Dehydrogenation of methanol to methyl formate: deuterium labeling studies

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The mechanism of methanol dehydrogenation to methyl formate (MF) was studied over a copper–zirconium alloy catalyst sample prepared from an amorphous precursor. As a result of a special activation procedure, a catalyst of stable activity was obtained suitable for mechanistic studies. A mixture of CH_3OD and CD_3OD was used in various ratios to study the isotope distribution of unreacted methanol and product MF. The D/H ratio in the formyl group is similar to that of the feed mixture. Similarly, considerable D/H randomization was found in the methyl group of methyl formate. These results suggest that fast dehydrogenation–hydrogenation equilibrium steps occur prior to the formation/desorption of methyl formate. The mechanism of the reaction can be rationalized assuming an intermediate which we call equilibrated surface formyl/formate group.

Keywords: methanol dehydrogenation; deuterium labeling; copper–zirconium; amorphous alloy; equilibrated surface formyl/formate

1. Introduction

Methyl formate is an important industrial intermediate in formic acid and formamide production [1]. Extensive research is being conducted in many groups using copper based catalysts to improve the activity and selectivity so far obtained [2–5]. The nature of the active site is debated, and the mechanism of the reaction is being questioned [6,7] from many aspects. In this paper we report the results of our mechanistic studies carried out over a copper–zirconium catalyst prepared from an amorphous precursor. This catalyst has previously been studied in the dehydrogenation of 2-propanol [8] and in the reaction of allyl alcohol [9]. The catalyst was characterized in detail [10–12]. When used for the dehydrogenation of methanol this catalyst exhibited stable activity over 150 h with fair selectivity following a special activation procedure [13].

As far as methanol adsorption is considered there are numerous single-crystal studies available [14–18] over various copper and copper oxide surfaces indicating rapid methoxy formation on the metal or metal oxide surface. Methoxy formation was also found by IR studies on the metal [2,19,20] or on the support of supported catalysts [2,21]. These studies all conclude that methoxy formation occurs rapidly via the dissociation of the OH group. This is followed by additional hydrogen dissociation steps to form surface bound CH_2O, CHO and CO species. The adsorption geometry of the resulting species is less understood [16,17]. Unfortunately, there is no unambiguous evidence that the observed or suggested surface species undergo the proposed methyl formate formation mechanisms since they are all based on homo-

geneous reaction pathways. These are the Tischenko [16] and the hemiacetal [17,22,23] type mechanisms (fig. 1). MF formation can also be affected by a transesterification [7] reaction (fig. 1).

The purpose of the present study is to find evidence for any of the above mentioned mechanisms or another relevant mechanism under the particular conditions we applied. An activated, stable catalyst prepared according to our previous study [13] was subjected to a mixture of CD_3OD and CH_3OD in various ratios. The reaction products were analyzed by GC-MS. Conclusions based on their isotope distribution are discussed below.

2. Experimental

A copper–zirconium alloy in the form of a thin, 2 mm wide ribbon with the elemental composition of 41 : 59 at% was prepared by the melt quenching method [24] under argon. A continuous flow-type microreactor was used for catalytic studies. Methanol vapor was introduced into the carrier gas stream via saturation. A carrier gas flow rate of 8 ml helium/min was applied over 50 mg catalyst samples [13]. The alloy catalyst was activated by means of reaction (reduction)/oxidation cycles at 300°C. Stable activity and selectivity were obtained at 240°C reaction temperature. Details are given in ref. [13].

The original Cu(0) surface area of the amorphous alloy ribbons was 0.02 m^2/g measured by N_2O titration [25,26]. After activation, the stabilized catalyst exposed a Cu(0) surface area of 0.66 m^2/g in situ and 2.3 m^2/g, after reduction at 300°C in hydrogen for 30 min.
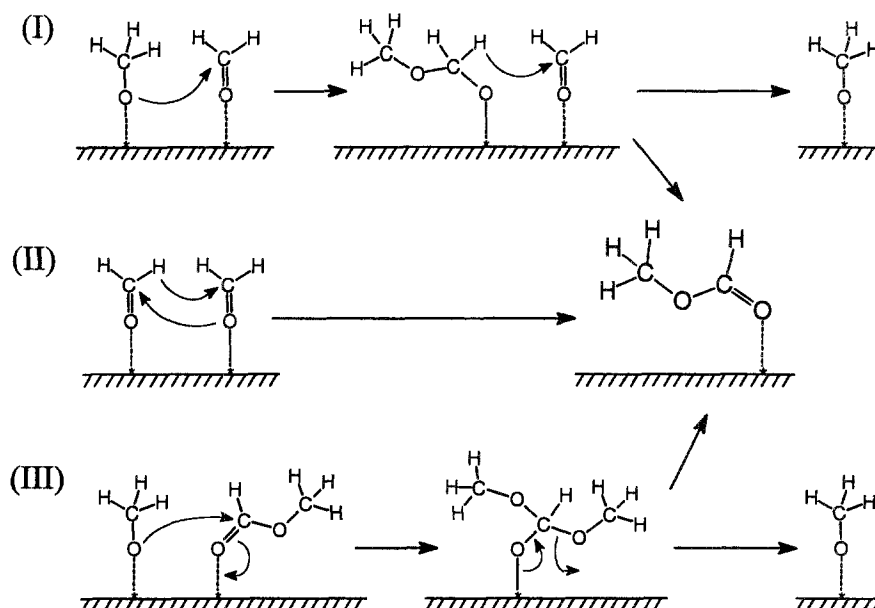
Fig. 1. The formation of methyl formate by the hemiacetal (I), Tischenko-type (II) mechanisms; methyl formate transesterification (III).

Product analysis was carried out with an HP 5890 GC equipped with FID and an HP-1 (0.2 mm × 50 m) column. A pneumatic gas sampling system automatically controlled by a DataApex Chromatography Station for Windows 1.5 was used [13]. Deuterium labeling experiments were carried out on an identical GC connected to an HP 5970 mass selective detector.

Methanol was a Merck product (for spectroscopy). CH_3OD (methanol-d_1, D = 76%) was prepared according to [27]. CD_3OD (methanol-d_4) was purchased from Cambridge Isotope Laboratory (D = 99%). Unlabeled methanol was applied for catalyst activation and the labeled compounds were used in various ratios for the isotope labeling studies.

deuterium labeling studies, since both the activity and the selectivity are fairly stable for long time on stream at this temperature. Our previous studies revealed that the activity of the catalyst can be maintained at 240°C for more than 150 h [13].

The mass spectra of both light methanol and methyl formate exhibit abundance at m/e 31 corresponding to the molecular formula CH_2OH^+. The values for the labeled compounds are 31 and 32 in CH_3OD and 34 in CD_4OD, respectively. When isotopomers are present, abundances appear at m/e 31, 32, 33 and 34, thus only the sum of them will correspond to the total amount of the given isotopically mixed molecules. Isotope distributions, therefore, were calculated by normalizing each of
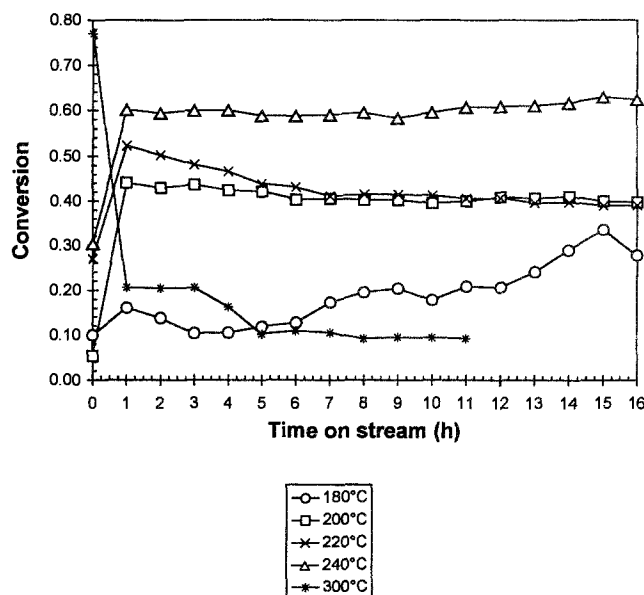
3. Results

The conversion of methanol on an activated Cu–Zr sample is plotted in fig. 2 as a function of time on stream at various temperatures. The initial activity is the highest at 300°C but it decreases rapidly. At 180°C in turn, the lowest initial activity is observed which increases slowly during the reaction. Stable activity is obtained at 240°C after a short induction period.

The methyl formate (MF) selectivity values are plotted in fig. 3 as a function of time on stream at various temperatures. The marked change in selectivity at the beginning of the reaction is due to the formation of the active surface rapidly generated by the reaction itself [13]. During this initial period the highest selectivity is observed at 180°C. Stable selectivities are obtained at 220 and 240°C. Although the highest stable selectivity of MF is obtained at 220°C, the activity of the catalyst is slowly decreasing (fig. 2). Therefore, it seemed to be a good compromise to use the catalyst at 240°C for the

Fig. 2. Methanol conversion as a function of time on stream at various temperatures over an activated Cu–Zr catalyst sample.
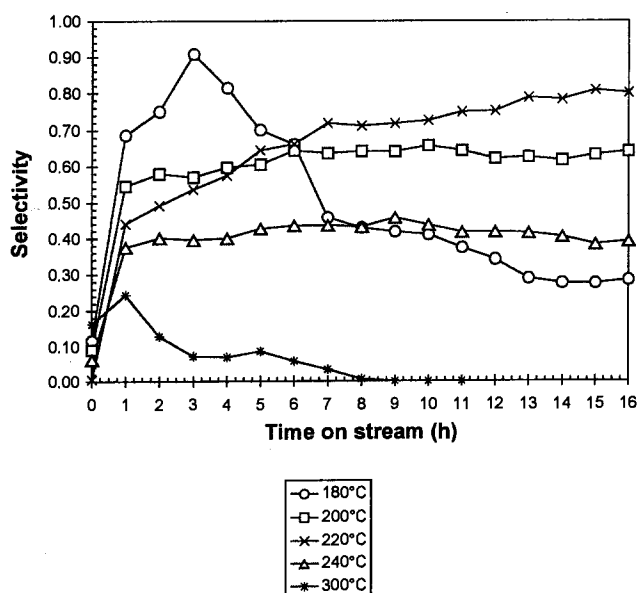
Fig. 3. Methyl formate selectivity data as a function of time on stream at various temperatures over the same catalyst sample.

these abundances with this sum. This procedure was carried out for m/e 15, 16, 17 and 18 for the methyl fragments, and m/e 60, 61, 62, 63 and 64 for MF. In addition, m/e 29 was also monitored since it corresponds to the formyl group in MF. Both background correction and overlapping fragmentation patterns were taken into account. In the latter case corrections were made on the basis of the fragmentation patterns of the pure starting compounds.

Fig. 4 displays the normalized abundances of the methyl fragment of methanol leaving the catalyst as a function of methanol-d_4 added to CH_3OD in the saturator. The relative amount of CH_3 groups (corresponding to CH_3^+ fragments) is decreasing, whereas CH_2D and CHD_2 intensities exhibit sharp increase at the first ali-

quot of CD_3OD. Additional aliquots result in a moderate decrease in their normalized intensity, but their ratio remains approximately the same. CD_3 exhibits a continuously increasing intensity in recovered methanol.

The amount of CH_3 fragments in recovered methanol is higher than that of CH_3 in the product MF shown in fig. 5. Although the tendency displayed is similar to approximately the same values as in the case of methanol, the relative abundances of CH_2D and CHD_2 exhibit saturation throughout the composition investigated. The normalized intensities of the molecular ions of MF (AMU 60, 61, 62, 63, 64) are plotted in fig. 6. According to expectations, the same trends are seen. However, molecules containing three or four deuteriums (AMU 63 and 64, Δ and $*$, respectively) show increasing ratios in fig. 6. It is obvious that AMU 64 corresponds to $DCOOCD_3$. Since the change in AMU 63 intensity is identical with that of AMU 18 (CD_3) in MF (fig. 5) AMU 63, consequently, corresponds to $HCOOCD_3$.

4. Discussion

A common feature of all mechanisms reported in the literature [7,16,17,22,23] is that, whenever methanol is adsorbed, a methoxy group is rapidly formed through the dissociation of the O–H bond. They suggest that the resulting hydrogen is considered to leave the surface and, therefore, it does not play any role during the following reaction steps. These studies are also common in the assumption that the methoxy group keeps its integrity without excessive H–D exchange (fig. 1). Once surface bound formaldehyde is formed [16], no further dissociation occurs and the reaction proceeds directly to form MF. Neither surface bound formyl, nor adsorbed CO is considered to take part in the reaction. If these mechanisms were fully applicable, keeping the assump-
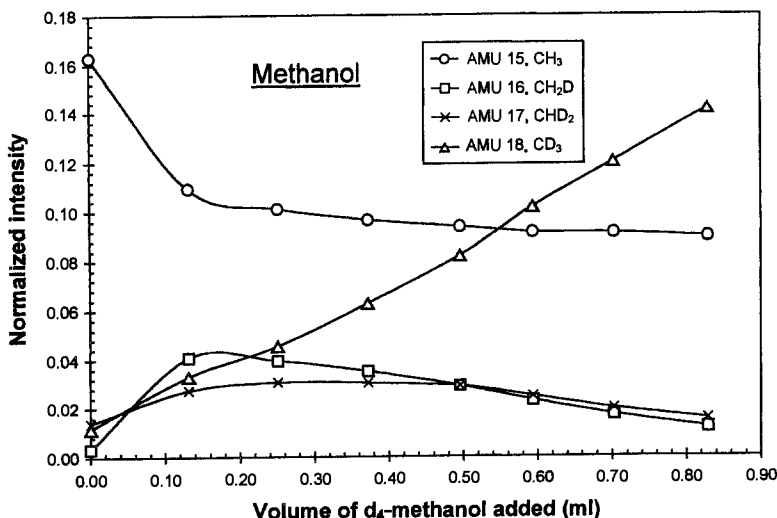

Fig. 4. Variation of normalized CH_xD_{3-x} fragment intensities in recovered methanol as a function of the volume of methanol-d_4 added to methanol-d_1 in the saturator.
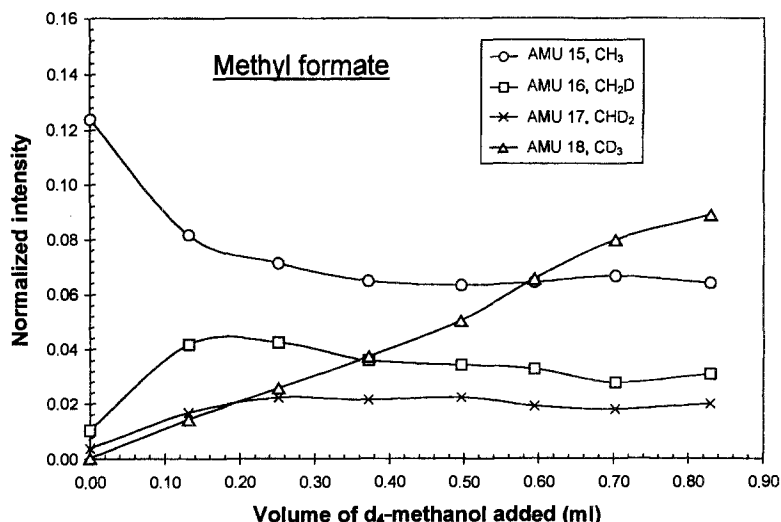
Fig. 5. Variation of normalized CH_xD_{3-x} fragment intensities in the product methyl formate as a function of the volume of methanol-d_4 added to methanol-d_1 in the saturator.

