 (m), 1464 (w), 1372 (w), 1279 (w), 1112 (m), 1050 (w) cm^{-1} .

GC/MS (70 eV): m/z (%) = 97 (50), 95 (10), 69 (10), 56 (34), 55 (67), 45 (12), 43 (10), 41 (27), 29 (13).

3. Results and discussion

In previously performed gas phase investigations under normal pressure, various acetals **1** have been used as reactants to form alcohols **2** [15]. The present work deals exclusively with the hydrogenation of 5,5-dimethyl-2-phenyl-[1,3]dioxane (**1a**) to 3-benzyloxy-2,2-dimethyl-propan-1-ol (**2a**) under elevated pressure in liquid phase. The reactions have been carried out in a batch as well as in a continuous flow

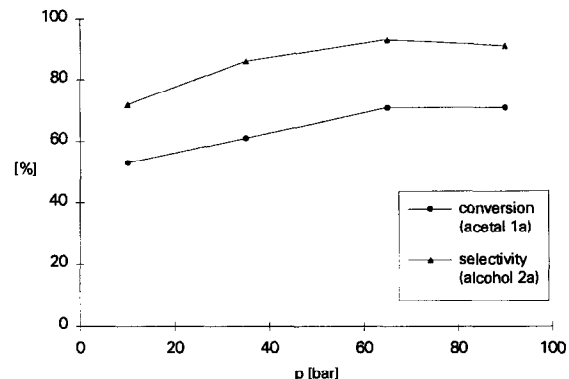


Fig. 1. Influence of the hydrogen pressure on the hydrogenation of 5,5-dimethyl-2-phenyl-[1,3]dioxane (**1a**); reaction conditions: $T = 190^\circ\text{C}$, 0.1 g Cu/H-[B]-silicalite-1 (4.0 wt% Cu, catalyst A), 2.0 g reactant in 13.4 g 1,4-dioxane, $t = 12$ h.

reactor. During these reactions 3-benzyloxy-2,2-dimethyl-propionaldehyde (see Eq. (1), $\text{X} = \text{CHO}$) which was the main by-product in the gas phase investigations, was produced only in some experiments and then to a negligible amount.

3.1. Batchwise hydrogenation under elevated pressure

The influence of hydrogen pressure as high as 90 bar on the hydrogenation reaction was investigated over Cu/H-[B]-silicalite-1 (4.0 wt% Cu, catalyst A). This catalyst and reaction temperature of 190°C were selected, since their application yielded good results in the gas phase hydrogenations [15]. The catalytic results obtained are demonstrated in Fig. 1.

As shown in Fig. 1, high hydrogen pressures led to the best results. Therefore, all following batchwise experiments were carried out with a hydrogen pressure of 90 bar. At this pressure, the alcohol selectivity of about 90% (see Fig. 1) was accepted to be high enough to compare various catalysts. Thus, the reaction conditions were not optimized further. The following groups of catalysts were used for the catalytic runs:

1. copper-doped zeolites having MFI type structure;

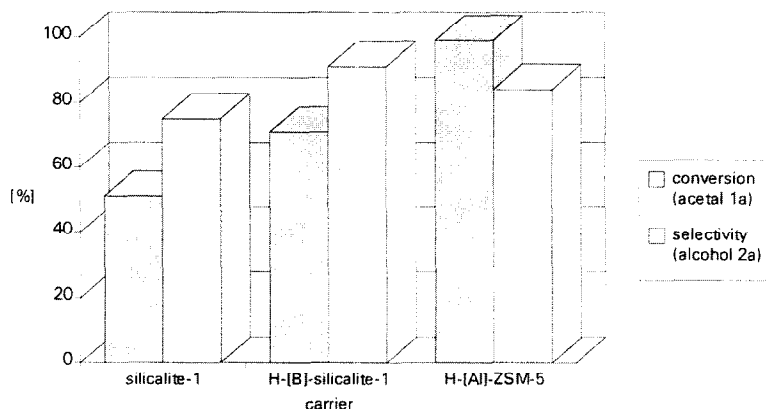


Fig. 2. Influence of various copper carriers on the hydrogenation of 5,5-dimethyl-2-phenyl-[1,3]dioxane (**1a**); reaction conditions: $T = 190^{\circ}\text{C}$, $p = 90$ bar H_2 , 0.1 g catalyst, 2.0 g reactant in 13.4 g 1,4-dioxane, $t = 12$ h.

