

**The Structure of the Na_2MoO_4 catalyst for water free
dehydrogenation of methanol to formaldehyde**

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Abstract: The Na_2MoO_4 has been found to have a peculiar catalytic behaviour. The CH_2O formation starts after a period of time stay at 670°C . Then the yield increases and reaches a maximum after some 12hrs. This work shows that the catalyst undergoes an extensive phase transformation prior to becoming active.

1. **Introduction**

Conventionally, formaldehyde is produced by partial oxidation or oxidative dehydrogenation of methanol. In these processes, water is formed as a by product. Sodium compounds have recently [1] been found to be active in water free formaldehyde production. Moreover, these catalysts were shown to deactivate very slowly. It was presumed that coking was the main factor of deactivation. Most of the catalytic activity could be recovered by burning the coke at high temperatures ($> 800^\circ\text{C}$). However, the change of color in Na_2MoO_4 appeared to be linked to the delayed catalytic activity; it can hardly be only explained by coking. This latter effect would hinder the catalytic activity instead of being parallel to it. In the following, we discuss the results and present the first conclusions of our current investigations on this new catalyst.

2. **Experimental**

The formaldehyde production is carried out at 670°C , following the heating sequence sketched in fig.1a. The activity of the catalyst during that time is shown on fig.1b. This behaviour is different from what happens when other sodium compounds (Na_2CO_3 or $\text{Na}_2\text{B}_4\text{O}_7$) are used as catalysts for the same reaction. For this investigation, samples were examined at various stages on fig. 1a (0h, 6h, 12h). The 0h sample corresponds to the time when 670°C is settled; and the 12h sample is normally the one which presents a full catalytic activity.

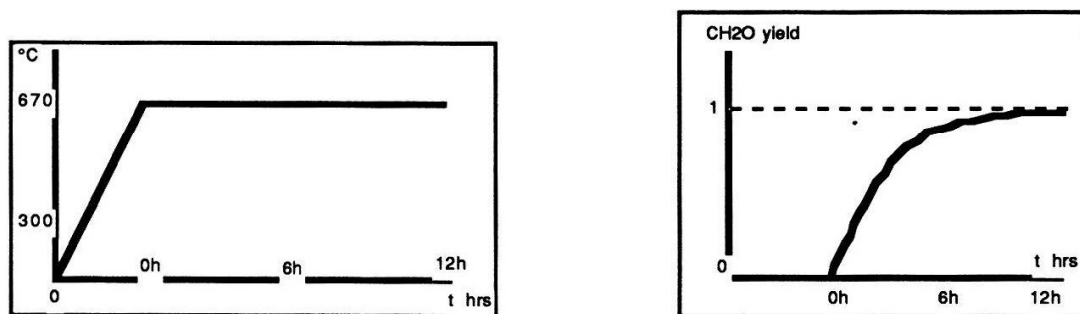


Fig. 1: a) Heating sequence. b) Catalytic activity vs time at 670°C

The formaldehyde production follows this reaction: $CH_3OH \rightarrow CH_2O + H_2$. A large amount of hydrogen is then formed. The effect of H_2 on the structure of the catalyst at reaction temperature (670°C) had to be understood. We therefore examined samples of Na_2MoO_4 which had been heated at 670°C for 12h.

3. Results

a. -Effect of heating for 6hrs at 670°C in methanol

When the catalyst bed is >10cm, the formaldehyde starts to form at this point. The powder has become a solid of black color outside and one sees an inner white part when it is broken. Our observations show that at this stage the material has undergone an extensive decomposition (fig.2). There is Na rich needlelike material stemming out from Mo rich areas. Until now, these sodium rich areas have been found to be amorphous.

