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LETTERS TO THE EDITORS

The Formation of C_2-Oxygenates from Synthesis Gas over Oxide-Supported Rhodium

The problem of selectivity in synthesis gas reactions and in particular the problem of how to maximize the selectivity in oxygenates has attracted much attention in recent years (*1*). Several models have been suggested to explain why with certain supports or promoters the selectivity of Rh for oxygenates is high:

(a) A support or a promoter influences the electronic structure of the metal (*2*).

(b) The support oxygen can be activated to take part in the formation of oxygenates, outside the metal surface (*3*).

(c) The promoter or the support material stabilizes the presence of Rh^{n+} centers and the reaction is "bifunctional." Rh^0 produces CH_x units and Rh^{n+} are the sites of CO insertion into these units (*4, 5*).

(d) The promoter placed on the metal surface accelerates CO dissociation and CO insertion (*6, 7*) whereby the Rh^{n+} centres play no role.

Our own results, to which we refer below, and some other recent data in the literature make it possible to reject some of the ideas mentioned above and to draw up a unifying model for the formation of C_2-oxygenates from synthesis gas. The starting point is the recent note published by Sachtler *et al.* in this journal (*7*).

Idea (a) above is not considered. Theoretically it is not well defendable (*8*) and the particles of Rh are sometimes so large (5–10 nm) that speculations on such an effect are not relevant at all.

Parts of other theories can be integrated into one model, schematically shown in Fig. 1. Figure 1 presents an "artist's view" of the following. Various forms of adsorbed CO, in single or multiple coordination, populate the Rh surface; CO can switch between these forms and competes for sites with other species including adsorbed hydrogen. When CO is activated by the cation of the promoter (Fig. 1, left) it can switch over into a chemisorbed species which has two more or less equivalent oxygens (Fig. 1, middle). In one of these forms, an attachment of a CH_x group (insertion) takes place. It is not known whether a single or multiple (*7*) bound CO is involved in these steps. After insertion, hydrogenation follows into CH_3CHO (indicated in Fig. 1) or C_2H_5OH. As already mentioned above, Rh^{n+} ions stabilize formyl groups and are beneficial for CH_3OH formation (Fig. 1, right).

Experimental support exists for all the intermediates and reaction steps shown in Fig. 1, and it is discussed below.

It has been shown that CH_2 ex CH_2Cl_2 (but not CH_3 ex CH_3Cl) can be converted into CH_3CH_2OH by adding CH_2Cl_2 to a $CO:H_2$ mixture (*9*). The formation of C_2-oxygenates by CO insertion into CH_x units has been further proven by isotopic labeling. Isotopic labeling also revealed (*10, 11*) that the oxygen of the support or promoter participates in the intermediates of the reaction. However, a certain caution is necessary with this information. A fast exchange of "O" between other intermediates and/or products and the solid oxides would serve the same purpose as direct participation of oxide in the formation of crucial intermediates. It would, however, be highly incidental that the degree of exchange of oxygen reaches almost exactly the value expected, when acetates operate as intermediates. Therefore, acetate formation, with participation of support oxygen, seems to be the better explanation of the data available and such participation of oxide oxygen is also assumed in the present model (Fig. 1).

It has also been shown that support mate-

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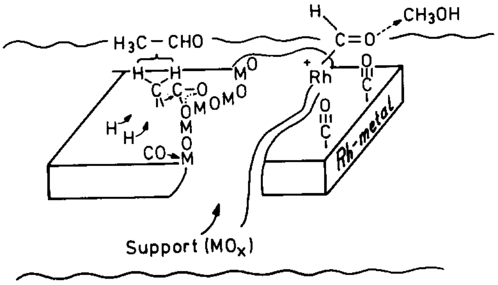

FIG. 1. Schematic model of the formation of C_2-oxygenates and methanol on the surface of a rhodium catalyst.

rial, which reaches the metal surface, either during high-temperature reduction (encapsulation) or during other stages of preparation, can play the role of the promoter of insertion (or other steps) in the sense of Fig. 1. Our suggestion is that also Rh_2O_3 plays this role (*12–14*).

The role of Rh^{n+} needs one more comment. The following two suggestions can be found in the literature: (i) Rh^{n+} (or ions of other metals) form the centers of CH_3OH formation (*4, 8*) and (ii) Rh^{n+} are centers of formation of higher oxygenates, whereby the mechanism is "bifunctional": metal surface supplies CH_x groups and recombination of these groups with CO takes place on Rh^{n+} (*4, 5*).

Our recent results (*15*) confirm suggestion (i) but are at variance with suggestion (ii). Thus it appears that the concentration of Rh^{n+} is sympathetically correlated with the activity in CH_3OH formation, but the correlation with higher oxygenates is antipathic and the most active and selective catalysts in C_2-oxygenate formation contain no extractable (Rh^{n+}) rhodium (*12*). However, the findings just mentioned do not exclude that Rh^{n+} on the metal can fulfill the role of the promoter in CO activation, in the sense of the theory in Ref. (*7*) and in compliance with the experimental data in Refs. (*13, 16*).

An equally important function of the oxide is to block the metallic (Rh) surface and to suppress the production of CH_x units through CO dissociation to an optimal level. Catalysts with optimal selectivity showed indeed a low CO and H_2 aerial adsorption (*12, 15*).

An inspection of the data in the references quoted above should convince the reader that the model [being a combination of ideas expressed by others, mainly in Refs. (*7, 10*)] presented in Fig. 1 is very well supported in all details discussed.

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