Homogeneous catalysis by evaporated solids

Steffen Ruf [1], Gerhard Emig *

Lehrstuhl für Technische Chemie I, Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany
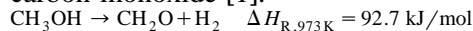
Abstract

About 10 years ago, sodium aluminate has been found as suitable catalyst for the pure dehydrogenation of methanol to anhydrous formaldehyde. At first, the reaction was supposed to follow a heterogeneous mechanism. Later on, experimental results with a special set-up were at variance. Recent investigations revealed the loss of catalytically active species from the solid aluminate into the vapour phase where the entire reaction is likely to take place. Furthermore, evaporated elemental sodium catalyses the dehydrogenation of methanol in a homogeneous vapour-phase reaction. With respect to additional investigations carried out lately, a conclusive reaction mechanism is proposed which explains both the reaction with sodium aluminate and evaporated elemental sodium as catalysts in a proper way. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Formaldehyde as an aqueous solution is commonly produced by the silver catalyst or formox process. As an alternative route, the pure dehydrogenation of methanol leads to anhydrous formaldehyde, required for the production of polyoxymethylenes. For the last 10 years, we have intensively studied this endothermic reaction using lithium–sodium aluminate $(Li_{1-x}Na_xAlO_2)$ and particularly sodium aluminate $(NaAlO_2)$ as catalyst yielding formaldehyde, hydrogen and carbon monoxide [1]:

$$CH_3OH \rightarrow CH_2O + H_2 \quad \Delta H_{R,973K} = 92.7 \text{ kJ/mol}$$
$$CH_2O \rightarrow CO + H_2 \quad \Delta H_{R,973K} = 12,4 \text{ kJ/mol}$$

Unfortunately, both catalysts suffer from deactivation phenomena as soon as the methanol fraction in the feed stream exceeds 10%. Furthermore, the two aluminates reach their activity at relatively high temperatures, i.e., not until 1150 K.

At these temperatures methanol is also converted homogeneously in absence of any catalyst resulting in remarkable lower selectivities of formaldehyde than catalytically obtained. The uncatalysed reaction is therefore superimposed to the dehydrogenation catalysed by lithium or sodium aluminate.

In previous experiments [2], a special experimental set-up gave rise to the assumption that sodium aluminate acts not as heterogeneous catalyst but that it is decomposed during the reaction emitting fragments into the vapour phase. Thermodynamic calculations identified these catalyst fragments as elemental sodium [2].

* Corresponding author. Tel.: +49-9131-8527420; Fax: +49-9131-8527421; E-mail: emig@tc.uni-erlangen.de
[1] Present address: Aventis Research and Technologies, Industriepark Höchst, G 811, D-65926 Frankfurt, Germany. E-mail: rufs@aventis.com.

Therefore, we supposed sodium to catalyse the reaction homogeneously in the vapour phase. According to additional examinations recently performed, these catalyst fragments could be identified by mass spectroscopy [3]. Furthermore, elemental sodium was evaporated in order to scrutinise the thesis whether sodium catalyses the dehydrogenation of methanol or not [4].

For the uncatalysed conversion a reaction scheme is presented consisting of only 12 elementary free-radical reactions and 13 different species. It was derived from kinetic simulation in order to describe experimental data. Afterwards three reactions considering the influence of the catalyst were added to this scheme. With respect to further examinations studying the reaction mechanism, a catalytic cycle with the formation of sodium methanolate and its repeated decomposition is proposed which is likely to be valid for both the solid sodium aluminate catalyst and the evaporated sodium.

2. Experimental

The reaction was carried out in a corundum tube reactor (12 mm × 8 mm × 1000 mm) with a reaction zone centred in the axis of the tube. The product stream was analysed by on-line gas chromatography. Further details are given in Refs. [2,4].

While studying the uncatalysed reaction, an empty tube was used heating the reaction zone to 1123 and 1173 K, respectively. The mole fraction of methanol in the feed stream was set to 10 or 20% with nitrogen as inert gas for balance varying the flow velocity between 0.75 and 1.5 m/s. The feed stream was pre-heated to 473 K.

