Journal of Thermal Analysis, Vol. 37 (1991) 1269-1279

Dedicated to Professor Dr. H. J. Seifert on the occasion of his 60th birthday

DECOMPOSITION OF METHANOL VAPOUR OVER SOLID CATALYST, MEASURED BY DSC

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(Received October 20, 1990)

The activity of copper containing catalysts for the formation of methanol from CO and H_2 is investigated by DSC measurement of the methanol decomposition. Calibration of the DSC signal can be performed by melting experiments with tin under reaction conditions. Comparison of catalysts is well possible by measurement of the standard activity at 240°, the apparent activation energy for the methanol decomposition reaction and the aging of the catalyst samples.

At our laboratory catalysts are developed for the low pressure synthesis of methanol and fuel methanol, consisting of a mixture of methanol and higher (C_2–C_6) alcohols [1]. One of the concerning reactions is:

$$CO + 2H_2 \rightleftarrows CH_3OH$$

The formation of methanol is exothermic, with an enthalpy change ΔH of [2,3]:

$$\Delta H = -(77.34 + 0.0429\ T/K) \quad \text{kJ/mol} \quad \text{methanol}$$

At normal pressure the equilibrium lies at the left side, giving little conversion into methanol. For this reason the reaction has to be performed at high pressures and at low temperatures. In a preceding publication a number of methanol catalysts is studied with high pressure DSC [4]. For a fast

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screening of catalysts however, DSC experiments at atmospheric pressure appear to be more convenient.

Since the synthesis of methanol, as discussed above, cannot be studied at atmospheric pressure, the activity of catalysts, nevertheless, can also be studied using the reverse reaction. Thus, the principle of microreversibility is applied, after which a catalyst, when active for the forward reaction, also is active for the reverse reaction under proper conditions. The decomposition of methanol vapour into H_2 and CO is endothermic, while the equilibrium at atmospheric pressure lies at the (H_2+CO) side (in the temperature region 200-400°).

For a quantitative evaluation of the DSC signal, calibration is performed by melting experiments of tin under reaction conditions, using a pan with a layer of catalyst powder and with a piece of tin on top of it.

Experimental

The catalysts were prepared by the coprecipitation method, as described before [1]. The precipitate was dried and calcined up to 450°, giving a catalyst precursor with an atomic composition $Cu_{1.26}Co_{0.84}Zn_{0.9}Al_{1.2}O_x$. For the testing of catalyst performance a Dupont 910 DSC apparatus was used.

A certain weight (1-17 mg) of catalyst powder was placed in an open aluminium pan (diameter 6 mm) on the sample side sensor.

As reference an empty pan was used.

A DSC experiment consists of several steps (see Fig. 1):

– First the catalyst is carefully reduced by heating at a constant rate (10 or 20 deg/min) up to 400° in a gas mixture containing 90% N_2 and 10% H_2,

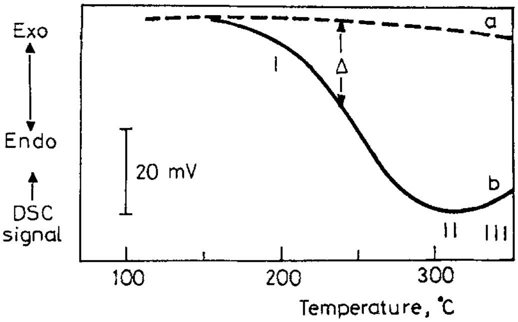

Fig. 1 DSC plot of methanol decomposition over 4.41 mg of catalyst. Heating rate 20 deg/min. a = baseline; b = reaction line
I = low temperature region, with increasing rate; II = region with maximum rate; III = decreasing rate

at a flow rate of 1 l/h (STP). In this step copper and cobalt oxides are reduced, but ZnO and Al_2O_3 remain unreduced.

– Secondly a baseline was measured by heating from 100-350° in the same gas mixture (Fig. 1, line a).