2. copper catalysts with non-microporous supports, copper oxides and metallic copper;
3. copper chromite and nickel oxide on silica.

3.1.1. Ad (1): Copper-doped zeolites having MFI type structure

The catalysts employed were Cu/H-[B]-silicalite-1 (4.0 wt% Cu, catalyst A), Cu/H-[Al]-ZSM-5 (3.8 wt% Cu, catalyst B) and Cu/silicalite-1 (12.3 wt% Cu, catalyst C) (see Fig. 2).

All three catalysts were active in the hydrogenation of 5,5-dimethyl-2-phenyl-[1,3]dioxane (**1a**). The acidic catalysts Cu/H-[B]-silicalite-1 and Cu/H-[Al]-ZSM-5 led to higher conversions of acetal **1a** and selectivities for alcohol **2a** than Cu/silicalite-1. This was an indication to the advantageous influence of Brønsted acidity. H-[Al]-ZSM-5 which should contain stronger acidic centers than H-[B]-silicalite-1 [16] gave also a higher conversion. However, the sequences in the conversion of acetal **1a** and in

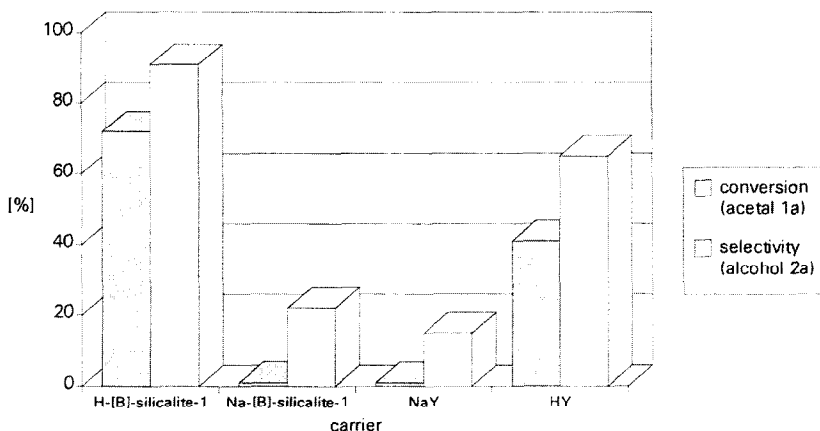


Fig. 3. Hydrogenation of 5,5-dimethyl-2-phenyl-[1,3]dioxane (**1a**) using Cu/H-[B]-silicalite-1 (4.0 wt% Cu, catalyst A) ion-exchanged with NaBr and Cu/NaY (5.4 wt% Cu, catalyst F) ion-exchanged with NH_4Cl and calcined; reaction conditions: $T = 190^{\circ}\text{C}$, $p = 90$ bar H_2 , 0.1 g catalyst, 2.0 g reactant in 13.4 g 1,4-dioxane, $t = 12$ h.

the selectivity for alcohol **2a** were not the same since Cu/H-[B]-silicalite-1 led to the highest selectivity for alcohol **2a** (compare Fig. 2).

A further investigation of the influence of acidity is illustrated in Fig. 3. The catalyst Cu/H-[B]-silicalite-1 (4.0 wt% Cu, catalyst A) has been ion-exchanged with sodium bromide (three times) resulting in a Cu/Na-[B]-silicalite-1 catalyst. The active sites of the catalyst have been deactivated by sodium (see Fig. 3). On the other hand, an inactive Cu/NaY catalyst (5.4 wt% Cu, catalyst F) after an ion exchange with ammonium chloride (three times) and subsequent calcination (Cu/HY catalyst) has shown a considerable increase in activity (see Fig. 3).

