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# Hydrogenation of dimethyl succinate over monolithic catalysts

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## Abstract

Hydrogenation of dimethyl succinate over monolithic copper and nickel catalysts was studied using a semibatch reactor in which liquid was circulated, while hydrogen was continuously passed through the mixture. Flow rates of both phases were adjusted, so the system operated in the Taylor flow regime. The process was investigated at 150–240°C and 3–7 MPa. A nickel catalyst was active, but was insufficiently selective. Higher loaded copper catalysts were active and selective with respect to γ-butyrolactone at relatively low conversions. Catalyst activity (initial rates) was similar to that for the liquid phase hydrogenation of maleic anhydride over conventional catalysts previously reported. The catalysts deactivated, but unlike the nickel catalyst, activity of copper catalyst was easily restored by high temperature treatment in hydrogen. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Hydrogenation; Monolithic catalysts; γ-Butyrolactone

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## 1. Introduction

Demand for 1,4-butanediol (BD), γ-butyrolactone (GBL) and tetrahydrofuran (THF) has grown in recent years. THF is used as a solvent and a monomer for the manufacture of polytetramethylene glycol. GBL is a starting material for *N*-methylpyrrolidone and 2-pyrrolidone that are used as solvents and raw materials for making pharmaceuticals. BD is a starting material for polyurethanes, poly(butylene terephthalate), and for GBL and THF. BD can be manufactured by condensing acetylene and formaldehyde to give butynediol followed by hydrogenation [1]. Problems associated with these processes led to the development of alternative routes. In fact BD, GBL, and THF could be manufactured by hydrogenation of maleic anhydride [2,3], dialkyl maleates [2,4,5], and dialkyl succinates [5,6]. Gas and gas–liquid phase processes using conventional catalysts have been proposed. Monolithic catalysts offer processing advantages, such as low pressure drop, short diffusion paths, and easy reactor scale-up [7], and in this paper, results of studies on the hydrogenation of dimethyl succinate (DMS) over selected monolithic nickel and copper catalysts are reported.

## 2. Experimental

### 2.1. Catalysts

Monolithic cordierite-based copper catalysts (Johnson Matthey) and nickel catalysts (Engelhard) had a cell density of 400 cpsi, and were prepared by washcoating techniques. The volumetric fraction of the catalyst layer $\varepsilon_{cat}$ was ca. 5.3%, and the density of the washcoat layer was about 1500 g/l. Further details are given in Table 1.

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Table 1
Characteristics of the monolithic catalysts tested

| | Catalyst code | | |
|---|---|---|---|
| | C116-10 | MVTAC-004 | MVTAC-005 |
| *Support* | | | |
| Type | 400 cpsi | 400 cpsi | 400 cpsi |
| Composition | Cordierite | Cordierite | Cordierite |
| Pore volume ($cm^3/g$) | 0.18–0.24 | 0.19–0.24 | 0.21–0.30 |
| Geometric surface area ($m^2/l$) | 2.64 | 2.64 | 2.64 |
| Voidage (open frontal area) (%) | 75 | 75 | 75 |
| *Preparation* | | | |
| Metal | Nickel | Copper | Copper |
| Washcoat thickness (μm) | ±15 | ±25 | ±25 |
| Metal loading (g/l) | 5.28 | 22 | 10 |
| Type | Calcined unreduced | Calcined unreduced | Calcined unreduced |
| *Analyses* | | | |
| Total surface area, BET[a] ($m^2/g$) | – | ±14 | – |

[a] Including the cordierite monolith.

### 2.2. Apparatus and procedures

A Naki-Twin Tubular Reactor (OL-10503) with ID 21.5 mm tubes was used. Catalysts were held in place in the usual way. Nine channels referred further as "reactive channels" were open to flow down to the mixture of liquid and gas. The remaining channels were open to gas only. The nickel catalyst length was 14.3 cm, and the copper catalyst 15.5 cm. The catalysts were reduced at 215–220°C in $H_2/N_2$ (4–7% $H_2$) for 16–20 h, followed by treatment in pure $H_2$ for 4–5 h. Temperature and pressure were set with a $H_2$ flow of 20 l/h, and the DMS reaction mixture was circulated at 300 ml/h. The initial liquid volume ranged from 100 to 400 ml. The superficial liquid velocity is ca. $1\,cm\,s^{-1}$, and the superficial gas velocity is of the same order of magnitude. However, the true gas velocity in "reactive channels" can be different from the superficial velocity because of backmixing of gas in channels open only to gas. Consequently, the hydrodynamics of gas in these channels is not known in detail. Andersson et al. [8] reported the velocity of typical liquids in very low pressure drop straight channels due to gravity to be $0.2\text{–}0.5\,m\,s^{-1}$. So this is the expected range of the gas flow through the "reactive channels", and under such conditions the flow of both phases falls in the Taylor flow regime. Runs were made at 150–250°C and 3–7 MPa (Table 2).

Table 2
Process conditions and kinetic constants

| Catalyst | Run No. | Temperature (°C) | Pressure (MPa) | Time-on-stream at the start of the run (h) | Kinetic constant ($10^6\,m^3\,kg_{cat}^{-1}\,s^{-1}$) |
|---|---|---|---|---|---|
| C116-10 | 1 | 150 | 3 | 0 | $4.54 \pm 0.16$ |
| | 2 | 200 | 3 | 22 | $2.40 \pm 0.35$ |
| | 3 | 250 | 3 | 50 | $3.32 \pm 0.30$ |
| MVTAC-004 | 4 | 220 | 7 | 0 | $2.00 \pm 0.22$ |
| | 5 | 240 | 7 | 25 | $2.38 \pm 0.25$ |
| MVTAC-005 | 6 | 220 | 7 | 0 | $8.89 \pm 1.44$ |
| | 7 | 220 | 7 | 8 | $1.11 \pm 0.39$ |
| | 8 | 220 | 7 | 46 | $6.80 \pm 0.86$ |
| | 9 | 220 | 7 | 69 | $8.32 \pm 1.88$ |

Reaction mixtures were analysed by chromatography: an HP 5710A equipped with FID and a stainless steel column (2 mm × 2 m) with OV17-FSAP (60:40) on WHP (120 mesh), and a Gide 18.3 with FID and a stainless steel column (2 mm × 2 m) with Carbowax 20M on Chemosorb W (60–80 mesh).

## 3. Results

Several products were identified, and based on previous work a reaction scheme was proposed involving consecutive and parallel reactions (Fig. 1). BD formed via GBL was hydrogenated to THF and possibly *n*-butanol. GBL was also hydrogenated to *n*-butanol that underwent transesterification with DMS. Transesterification of DMS with ethanol also took place and the product most likely hydrolysed to monomethyl succinate (MS). Methanol probably reacted with water as suggested by Turek et al. [6] in the gas phase hydrogenation of DMS. Ethanol was formed in an unidentified reaction. Conversions of DMS as a function of time over both catalyst types are shown in Figs. 2 and 3. Absolute hydrogenation rates were low because of the small amount of catalyst, but kinetic analysis showed high activity. Rates of DMS hydrogenation over nickel catalyst decreased with time, and after 75 h activity was nearly zero, in spite of increasing the pressure to 7 MPa. The product was mainly dibutyl succinate (DBS) formed in 84–100% selectivity. Rates of hydrogenation of GBL and BD to *n*-butanol were higher than for formation of GBL and BD. The transesterification rate of DMS with *n*-butanol was high enough to produce DBS, and methanol that was formed was probably consumed in reaction with water as mentioned above. Attempts to regenerate the nickel catalyst failed. Conversions for the copper catalyst MVTAC-004 at 7 MPa reached 22–26 mol% for more than 20 h, and similar conversions were obtained with the nickel catalyst at lower pressure (3 MPa). Activity of a different copper catalyst (MVTAC-005) was higher, but this decreased during use. However, heating at 500°C in $H_2$ for 2 h restored full activity. Copper catalysts were active for formation of GBL (91–100%). BD was formed only with MVTAC-004; selectivity was low (3–9%). No trace of *n*-butanol or THF was found.

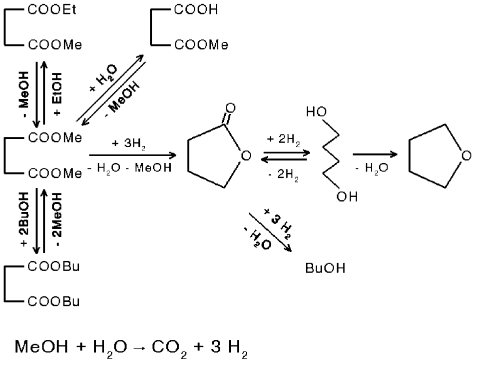

Fig. 1. Reaction scheme.

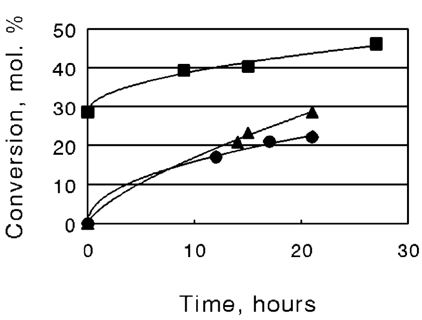

Fig. 2. Conversion vs time for the nickel catalyst (3 MPa): (▲) run 1 (150°C, 0 h on stream); (●) run 2 (200°C, 22 h on stream); (■) run 3 (250°C, 50 h on stream).

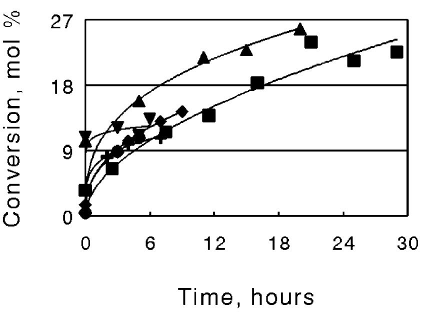

Fig. 3. Conversion vs time for the copper catalyst (7 MPa): (▲) run 4 (MVTAC-004, 220°C, 0 h on stream); (■) run 5 (MVTAC-004, 240°C, 25 h on stream); (●) run 6 (MVTAC-005, 220°C, 0 h on stream); (▼) run 7 (MVTAC-005, 220°C, 8 h on stream); (◆) run 8 (MVTAC-005, 220°C, 46 h on stream); (+) run 9 (MVTAC-005, 220°C, 69 h on stream).

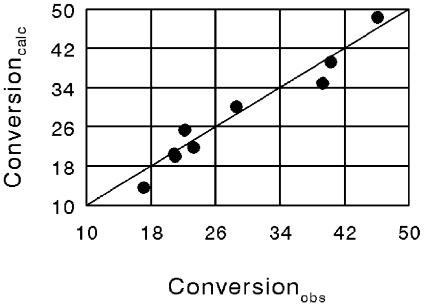

Fig. 4. Parity diagram for the nickel catalysts.