– Then a reaction line was measured with the same heating rate in a methanol containing gas mixture (Fig. 1, line b). During the heating an endothermic heat effect becomes visible, corresponding to the decomposition of methanol. The difference Δ between baseline and reaction line is a measure for the rate of the reaction. This reactant gas mixture is made by bubbling a nitrogen flow through an evaporator, filled with liquid methanol, at 0°. At this temperature methanol has an equilibrium pressure of 29.39 mm. Hereafter hydrogen was added, giving a gas mixture consisting of 9.97% H_2, 3.48% CH_3OH and 86.55% N_2 at a flowrate of 1.053 l/h (STP). So the total methanol flow through the DSC cell (r_{100}) correspond with $4.55\cdot10^{-7}$ mol/s. The hydrogen in the reactant gas is necessary for keeping the catalyst in the reduced form during the experiments.
Testing of the catalyst stability could be performed by measuring the reaction line several times in succession.

– At last the DSC cell was cooled down to room temperature and opened. Then a flat piece of tin (5-20 mg) was placed on the top of the catalyst sample, after which the melting of tin was studied in the reduction or reaction gas mixture.
Since reoxidation of the catalyst occurred during the contact with air, the sample had to be reduced first (up to 280°) before the melting peak of tin could be measured quantitatively. The values, used for tin, are: melting temperature 232° and heat of metling 60.58 J/g.

Results

The DSC experiment of Fig. 1 shows that the difference Δ between the baseline and the reaction line increases with increasing temperature. Several regions are visible:

I The kinetic region, where Δ increases according to an Arrhenius relation.

II The rate of increase diminishes until a maximum value of Δ is reached (II). Here the catalyst activity is so high, that all the methanol vapour, which reaches the catalyst, is decomposed. Now the diffusion of methanol from the bulk gas to the catalyst surface is rate determining.

III In most cases a region III is visible at high temperature, where Δ decreases with temperature. An important reason is the occurrence of the strongly exothermic reaction of CO and H_2 into methane [5,6], preceeding at high temperature (ΔH = about 215 kJ/mol methane).
Therefore the value of Δ decreases, being the sum of both effects, a nearly constant endothermic effect and an, at increasing temperature, growing exothermic effect.
Another reason, in particular for thick catalyst layers, can be the fact, that at high temperatures the catalyst becomes so active, that only the top layer of the catalyst sample reacts with the methanol vapour. This can lead to a decrease of the fraction of heat, going to the DSC sensor, and an increase of the fraction of the heat effect, going to the gas phase.
Besides the layer thickness, also the thermal conductivity of the catalyst sample plays an important role for this effect.

Discussion of the results

Results of the DSC experiments are given in the Figs 2-4 and in Tables 1 and 2. Table 1 deals with the results of the calibration with the melting of tin on top of the catalyst samples. The calibration factor *C.F.* is determined by calculation of the quotient of the real heat of melting of the piece of tin (mJ) and the DSC surface area of the melting peak (mV·seconds), resulting in a *C.F.* value with the dimensions:

$$\mathrm{mJ/(s \cdot mV) = mW/mV}$$

– For control in experiment 'a' one *C.F.* value is determined in a different way, namely by measurement of the methanation reaction over a nickel catalyst (see ref. [7]).
In this publication the methane formation rate has been measured both by gas chromatography and by DSC.
At 395° the maximum methanation rate = $\xi_{395} \cdot r_{100}$
$r_{100} = 5.187 \cdot 10^{-7}$ mol/s
$\xi_{395} = 65.3\%$ (for a pan with diameter 6 mm)
So the total heat of reaction per second at 395° is:

$$\xi_{395} \cdot r_{100} \cdot \Delta H$$

Since ΔH = 217 kJ/mol, this results in a heat flow of 73.50 mW at this temperature. In a DSC experiment the signal Δ is measured. It amounts to be 191.0 mV, so the calibration factor $C.F.^*$ = 73.50/191.0 = 0.385 mW/mV. According to this publication [7], the calibration factor is nearly constant between 200 and 400° , so comparison with the tin melting experiment at 232° is allowed. As can be seen in experiment "a" there is a good agreement between both $C.F.$ values (0.388 respectively 0.385 mW/mV).