Fig. 1 shows the special experimental set-up which has led to the assumption that catalyst fragments leave the solid aluminate. The mixture of methanol and nitrogen is fed to the reaction zone through an inner tube without contacting the aluminate packing (feed stream
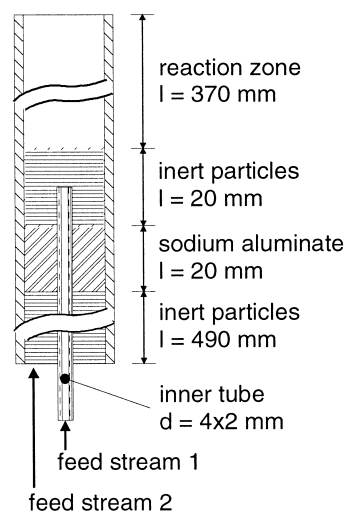

Fig. 1. Experimental set-up with two splitted feed streams.

1). A second stream (feed stream 2), alternatively consisting of nitrogen, nitrogen/water or nitrogen/hydrogen, was passed through the catalyst layer ($Li_{0.5}Na_{0.5}AlO_2$) and mixed with feed stream 1 afterwards. Varying the composition of feed stream 2, the degree of methanol conversion and the yield of formaldehyde changes dramatically. The reactor temperature was kept at 1173 K, the mole fraction of methanol at 10%.

In order to study whether sodium catalyses the dehydrogenation of methanol a tee carrying a flat crucible with elemental sodium was attached to an empty tube reactor (Fig. 2). A separate nitrogen stream was passed over the crucible to transport evaporated sodium to the reaction zone. The amount of sodium in the reaction zone was varied by changing the crucible temperature. A second, smaller inner tube (6 mm × 4 mm) enabled the feed of methanol (diluted with nitrogen) to be supplied directly into the reaction zone without contacting elemental sodium placed in the crucible. Meanwhile, the reactor temperature was kept constantly at 973 K as the mole fraction of methanol in the feed was held at 10%.

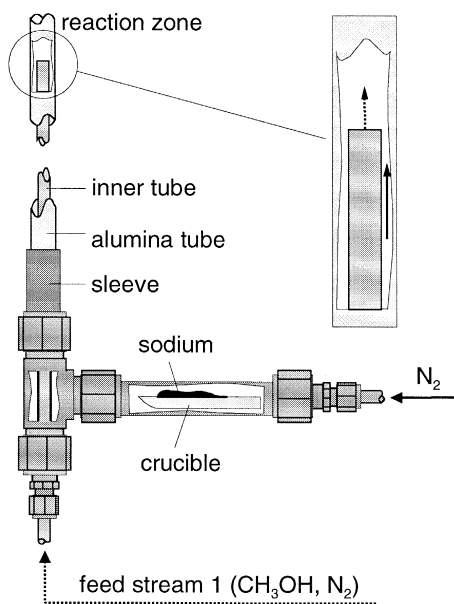For the additional experiments with the aim to examine more details of the reaction mecha-

Fig. 2. Experimental set-up for evaporating sodium.

nism, first methanol was substituted by methane and second sodium as catalyst was substituted by sodium methanolate. A commercial methanolic solution (30%, Merck) was diluted to 0.05% by mixing with the methanol feed stream. Changing the direction of flow in the reactor, it was dripped directly from the top to the reaction zone realising a methanol mole fraction of 10% at 973 K reactor temperature.

3. Results

The dehydrogenation of methanol to formaldehyde was performed non-catalytically in an empty tube as well as catalytically with sodium aluminate as solid and elemental sodium as vaporised catalyst. Supplementary experiments gave special insights to the reaction mechanism.

3.1. Uncatalysed reaction

Methanol is converted homogeneously without catalyst as soon as the reaction temperature exceeds 1073 K. With increasing temperature the degree of methanol conversion is increasing while the selectivity to formaldehyde decreases. The maximum yield is approximately 19%. Carbon monoxide appears as by-product while methane and water can only be detected in small traces. At 1173 K reactor temperature, 10% methanol mole fraction in the feed stream and 1.0 m/s flow velocity, the degree of methanol conversion and the formaldehyde selectivity are approximately 30 and 48%, respectively.