It is then obvious that acidity resulting from protons is decisive for the catalytic performance of the zeolite catalysts.

3.1.2. Ad (2): Copper catalysts with non-microporous supports, copper oxides and metallic copper

The following catalysts were applied: Cu/SiO₂ (4.4 wt% Cu, catalyst D), Cu/Al₂O₃ (4.8 wt% Cu, catalyst E), copper(I) oxide, copper(II) oxide and metallic copper. The catalytic results obtained with these materials are shown in Fig. 4.

The conversion obtained over the catalyst Cu/SiO₂ is negligible and the use of metallic copper or copper(I) oxide also did not give satisfactory results (the yields of alcohol **2a** were lower than 1%). The catalyst Cu/Al₂O₃ gave results comparable to those obtained with Cu/H-[B]-silicalite-1 and Cu/H-[Al]-ZSM-5. A conversion of almost 80% was achieved while the selectivity for alcohol **2a** was about 90%. With copper(II) oxide, a selectivity of 95% for alcohol **2a** was obtained indicating that the properties of the carriers were not essential for catalysis. However, the conversion of 25% was rather low. A big disadvantage of this material was the formation of a metallic copper layer on the surface of the glass inlet. Therefore, it was better to use catalysts containing a small amount of copper distributed on a support.

3.1.3. Ad (3): Copper chromite and nickel oxide on silica

The hydrogenation proceeded over copper chromite and nickel oxide on silica as described already in the literature [6] (Fig. 5).

Copper chromite turned out to be the best of the investigated catalysts under the applied reaction conditions.

In the case of the hydrogenation of aromatic

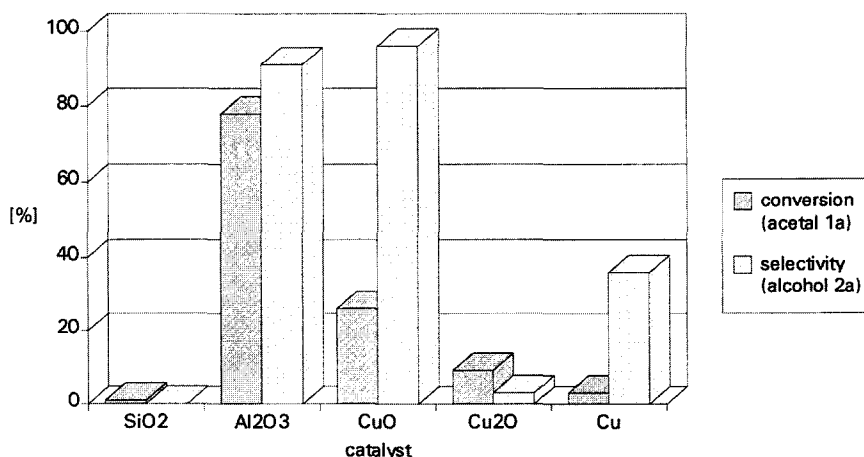


Fig. 4. Influence of various copper catalysts on the hydrogenation of 5,5-dimethyl-2-phenyl-[1,3]dioxane (**1a**); reaction conditions: $T = 190^{\circ}\text{C}$, $p = 90$ bar H_2 , 0.1 g catalyst, 2.0 g reactant in 13.4 g 1,4-dioxane, $t = 12$ h.