tion that hydrogen desorbs rapidly, the reaction of pure CH_3OD would not produce deuterium-containing MF.

If the desorption of alcoholic deuterium, however, is slower than the randomization reaction the dehydrogenation of methanol should produce deuterated MF. Indeed, according to our measurements, both carbon atoms in the MF molecule accommodate deuterium(s), thus H–D exchange must take place prior to these steps, prior to the desorption of MF. Since MF was shown to have low heat of adsorption [28] it is reasonable to assume that once formed it leaves the surface without participating in further isotope exchange. The exchange appears even less likely if one considers the surface geometry of MF since the formyl hydrogen points away from the surface.

Theoretically, when in the kinetic region, all methanol molecules can undergo adsorption on the catalyst surface. Some of them desorb unchanged, others dissociate forming surface methoxy and other surface bound species. Since carbon atoms in the MF molecule are of different oxidation states (fig. 1) one can assume different reaction paths operating for these components. The oxidation of methoxy proceeds with stepwise hydrogen losses producing surface bound formaldehyde (CH_2O), formyl (CHO) and CO species. Some studies report that CO can be further oxidized producing CO_2 or formate [29,30]. In our experiments no evidence was found for formic acid formation. We did observe, however, CO_2 among the products but only during the short induction periods during which the catalysts reached their stable activity and selectivity [13].

Therefore, various surface bound species ranging from methanol to CO as well as hydrogen are assumed
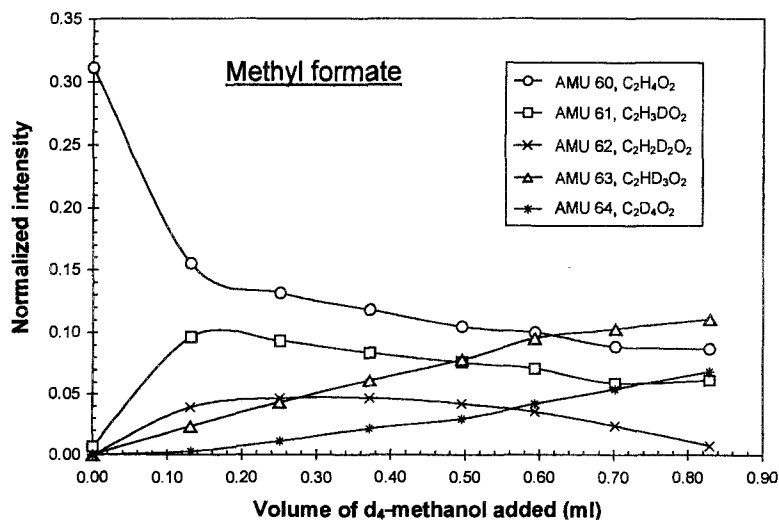

Fig. 6. Variation of normalized molecular ion intensities in the product methyl formate as a function of the volume of methanol-d_4 added to methanol-d_1 in the saturator.
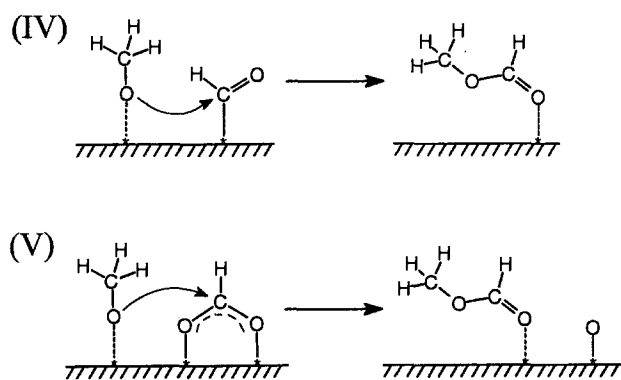
(IV)

