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Promoter Action in Fischer–Tropsch Catalysis

One of the early discoveries in Fischer–Tropsch catalysis was that the addition of a small amount of a metal ion, which is not reduced to the zero-valent state under prevailing reaction conditions, has a significant effect on the activity and selectivity of the catalyst. Generally this promoter was an alkali metal ion (*1*). More recently it was discovered that early transition metal ions exert a similar influence on CO hydrogenation over supported Rh (*2–4*). For example, manganese, which is present as Mn^{2+}, increases the catalytic activity of silica-supported rhodium by roughly one order of magnitude, without impairing selectivity to convert synthesis gas into oxygenates, i.e., alcohols and aldehydes (*3*). X-Ray line broadening shows that this activity increase is not caused by an enhanced dispersion of Rh; chemisorption of H_2 or CO and the intensity of ir bands due to adsorbed CO are actually found to be lower for the promoted than the unpromoted catalyst (*4*).

In this communication we discuss a model for these promoter effects based on the activation of CO by interaction of a promoter ion with the oxygen atom of a chemisorbed carbonyl. A schematic representation of this type of bonding is outlined in Fig. 1, where the CO is carbon bonded to two or more surface metal atoms, M, and the promoter, P, is bonded to oxygen. B is an anion which compensates the charge of P.

Precedence for carbon and oxygen-bonded carbon monoxide may be found in many structurally characterized organometallic compounds (*5, 6*). In these compounds a formally positive metal ion may be bound to the carbonyl oxygen alone, or sometimes simultaneously bonded to both the carbon and oxygen of the carbonyl (*6*). It also has been found that carbon and oxygen bonding promotes a variety of organometallic reactions, including two which are important to the surface catalytic chemistry of carbon monoxide: CO cleavage and CO insertion into metal alkyl bonds. For example, rate enhancements of the order of 10^3 for the CO insertion reaction result in the presence of alkali metal ions which are known to bind to carbonyl oxygen (*7*), and aluminum trihalides bring about enhancement factors of the order of 10^8 (*8*). Carbon and oxygen bonding also is strongly implicated in the cleavage of a CO ligand to produce carbidic cluster compounds (*9*).

Upon interaction with an acceptor ion, the C–O bond of coordinated carbon monoxide in molecular compounds is weakened, as judged from an increase in bond length and a lowering of the CO stretching frequency (*6*). Indeed, the decreased CO infrared stretching frequency provides a useful diagnostic feature for the identification of C- and O-bonded molecular systems. Frequency decreases on the order of 100 to 300 cm^{-1} are common. Table 1 summarizes CO stretching frequencies in some representative C- and O-bonded carbonyl compounds. These low carbonyl stretching frequencies are to be compared with molecular frequencies between 1950 and 2130 cm^{-1} which are typical for a terminal CO bonded to a neutral metal center, 1850 to 1950 cm^{-1} for a CO which is C-bridging between two neutral metal atoms, and 1750 to 1900 cm^{-1} for C-bridging of three metal atoms. Similar frequencies are seen on metal surfaces (*10*).

Significantly, the Mn^{2+}-promoted Rh catalyst exhibits a band around 1530 cm^{-1}, suggesting that C- and O-bonded carbon monoxide is present (*11*). A CO stretching

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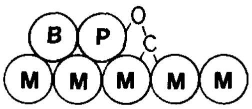

FIGURE 1

TABLE 1

CO Stretching Frequencies for M–C–O–M′ Moieties

M	M′	ν (cm^{-1})	Compound[a]	Reference
Mo	Nb	1580	$Cp_3NbW(CO)_3$	*29*
Mo	Ti	1623	$CpMo(CO)_3Ti(CH_3)C'_{p_2}$	*30*
Fe	Fe	1380–1420	$[HFe_4(CO)_{13}]^-$ (Fig. 2)	*31*
Ru	Al	1535	$Ru_3(CO)_{12}AlBr_3$	*32*
		2143	Gaseous CO	

[a] C_p,η^5-cyclopentadiene; C'_p,η^5-pentamethylcyclopentadiene.

mode at this same frequency has been reported for CO on a stepped Ni surface Ni[5(111) × (1$\bar{1}$0)] (*12*) and on Fe(111) (*13*). It is relevant to the present discussion of reactivity that the 1530-cm^{-1} band on the stepped Ni surface virtually disappears upon increasing the temperature to only 310 K, and a concomitant appearance of bands at 470 and 700 cm^{-1} occurs. These observations indicate that the adsorbed C- and O-bonded CO dissociates to C_{ads} and O_{ads} with extraordinarily low activation energy. The binding of CO to these stepped surfaces is likely to be analogous to the C- and O-bonded CO in $[HFe_4(CO)_{13}]^-$ (Fig. 2), which has been induced to dissociate in homogeneous reactions (*9*). Based on these observations, it is likely that the protruding atom of a stepped surface acts as an oxophilic promoter. According to the Smoluchowski theory this atom should indeed have a positive charge (*14*).

Up to this point the resemblance of the chemistry between molecular carbonyl complexes and that of chemisorption complexes has been stressed; however, in homogeneous solution reactants are free to diffuse into configurations which are appropriate for attachment to both C and O of a carbonyl ligand. The configurations which can be achieved by the reactants in a solid catalyst are likely to be more limited. Thus the oxide or hydroxide of an electropositive promoter ion might be expected to form a phase which is separate from the catalytic metal particles. In this condition, it is difficult to imagine how the promoter would be effective. This difficulty has been overcome by recent results on the interaction of metal particles with certain metal oxides under reducing conditions. Investigations of the so-called SMSI effects show that transition metal ions are bound rather strongly to the surface of metal particles. Several groups have found that under reducing conditions, transition metals (Rh (*15–17*) and Ni (*18, 19*) have been studied to date) supported on TiO_2 become partially covered by Ti^{n+} ($n < 4$) and O^{2-} ions. A similar phenomenon might occur with suboxides of other electropositive promoter elements. The ions of an electropositive metal on the surface of a metal particle might provide sites at which CO may be C bonded to a metal surface and O bonded to the coadsorbed ion, as has recently been proposed to explain SMSI effects (*20, 21*).

It is to be emphasized that we do not propose that activation by C and O bonding is the exclusive mechanism for promoter effects. However, the evidence which has accumulated to date suggests that this mechanism is highly plausible and deserves careful study. In this connection, we make a plea that vibrational spectroscopic studies of promoted systems be extended to the low-frequency region (1600–1300 cm^{-1}) which may reveal the presence of C- and O-bonded CO (*11*). Care must be taken in this frequency range to distinguish the carbon monoxide shell from infrared absorptions

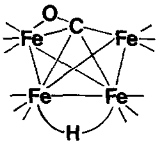

FIGURE 2

due to formate, acetate, carbonate, and water (*22–28*). Much of the reported material does not extend to this critical region.

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