Table 1 Calibration of the DSC signal by melting of tin. The value of $C.F.^*$ is determined with the methanation reaction [7]

Experiment	Catalyst$^{1)}$	Weight, mg	Gasphase % H_2	% N_2	$C.F.$, mW/mV	$C.F.^*$, mW/mV
a	Ni_3AlO_x	3.10	98	2	0.388	0.385
b	Ni_3AlO_x	3.10	10	90	0.251	
c	–	0.00	10	90	0.244	
d	A	1.42	10	90	0.280	
e	A	4.41	10	90	0.284	
f	A	5.99	10	90	0.290	
g	A	16.85	10	90	0.338	

$^{1)}$$Ni_3AlO_x$: methanation catalyst

A : methanol and higher alcohol catalyst $Cu_{1.26}Co_{0,84}Zn_{0.9}Al_{1.2}O_x$

–: empty cup

– Further it can be concluded from Table 1 that the calibration factor depends on the composition of the gas phase (experiment a and b) and on the amount of catalyst (b and c, respectively c-g).

These observations can be explained by the fact that the calibration factor is a measure for the relative amount of the heat effect that is transported to the sensor and to the gas phase. Going from hydrogen to nitrogen the thermal conductivity of the gas phase decreases, and also the heat flow to the gas phase. Then the heat flow to the sensor increases, resulting in an increase of the DSC signal and a decrease of the $C.F.$ value. The same effect appears when the thermal conductivity of the solid catalyst increases (experiment e and b) or the layer thickness decreases (experiment g → c).

It can be concluded that the calibration must be performed with identical amounts of catalysts and in a gas phase with identical thermal conductivity as is the case in the catalytic reaction itself. Since the thermal conductivity

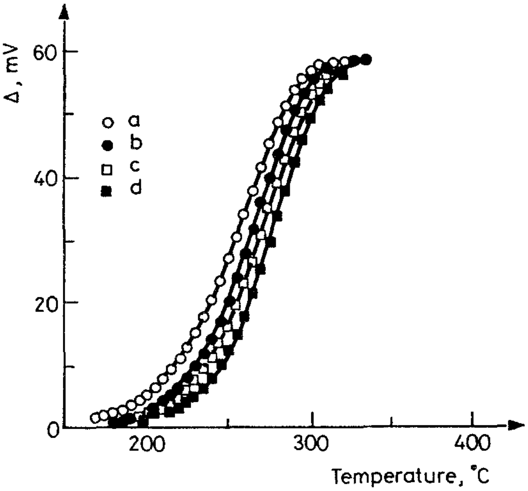

Fig. 2 Plot of Δ (mV) against temperature (°C) for four successive runs (a, b, c, d) with 1.42 mg of catalyst. Heating rate 20 deg/min

of CO and N_2 is the same, calibration can be performed both in a CO/H_2 or a N_2/H_2 mixture.

In Figs 2 and 3 DSC experiments are shown for a small amount of catalyst (1.42 mg) and for a large amount (16.85 mg). From these figures it can be seen that the reaction rate increases with temperature and decreases with successive runs.

Figure 4 shows the Arrhenius plot in a low temperature region for the successive runs with a small amount of catalyst. From this figure the apparent activation energy can be determined for the successive runs.

Table 2 gives a summary of the results for three different amounts of catalyst. For comparison the standard activty r_S is determined at 240°. This value can be derived from the value of Δ at 240° and the *C.F.* value of the concerning amount of catalyst (see Table 1).

$$r_s = \Delta \cdot C.F. \cdot \frac{1000}{\text{weight/mg}} \cdot 3600 \cdot \frac{1}{|\Delta H|} \cdot M \qquad \frac{\text{g methanol}}{\text{g cat.hr}}$$

In this formula M is the molar weight of methanol, being 32 g/mol, and $|\Delta H|$ is the absolute value of the enthalpy change per mole methanol at 240°.

$$|\Delta H| = (77.34 + 0.0429\ \text{T/K}) \cdot 10^6 = 99.35 \cdot 10^6 \quad \text{mJ/mol}$$

Comparison of the standard activities and E_A values delivers:

Small amounts of catalyst show a high initial activity and a fast decrease of activity during successive runs, compared to large amounts. An explanation can be found in the applied reduction procedure: for small amounts the water vapour, generated during the reduction, can easily diffuse away, giving a low water vapour pressure inside of the catalyst sample. For large amounts however, more water vapour is evolved in a thick catalyst layer, resulting in a higher water vapour pressure inside of the catalyst, and therefore the growth of larger metal particles. Since the catalytic activity will be proportional to the metal area inside of the catalyst, the initial activity of small amounts of catalyst will be higher than when large amounts are used. Of course, a different amount of catalyst leads to different values of effectness factor, Thiele modulus and Turn Over Number [8].