(V)

Fig. 7. The formation of methyl formate through equilibrated surface formyl (IV) and bidentate surface formate (V) surface intermediates containing one hydrogen atom.

to populate the surface. The step-wise hydrogen dissociation equilibria, rapidly established between various surface species, can be monitored using deuterated methanol. Since the OH and CH_3 groups contain different numbers of hydrogen atoms, there is an excellent opportunity to modify the isotope ratio by changing the composition of the reacting labeled molecules. Our starting point is that, if the alcoholic hydrogen leaves the surface before the randomization, then it has no effect on the deuterium distribution of MF. If it is not the case, however, alcoholic hydrogen will also affect isotope distribution.

Unfortunately, in our catalytic system we cannot distinguish between some surface species. Rather, they can all be treated as one reactive intermediate. As it will be described later, this intermediate very probably contains one hydrogen on the precursor of the formyl carbon. It is also reasonable to assume that it has the same oxidation state as MF, thus it might be its immediate ancestor. This emerging intermediate, therefore, can be regarded

as an equilibrated surface formyl (ESF) group. Furthermore, on oxide surfaces, bidentate formate species have been reported in methanol synthesis [31,32]. The existence of such an intermediate is also possible, and it is also common with ESF in its most important feature, i.e., it also contains one hydrogen atom. These surface species react with a methoxy group producing MF (fig. 7).

Bowker et al. measured total isotope scrambling above 470 K over oxygenated copper surface [33]. Since our experimental observations indicate complete D/H randomization, ESF should exhibit the same D/H ratio as introduced with the reactants. Fig. 8 shows the D/H ratio in the formyl group of MF as a function of the amount of methanol-d_4 introduced. The dashed line shows the calculated D/H ratio based on the D/H ratio in the feed. Calculations were done by taking into account the fraction of methanol converted to ESF to make MF. Theoretically, it means that we remove all hydrogens from the adsorbed methanol molecule, randomize them and simply build MF molecules again. Except for the starting region, experimental data points (squares) fit well this calculated (dashed) line.

On the basis of the above discussion we can state that the D/H ratio in the formyl group of the MF molecule corresponds to the D/H ratio in the reactant mixture, thus complete mixing occurs prior to MF desorption. In other words, the recombination of hydrogen atoms to form hydrogen molecules is considerably slower than the dissociation equilibria of CH_xO species. This is also supported by the fact that methyl formate formation is strongly inhibited by hydrogen [13].

Let us investigate the possibility we cited previously that hydrogen leaves the surface without its involvement in any reaction. This should be the case in a Tischenko type reaction and in a transformation with the involvement of hemiacetal [16]. In both cases methoxy or form-
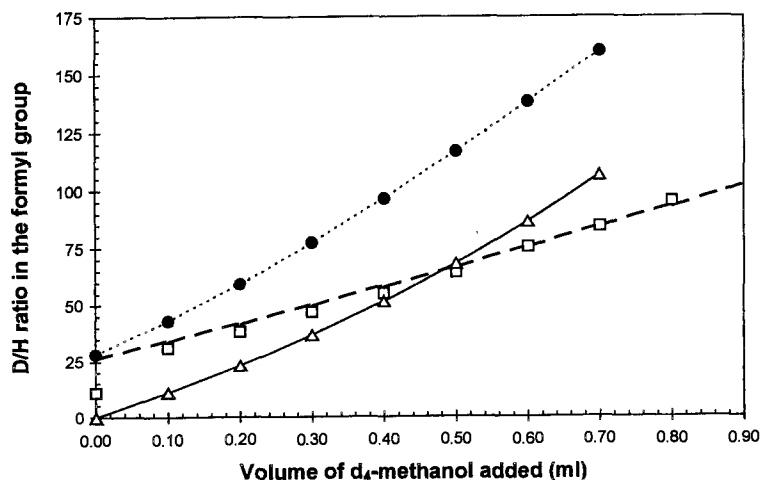