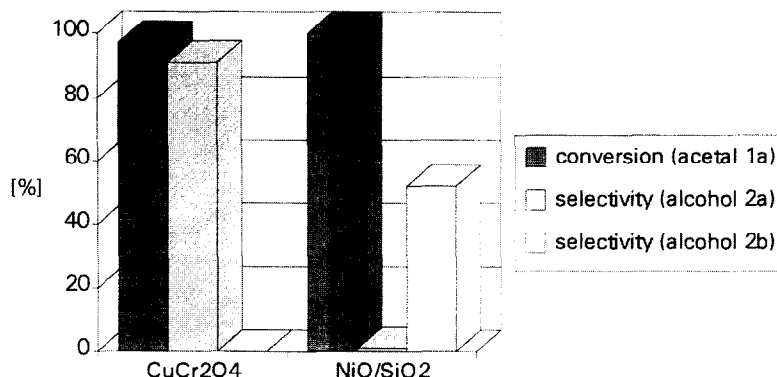


Fig. 5. Hydrogenation of 5,5-dimethyl-2-phenyl-[1,3]dioxane (**1a**) using copper chromite and nickel oxide on silica as catalysts; reaction conditions: $T = 190^{\circ}\text{C}$, $p = 90$ bar H_2 , 0.1 g catalyst, 2.0 g reactant in 13.4 g 1,4-dioxane, $t = 12$ h.

substituted reactants **1** using nickel oxide on silica as the catalyst, an undesired additional reaction occurred to a high proportion. This was the hydrogenation of the aromatic substituent; the desired aromatic alcohol **2a** was formed only to a low extent of approximately 1%, while saturated alcohol **2b** was achieved with a selectivity of 50%. The selectivities for alcohols **2a** and **2b** represent also maximum values. The reason was the formation of methylcyclohexane. The amount of this compound could not be determined precisely by gas chromatography because of its unfavorable peak position near the peak of the solvent. Thus, nickel oxide on silica was not further used as catalyst throughout this work.

Considering the selectivities for alcohol **2a** obtained in the batchwise hydrogenations of acetal **1a**, various catalysts (e.g. Cu/H-[B]-silicalite-1, Cu/H-[Al]-ZSM-5 or Cu/ Al_2O_3) were suited for a comparison with the literature-known (and so far best) catalyst, copper chromite. Ultimately, Cu/H-[B]-silicalite-1 (4.0 wt% Cu, catalyst A) was selected, because this catalyst system led to the best results when applied in the gas phase hydrogenations under normal pressure [15]. The reaction temperature was varied between 150°C and 220°C (see Figs. 6 and 7).

At low temperature, copper chromite was better than Cu/H-[B]-silicalite-1 but at 220°C both catalysts yielded the same results.

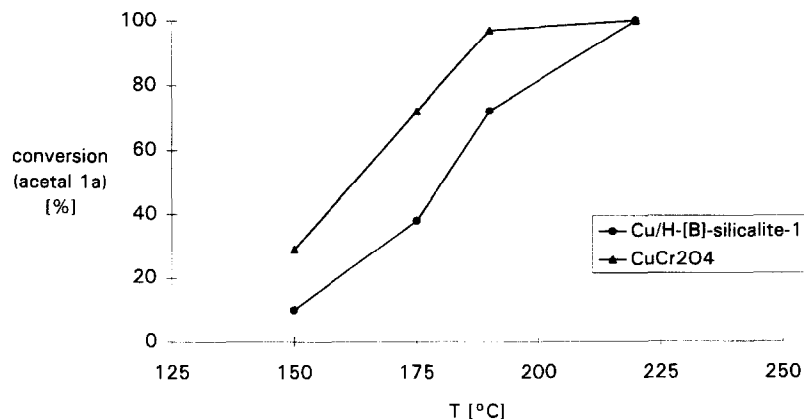


Fig. 6. Influence of temperature on the conversion in the hydrogenation reaction of 5,5-dimethyl-2-phenyl-[1,3]dioxane (**1a**) using copper chromite and Cu/H-[B]-silicalite-1 (4.0 wt% Cu, catalyst A) as catalysts; reaction conditions: $p = 90$ bar H_2 , 0.1 g catalyst, 2.0 g reactant in 13.4 g 1,4-dioxane, $t = 12$ h.

