CONTROLLED RE-OXIDATION OF LOW-PRESSURE METHANOL SYNTHESIS CATALYST, FOLLOWED BY MEANS OF DSC

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Abstract

The re-oxidation of low-pressure methanol synthesis catalyst was followed by means of DSC, with the aim of contributing to a better understanding of the processes taking place during catalyst blanketing, stabilization and re-oxidation. The investigations were carried out with previously hydrogen-reduced samples, and their successive re-oxidation was performed with different oxygen contents in the oxygen/nitrogen gas mixtures. A procedure for catalyst stabilization and/or catalyst discharge is proposed.

Keywords: low-pressure methanol synthesis catalyst, re-oxidation, stabilization, DSC

Introduction

Many metal-based catalysts are pyrophoric in their reduced state, therefore requiring special handling procedures when not in use. Blanketing under static conditions with an inert gas, usually nitrogen, readily available with an oxygen content of less than 10 ppm, is the most widely applied procedure [1].

When discharge of the catalyst from the vessel is necessary, catalyst stabilization by successive oxidation is the usual procedure. Catalyst that is to be re-used must be stabilized very carefully to minimize loss of activity. When the catalyst is to be discarded, more rapid stabilization is possible, but care is still required to avoid excessive temperatures causing intensive sintering with block formation in the catalyst bed, in extreme cases even damaging the vessel. The re-oxidation process is carried out in a diluted oxygen/nitrogen mixture, with gradually increase of the oxygen content during the stabilization process to control the temperature profile in the vessel. During the discharge operation, only the discharge port should be open, to prevent air from being drawn into the vessel by the chimney effect. It is necessary to control the output rate of the catalyst to reduce the chance of air entering the vessel.

When the vessel is made of stainless steel, it can be filled and drained several times with water before the catalyst is discharged. Water prevents easy access of air to the active surface, at the same time cooling the catalyst and so markedly slowing down oxidation of the reduced catalyst. Usually, the catalyst is not completely stabilized by water and will become pyrophoric again if it is allowed to dry out. Once the catalyst is discharged, it should be kept away from all inflammable materials.

In this work an investigation was carried out on the controlled re-oxidation of the commercial copper-based low-pressure methanol synthesis catalyst, $CuO-ZnO-Al_2O_3$. The catalyst is active in the reduced form, the active structure consisting of different copper species, being stabilized by an Al_2O_3 promoter on a ZnO support [2]. There are not enough data in the literature as concerns the mechanism of oxidation of the complex active structure in the reduced catalyst, the temperature range of different oxidation processes and the resulting heat effects. Investigations have mainly been directed to the reduction mechanism and the formation of different active copper species in catalyst activation [2–6]. The present investigations were carried out with the aim of contributing to a better understanding of the processes taking place during partial or complete re-oxidation of the catalyst in the blanketing and stabilization procedure. We believe that the data published in the present paper can serve as a good basis in technical heat balance calculations relating to the catalyst stabilization processes, owing to the safe re-oxidation of the catalyst before its discharge from the vessel.

Experimental

The investigations were carried out on a typical commercial low-pressure methanol synthesis catalyst, as described in a previous paper [7]. The chemical composition of the catalyst was $CuO:ZnO:Al_2O_3=69:24:7$ wt.%. The quantity of heat released during the catalyst reduction and re-oxidation was measured with a differential scanning calorimeter, DSC, Du Pont Thermal Analyzer 1090. The catalyst was reduced in a hydrogen flow of 20–25 ml/min, at a heating rate of 10 deg·min^{-1}, from ambient temperature to 350°C. Subsequently, the catalyst was cooled down in a static hydrogen atmosphere in the DSC cell. The catalyst stabilization experiments were carried out in a subsequent flow of oxygen/nitrogen gas mixture containing 0.1, 1.0 or 5.0 vol.% O_2, the highest concentration being applied twice; the oxidation was completed in an air flow. The gas mixture flow rate was 20–25 ml/min, the temperature interval was from ambient to 350°C, and the heating rate was 10 deg·min^{-1}. After each treatment, the samples were cooled down in situ to ambient temperature in the gas

mixture applied. In all DSC experiments, initially 10 mg of well-powdered fresh catalyst was used.