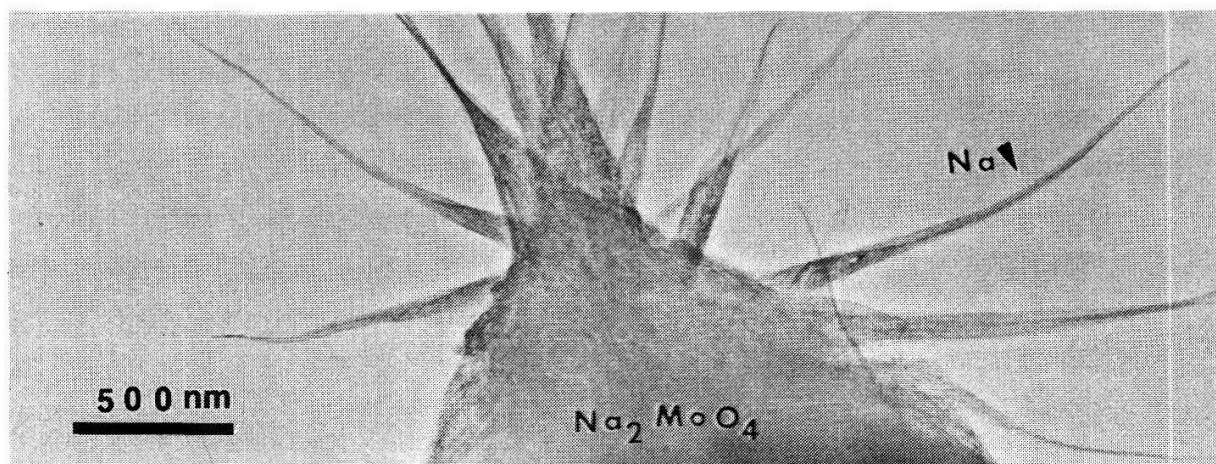


fig. 2: The catalyst after 6hrs in methanol at 670°C

c. -Heating for 12hrs in methanol

The catalyst has now become an entirely black solid, as the catalytic activity reaches its maximum. The decomposition has proceeded much further. The Na rich needles are now much bigger (fig.3) and most of the time the areas rich in Na_2MoO_4 , are covered with carbon (fig.3b). Moreover dendritic formations rich in Mo have taken place.

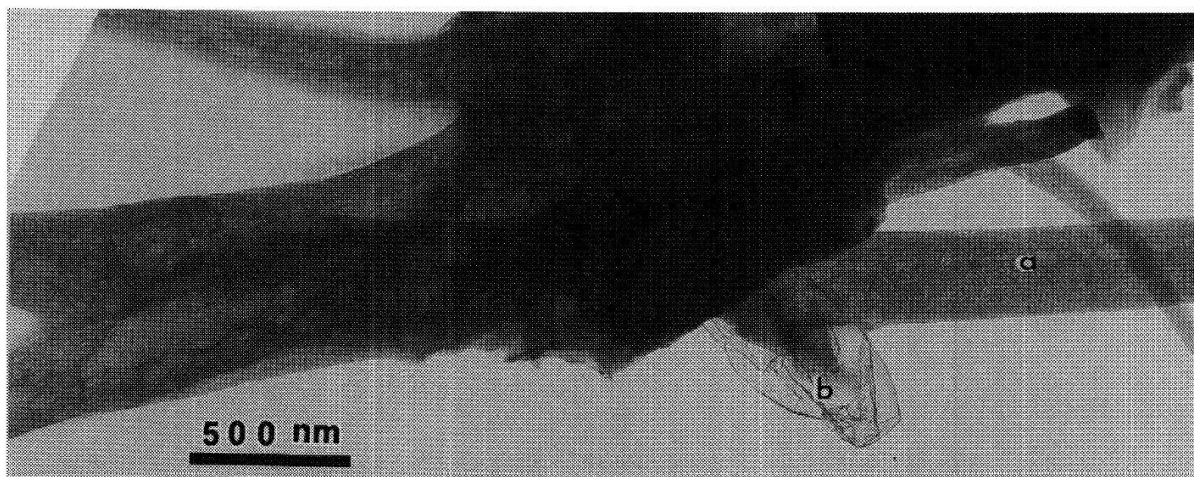


fig. 3: a) Na rich needle-like material, b) coking of the remaining Na_2MoO_4

When this material is put into water, it separates into a soluble, whitish compound and a black non soluble phase. The soluble material is mostly $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ from the initial phase. In addition we find a Na rich compound which does not contain any detectable Mo. This material appears to be microcrystalline after drying. Its structure as determined by electron diffraction seems to be that of a sodium carbonate compound. There seem to be two candidates NaCO_3 and $\text{NaCO}_3 \cdot 10\text{H}_2\text{O}$. The non soluble material is made of Mo rich phases. We have found some MoO_3 microcrystals and a material made of mixed Mo (Mo_9O_{26} , MoO_3 , ...) oxides.