## 4. Kinetic analysis

Kinetic analysis of experimental data was performed to compare monolithic catalysts with particular catalysts. Plug-flow through the catalyst and ideal mixing of liquids in the recirculation vessel were assumed. Results were analysed assuming the reaction was first order in DMS. An apparent rate constant *k*, that was a function of $H_2$ partial pressure, was estimated by a Marquardt–Levenberg procedure [9]. Graphs of conversion$_{calc}$ against conversion$_{obs}$ for DMS are shown in Figs. 4 and 5, and derived kinetic constants are in Table 2. Agreement between calculated and observed conversions were reasonable, and so this model was considered suitable for comparing different monolithic catalysts and particulate catalysts. The apparent rate constant (*k*) for the fresh nickel catalyst at 3 MPa ($4.54\times10^{-6}\,m^3\,kg_{cat}^{-1}\,s^{-1}$) was ca. 50% lower than that for the copper catalyst (MVTAC-005) at 7 MPa ($8.89\times10^{-6}\,m^3\,kg_{cat}^{-1}\,s^{-1}$). The solubility of $H_2$ increases by 2.3 on going from 3 to 7 MPa. Herrmann and Emig [2,3] found that the order in $H_2$ was ca. 0.33, so the expected rate constant for the nickel catalyst at 7 MPa ($5.97\times10^{-6}\,m^3\,kg_{cat}^{-1}\,s^{-1}$) would be still lower than that for this copper catalyst at the same pressure and at the higher temperature. Thus, the activities of both nickel and copper catalyst are similar, but their selectivities are very different. Rate constants for both catalyst types decreased during use indicating catalyst deactivation, but the initial activity of the copper catalyst returned after treatment in $H_2$.

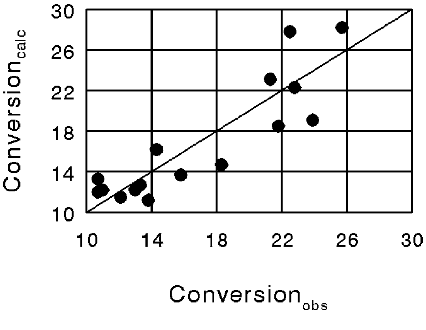

Fig. 5. Parity diagram for the copper catalysts.

The activity of the copper monolithic catalysts was compared with data for conventional ones reported previously. Initial rates for liquid phase hydrogenation of maleic anhydride in dioxane at a concentration of 560 mol/m$^3$ at 240°C and 7.5 MPa were reported to be 0.009–0.0014 mol $kg_{cat}\,s^{-1}$ [2,3]. Based upon the kinetic constants and evaluation of liquid hold-up (0.04), we estimated the initial rate of hydrogenation of DMS (7650 mol/m$^3$) at 220°C and 7 MPa to be 0.0027 mol $kg_{cat}^{-1}\,s^{-1}$. If the DMS concentration was reduced to that for maleic anhydride, the rate would be slightly below the rate for hydrogenation of maleic anhydride that is hydrogenated more easily than esters. So monolithic catalysts can be considered to have advantages in these systems that have the additional benefit that no solvent is needed because the reactants are liquid. However, the volumetric fraction of the catalyst layer ($\varepsilon_{cat}$) for trickle bed reactors is ca. 0.5, that for slurry reactors is at most 0.2, and for the monolithic catalysts with a thin washcoat it is only 0.053. So the volumetric hydrogenation rates for monolithic catalysts is an order of magnitude lower than conventional reactors. This situation can be improved by having thicker washcoat layers. With a washcoat thickness of 50 or 100 μm (Herrmann and Emig [2,3] used catalyst particles ca. 150 μm in size), $\varepsilon_{cat}$ would be increased to 0.17 and 0.32, respectively, and would make the catalyst load comparable to conventional catalysts. This would make a monolithic catalyst process industrially attractive for BD or THF production, that was possible with conventional copper catalysts for GBL, BD and THF production via gas phase hydrogenation of DMS [6] and diethyl maleate [4].

## 5. Conclusions

The monolithic catalysts studied were active in hydrogenation of DMS. A nickel catalyst was insufficiently selective for BD, GBL and THF. Here *n*-butanol was the main product, and this underwent transesterification forming DBS. Copper catalysts are highly selective for GBL formation, and to a smaller extent, for BD, but they are insufficiently selective with respect to THF. The nickel and copper catalysts deactivated, but copper catalyst was fully regenerated by treatment with hydrogen.

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