Looking at the reaction scheme of the uncatalysed dehydrogenation, the formation of carbon monoxide is discussed in the literature as parallel reaction from both formaldehyde and methanol [5,6] in a triangular (parallel-consecutive) scheme. However according to our investigations, the exclusive formation of carbon monoxide from formaldehyde in a consecutive reaction and not directly from methanol seems to be more likely taking elementary reaction steps into account. Varying the residence time, the decision, whether the reaction follows a consecutive reaction or triangular scheme, can be made by plotting reactant concentrations vs. residence time. In case of a consecutive reaction the slope of carbon monoxide vs. time curve must be zero in the origin showing simultaneously a maximum of the formaldehyde curve. Otherwise, in case of a parallel reaction, the slopes of both formaldehyde and carbon monoxide curves are larger than zero in the origin.

The variation of residence time reveals experimentally that carbon monoxide is formed from formaldehyde in a consecutive reaction (Fig. 3). As expected, the mole fraction of formaldehyde shows a maximum while the slope of the carbon monoxide curve is zero in the origin and the curve increases monotonically with longer residence times. Carbon monoxide is therefore exclusively formed from formaldehyde and not directly from methanol. The reaction was simulated with a consecutive reaction scheme under isothermal conditions; the corresponding curves show good agreement with the experimental data.
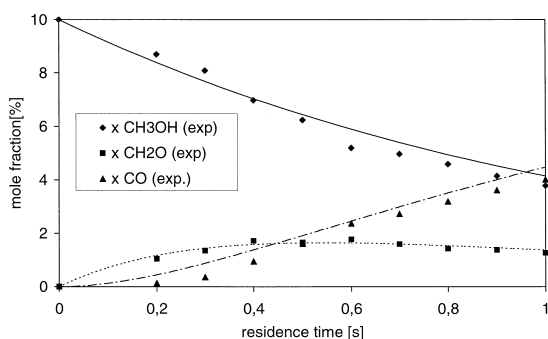
Fig. 3. Reactants concentration under variation of residence time.

3.2. Aluminate catalyst

With sodium aluminate as catalyst in both fixed bed and catalytic tube wall reactor the maximum formaldehyde yield of 65% is achieved at nearly total methanol conversion at 1173 K reactor temperature and 10% methanol mole fraction in the feed stream. Outside this range at only 50 K lower reactor temperature, the catalyst loses 60% of its full activity within only 6 h. Therefore, the catalyst must be kept at temperatures of 1153 or higher for stationary operation.

Fig. 4 shows experimental results applying the special set-up of Fig. 1 with different compositions of the second feed stream which passed through the catalyst bed. During the first 150 min the feed consisted exclusively of nitrogen. After a short induction period, the degree of methanol conversion reached 30% with a
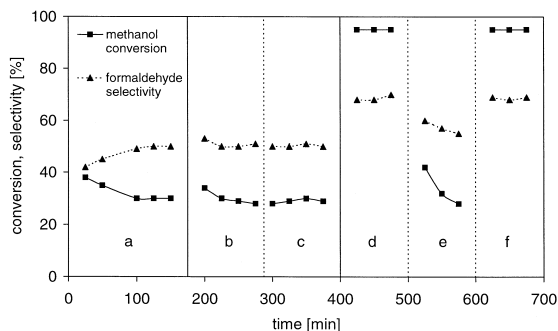
formaldehyde selectivity of 48%, known as typical values of the uncatalysed reaction.

