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ON THE JUNCTION EFFECT THEORY OF ACTIVITY IN METHANOL SYNTHESIS CATALYSTS

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The junction effect theory which has been propounded to account for the activity in methanol synthesis of oxide supported copper catalysts has been examined in the light of published data on the mechanism of methanol synthesis on copper/zinc oxide/alumina catalysts. The absence of a formate species on the surface of the zinc oxide component of the catalyst after methanol synthesis (the formate species has been shown to be the pivotal intermediate in methanol synthesis on zinc oxide) precludes its involvement in the reaction and negates the applicability of the theory to the copper/zinc oxide/alumina system.

The view has been promulgated that, for oxide supported metal catalysts in general, and for zinc oxide supported copper in particular, the activity of these catalysts in methanol synthesis derives from the increase in the number of defects in the oxide, brought about by the stabilisation of the defects by the vicinal metal–the junction effect [1]. Indeed it has been proposed that the metal/oxide junction effect can produce a one thousand fold increase in the number of oxide defects. Their exact role in the synthesis of methanol has, as yet, not been completely specified other than as a site for hydrogen dissociation and thereafter of hydrogenation of carbon monoxide or carbon dioxide. It is proposed that this is a unifying view of the mechanism of methanol synthesis and, while it is attractive, a detailed examination of our published data shows that it does not hold for the copper/zinc oxide system [2–5] and is therefore not general.

In respect of methanol synthesis by zinc oxide, we have shown that the formate species is the longest lived and therefore pivotal intermediate in this reaction [2–4]. It is characterised in a temperature programmed reaction spectrum after the adsorption of formaldehyde or methanol [2] or methyl formate [3] by the coincident desorption of carbon monoxide and hydrogen at 580 K (together with some carbon dioxide, depending on the formate coverage and the defect state of the zinc oxide). We have further shown, again by temperature programmed reaction spectroscopy, that the formate species is formed by the activated

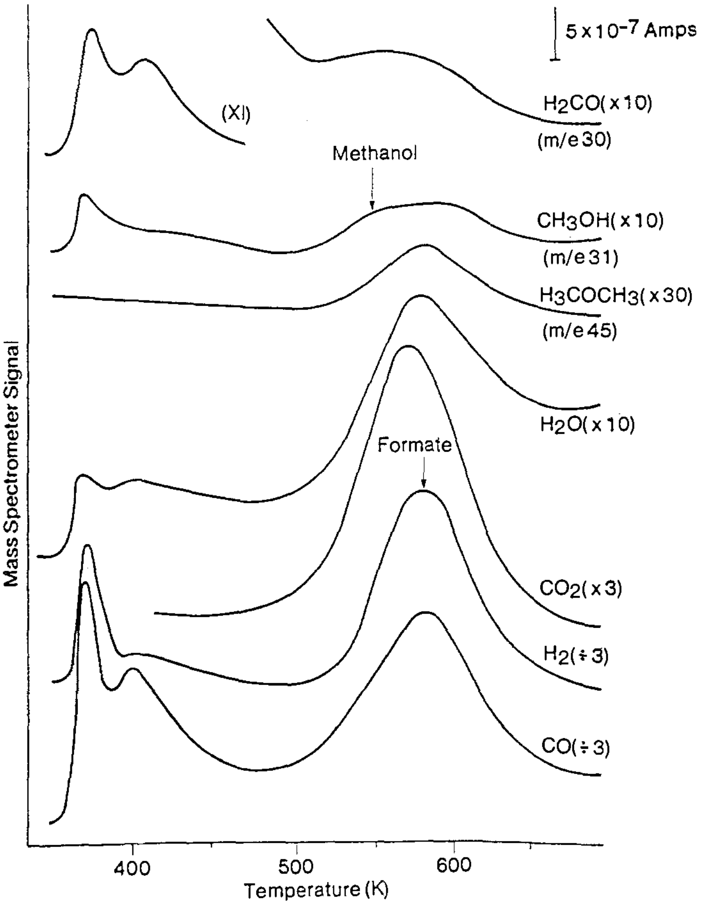

Fig. 1. The formate temperature programmed desorption spectrum from a defect zinc oxide characterised by the coincident desorption of carbon monoxide and hydrogen at 580 K, resulting from room temperature adsorption of formaldehyde.

co-adsorption of carbon dioxide and hydrogen [2]; the role of the carbon dioxide in the carbon monoxide/carbon dioxide/hydrogen feed is to produce defects in the zinc oxide which are the sites for carbon dioxide adsorption and its specific hydrogenation to methanol [4]. Fig. 1 shows a typical formate reactive desorption spectrum in this instance produced by temperature programming after the room temperature adsorption of formaldehyde [2].

The reaction pathway for methanol synthesis on copper alone is similar to, but of lower energy than, that on zinc oxide. Here, again, the formate species is the dominant intermediate identified by the coincident desorption at 440 K, of carbon dioxide and hydrogen, resulting from the room temperature adsorption of formaldehyde or methanol or after the co-adsorption of carbon dioxide and hydrogen at 305 K [5] (fig. 2). The role of the carbon monoxide in the carbon

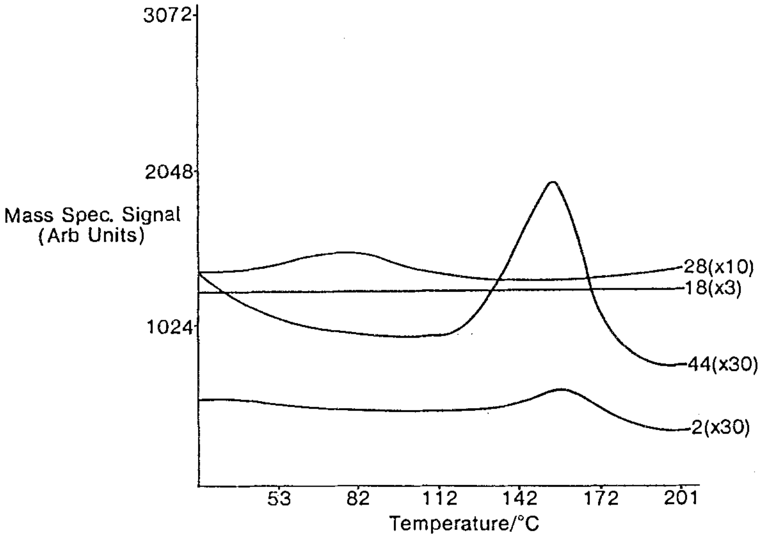

Fig. 2. The formate temperature programmed desorption spectrum from polycrystalline copper characterised by the coincident desorption of carbon dioxide and hydrogen at ~ 440 K, resulting from the co-adsorption of carbon dioxide and hydrogen at 305 K.

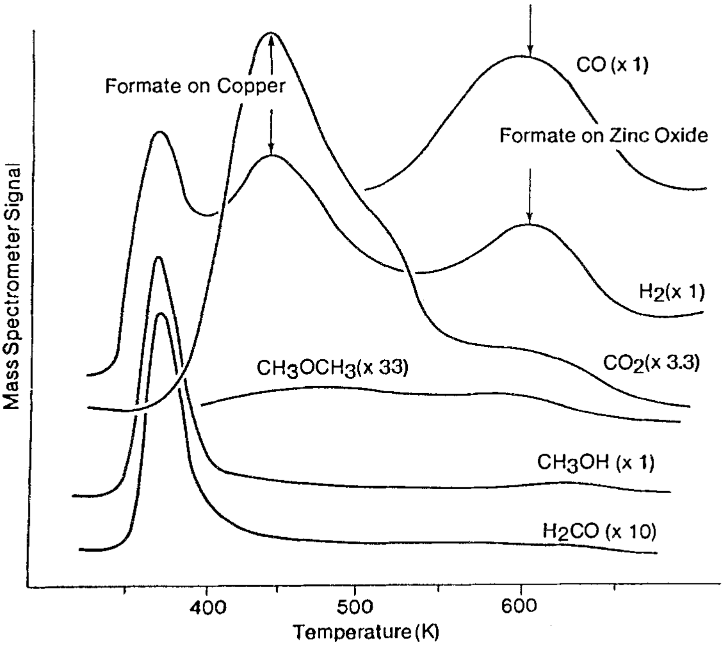

Fig. 3. The formate temperature programmed desorption spectra from the copper and zinc oxide components of a copper/zinc oxide/alumina catalyst, resulting from room temperature methanol adsorption on the catalyst.

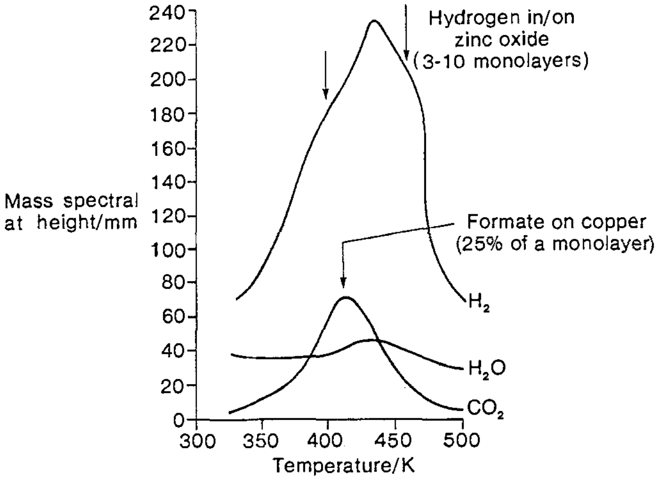

Fig. 4. The temperature programmed desorption spectrum from a copper/zinc oxide/alumina catalyst which had been producing methanol from a carbon dioxide/hydrogen feed. The formate on the copper component of the catalyst is evident by the coincident desorption of carbon dioxide and hydrogen at 440 K, but no formate is observed on the zinc oxide component.

monoxide/carbon dioxide/hydrogen feed is to keep the copper in a highly reduced, more active state [5].

Dosing formaldehyde or methanol on to a reduced copper/zinc oxide/alumina catalyst shows the catalyst to act merely as the sum of its parts [5]. The temperature programmed reaction spectrum obtained on temperature programmed after having dosed methanol onto the reduced catalyst is shown in fig. 3. The coincident desorption of carbon dioxide and hydrogen at 440 K is characteristic of formate decomposition from the copper component, while the coincident desorption of carbon monoxide and hydrogen at 580 K is a finger print of formate having formed on the zinc oxide component of the catalyst.

However when the surface of the catalyst is interrogated after having synthesised methanol from a carbon dioxide/hydrogen stream at 500 K, (cooling to ambient in the mixed gas before temperature programming in helium) only the formate species on copper is observed by the coincident desorption of carbon dioxide and hydrogen (as a shoulder on a larger peak) at 440 K (fig. 4). There is no coincident desorption of carbon monoxide and hydrogen which would be manifestly evident were the zinc oxide component of the catalyst to be producing methanol on its significantly increased defect surface.

In conclusion therefore while the junction effect is an attractive theory which may well account for the activity of copper/thoria catalysts in methanol synthesis whose activity appears to depend on quite different factors, it does not account for the activity of copper/zinc oxide/alumina catalysts in methanol synthesis and therefore unfortunately cannot be described as a unifying theory.

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