Table 2 Decomposition of methanol. Results of DSC experiments at standard conditions with different weights of catalyst precursor. Heating rate 20 deg/min.
r_s = standard activity at 240°C (dimension: g methanol/g cat.hr),
ξ_{max} = maximum relative methanol conversion, %

Sample weight mg	Run number	Δ at 240°C mV	r_S	EA, kJ/mol	Tmax, °C	Δmax, mV	ξmax, %
1.42	1	19.8	4.52	70	330	58.0	34.6
1.42	2	14.2	3.24	90	330	58.0	34.6
1.42	3	11.1	2.54	92	–	–	–
1.42	4	8.0	1.83	103	–	–	–
4.41	1	27.0	2.02	69	300	59.0	36.1
16.85	1	37.7	0.88	51	280	58.0	42.6
	2	31.9	0.74	84	280	57.8	42.5
	3	31.9	0.74	84	280	57.8	42.5

During the reaction sintering of the metal particles occurs. Since small particles are more sinteractive than large particles, the decrease of activity will be higher for small amounts of catalyst. The increase of the activation energy during the successive runs of one sample similarly can be explained, since small particles will be more reactive than large particles, resulting in a lower initial activation energy. For the rest, other effects, such as different Cu/Co alloy formation during the reduction and carbonization of the catalyst during the reaction, will play a role as well. Therefore the proportion between activation energy and activity and the end values after aging

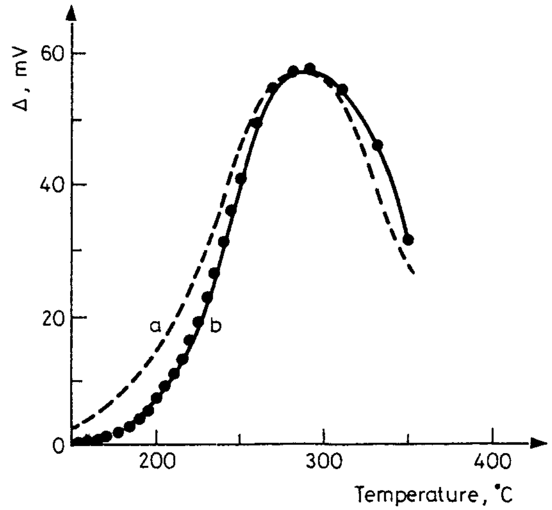

Fig. 3 Plot of Δ(mV) against temperature (°C) for two successive runs (a, b) with 16.85 mg of catalyst. Heating rate 20 deg/min. A third run (c) coincides completely with the second run (b)

will not be the same for different amounts of catalyst. The 16.85 mg sample reaches already a constant activity after the second run, but the 1.42 mg sample is still changing at the fourth run.

Probably different amounts of catalyst will behave more identically, when the reduction procedure should be changed: lower heating rates and higher flow rates of the reduction gas should give lower water vapour pressures inside the sample and more comparable results for different amounts. These results indicate that the best way for comparing different catalysts will be the use of the same low amount of catalyst sample, for instance 4 mg.

