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The Formation of C_2-Oxygenates from Synthesis Gas over Oxide-Supported Rhodium. Reply to van der Lee and Ponec

We are glad to note that the views expressed by van der Lee and Ponec (*1*) are very similar to our own. In this letter we briefly discuss two points where some differences in interpretation exist: (1) the nature of positive metal ions on metal surfaces, and (2) the role of surface carboxylates in aldehyde formation.

(1) A rhodium surface, which is partially covered with Mn^{2+} and O^{2-} ions, is superior to rhodium alone in the yield of oxygenates. Two models have been proposed to rationalize this observation: (a) Positive Mn ions interact with the O atom of CO which is coadsorbed on an adjacent site, and this interaction promotes CO cleavage and/or migratory insertion into metal alkyl bonds (*2*). (b) The presence of positive Mn ions stabilizes positive Rh ions, which have increased catalytic activity (*3–5*).

We believe that these models have strong commonality. The large difference between the work function of Rh (4.98 eV) and the second ionization potential of Mn (15.64 eV) shows that a neutral Rh surface sparsely covered with Mn^{2+} ions would be unstable. In reality the positive charge will be distributed over adsorbing and adsorbed metal atoms. This also holds for other "strong metal–support interaction" (SMSI) systems because the negative charge of O^{2-} ions is compensated by a positive charge which is spread over metal atoms in its immediate vicinity, including the promoting and the adsorbing metal element. This conclusion is in line with experience from organometallic clusters containing metal–metal bonds, where various lines of physical evidence indicate that charge is delocalized over the metal system.

(2) van der Lee and Ponec (*1*) assume that acetaldehyde is formed via acetyl and acetate intermediates. That is, the surface acetyl group reacts with surface oxygen to form surface-bound acetate, which is subsequently reduced by hydrogen to the aldehyde. We agree that interconversion of acyl and carboxyl groups can explain the oxygen scrambling reported by Orita *et al.* (*6*) but we hesitate to accept that the carboxylate is a necessary intermediate in the formation of aldehydes. Aldehyde formation by CO insertion followed by hydrogen addition is a step common to Fischer–Tropsch synthesis (*6, 7*) and hydroformylation. Both reactions are catalyzed by the same rhodium catalysts (*8–10*). No oxygen isotope scrambling has, to our knowledge, ever been reported for supported hydroformylation catalysts. The fact that the best hydroformylation catalysts are unsupported Rh complexes proves that carboxylate formation is not a necessary step in this process. Under Fischer–Tropsch conditions, unlike hydroformylation, H_2O vapor and adsorbed OH groups are abundantly present and provide vehicles for oxygen exchange between acyl groups and oxide surfaces (*11, 12*). Orita *et al.* (*6*) report that the extent of this exchange is different for promoted and unpromoted Rh samples. While we agree that the interconversion of surface acyl and carboxylate may be facile, we prefer the view that the hydrogenation of surface acyl is the predominant route to aldehyde products.

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