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NOTES

Comparison of the Fischer-Tropsch Synthesis of Hydrocarbons and the Haber Synthesis of Ammonia

The Fischer-Tropsch reaction in its simplest form (the methanation reaction) can be represented formally as:

$$CO + 3H_2 \xrightarrow{\text{catalyst}} CH_4 + H_2O$$
$$\Delta H^0 = -\ 207 \text{ kJ mole}^{-1}. \quad (1)$$

The Haber reaction is:

$$N_2 + 3H_2 \xrightarrow{\text{catalyst}} NH_3 + NH_3$$
$$\Delta H^0 = -\ 92 \text{ kJ mole}^{-1}. \quad (2)$$

The most efficient catalysts for both processes are the Group VIII metals (*1, 2*) generally combined with a promoter such as potassium oxide and in some cases with a support such as alumina.

The conditions for each process have common features. Both are high-pressure, high-temperature processes. Typical conditions using an iron catalyst are 30 atm, 573°K (Fischer-Tropsch) and 100 atm, 723°K (Haber).

It has become apparent from recent work that carbon monoxide and nitrogen are capable of both associative and dissociative adsorption on Group VIII and other metals (*3–5*). Table 1 summarizes results where evidence for associative adsorption has been found and Table 2 presents data interpreted in favor of dissociative adsorption. It is clear from these tables that at low temperatures both carbon monoxide and nitrogen can be adsorbed associatively while at high temperatures they can both be adsorbed dissociatively.

The dissociative adsorption of nitrogen is taken as the first elementary step (and even the rate-determining step) of the mechanism of the Haber process (*34, 35*). It is clear from Table 2 that at the temperatures used in the Haber process nitrogen is adsorbed dissociatively on those metals for which data are available. At lower temperatures (<670°K) as shown by Brill *et al.* (*23*) synthesis of ammonia can occur via secondary dissociation of a hydrogenated nitrogen molecule. However, the dissociative adsorption of carbon monoxide is in conflict with current mechanisms for the Fischer-Tropsch process where associative adsorption is believed to occur (*1*). On the basis of the data in Tables 1 and 2 it can be seen that at the temperatures involved in Fischer-Tropsch synthesis dissociation of carbon monoxide can occur.

Following the dissociative adsorption of nitrogen in the Haber process the formation of ammonia occurs by stepwise hydrogenation of nitrogen atoms, imino and amino radicals, respectively. