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METHANOL FORMATION ON Cu/ZnO CATALYSTS, MEASURED BY HIGH PRESSURE DSC.

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The activity of copper containing catalysts for the formation of methanol from CO and H_2 is investigated with High Pressure DSC. The activity is measured at 40 atm. and 230 °C. The DSC signal has been calibrated with melting experiments with tin under reaction conditions. Comparison with flow reactor measurements shows a good relation with the DSC experiments.

At our laboratory catalysts are developed for the low pressure synthesis of methanol and fuel-methanol, consisting of a mixture of methanol and higher alcohols [1].

The concerning reaction is

$$CO + 2H_2 \rightleftharpoons CH_3OH \tag{1}$$

This reaction is exothermic. At 500 K the value of $\Delta H = -97.7$ kJ/mol CO [2, 3]. At normal pressure the equilibrium lies at the left side, giving nearly no conversion into methanol. For this reason the reaction has to be performed at high pressures and at low temperatures. A formula for the rate equation is for instance [3]:

$$r = k P_{CO}^{0.5}\ P_{H_2}/P_{MeOH}{}^{0.66}\quad (1 - P_{MeOH}/P_{CO}P_{H_2}^2\, K_{eq}) \tag{2}$$

with $K_{eq} = (P_{MeOH}/P_{CO} \cdot P_{H_2}^2)$ in equilibrium conditions.

This formula shows the influence of pressure and equilibrium condition. Further the reaction rate is sharply increased when a little part of the CO is replaced by CO_2. With alumina containing catalysts at high temperatures also dimethylether is formed, according to the reaction:

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \tag{3}$$

Normally the activity of catalysts is investigated by flow reactor measurements, using gaschromatography for analysis of the degree of conversion.

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This investigation concerns the use of high pressure DSC. In that case the degree of conversion is determined from the reaction heat. For testing, catalysts were investigated, which were also analysed by reactor measurements.

In preceding publications [4, 5] DSC measurements of the methane formation over nickel catalysts were described. In that case the equilibrium is situated at the methane side. So a quantitative calibration of the DSC plot becomes possible by measurement of the DSC signal at high temperature where the reaction reaches a complete conversion.

In the case of methanol synthesis a complete conversion into methanol cannot be reached, so calibration from the DSC plot itself is not possible. In this case calibration can be performed by melting experiments with tin under reaction conditions, using a pan with catalyst powder and with a piece of tin on top of it.

Experimental

The catalysts were prepared by coprecipitation of the hydroxides of copper, zinc, aluminium and lanthanum [1]. The precipitate is dryed and calcined at 300 to 350°.

A Dupont High Pressure DSC cell is used. Because the cooling speed of the original cell was very slow, a water cooled jacket was constructed, that fits very closely round the pressure cylinder (Fig. 1). With this device the cell is cooled from 300 to 100° in less than 10 minutes.

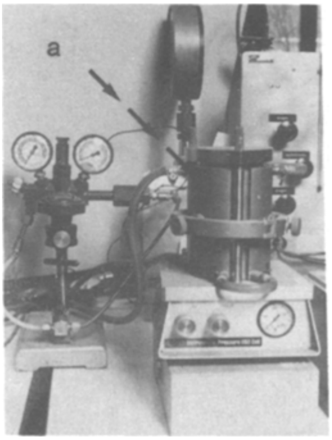

Fig. 1 High pressure DSC cell; *a* is the cooling jacket

The reaction gases were premixed in a pressure cylinder, fitted with a high pressure regulator for control of the pressure in the DSC cell. The outlet of the DSC cell was connected with a pressure regulator, where the pressure was reduced to a few atmospheres, and a mass flow controller for control of the gas flow rate.

A DSC experiment consisted of several steps (Fig. 2):

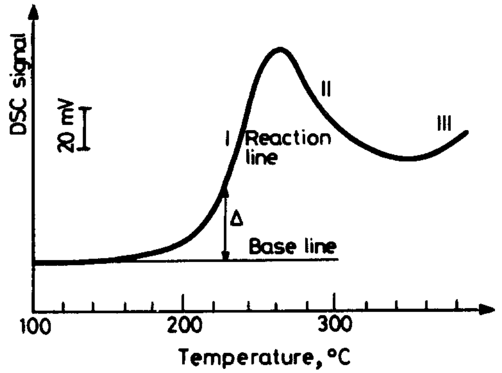

Fig. 2 DSC plot of the methanol synthesis. 31.19 mg cat.h, reaction 2 deg min^{-1}, 0.70% CO_2, 9.82% CO, 89.49% H_2; pressure: 40 bar, flowrate: 25 min min^{-1}.

- Reduction of about 30 mg catalyst in a gas mixture of 2% H_2 in N_2 with a flowrate of 1 l hr^{-1} at a pressure of 2 atm. The sample was heated with 1 deg min^{-1} from 20 to 240° and kept at 240° during 18 hours.

  The reduction procedure is very important for the ultimate catalytic activity.
- A baseline is measured in the reduction gasmixture, from 100 to 240° with deg min^{-1}.
- The reaction line is measured from 100 to 240° (or to higher temperatures) with 2 deg min^{-1}) at a pressure of 40 atm. The composition of the reaction gas is 0.7% CO_2, 9.82% CO and 89.48% H_2. The flowrate is 25 nml min^{-1}, so the CO flow corresponds with $1.83 \cdot 10^{-6}$ mole CO s^{-1}.