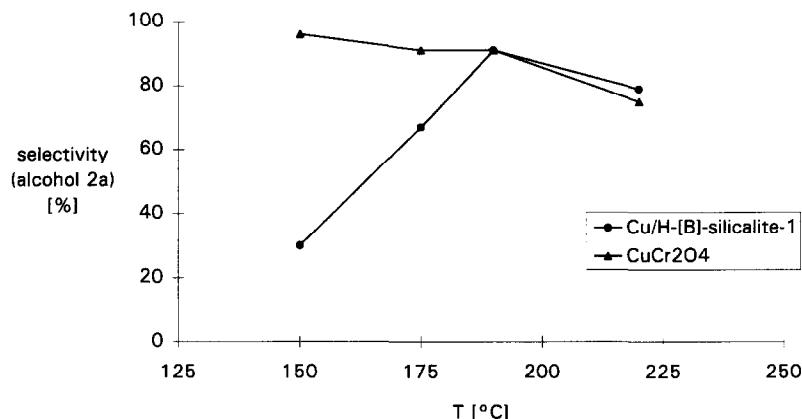


Fig. 7. Influence of temperature on the selectivity for alcohol **2a** in the hydrogenation reaction of 5,5-dimethyl-2-phenyl-[1,3]dioxane (**1a**) using copper chromite and Cu/H-[B]-silicalite-1 (4.0 wt% Cu, catalyst A) as catalysts; reaction conditions: $p = 90$ bar H_2 , 0.1 g catalyst, 2.0 g reactant in 13.4 g 1,4-dioxane, $t = 12$ h.

As was demonstrated, the Brønsted acidity of Cu/H-[B]-silicalite-1 had a positive effect on catalysis at 190°C (compare Figs. 2 and 3). However, this acidity was likely also the determining factor for worse results at lower temperatures of 150°C and 175°C. The acid sites of Cu/H-[B]-silicalite-1 could promote the cleavage of 1,3-dioxane **1a** into benzaldehyde and 2,2-dimethyl-propan-1,3-diol (reverse reaction of the synthesis of acetal **1a**). This undesired side-reaction requires presence of water. However, the ensuing reduction of benzaldehyde to toluene produces water again. Thus, even traces of water — e.g. from the catalyst itself — can have a considerable influence under the applied reduction conditions. At higher temperatures of approximately 190°C, the formation of alcohol **2a** seemed to compete with the cleavage of acetal **1a** and so the selectivity for alcohol **2a** increased using Cu/H-[B]-silicalite-1 at this temperature. At even higher temperature of 220°C, consecutive reactions — e.g. the hydrogenation of alcohol **2a** to toluene and 2,2-dimethyl-propan-1,3-diol — appeared to grow stronger. This resulted in a decrease of the selectivity for alcohol **2a** using Cu/H-[B]-silicalite-1 as catalyst.

Copper chromite is much less acidic than Cu/H-[B]-silicalite-1 and so it did not cleave acetal **1a** to a large extent. Therefore, a high

selectivity for alcohol **2a** was observed at low temperatures. In contrast, the good hydrogenation activity of copper chromite seemed to accelerate consecutive reactions with increasing temperature, e.g. the above mentioned hydrogenation of alcohol **2a**. This could explain why the selectivity for alcohol **2a** decreased continuously with increasing temperature using copper chromite as catalyst.

At 190°C under the applied reaction conditions, copper chromite was the best catalyst to hydrogenate 5,5-dimethyl-2-phenyl-[1,3]dioxane

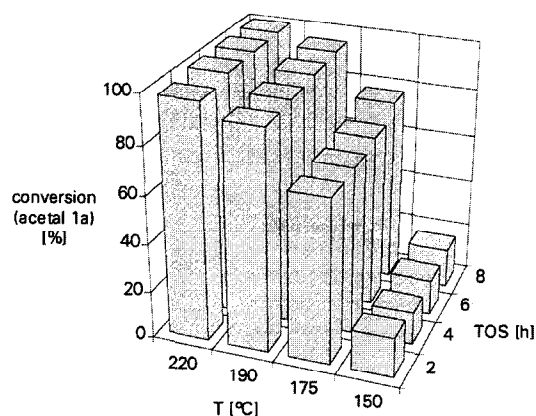


Fig. 8. Influence of temperature and TOS on the conversion of 5,5-dimethyl-2-phenyl-[1,3]dioxane (**1a**) using Cu/H-[B]-silicalite-1 (4.0 wt% Cu, catalyst A) as catalyst; reaction conditions: $p = 80$ bar H_2 , $\dot{V}_{H_2} = 10$ l/h, $WHSV = 1$ h⁻¹, $\dot{m}_{\text{reactant solution}} = 46$ g/h, 1.0 g reactant in 13.4 g 1,4-dioxane.