The morphology and the phase composition of the fresh, reduced and re-oxidized catalysts were investigated by scanning electron microscopy (SEM, JEOL, JSM-35) and X-ray diffraction (XRD, Philips PW 1050).

Results and discussion

Preferred catalyst testing conditions for DSC

The reproducibility of DSC measurements in a dynamic regime could be a serious problem, as recognized in previous investigations [8, 9]. The sample size, the gas flow rate and the catalyst particle size have a great influence on the accuracy and reproducibility of DSC measurements.

It has been shown that a correct choice of the quantity of the copper-based catalyst sample is very important for correct catalyst evaluation [8]. Increase of the sample size causes a lowering of the reduction temperature in the DSC experiment. The delivered heat sometimes disturbs the appropriate heat flow in the equipment, preventing correct evaluation of the results. We recommend the constant use of the same size of samples, this being selected on the basis of the optimal heat flow regime. The heat quantity released is strongly dependent on the flow rate of the applied gases. For instance, at the selected flow rate of 20–25 ml/min, the reduction temperature of the powder catalyst is 241.8°C, and the heat quantity released is 781 J/g; in a static hydrogen atmosphere, the corresponding values were 210.4°C and 604 J/g. The reduction temperature of the catalyst pellet in the flow regime was 222.1°C and the heat quantity released was 199 J/g, the lower value relative to the powder form being caused by incomplete reduction of the bulk catalyst.

Reduction of the catalyst sample

The low-pressure methanol synthesis catalyst is delivered to the plant in the oxidized form as CuO. Reduction is necessary to activate the catalyst, since the $Cu(0)/Cu(I)$ species represent the active sites of the catalyst [10–12]. The reduction is exothermic ($\Delta H = -81$ kJ/mol) and the temperature front will pass down the catalytic bed as the reduction proceeds [1]. The catalyst activity is mainly dependent on the surface area of the copper crystallites formed during the reduction [1–6]. Copper has a low sintering temperature and the catalyst temperature should be kept below 230°C during reduction to ensure maximum activity, although the low-pressure methanol synthesis catalyst can be operated at higher temperatures when it has been reduced [1, 13].

Complete reduction of the active structure was necessary as the initial step to obtain samples for re-oxidation experiments. Preliminary reduction experiments on the catalyst with 1.0 vol.% H_2 and 0.5 vol.% CO in nitrogen, as the preferred composition of the activation mixture under industrial conditions, showed incomplete reduction under the conditions of the DSC experiments, even well in excess of the optimal reduction temperature; the very weak exo effect and the subsequent XRD analysis confirmed this.
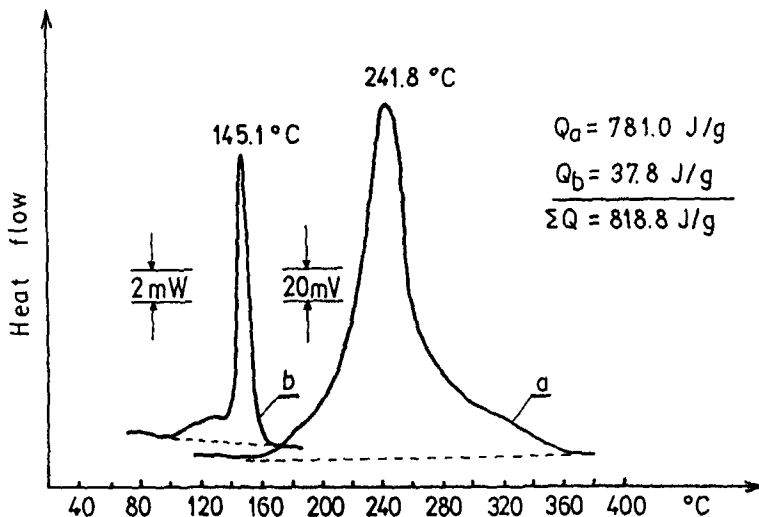

Fig. 1 DSC reduction curve (a), and repeated reduction curve (b) of the catalyst in a hydrogen flow