d. -Heating in Hydrogen 670°C 12hrs

After these 12hrs the catalyst becomes a whitish solid in a large inner part. The black outer part is extended on less than 1mm. On fig.4, it appears that the Na_2MoO_4 has undergone transformation as well. The Na separated material bares the needlelike aspect. However the Mo rich area do not seem to separate away from the initial Na_2MoO_4 material. They are found to form an intimate mix-

ture with it (fig.4b). In the inner part of the solid, we do not notice any phase separation. All the analyzed samples exhibit the original composition.

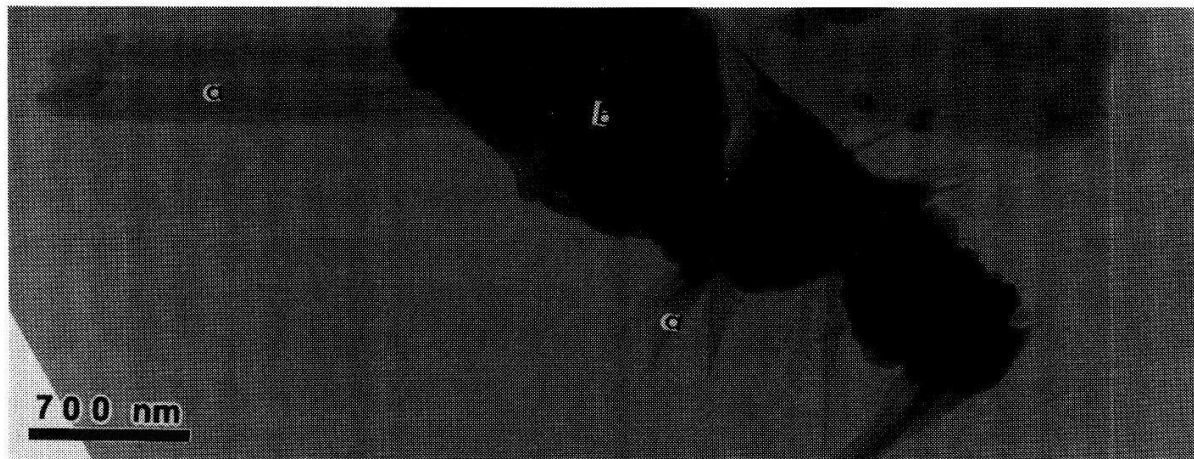


Fig. 4: 12 hours in H₂, a) separation of Na rich areas, b) intimate mixture of Mo rich areas and original material-Na₂MoO₄

When this sample is put into water, we only find two separate phases: A non soluble compound which show small crystals of MoO₂ and microcrystals of Mo₄O₁₁ of monoclinic structure. In the soluble phase we only have found the hydrated form of Na₂MoO₄.

3. -Conclusion

These preliminary results show that the catalytic activity of Na₂MoO₄ does not start until it undergoes an extensive decomposition. From morphological point of view, it appears that Na separates in similar ways in the methanol or in hydrogen treated samples. This does not imply that we have the same phases in both cases. For the Mo rich phases there seems to be some difference: a) We do not find any dendritic formation in the H₂ treated samples. b) The Mo rich phases remain mixed with the original Na₂MoO₄ material. c) From the electron diffraction analysis, we can draw these preliminary results : -In the H₂ treated sample there seems to form MoO₂ small crystals and Mo₄O₁₁ microcrystals. -In the CH₃OH treated one, lesser reduced forms of Mo oxides are produced (MoO₃ small crystals, and a mixture of MoO₃ and Mo₉O₂₆, etc... in the dendrites.

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