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$Cu–B_2O_3/SiO_2$, an effective catalyst for synthesis of fatty alcohol from hydrogenolysis of fatty acid esters

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This work demonstrates that $Cu–B_2O_3/SiO_2$ is an effective catalyst for synthesis of fatty alcohols from hydrogenolysis of fatty acid esters. Boron oxide not only acts as a textural promoter to increase the dispersion of copper, but also as a structural promoter to decrease the activation energy of hydrogenolysis by 10 kJ/mol. The optimum loading of boron oxide doped is around 6.4 wt%. This chromium-free copper catalyst is seven times as active as the commercial copper chromite (Engelhard Cu-1234E) in the hydrogenolysis of methyl esters at 240°C, 110 bar. $Cu–B_2O_3(6.4\%)/SiO_2$ is a promising catalyst for lower pressure (<150 bar) hydrogenolysis processes.

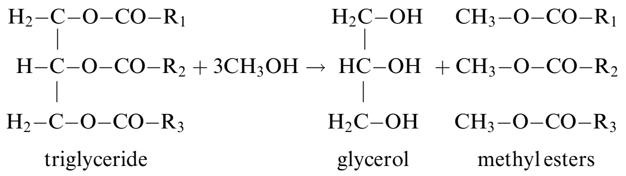
Keywords: Cu catalyst, hydrogenolysis, methyl ester, fatty acid ester, fatty alcohol

1. Introduction

Catalytic hydrogenolysis of esters to two alcohols,

$$RCOOR_1 + 2H_2 \rightarrow RCH_2OH + R_1OH\,,$$

was first described by Folkers and Adkins in 1931 [1] and has found extensive application in industrial processes, especially for deriving fatty alcohols from fatty acid esters. Fatty alcohols in carbon chain length from C_6 to C_{22} are widely employed as intermediates in detergents and cosmetics. Fatty acid methyl esters, major raw materials for fatty alcohols synthesis, are produced by transesterifying triglycerides from natural sources with methanol:



$$\begin{array}{ccccc} H_2{-}C{-}O{-}CO{-}R_1 & & H_2C{-}OH & & CH_3{-}O{-}CO{-}R_1 \\ | & & | & & \\ H{-}C{-}O{-}CO{-}R_2 & +\,3CH_3OH \rightarrow & HC{-}OH & + & CH_3{-}O{-}CO{-}R_2 \\ | & & | & & \\ H_2{-}C{-}O{-}CO{-}R_3 & & H_2C{-}OH & & CH_3{-}O{-}CO{-}R_3 \\ \text{triglyceride} & & \text{glycerol} & & \text{methyl esters} \end{array}$$

Commercial hydrogenolysis of fatty acid esters is performed utilizing copper-based catalysts, typically at temperatures ranging from 200 to 250°C and at pressures of 200 to 300 bar. Traditionally used catalysts are essentially comprised of copper and chromium oxides, sometimes supported and doped with additives such as barium [2–6]. Developing low-pressure processes has long been a prime industrial target. Therefore, research effort nowadays focuses on creating active catalysts to allow processing below 150 bar and on chromium-free copper catalysts to reduce environmental pollution. This study confirms that the chromium-free $Cu–B_2O_3/SiO_2$ catalysts are effective in hydrogenolysis of fatty acid esters.

For catalytic studies, methyl acetate is an appropriate model compound for C_{12}–C_{18} esters for industrial interest. The hydrogenolysis reaction equation of methyl acetate can be described by:

$$CH_3{-}CO{-}O{-}CH_3 + 2H_2 \rightarrow$$
$$CH_3{-}CH_2{-}OH + CH_3{-}OH$$

In addition to the main products ethanol and methanol, some other compounds, e.g. ethyl acetate, ethanal and ethane may be formed. Ethyl acetate is produced by transesterifying methyl acetate and the product of ethanol, and is merely an intermediate that reacts with hydrogen to form two equivalent ethanols:

$$CH_3{-}CO{-}O{-}CH_3 + CH_3{-}CH_2{-}OH \rightarrow$$
$$CH_3{-}CO{-}O{-}CH_2{-}CH_3 + CH_3{-}OH$$

$$CH{-}CO{-}O{-}CH_2{-}CH_3 + 2H_2 \rightarrow 2CH_3{-}CH_2{-}OH$$

Ethanal arises from the incomplete hydrogenation of ester or from the dehydrogenation of ethanol:

$$CH_3{-}CO{-}O{-}CH_3 + H_2 \rightarrow CH_3{-}CO{-}H + CH_3OH$$

Ethane results from the reaction of ester with three equivalents hydrogen:

$$CH_3{-}CO{-}O{-}CH_3 + 3H_2 \rightarrow$$
$$CH_3{-}CH_3 + CH_3OH + H_2O$$

In this reaction system, Cu/SiO_2 catalysts are well established and have been studied by Trimm and co-workers [7–10]. Iron, magnesium, manganese and zinc as promo-