Further experiments in a pure hydrogen flow show a one-step reduction, with maximum at 241.8 °C and a released heat quantity of 781 J/g (Fig. 1a). After the reduction, the catalyst was cooled down in a static hydrogen atmosphere and re-heated in a hydrogen flow (Fig. 1b). The reduction temperature diminished to 145.1 °C, and the heat quantity released was only 37.8 J/g, i.e. less than 5.0% of the heat quantity released in the first experiment, demonstrating the high degree of reduction obtained in the previous step. The lowering of the reduction temperature on repeated hydrogen treatment is an unexpected trend. In explaining this phenomenon, confirmed in repeated experiments, we consider some surface re-oxidation of copper species to be possible during the cooling process, initiated by the water present as a reduction product in the cell atmosphere. The subsequent reduction, in a repeated reduction process, involves these surface oxidized species, at lower temperature and with a very low heat effect.

XRD results on the one-step reduced sample confirmed that CuO was reduced to metallic Cu(0). The most intensive XRD signals of CuO (d=0.251

and 0.231 nm) disappeared on reduction treatment. New, intensive and sharp signals of metallic copper Cu(0) ($d=0.208$ and 0.181 nm) in the reduced sample indicate the completeness of the reduction of the active phase. At the same time, the rearrangement of the ZnO lattice takes place, confirmed by the sharpening of the characteristic XRD signals ($d=0.2476$ nm). There is no XRD indication of the Al_2O_3 phase in either oxidized or reduced samples, owing to the low quantity and/or the low crystallinity of the Al_2O_3 forms in the system. The SEM pictures (Fig. 2) show the hexagonal plate-like ZnO and monoclinic CuO crystals in the fresh catalyst (Fig. 2a). The SEM picture of the reduced sample is mainly characterized by the presence of metallic copper, the crystals of ZnO no longer being visible on the sample surface (Fig. 2b).
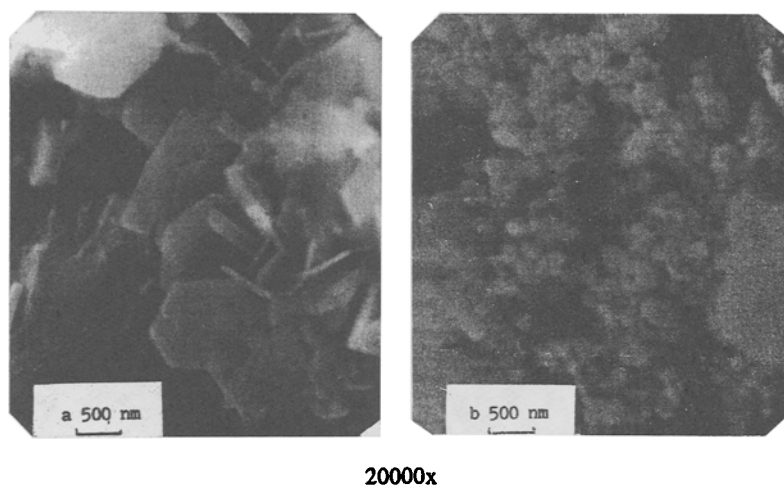

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Fig. 2 SEM pictures of fresh catalyst (a) and catalyst reduced in a hydrogen flow (b)

Since the previous results confirmed the complete reduction of the active phase, in further investigations the fresh catalyst was reduced in only one step in a hydrogen flow.

Stabilization of the reduced catalyst

The heat released during the re-oxidation of the typical copper-based low-temperature shift catalyst is $\Delta H=-647$ J/g [1]. As both the chemical compositions and the physicochemical properties of the low-temperature shift catalyst and the low-pressure methanol synthesis catalyst are very similar, the experimental results were referred to these data.

The re-oxidation experiments were carried out in four cycles, each starting with freshly reduced catalyst and with increasing oxygen content in the initial gas mixture. XRD analysis of the samples after each of the re-oxidation cycle confirmed the completeness of copper oxidation.