The tubular reactor measurements were different from the DSC experiments: the heating rate during the reduction was 0.5 deg min^{-1} and the activity was determined at 75 atm and 240° after 24 hours of isothermal reaction. For the reaction a gasmixture was used with composition: 82.2% H_2, 10.2% CH_4, 4% CO and 3.6% CO_2.

Results and conclusions

In Fig. 2 a DSC plot is given. Three regions can be distinguished: region I shows an increasing reaction rate. An arrhenius plot of the difference signal Δ shows a straight line until about 230°. At higher temperatures the reaction rate is influenced by the vicinity of equilibrium conditions, resulting in a decrease in region II. Region III shows again an increasing DSC signal, caused by formation of dimethylether.

From the DSC signal Δ (mV) the catalytic activity r_{DSC} (dimension: g methanol/g catalyst.) can be calculated with help of the tin calibration, according to the formula:

$$r_{\mathrm{DSC}} = \Delta \cdot (1000/g) \cdot (\mathrm{C.\ F.}) \cdot M/\Delta H \cdot 3600 \qquad (4)$$

C. F. is the calibration factor, determined with tin (m.p. 232°), and amounts to 0.4434 mW/mV; g is the catalyst weight in mg; $M = 32$, the molar weight of methanol, and ΔH is the heat of reaction = 97.7 kJ/mol methanol. The maximum rate at 270° ($\Delta = 138.0$ mV) corresponds to a CO conversion rate of $6.26 \cdot 10^{-7}$ mole s^{-1}, so 34% of the CO flow is converted into methanol. This can be compared to the equilibrium conversion of 48% of the CO flow at this temperature [2].

Apparently the gases in the DSC cell are not ideally mixed: at the maximum the equilibrium conditions are attained in the vicinity of the catalyst sample, but not in the rest of the cell.

Table 1 gives the catalyst composition and the rates, measured by DSC and tubular reactor. Further the activation energy for the low temperature part of region I (below 230°) is given.

Table 1 Comparison of catalysts

Cat.	Composition, mol %	E_a,	Activity, g methanol/g cat.h	
	Cu – Zn – Al – La	kJ/mol	DSC (230 °C)	Reactor (240 °C)
a	25 – 51 – 24 – 0	103	0.38	0.60
b	28 – 55 – 17 – 0	95	0.43	0.68
c	28 – 55 – 17 – 0	124	0.44	0.68
d	67 – 33 – 0 – 0	120	0.53	0.90
e	28 – 55 – 17 – 0	113	0.63	1.10
f	50 – 25 – 25 – 0	111	0.40	1.20
g	45 – 45 – 9 – 1	116	0.74	1.40
h	56 – 26 – 17 – 1	110	0.93	1.80

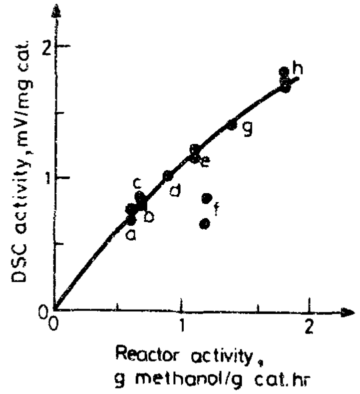

Fig. 3 Comparison of H. P. DSC and tubular reactor measurements. The DSC activity is determined at 40 atm. and 230 °C, the reactor activity at 70 atm. and 240 °C.

In Fig. 3 activities, measured by DSC and flow reactor are plotted against each other. The following can be remarked:

- There is a good relation between both kinds of measurements. At high activities the DSC activity is relatively low compared to the reactor activity. This is caused by the fact that the products in the DSC cell remain in the vicinity of the catalyst sample during a relatively long time, compared to the flow reactor experiments, resulting into lower reaction rates because of the approach of equilibrium conditions near the sample.
- The activation energies are in the range from 95–124 kJ/mol. This value corresponds to a complicated overall process.
- Catalyst f behaves differently from the other catalysts. There is also a big difference between both DSC experiments. Perhaps little variations in reduction of reaction conditions are responsible for this behaviour.
- Determination of the reaction rate from DSC experiments is poblematic, when not only methanol but also other products like higher alcohols or dimethylether are formed.
- Comparison with DSC measurements of the formation of methane over nickel catalysts leads to the conclusion that in this last case less problems arise with the determination of the catalytic activity from DSC experiments [4, 5].

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Zusammenfassung – Die Aktivität kupferhaltiger Katalysatoren bei der Bildung von Methanol aus CO und H_2 wurde mittels Hochdruck-DSC untersucht. Sie wurde bei 40 bar und 230 °C gemessen.

Die Eichung des DSC-Signals erfolgt mittels Schmelzen von Zinn unter Reaktionsbedingungen. Ein Vergleich mit Messungen im Strömungsreaktor zeigte eine gute Korrelation mit den DSC-Ergebnissen.

РЕЗЮМЕ — Методом ДСК высокого давления изучена активность медь-содержащих катализаторов, используемых для получения метанола из окиси углерода и водорода. Активность катализаторов была измерена при давлении 40 атм и температуре 230°. Градуировка ДСК сигналов была проведена с оловом в тех же самых условиях реакции. Сопоставление полученных данных с измерениями в проточном реакторе показало хорошее совпадение.