CO Hydrogenation in the Presence of Added Oxygen: New Evidence on the Reaction Mechanism

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The title reaction produces significant increases in the formation of C_2 but not C_1 or C_3 oxygenates which provide mechanistic evidence concerning carbon–carbon bond formation.

CO hydrogenation to produce hydrocarbons and oxygenates remains a well studied and important reaction. In addition the mechanism by which carbon–carbon bond formation occurs continues to be an area of controversy. Proposals that have received some experimental support to-date include the involvement of surface carbide[1] (generated *via* dissociative adsorption of CO), surface methylene carbene,[2] and the involvement of oxygenated intermediates, *e.g.* hydroxy carbene.[3] Recently Brady and Pettit[4] have reported a study of the reaction of CH_2N_2 with H_2 and with $CO–H_2$ over a range of catalysts and concluded that the results support the involvement of a surface methylene carbene intermediate in carbon–carbon bond formation. However, as has been indicated by Henrici-Olivé and Olivé[5] these results cannot be cited as evidence to preclude a mechanism in which oxygenated surface spècies are dominant. Oxygenates as well as hydrocarbons are generally considered to be primary products of the reaction but the mechanistic proposals based on carbide or methylene carbene can only account for oxygenates *via* CO insertion,[6] which is also a central feature of the proposals of Henrici-Olivé and Olivé. We have recently[7] used oxygen as an informative probe in the study of carbon–carbon bond formation in the zeolite catalysed methanol to gasoline process and we have now utilized this approach to provide new information for carbon–carbon bond formation in CO hydrogenation using a cobalt manganese oxide catalyst.[8] In this communication we comment on the nature of the C_1 intermediates and the possible mechanistic role of water. Furthermore we present clear evidence against a number of previous mechanistic proposals for this catalyst.

Co/Mn 1:1 catalyst (0.2 g), prepared as previously described,[8] was studied for CO hydrogenation in a glass microreactor. In a typical experiment CO/H_2 (1:1) was reacted over the catalyst [220 °C, gas hourly space velocity (GHSV) = 455 h^{-1}] for 24 h in which time the product distribution stabilised as determined from g.c. analysis of the reactor effluent. Following this a small flow of a N_2/O_2 mixture (0.4 mole % O_2) was added to the CO/H_2 so that the reactant ratio was $CO:H_2:O_2$ 1359:1351:1 (*i.e.* 0.037 mole % O_2) and the product distribution was again monitored. The results, shown in Figure 1, demonstrate that on addition of the oxygen the C_2 oxygenates, ethanal and ethanol markedly increase by factors of *ca.* 5 and 4, respectively, before declining. Significantly, no enhancement in methanol or CO_2 selectivity was observed nor in the other C_1 oxygenates, formaldehyde and formic acid. Prior to O_2 co-feeding CO conversion was *ca.* 5%, and during O_2 co-feeding the catalyst activity was observed to decline slowly. On removal of the oxygen from the reactant gases the product selectively returned to that observed prior to O_2 addition but with decreased activity. Re-reduction of the catalyst with a hydrogen atmosphere returned the performance to that observed for a fresh catalyst. Experiments with

higher O_2 concentrations of *ca.* 0.08 and 0.5 mole % gave similar results.

Addition of trace levels of oxygen leads to a significant perturbation of the system which we consider to have considerable mechanistic significance. The role of oxygen is most likely to be to (i) bring about oxidative cleavage of a C_2 surface intermediate or (ii) remove adsorbed H as H_2O with change of oxidation state of the metal. Detailed ^{18}O tracer studies would help to distinguish between these possibilities. However, on the basis of the results it is considered that possibility (i) is mitigated against because oxidative cleavage by O_2 would not be expected to be significant for just a C_2 species and an increase in C_1 and C_3 oxygenates would also have been expected which was not observed. The removal of adsorbed hydrogen as H_2O seems an attractive possibility because it would result in C_2 desorption at a higher oxidation state (by the H_2O produced). Furthermore, since the increase in C_2 oxygenates is accompanied by a corresponding decrease in both alkane and alkene selectivities it follows that the latter could be formed *via* reduction by adsorbed hydrogen (now depleted) of the same C_2 intermediate which gives rise to the
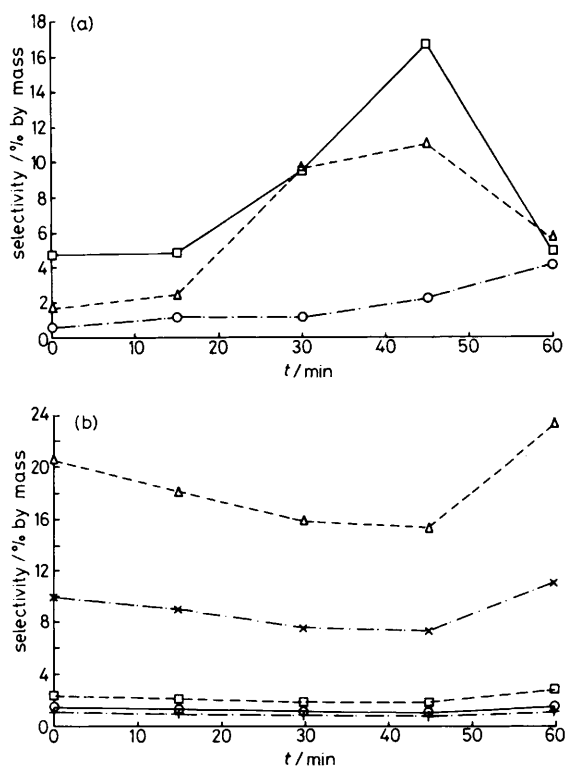