First cycle of catalyst oxidation

The first cycle of catalyst oxidation started with 0.1 vol.% O_2 in the oxygen/nitrogen gas mixture, followed by 1.0, 5.0 and again 5.0 vol.% O_2 and was completed in an air flow. Figure 3 presents the corresponding DSC curves and the released heat quantities.
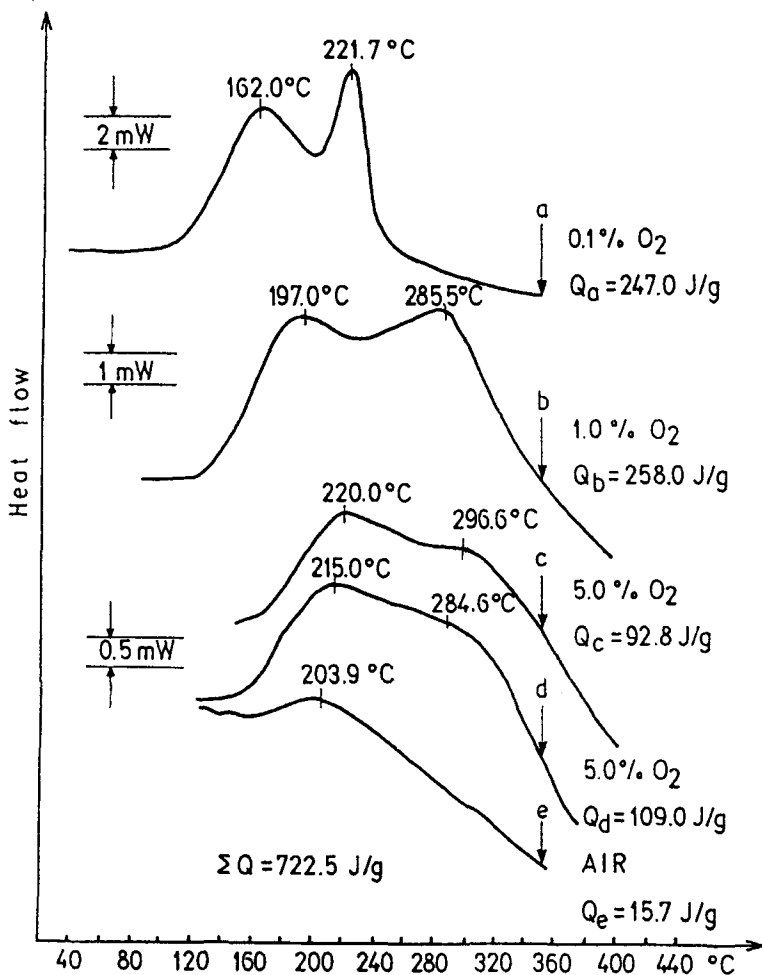

Fig. 3 DSC curves obtained during consecutive catalyst oxidations with different oxygen contents in the gas mixture: a) 0.1; b) 1.0; c) and d) 5.0 vol.% O_2; e) in an air flow

The DSC curve obtained during the heat treatment of the catalyst with 0.1 vol.% O_2 in the gas mixture has two large exo signals, at 162 and 221.7°C (Fig. 3a). The former is broad and is presumed to reflect the re-oxidation of the large, sintered metallic Cu(0) particles at the catalyst surface. The sharper signal at 221.7°C probably reflects the oxidation of smaller copper particles, which are in stronger interactions with the ZnO catalyst carrier. However, this signal could also originate from the oxidation of Cu(I) to Cu(II). The quantity of heat released is 247 J/g, i.e. well below the reference value for the complete oxidation of such type of catalyst [1].

The following oxidation step was performed with a gas mixture containing 1.0 vol.% O_2. The oxidation processes are accompanied by a large double exo effect in the DSC curve, the two having the same shape and intensity (Fig. 3b), at 197°C and 285.5°C. The shifts in the oxidation temperatures towards higher temperatures are coused by the oxidation of copper in deeper layers of catalyst perticles. The quantity of heats released is 258 J/g.

