

Heterogeneous Catalytic Insertion Mechanism of the C₂ Oxygenate Formation

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Experiments on the mechanism of formation of ethanol and acetaldehyde from CO-H₂ (2 : 1), performed by adding methylene chloride to the mixture, show that C₂ oxygenate formation proceeds *via* CO insertion.

Formation of ethanol, acetaldehyde, and other oxygen containing molecules ('oxygenates') from 'syngas' (CO-H₂) catalysed heterogeneously is a commercially attractive reaction^{1,2} for which a number of fundamental questions concerning the mechanism remain open. One question is whether or not the C₂ oxygenates are formed by a CO insertion reaction, as the C₃ and higher oxygenates^{3,4} most likely are. Orita *et al.*⁵ have proved that C₂ oxygenates are formed in two steps, with the first step leading to the methyl group using the carbon from the reservoir resulting from CO dissociation. However, it is not evident from the data that the second step involves only CO insertion. Moreover, Takeuchi and Katzer,⁶ using double labelling of CO, discovered that processes other than a simple insertion (for example those involving dissociation of CO) could be fully or partially responsible for C₂ oxygenate formation. Additional information on the possible CO insertion in C₂ oxygenate formation is thus still desirable.

It would also be interesting to explain why Pd and Rh differ so much in their propensities to form the C₂ oxygenates. A rhodium catalyst can be prepared in such a way that of all the oxygenates it selectively makes either methanol^{7,8} or ethanol.^{9,10} On the other hand there are no reports on Pd catalysts producing ethanol although methanol formation can be very selective.^{11,12} The reason for this is not fully known and we addressed ourselves to this problem.

In this paper 'syngas' reactions were followed at one temperature (473 K) and standard conditions (1 bar pressure; continuous flow, 12 ml/min; H₂ : CO, 2 : 1). The products were analysed by g.c. When the reaction of the 'syngas' mixture had reached its steady state, CH₂Cl₂ was added at its saturation pressure (*ca.* 160 Torr) at 273 K. Catalysts were prepared by impregnating the supports (V₂O₅, La₂O₃, *etc.*) with either PdCl₂ or RhCl₃, loading 4.5% wt. Catalysts were dried (16 h; 383 K in air) and reduced overnight, the Pd catalysts at 473 K and the Rh catalysts at 673 K. The results are shown in Figure 1.

The main points arising from the data in Figure 1 are as follows. (i) Pd, which is a poor catalyst for MeOH production in combination with V₂O₅ and shows no production of C₂ oxygenates, starts to produce C₂ oxygenates when CH₂Cl₂ is added. (ii) The change caused by CH₂Cl₂ addition in the product pattern of Rh is much less pronounced. (iii) Methanol production is also enhanced after CH₂Cl₂ addition. This effect is only temporary, for after 2 h the production of MeOH has reached the same value as before addition.

It should be noted that those Pd catalysts which show a much higher activity and selectivity for MeOH, such as Pd/La₂O₃, also show the same behaviour as Pd/V₂O₅ catalysts.

We have also obtained results with MeCl as an additive. The species formed from MeCl (methyl radicals most likely) appeared to increase the rate of production of MeOH but not that of EtOH. With regard to the interpretation of these results, we note that it is known that the C-Cl bond of CH₂Cl₂ is easily broken^{13,14} and that this leads to an enhancement of production of CH₄ and other hydrocarbons. This has been explained by the enhancement of the concentration of CH_x species on the surface by the external supply.

On the other hand, a possible localized formation of PdCl_x species would not increase the rate of CO dissociation, since

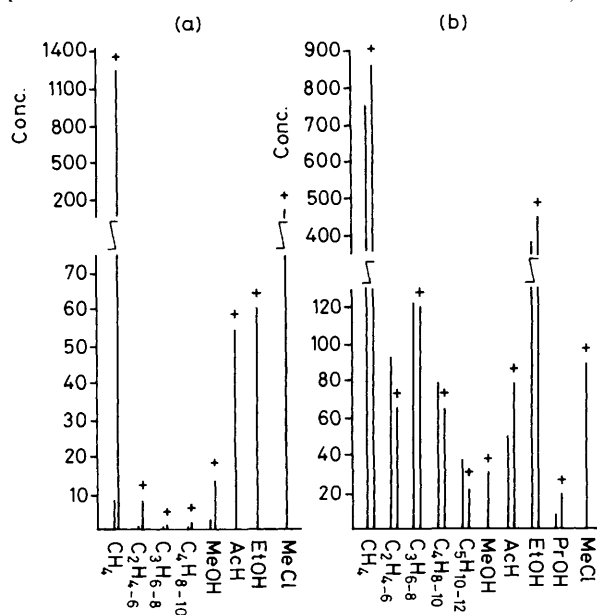


Figure 1. Reaction of 'syngas' (CO : H₂, 2 : 1) into hydrocarbons and oxygenates: representative results for Pd and Rh metals on the same support (V₂O₅). Bars indicate the concentrations (in arbitrary units, proportional to molar concentrations) of the respective products, without or with (+) the methylene chloride as an additive, upon reaction at 1 bar, 473 K. (a) Pd/V₂O₅; CO conversion 0.02%; S(MeOH) 27%; (b) Rh/V₂O₅; CO conversion 4.0%; S(C₂ oxygenates) 29%.

the methanation activity of the Pd catalysts increases steadily in the course of the reduction of PdCl₂.^{15,16} (*N.b.* In compliance with all modern literature we assumed above that methanation and hydrocarbon formation can proceed *via* CO dissociation). Conclusions from the data are then straightforward, as follows. (i) Pd can form C₂ oxygenates when CH_x groups are supplied by sources other than CO dissociation which is a difficult step on Pd metal. (ii) Since CO dissociation and the resulting formation of CH_x is not expected to play a role on palladium in the transition from CH_x to EtOH (and similar), the data presented strongly suggest that the C₂ oxygenates are formed by CO insertion. (iii) On Rh, where the supply of CH_x groups from CO is probably sufficient (Rh dissociates the C–O bond better than Pd), the enhancement of the C₂ oxygenate production by CH₂Cl₂ is only marginal. (iv) It is not the lack of the propensity of Pd to catalyse insertion which causes the low activity in the formation of C₂ oxygenates, but it is rather the insufficient supply of CH_x groups on Pd which is responsible.

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