Fig. 8. D/H ratio in the formyl group of product methyl formate as a function of the volume of methanol-d_4 added to methanol-d_1 in the saturator. (□) Experimental points, (———) line calculated by using ESF as an intermediate, (△) and (———) show calculated results using the Tischenko-type mechanism, (· · ·) and (●) correspond to the Tischenko-type mechanism modified by a kinetic isotope effect.

aldehyde is formed in fast reaction steps. According to this, two hydrogen isotopes produced during the formation of formaldehyde or methoxy desorb as a hydrogen molecule liberating surface sites for further dissociation. For this calculation, the same fraction of methanol to be converted to MF is used but only the methoxy group is considered. The calculated D/H ratio is also plotted in fig. 8 (solid line). Evidently, experimental points do not support this assumption.

One should also explain the apparent lack of kinetic isotope effect. Theoretically, C–H dissociation is expected to be faster than C–D dissociation. Therefore, without the involvement of randomization the D/H ratio in the surface species should be higher than that in the original mixture. Since both the Tischenko and hemiacetal type mechanisms are based on (lighter) hydride anion transfer to form formyl carbon, a further deuterium enrichment on the formyl carbon should be observed. According to figs. 6 and 8 no such effect can be seen. Furthermore, it must be emphasized that deuterium enrichment on the formyl carbon should be found even when completely randomized surface species are transformed either according to the Tischenko mechanism or via the hemiacetal. Again, this is not the case. (See dotted line in fig. 8. An isotope effect $k_H/k_D = 2.1$ was used in the calculations [7].)

If MF formation involves a surface species possessing a single hydrogen, as it is suggested here (ESF), the transformation becomes very simple. In this case the oxidation state of the surface intermediate and that of the product are the same. As a result, no further hydrogen transfer is involved and, consequently, kinetic isotope effect is eliminated. This finding also puts emphasis on the role of equilibria between surface species, thus the reaction can be formalized by introducing ESF as a possible reaction intermediate which contains one hydrogen atom.

Finally Wainwright's transesterification mechanism [7] (fig. 1, reaction III) should also be discussed. This mechanism, however, is not an independent reaction route, since it assumes the secondary transformation of MF already formed. It is obvious that there is no hydrogen transfer and there is no change in the oxidation number of the reaction partners. The hydrogen (deuterium) of the formyl carbon, therefore, remains intact during this process. So the observed D/H ratio on the formyl group of MF is established prior to MF formation, i.e., ESF should exhibit exactly the same D/H ratio as introduced into the reactor. It follows that a possible transesterification does not change the deuterium distribution of the product MF.

Further experiments as well as computer modeling are under way by using other labeled compounds and various copper catalysts to trace reaction intermediates in order to exactly formulate a mechanism, involving the H–D exchange reported above.

5. Conclusion

The isotope distribution of product methyl formate formed in the dehydrogenation of labeled methanols suggests that the actual mechanism of MF formation on copper should involve dehydrogenation–hydrogenation steps prior to the formation/desorption of MF. The observed D/H distribution can be explained by assuming a surface intermediate containing one hydrogen atom, which is in a rapid H–D exchange equilibrium. Therefore, equilibrated surface formyl (formate) group is introduced to denote a reaction intermediate. This rules out both the Tischenko mechanism and the transformation with the involvement of a hemiacetal intermediate.

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