The DSC curve obtained during oxidation of the catalyst with 5.0 vol.% O_2 in the gas mixture is very similar to the previous DSC curve, but the maxima of the exo signals are less pronounced and shifted towards higher temperatures, 220 and 296.6°C (Fig. 3c). The heat quantity released is 92.8 J/g, which, together with the previous quantities, is still below the reference value.

The following experiment was carried out again with 5.0 vol.% O_2 in the gas mixture. The DSC curves obtained for the two consecutive oxidation with 5.0 vol.% O_2 are very similar as concerns the oxidation temperatures and the heat quantity released (Fig. 3d). In the DSC curve, the two exothermal peaks almost overlap, the maxima possibly being assigned to 215°C and 284.6°C, being, the inflection point of the DSC curve. The heat quantity released is 109 J/g, indicating completion of the oxidation.

The last step of catalyst oxidation was carried out in an air flow. This DSC curve is very broad, with a maximum at 203.9°C (Fig. 3e). It is difficult to say where the small exo effect ceased. The estimated heat quantity released is only 15.7 J/g. The total heat quantity released during the five-step oxidation is 722.5 J/g, which is comparable to the reference value for a similar type of catalyst, i.e. 647 J/g.

Second cycle of catalyst oxidation

The second cycle of catalyst oxidation started with 1.0 vol.% O_2 in the gas mixture. Figure 4 shows the DSC curves and the heat quantities released as functions of the oxygen content in the gas mixture.

The DSC curve obtained during oxidation of the catalyst with the gas mixture containing 1.0 vol.% O_2 is very simple (Fig. 4b). There is a large exo peak, with maximum at 203.1°C. The quantity of heat released is 248 J/g.

The following treatment was carried out with 5.0 vol.% O_2 in the gas mixture (Fig. 4c). The shape of the DSC curve is simple and shows a large exo ef-
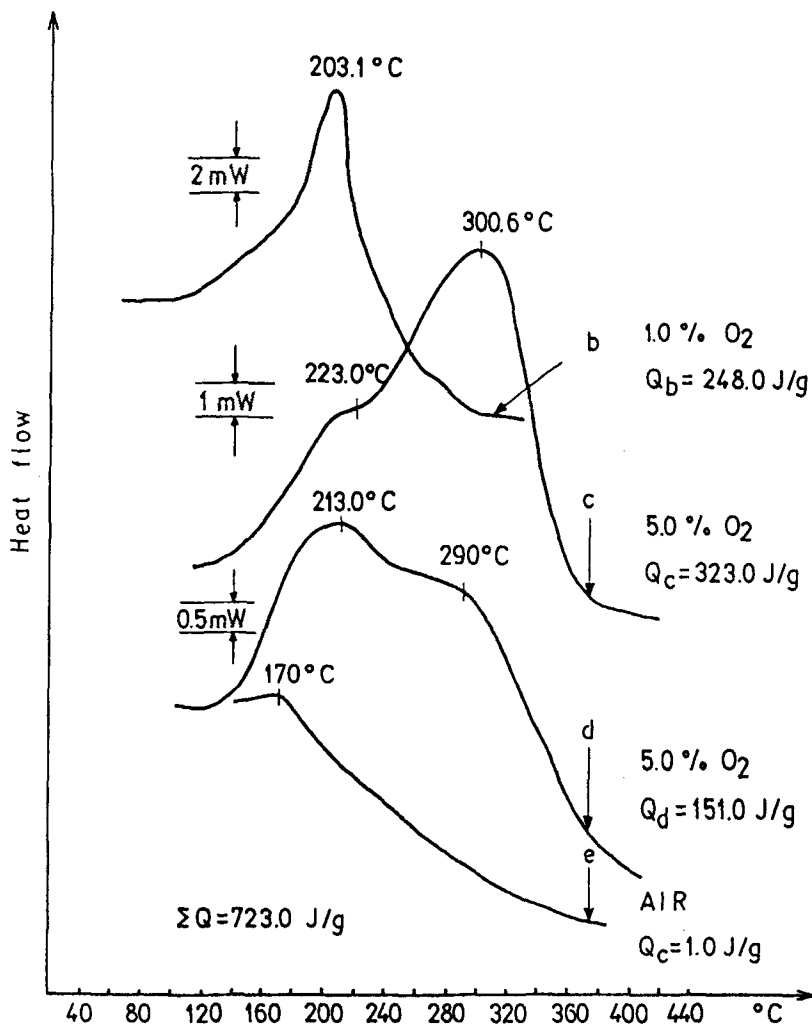
Fig. 4 DSC curves obtained during consecutive catalyst oxidations with different oxygen contents in the gas mixture: b) 1.0 vol.% O_2; c) and d) 5.0 vol.% O_2; e) in an air flow