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ters have been described by Claus et al. [11], and Staal and co-workers [12,13] have investigated the effects of zinc. The profound influence of boron oxide on a Cu/ SiO_2 catalyst was examined in our previous studies concerning the hydrogenolysis of methyl formate [14]. In this study Cu–B_2O_3/SiO_2 catalysts were used for hydrogenolysis of methyl esters, and some catalytic results are presented here.

2. Experimental

Cu–B_2O_3/SiO_2 catalysts with 15 wt% copper loading were prepared by incipient co-impregnation of copper nitrate and boron oxide dissolved in water, dried at 100°C for 6 h and calcined in air at 300°C for 3 h. A commercial copper chromite catalyst (Engelhard Cu-1234E) was used for comparison.

The slurry-phase hydrogenolysis of methyl acetate was performed batchwise in a magnetically stirred autoclave (Par-4546) of 100 ml capacity in the temperature range of 220–250°C and at pressures of 110–150 bar. Before reaction, the copper-based catalyst was pre-reduced in hydrogen up to 200°C at a rate of 5°C/min maintained for 3 h. The amount of catalyst used was sufficiently small and the stirring speed high enough to minimize the mass transfer resistance. The reaction system was quenched after an appropriate period (2–20 h), and the product sample was withdrawn for analysis by a gas chromatograph equipped with a flame ionization detector and a $1/8'' \times 6'$ Porapak Q column.

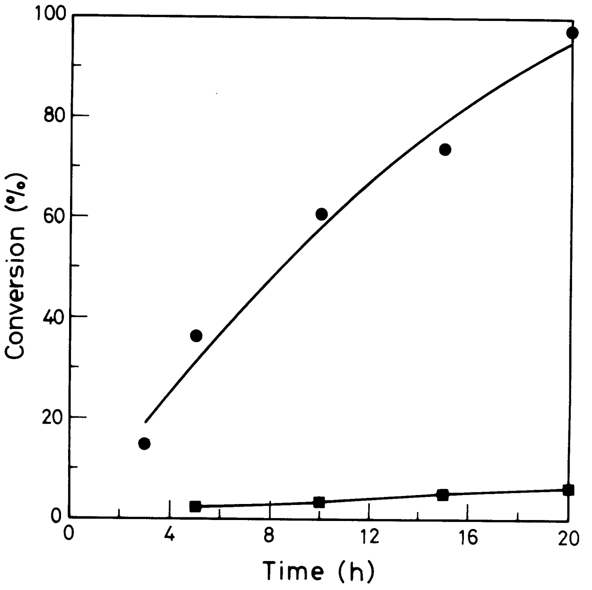

Figure 1. Comparison of Cu–B_2O_3/SiO_2 and copper chromite catalysts for hydrogenolysis of methyl acetate (240°C, 110 bar, methyl acetate/cyclohexane = 10 ml/70 ml; Cu–B_2O_3(6.4%)/SiO_2 = 1 g, copper chromite = 0.68 g).

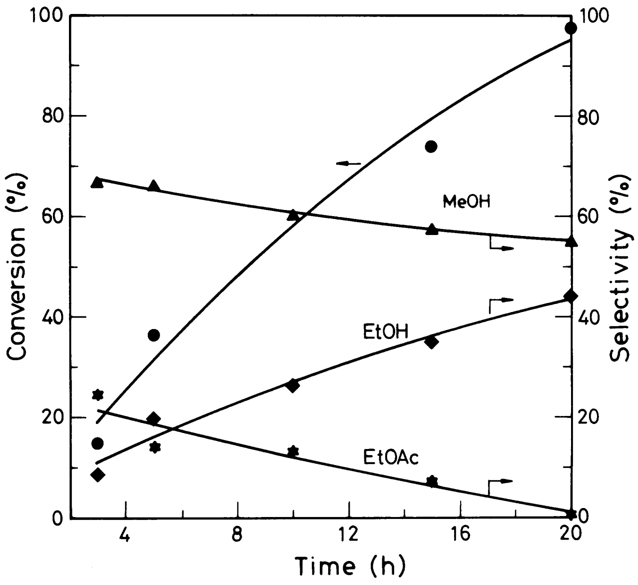

Figure 2. Distribution of products for hydrogenolysis of methyl acetate (240°C, 110 bar, methyl acetate/cyclohexane = 10 ml/70 ml, Cu–B_2O_3(6.4%)/SiO_2 = 1.0 g).