Figure 1. Influence of O_2 cofeeding on product selectivity during CO hydrogenation. (a) Oxygenate selectivity □ ethanal, △ ethanol, ○ propanol; (b) hydrocarbon selectivity △ methane, □ ethene, ○ ethane, × propene, + propane.
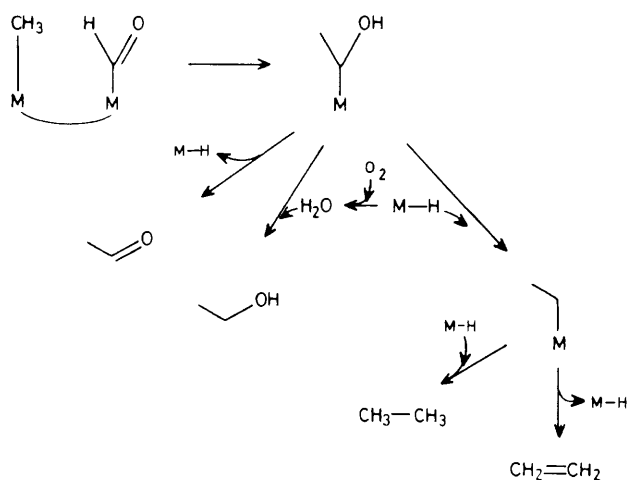
Figure 2. Scheme for product formation.

ethanol and ethanal. Similarly the drop in methane selectivity would imply that it is formed *via* hydride reduction of a surface methyl. Separate experiments with ethanal/H_2 and ethanol/H_2 mixtures showed that, under comparable reaction conditions, both were active species for chain growth and also were interconvertible on this catalyst.

The results of the study provide evidence against a number of previous proposals operating on this catalyst. In particular it is apparent that carbon–carbon bond formation is unlikely to occur at a single metal site, *e.g. via* CO insertion,[6] since O_2 would also be expected to be reactive and this would lead to the formation of enhanced C_1 oxygenates with chain growth termination and this is not observed. Moreover the proposals of Brady and Pettit[4] and Biloen and Sachtler,[2] which involve reaction between a surface methyl and surface methylene carbon, are also not consistent with the perturbation caused by oxygen addition. Both C_1 intermediates (surface methylene and methyl) could be expected to be highly reactive towards oxygen and lead to the formation of C_1 oxygenates in addition to terminating chain growth which is not observed. It is also apparent that the proposal that surface carbide[1] is a key

reactive intermediate must also be discounted since no increase in CO_2 is observed with O_2 addition.

We consider that these results for this particular catalyst point towards carbon–carbon bond formation involving two intimately connected C_1 intermediates involving two adjacent metal sites such that one of them is fairly inert to O_2 (high C_1 oxidation state) and that the rate of reaction with the other (lower oxidation state) is faster than with oxygen. We propose the most likely structure for the precursor to the C_2 oxygenates to be an α-hydroxylated metal alkyl which would normally be reduced to a surface ethyl group and desorb as ethene or ethane. Such an intermediate could arise *via* attack by either a metal carbene or methyl on a surface formyl group which we consider to be an attractive electrophilic centre for chain propagation (see Figure 2). This is consistent with recent *X*-ray photoelectron spectroscopic (x.p.s.) results we have obtained for CO/H_2 adsorption on a polycrystalline iron surface in which evidence was given for formation of a 'C_2H_xO' species.[9]

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