fect at 300.6°C. On the left side of the peak, there is a slight maximum at 223°C. The heat quantity released is 323 J/g. The repeated oxidation with 5.0 vol.% O_2 (Fig. 4d) produced a DSC curve with two local exo effects, at 213 and 290°C, the heat quantity released being 151 J/g.

As concerns the shape of the DSC curve and the released heat quantity of 1 J/g obtained during catalyst oxidation in the air flow (Fig. 4e), it can be considered that the oxidation of the catalyst is completed in the previous stage.

The first (Fig. 4b) and the second (Fig. 4c) DSC curves obtained in the second oxidation cycle are different from those obtained at the same oxygen con-

tent in the first cycle (Fig. 3b and Fig. 3c), as regards both the shape and the released heat quantities. This shows that the oxidation course of the copper species and the fraction of copper oxidized are defined by the initial oxygen content in the gas mixture used for treatment. It is necessary to point out that the quantity of heat released obtained in the first oxidation step of both cycles, i.e. with 0.1 vol.% O_2 in the first and 1.0 vol.% O_2 in the second, are similar, 247 J/g and 248 J/g, respectively (Fig. 3a and Fig. 4b). However, the different shapes of these curves and the lower re-oxidation temperatures of the copper species for 0.1 vol.% O_2 in comparison with the 1.0 vol.% O_2 treatment indicate different mechanisms of oxidation, depending on the oxygen content. If it starts with a lower oxygen content, selective oxidation of the copper species, depending on the metal-support interaction (MSI), proceeds, starting with large copper crystallites loosely attached to the support, followed by re-oxidation of smaller particles at higher temperature. At a higher oxygen content, there is a one-stage oxidation independent of the particle size.

The DSC curve obtained at 5.0 vol.% O_2 in the second cycle (Fig. 4d) is similar to the corresponding DSC curve in the first cycle (Fig. 3d). The characteristic exo signals appear at similar temperatures, i.e. 213/215 and 290/284.6°C, but the released heat quantity is different, 151 J/g, which is more than the quantity of heat released in the corresponding experiment in the first oxidation cycle, 109 J/g. The same conclusion could be drawn for the final oxidation steps in the two cycles (Fig. 3e and Fig. 4e). This indicates that the final oxidation steps in both cycles are obviously less dependent on the initial oxygen content.

Third cycle of catalyst oxidation

The third cycle of catalyst oxidation started with 5.0 vol.% O_2 in the gas mixture (Fig. 5)

The DSC curve obtained with 5.0 vol.% O_2 is very simple, with a slight local maximum at 195°C and a maximum at 226.8°C (Fig. 5c). The released heat quantity of 1960 J/g could not be interpreted as realistic, because it is about three times more than the customary heat quantity released for such types of catalyst [1]. It could be supposed that the tremendous heat quantity released in a dramatic exo process, caused by the high initial content of oxygen in the gas mixture, disrupts the heat balance in the DSC cell, giving unrealistic values in an analytical sense. The subsequent treatment with 5.0 vol.% O_2 in the gas mixture confirmed that the oxidation of the catalyst was not completed in the previous experiment (Fig. 5d). This DSC curve has a slight local maximum at 200°C, similar to curve 5c, but the maximum is achieved at 313.2°C, the heat quantity released being 280 J/g. The third cycle finished with an air flow treatment (Fig. 5e). The heat signal is represented by a very stretched DSC curve, with a slight local maximum at 193°C. The estimated heat quantity is 17 J/g and thus the catalyst oxidation after the air treatment can be regarded as complete.

The results obtained in the third cycle were confirmed in several repeated experiments, giving similar values of the released heat.