3. Results and discussion

Our previous studies revealed the chromium-free Cu–B_2O_3/SiO_2 catalyst as a potential candidate for the hydrogenolysis of methyl formate with 1.5 times the reactivity of the commercial copper chromite (Engelhard Cu-1234E) [14]. In this work, a Cu–B_2O_3/ SiO_2 catalyst was again used in a preliminary test for hydrogenolysis of methyl acetate at 240°C and 110 bar in cyclohexane as a solvent. Compared with the copper chromite, shown in figure 1, the Cu–B_2O_3/SiO_2 catalyst proved much more active. As figure 2 indicates, methanol and ethanol are the major products, and the only byproduct is ethyl acetate from transesterifying ethanol with methyl acetate. The ethyl acetate is simply an intermediate that successively reacts with hydrogen to form two ethanols. Obviously, the Cu–B_2O_3/SiO_2 catalyst was a promising candidate for a low-pressure hydrogenolysis process. Hydrogenolysis of methyl acetate in dif-

Table 1
Effect of solvent on hydrogenolysis of methyl acetate

Solvent [a]	Conversion [b] (%)	Rate [b] (mmol/(h g-cat.))
n-hexane	44.7	5.7
cyclohexane	49.7	6.3
n-octane	65.7	8.5
methyl acetate [c]	18.6	18.2

[a] Solvent/methyl acetate = 70 ml/10 ml.
[b] Conversion and average rate in 10 h; $T = 240°C$, $P = 110$ bar, Cu–B_2O_3(6.4%)/SiO_2 = 1 g.
[c] Methyl acetate = 80 ml.

Table 2
Rates of Cu–B_2O_3(x%) / SiO_2 catalysts for hydrogenolysis of methyl acetate

B_2O_3 (x%)	Cu surface[a] area (m^2/g-cat.)	Dispersion[a] (%)	Rate[b]	
			(mmol/(h g-cat.))	(mmol/(h g-Cu))
0	11.0	10.8	4.7	31.5
1.6	15.9	15.7	6.1	40.0
3.2	39.3	38.7	10.6	70.8
4.8	32.2	31.8	15.3	101.9
6.4	23.2	22.9	17.1	114.4
8.0			13.5	90.2
10			10.8	72.1
Cu–Cr[c]	27.6		3.6	15.5

[a] Data from ref. [14] for similar catalysts.

[b] Average rate in 10 h ; $T = 240°C$, $P = 110$ bar, MeOAc = 80 ml; Cu–B_2O_3/SiO_2 = 1 g, Cu–Cr = 0.68 g.

[c] Copper chromite, Engelhard Cu-1234E.

ferent solvents was also examined, as illustrated in table 1. The rate of hydrogenoloysis without solvent is 2–3 times as large as the rate in a solvent of n-hexane, of cyclohexane or of n-octane. Therefore the following results and discussion are based on the hydrogenolysis of methyl acetate without solvent.

Similar to how the Cu–B_2O_3/SiO_2 catalysts behaved during the hydrogenolysis of methyl formate [14], the activity during hydrogenolysis of methyl acetate was enhanced as the amount of B_2O_3 doped was increased and reached a maximum at 6.4 wt% (table 2). Cu–B_2O_3/SiO_2 is seven times as active per gram Cu as the commercial copper chromite. Our previous studies had revealed that B_2O_3 not only acted as a textural promoter facilitating the dispersion of copper on a catalyst, but also as a structural promoter inducing a partially oxidized state in the copper [14]. This partially oxidized state of copper may promote the dissociative adsorption of hydrogen or methyl acetate [7], and facilitate the hydrogenolysis reaction.

In order to obtain kinetic information, the initial rates were evaluated at conversions around 10%. The rates increased with increasing temperature and no obvious byproduct except ethyl acetate formed below 250°C. The activation energy of 86.6 kJ/mol, estimated from an Arrhenius diagram in the range of 220–250°C (figure 3) was less than that of a Cu/SiO_2 catalyst [8] by 10 kJ/mol. The initial rates increased with pressures from 110 to 150 bar with the H_2 partial pressure having an order of 1.2, as indicated in figure 4.