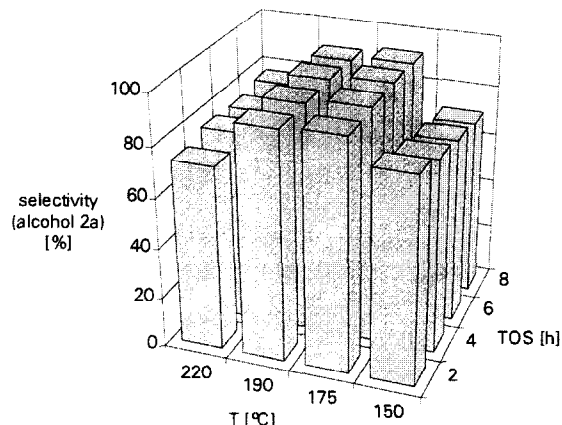


Fig. 9. Influence of temperature and TOS on the selectivity for alcohol **2a** in the hydrogenation reaction of 5,5-dimethyl-2-phenyl-[1,3]dioxane (**1a**) using Cu/H-[B]-silicalite-1 (4.0 wt% Cu, catalyst A) as catalyst; reaction conditions: $p = 80$ bar H_2 , $\dot{V}_{H_2} = 10$ l/h, WHSV = 1 h^{-1} , $\dot{m}_{\text{reactant solution}} = 46$ g/h, 1.0 g reactant in 13.4 g 1,4-dioxane.

1a to 3-benzyloxy-2,2-dimethyl-propan-1-ol **2a**. As was shown, Cu/H-[B]-silicalite-1 and copper chromite led to comparable hydrogenation results at elevated reaction temperature of 220°C. The aim of the following experiments was to investigate whether Cu/H-[B]-silicalite-1 can be an alternative catalyst in a continuous flow reactor.

3.2. Hydrogenation under elevated pressure in a continuous flow reactor

The hydrogenation reaction was investigated between 150°C and 220°C using Cu/H-[B]-silicalite-1 (4.0 wt% Cu, catalyst A) in a continuous flow reactor under elevated pressure (see Figs. 8 and 9). The following reaction conditions were applied: $p = 80$ bar, $\dot{V}_{H_2} = 10$ l/h hydrogen, WHSV = 1 h^{-1} , $\dot{m}_{\text{reactant}} : \dot{m}_{1,4\text{-dioxane}} = 1.0\text{ g} : 13.4\text{ g}$, $\dot{m}_{\text{reactant solution}} = 46$ g/h. By increasing the reaction temperature, the same tendencies as in the batch reactor were obtained. The conversion increased (see Fig. 8) and the selectivity for alcohol **2a** had a maximum between 175°C and 190°C (see Fig. 9). At this maximum, the conversion and the selectivity were of 90%.

In the continuous flow reactor, dibenzyloxy-2,2-dimethyl-propane **4a** was formed as by-product. This product could not be observed in the batch reactor. It could be formed by the condensation of 3-benzyloxy-2,2-dimethyl-propan-1-ol **2a** and phenyl-methanol in an acid-catalyzed reaction. Benzyl alcohol resulted from the acid catalyzed cleavage of the reactant **1a** into benzaldehyde and 2,2-dimethyl-propan-