The addition of small amounts of water to feed stream 2 afterwards influenced neither the degree of methanol conversion nor the selectivity to formaldehyde. After adding hydrogen to feed stream 2, the degree of methanol conversion however jumped to 98% while the formaldehyde selectivity increased from 48% to approximately 70%. Interrupting the supply of hydrogen, a breakdown of methanol conversion to the value of the uncatalysed reaction of 30% is observed. Likewise, the selectivity of formaldehyde decreased to the initial value of 48%. The procedure of adding hydrogen and interrupting the supply leads always to the same result. As long as hydrogen or, alternatively, methanol as reducing gases were added in small amounts, a similar conversion and selectivity is obtained as in the fixed bed or tube wall reactor with sodium aluminate as catalyst-although, in this case, the direct contact between methanol and catalyst is excluded.

In another experiment, the thermal behaviour of sodium aluminate under inert atmosphere was examined by mass spectroscopy [3]. Fig. 5 shows a temperature-dependent increase of the ion stream of the mass $m/e = 23$ (sodium). Sodium aluminate loses sodium (Na, as shown) and simultaneously sodium oxide (NaO, not shown) at elevated temperatures by decomposition.

Fig. 4. Results of set-up with splitted feed streams [(a) 100% N_2; (b) 99.3% N_2, 0.7% H_2O; (c) 98.7% N_2, 1.3% H_2O; (d) 87% N_2, 13% H_2; (e) 100% N_2; (f) 87% N_2, 13% H_2].
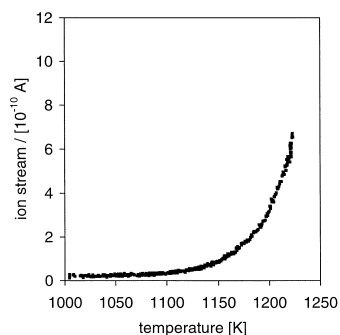

Fig. 5. Emission of sodium from sodium aluminate plotted vs. temperature [3].
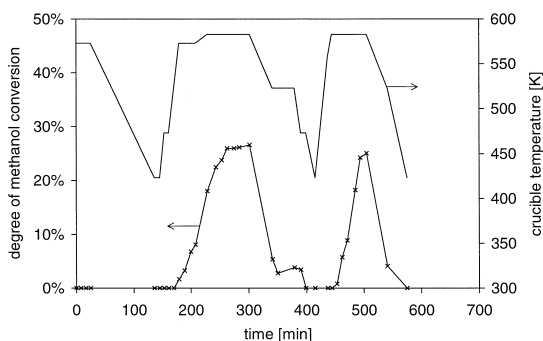
Fig. 6. Conversion of methanol in dependency on temperature of the crucible at a reaction temperature of 973 K (0–150 min: no sodium present, 150–600 min with sodium).

3.3. Elemental sodium as catalyst

Fig. 6 depicts the results of the basic experiment which obviously demonstrates the influence of evaporated sodium on the dehydrogenation reaction at a reaction temperature of 973 K. During the first 130 min no methanol conversion was detected according to the fact that no sodium was placed in the crucible. Under these conditions no homogeneous reaction is taking place, considering the experimental set-up as inert. Placing sodium in the crucible and increasing its temperature to 583 K, the degree of methanol conversion reached 25% with formaldehyde as the main product. Hydrogen and carbon monoxide were detected as the other reaction products. After lowering the crucible temperature to 423 K, no further methanol conversion was observed. As long as the temperature, or more precisely the partial pressure of sodium in the vapour phase is high enough, methanol is converted within the vapour phase to formaldehyde.

The repeated cycles of heating and cooling of the crucible and the appearance of formaldehyde show that sodium is essentially needed for the dehydrogenation reaction. Only as long as sodium is present in the vapour phase, methanol is converted to formaldehyde. The reaction is likely to take place entirely in the vapour phase. The conversion of methanol can be successfully conducted at 973 K, 200 K

lower than using sodium aluminate as solid 'catalyst'.

In order to decide whether sodium is consumed stoichiometrically or acts as catalyst the turnover number is determined. It is calculated as ratio of the molar consumption of methanol to sodium and resulted in values between 500 and 700 at 973 K reactor temperature. With one sodium atom between 500 and 700 methanol molecules were converted. The influence of sodium is therefore definitively a phenomenon of catalysis, the dehydrogenation of methanol to formaldehyde is therefore a homogeneously catalysed vapour-phase reaction.