To explore the availability of Cu–B_2O_3/SiO_2 for other methyl esters, hydrogenolysis of methyl propionate, of methyl butyrate and of methyl n-hexanoate was also performed at 240°C, 110 bar and compared with

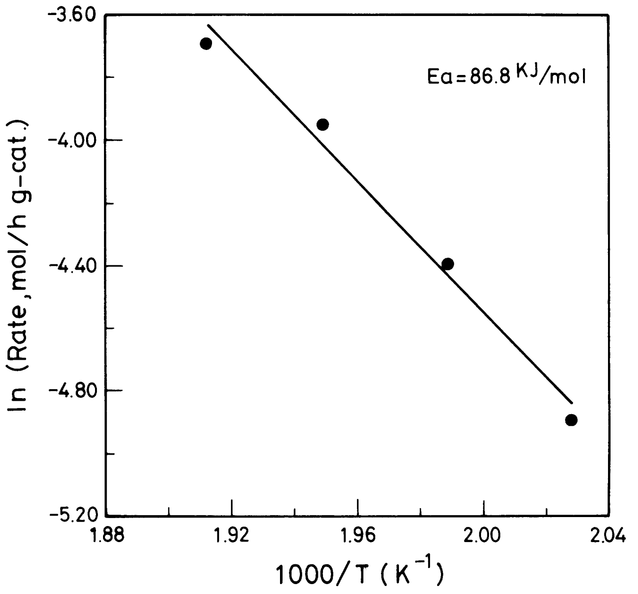

Figure 3. Arrhenius plot for hydrogenolysis of methyl acetate (240°C, methyl acetate = 80 ml, Cu–B_2O_3(6.4%)/SiO_2 = 1 g).

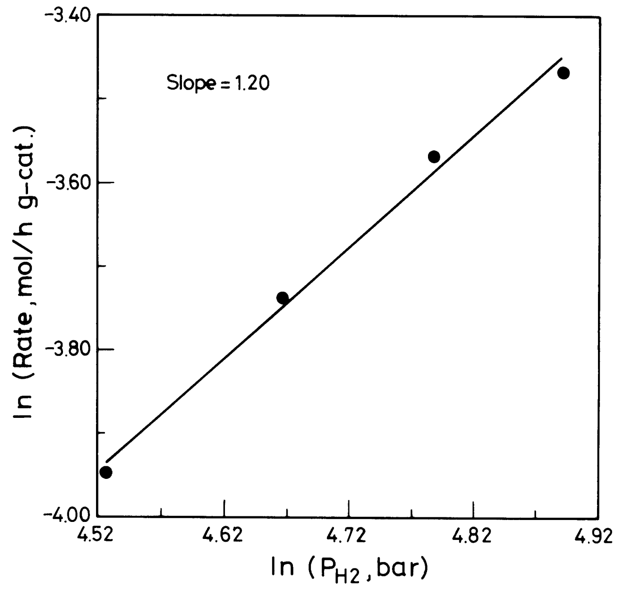

Figure 4. Effect of H_2 partial pressure on hydrogenolysis of methyl acetate (240°C, methyl acetate = 80 ml, Cu–B_2O_3(6.4%)/SiO_2 = 1 g).

Table 3
Hydrogenolysis of higher fatty acid methyl esters over Cu–B_2O_3/SiO_2 and coppper chromite

Ester [b]	Rate [a] Cu–B_2O_3(6.4%)/SiO_2		Rate [a] Cu–Cr	
	(mmol/(h g-cat.))	(mmol/(h g-Cu))	(mmol/(h g-cat.))	(mmol/(h g-Cu))
MeOAc	18.6	123.7	3.6	16.1
MeOPr	15.9	105.7	3.4	15.6
MeOBu	17.6	117.4	3.5	15.9

[a] Average rate in 10 h; $T = 240°C$, $P = 110$ bar, ester = 80 ml; Cu–B_2O_3/SiO_2 = 1 g, Cu–Cr = 0.68 g.

[b] MeOAc: methyl acetate, MeOPr: methyl propionate, MeOBu: methyl butyrate.

copper chromite. The quantitative results of methyl acetate, methyl propionate and methyl butyrate in table 3, and the approximate result of methyl hexanoate indicate that the rates were close for methyl esters with different carbon numbers and approximately seven times as active per gram Cu as the commercial copper chromite (Engelhard Cu-1234E). Methyl acetate proved itself an appropriate model compound for the hydrogenolysis of fatty acid methyl esters. Clearly, Cu–B_2O_3/SiO_2 is an effective catalyst for low-pressure fatty alcohol synthetic processes.

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