In Table 2 also the maximum conversion ξ_{max} of the methanol flow is given, together with the temperature T_{max}, where Δ reaches its maximum value Δ_{max}. The value of ξ_{max} is calculated according to the formula:

$$\xi_{max} = C.F. \cdot \Delta_{max} \cdot 100/|\Delta H|_{\text{max}} \cdot r_{100} \quad \%$$

$|\Delta H|_{\text{max}}$ is the absolute value of ΔH at T_{max} being $102 \cdot 10^6$ mJ/mol at 300°. r_{100} is the total methanol flow trough the DSC cell.

$$r_{100} = 4.55 \cdot 10^{-7} \quad \text{mol/s}$$

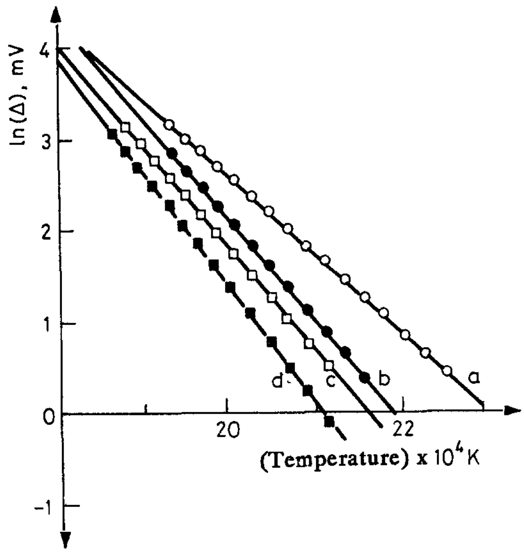

Fig. 4 Arrhenius plot for the low temperature region of four successive runs (a, b, c, d) with 1.42 mg of catalyst

As can be seen, the maximum conversion increases from 34.6% for 1.42 mg into 42.5% for 16.85 mg of sample, caused by the better contact with the bulk gas for thick catalyst layers.

The value of Δ_{max} is not only dependent on the diffusion of methanol to the catalyst surface, but also on the rate of methane formation at high temperatures (see Figs 1 and 3). Since this methanation rate strongly depends on the catalyst composition, it is not suitable to use the value of Δ_{max} as an internal calibration standard when comparing different catalysts. This is in contrast with the study of the methanation reaction over nickel catalysts [7].

When the methanol decomposition is compared with the methanation reaction, it appears that the value of ξ_{max} is different:

ξ_{max} = 65% for 3.10 mg Ni_3Al catalyst, compared to ξ_{max} = 36% for an equal amount of methanol catalyst. This can be explained by the difference in diffusion rates: the diffusion of CO in H_2 is much faster than the diffusion of methanol vapour in N_2.

Conclusions

– Since a catalyst accelerates both the formation and the decomposition of methanol in the same measure, methanol formation catalysts can be studied by investigation of the decomposition of methanol.

– Calibration can be performed by melting experiments of tin under reaction conditions.

– DSC experiments are well suitable for study of the effect of reduction conditions.

– Using the relatively simple and fast DSC experiments on the decomposition of methanol, a first selection of promising catalyst for MeOH synthesis and fuel methanol synthesis can be made. These catalysts can be further tested in more expensive reactor set-ups using GC for accurate rate analysis.

– For catalyst comparison only the low temperature part of the DSC curve should be used, since at high temperatures side reactions occur, e.g. the exothermic methanation reaction.

– Also the aging and pretreatment of catalysts can be studied with DSC.

– Fast screening of catalysts has to be performed with a standard small amount of catalyst and at standardized conditions concerning heating rate, gas flow and gas composition.

– Although determination of the qualitative activity of methanol catalyst is well possible by the DSC experiments, actual performance of the methanol synthesis catalysts can only be measured under real synthesis gas conditions. Since the conditions used for MeOH synthesis and for MeOH decomposition, as described in this paper, are quite different, the exact value of the catalyst activity cannot be found by the DSC method, as described in this article.

– Catalysts with a high decomposition activity, however, are also very active for MeOH synthesis, as found with reactor/gas analysis.

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Zusammenfassung — In DSC-Messungen an der Zersetzung von Methanol wurde die Aktivität von kupferhaltigen Katalysatoren für die Bildung von Methanol aus CO und H_2 untersucht. Das DSC-Signal kann mittels Zinn-Schmelzexperimenten unter Reaktionsbedingungen kalibriert werden. Ein Vergleich der Katalysatoren ist ohne weiteres durch die Messung der Standardaktivität bei 240°C, der scheinbaren Aktivierungsenergie der Methanol-Zersetzungsreaktion und des Alterns der Katalysatorproben möglich.