3.4. Investigations of the reaction mechanism

Additional experiments in order to elucidate the reaction mechanism of the sodium catalysed methanol dehydrogenation were performed first by substituting sodium by sodium methanolate and second by the simultaneous supply of methane (instead of methanol) and sodium.

Discussing the mechanism, the product formed in the reaction between methanol and sodium is of great importance. A special experiment should reveal whether there is a reaction between sodium and the hydrogen atoms of the methyl group in methanol or not. Sauer [7] proposed the reaction between methanol and sodium to sodium hydride and hydroxy-methyl radicals.

Although the reactor temperature was increased to 1223 K no conversion of methane was observed. Under these reaction conditions hydrogen atoms of methane are inactive against an attack of sodium. Hence, a reaction of sodium and methanol yielding sodium hydride (NaH) and hydroxy-methyl radicals (CH_2OH) is unlikely, without regarding this test as final proof but as a strong indication. In accordance with the known reaction in the liquid phase, the reaction to sodium methanolate and atomic hydrogen seems very likely.

Finally, the substitution of sodium by sodium methanolate as catalyst should reveal the precise

mechanistic role of sodium, which is discussed later. With sodium methanolate as catalyst similar methanol conversions and turnover numbers (450–800) are achieved under comparable reaction conditions, especially concerning catalyst concentrations and reactor temperature (973 K).

4. Discussion

4.1. Homogeneous reaction

The uncatalysed reaction as well as the sodium-catalysed reaction are taking place homogeneously in the vapour phase. Kinetic simulations turned out H-atoms to act as chain carriers while at the same time 12 elementary reactions with 13 different species are sufficient to describe the experimental data [8] The simplified reaction scheme is shown in Fig. 7.

The uncatalysed methanol decomposition is induced by homolytic C–O cleavage forming first methyl and hydroxyl radicals and then by reacting with methanol to methane, water and particularly hydroxy-methyl radicals. From these hydroxy-methyl radicals formaldehyde is formed which is further decomposed to carbon monoxide via formyl radicals by reaction with H-Atoms or by collision with an inert partner M.

Looking at the sodium-catalysed reaction, the determination of the turnover number revealed a catalytic effect of sodium on the dehydrogenation of methanol in the vapour phase. Concerning the reaction mechanism, two questions are of major interest. On the one hand, the product
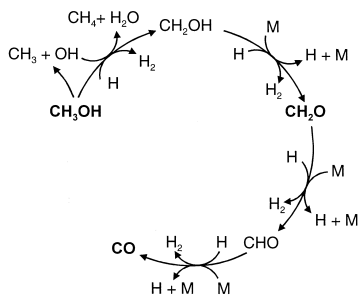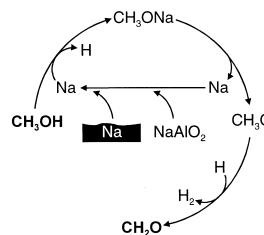

Fig. 8. Reaction cycle of the catalysed reaction with Na or NaAlO$_2$ as catalyst.

of the reaction of sodium and methanol is crucial, on the other hand the precise role of sodium is of great importance. As the methane experiment revealed, there is no reaction between methane and sodium although the reactor temperature was elevated to 1223 K. Moreover, in solution under normal conditions the product is definitely sodium methanolate. Therefore, we suppose the latter to be formed also in the vapour phase. The second question refers to the role of sodium, precisely whether there is a repeated decomposition of sodium methanolate during the reaction or not. The latter would mean that the only function of sodium is to generate H-atoms which could act as chain carrier analogous to the uncatalysed reaction.

The experiments using sodium methanolate as catalyst show two substantial clarifying results. First, sodium methanolate is decomposed under reaction conditions and acts also as catalyst for the pure dehydrogenation. Second, similar turnover numbers are calculated in comparison to elemental sodium as catalyst. The first result proves sodium methanolate not to be inert which means that the function of sodium is definitely not only to produce H-atoms; there would be no methanol conversion, if sodium methanolate was inert. The second result shows that it is irrelevant for the reaction mechanism whether the catalytic cycle is started by supplying sodium or sodium methanolate as catalyst (Fig. 8); offering sodium, the actual catalyst is supplied, offering sodium methanolate the intermediate is supplied.