Fourth cycle of catalyst oxidation

The last cycle was carried out in one step, directly in an air flow (Fig. 6).

The heat signal obtained shows a large and stretched exo peak with maximum at 261.7°C, preceded by two local maxima, at 153 and 210°C. It is presumed that these reflect the oxidation of the different copper species on the catalyst surface and in the subsurface layers. The slight maximum at 153°C is ascribed to the oxidation of the large metallic copper particles Cu(0), at higher temperature, *i.e.* at 210°C, while the oxidation of smaller metallic particles located deeper in the catalyst bulk proceeds at 261.7°C [10, 11]. The released heat of 2260 J/g could again be regarded as unrealistic and caused possibly by
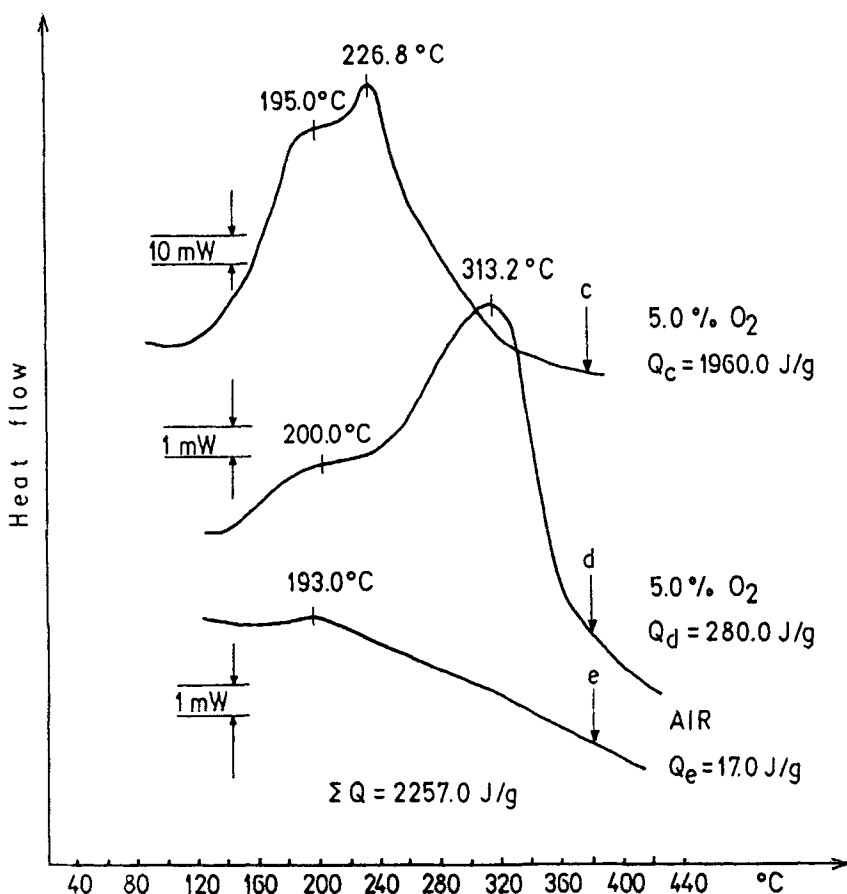

Fig. 5 DSC curves obtained during consecutive catalyst oxidations with different oxygen contents in the gas mixture: c) and d) 5.0 vol.% O_2; e) in an air flow
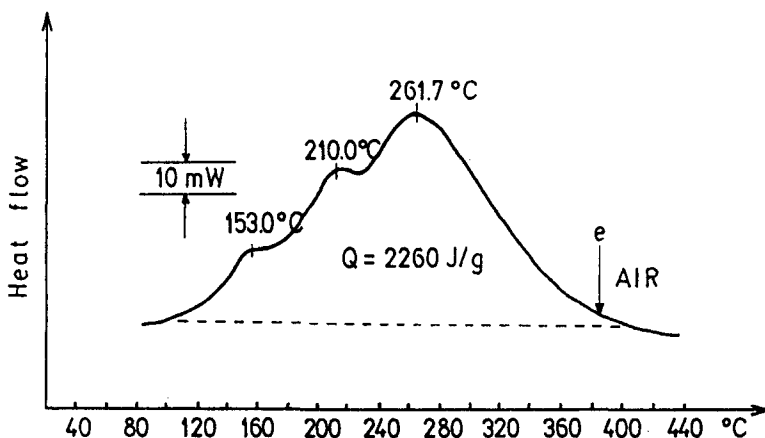
Fig. 6 DSC curve obtained by catalyst oxidation in an air flow

a disturbance of the heat balance in the DSC cell in an uncontrolled re-oxidation.