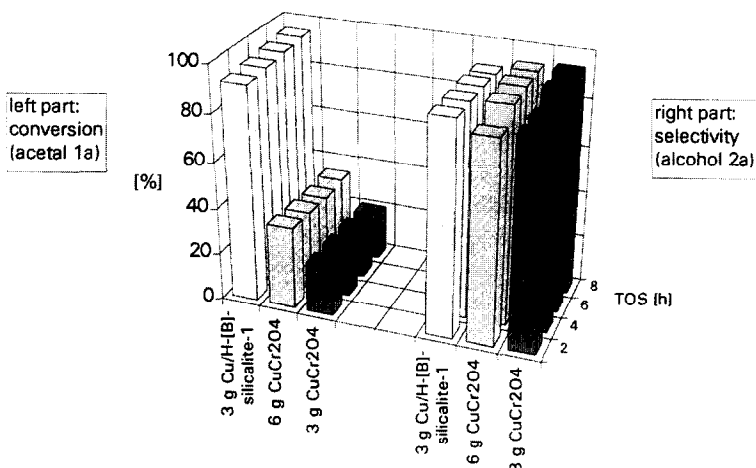


Fig. 10. Comparison of copper chromite and Cu/H-[B]-silicalite-1 (4.0 wt% Cu, catalyst A) in the hydrogenation of 5,5-dimethyl-2-phenyl-[1,3]dioxane (**1a**) in a continuous flow reactor under elevated pressure; reaction conditions: $T = 190^\circ\text{C}$, $p = 80$ bar H_2 , $\dot{V}_{H_2} = 10$ l/h, WHSV = 1 h^{-1} , $\dot{m}_{\text{reactant solution}} = 46$ g/h, 1.0 g reactant in 13.4 g 1,4-dioxane.

1,3-diol which was induced by traces of water and subsequent hydrogenation of benzaldehyde. The formation of 1 mol diether **4a** out of 2 mol alcohol yielded 1 mol water that could initiate the reaction again. Thus, the yield of desired alcohol **2a** could be increased by the avoidance of water in the case of acidic catalysts.

In the presence of copper chromite which is less acidic than Cu/H-[B]-silicalite-1, dibenzyloxy-2,2-dimethyl-propane **4a** was not formed. The catalytic results for copper chromite and a comparison with those obtained over Cu/H-[B]-silicalite-1 are demonstrated in Fig. 10.

As can be seen from Fig. 10, the catalyst system Cu/H-[B]-silicalite-1 seems to be a good alternative to copper chromite in a continuous flow reactor. Using equal masses and volumes of catalyst at 190°C and 80 bar total pressure, 5,5-dimethyl-2-phenyl-[1,3]dioxane **1a** is converted over Cu/H-[B]-silicalite-1 to a higher extent and at similar selectivities (conversion and selectivity for alcohol **2a** of about 90%). Further advantages of the zeolite catalyst as compared with copper chromite are:

- The obtained yield of 3-benzyloxy-2,2-dimethyl-propan-1-ol **2a** is comparable to the yields of other 3-alkoxy-2,2-dimethyl-propan-1-ols **2** synthesized by Otte et al. [6]. These authors worked within the same temperature range (preferably at 180°C to 220°C) but the total pressures were substantially higher (200 bar to 300 bar) than those used throughout our investigations.

- Applying Cu/H-[B]-silicalite-1, the toxic chromium of copper chromite can be avoided. In addition, the copper content of the employed Cu/H-[B]-silicalite-1 is lower than that of copper chromite.

4. Conclusions

The hydrogenation of 5,5-dimethyl-2-phenyl-[1,3]dioxane **1a** to 3-benzyloxy-2,2-dimethyl-propan-1-ol **2a** has been investigated under ele-

vated pressure. The reductions have been carried out not only in a batch reactor but also in a continuous flow reactor. Temperatures from 150°C to 220°C and pressures as high as 90 bar have been applied. In the batchwise hydrogenations, the literature-known but environmentally not benign catalyst copper chromite turned out to be the best catalyst, but in a continuous flow reactor, Cu/H-[B]-silicalite-1 was better. At 190°C and 80 bar total pressure, conversions and selectivities for alcohol **2a** of about 90% have been obtained with Cu/H-[B]-silicalite-1. This has appeared to be the most interesting result because such a catalyst system has allowed to avoid toxic chromium completely at a much lower copper content than in copper chromite.

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