The reaction between methanol and sodium leads to H-atoms and sodium methanolate. The

Fig. 7. Scheme of uncatalysed dehydrogenation reaction.

latter decomposes to methoxy radicals and sodium which is able to react repeatedly with methanol. Formaldehyde is formed from methoxy radicals. Unfortunately, H-atoms can also trigger chain reactions mentioned in the uncatalysed cycle explaining the occurrence of carbon monoxide. Obviously, the formaldehyde selectivity is therefore lower than 100%.

4.2. Effect of sodium aluminate on methanol dehydrogenation

Sodium aluminate is decomposed at elevated temperatures leading to a loss of sodium (Na) and sodium oxide (NaO) and the formation of alumina:

$$2\,NaAlO_2 \rightarrow Na + NaO + Al_2O_3$$
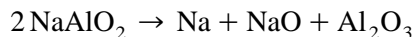
The temperature of 1150 K, when decomposition starts to be significant, coincides well with the temperature when sodium aluminate obtains its activity for the dehydrogenation reaction. At 1123 K, only in the very first beginning of the reaction enough sodium is emitted into the vapour phase. Later on, the temperature of the aluminate is too low to emit sufficient sodium for total conversion causing the decrease of catalyst activity within only 6 h. This may be caused by the slow process of diffusion in solid state. Furthermore, the plots of the ion stream of sodium and the degree of methanol conversion vs. temperature show a parallel behaviour.

The catalyst does not act heterogeneously but emits catalytically active sodium into the vapour phase. Within the vapour phase, the reaction is taking place homogeneously catalysed by emitted sodium. Therefore, sodium aluminate is consumed during the reaction and acts only as reservoir for the catalytically active sodium. In this case, deactivation of the solid 'catalyst' by loss of active species is not undesirable but imperative for the activity of sodium aluminate for the dehydrogenation of methanol.

The high reactor temperature of 1173 K is necessary for the production of formaldehyde when sodium aluminate is used as catalyst because decomposition of aluminate begins not until 1150 K. On the other hand a temperature of 973 K is enough for the chemical reaction as the results with elemental sodium show. The additional difference of 200 K is only required for the activation of sodium aluminate.

As the experiments with the two splitted feed streams (Fig. 4) revealed, the degree of methanol conversion could only be increased when reducing gases were led over the aluminate. On the other hand, sodium aluminate also emits catalyst fragments under non-reducing conditions. The divergent results can be explained by the design of the experimental set-up (Fig. 1). A fixed bed of aluminate with a following inert bed has been used as sodium source. We suppose sodium (Na) and sodium oxide (NaO) to recombine within the bed forming gaseous Na_2O before getting in contact with methanol. Na_2O is very likely to be catalytically inert under reaction conditions. There is neither a thermal decomposition forming sodium nor a reaction with methanol to form sodium methanolate and therefore no enhanced degree of methanol conversion. Under reducing atmosphere the recombination is probably hindered. Sodium can reach the reaction zone and catalyses the dehydrogenation reaction.

5. Conclusions

On a first glance, lithium and sodium aluminate as solid catalysts on the one side and evaporated sodium on the other side seem to be two different catalyst systems acting differently. However, our experimental results revealed sodium as active species in both cases. The solid catalyst acts not classically by adsorbing methanol and lowering thus the activation energy of the dehydrogenation reaction but by emitting active fragments into the vapour phase where the reaction is taking place. The 'heterogeneous' aluminate catalyst as well as the evaporated sodium turned out to catalyse the dehydrogenation in a homogeneously catalysed vapour phase reaction.

The dehydrogenation of methanol follows the same mechanism, independent whether sodium or sodium aluminate is applied. Sodium methanolate is repeatedly decomposed forming sodium and closing the catalytic cycle to form formaldehyde from methanol.

Acknowledgements

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