The results of DSC investigations of all the re-oxidation cycles are summarized in Table 1.

The temperature of re-oxidation of the first step in each of the cycles is always lower than the subsequent one, as expected. However, a lowering of the temperature is observed in the final step of re-oxidation in each cycle, i.e. at a highly oxidized state of the catalyst, as shown also by the low heat effect associated with the step.

From a comparison of the heat quantities released in the third and fourth re-oxidation cycles, both starting with high initial oxygen content (5 vol.%, air), it can be concluded that the process proceeds dramatically, not being controllable even on the laboratory level, not to mention an industrial scale ($120 \ m^3$ of catalyst in the plant vessel). Even though the results were unrealistic in an analytical sense, we consider that they are very illustrative in the sense of the uncontrolled re-oxidation that would proceed in the plant vessel in the event of an improper oxygen content in the initial and subsequent gas mixtures during re-oxidation of the catalyst.

Conclusions

DSC is recommended for simulation of the pyrophoric catalyst re-oxidation process, definition of the optimal experimental conditions (sample size, gas flow rate and particle size) being the prerequisite for a successful procedure.

Experiments on low-pressure methanol synthesis catalyst re-oxidation *in situ* in the DSC cell permitted formulation of the optimal controlled procedure for catalyst stabilization and/or catalyst discharge.

Table 1 Temperatures of maxima of thermal effects and heat effects of catalyst re-oxidation as a function of oxygen content in gas flow (vol.%)

	Re-oxidation cycles												
	First					Second				Third			Forth
	a	b	c	d	e	b	c	d	e	c	d	e	e
O₂ cont. vol. %	0.1	1.0	5.0	5.0	air	1.0	5.0	5.0	air	5.0	5.0	air	air
Temperature, °C	162.0	197.0	220.0	215.0	203.9	203.1	223.0	213.0	170.0	195.0	200.0	193.0	153.0
	221.7	285.5	296.6	284.6			300.6	290.0		226.8	313.2		210.0
													261.7
Heat effect, J/g	247.0	258.0	92.8	109.0	15.7	248.0	323.0	151.0	1.0	1960.0	280.0	17.0	2260.0
Total heat, J/g			722.5				723.0				2257.0		2260.0

In catalyst stabilization, in order to minimize the loss of catalyst activity, an initial low oxygen content mixture is preferred (0.1 vol.% O_2 or less), eventually followed by a higher oxygen content in the gas mixture (1.0 vol.% O_2 at most).

Complete oxidation of the catalyst, necessary for catalyst discharge, also has to proceed in steps, with rising oxygen content in the gas mixture. However, more rapid oxidation is possible, the initial concentration not exceeding 1.0 vol.% O_2, with subsequent increase of the oxygen content in the gas mixture up to the content in air. In this way, controlled re-oxidation proceeds, overheating and sintering of the catalyst in the vessel being avoided.

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Zusammenfassung — Als Beitrag zum besseren Verständnis der Vorgänge während Katalysator-Blanketing, -Stabilisation und -Reoxidation wurde mittels DSC die Reoxidation des Niedrigdruck-Katalysators für die Methanolsynthese verfolgt. Die Untersuchungen wurden mit zuvor wasserstoffreduzierten Proben durchgeführt, die anschließende Reoxidation hingegen mit Sauerstoff/Stickstoff-Gasgemischen unterschiedlichen Sauerstoffgehaltes. Es wird eine Methode zur Katalysatorenstabilisation und/oder zur Katalysatorenbeseitigung vorgeschlagen.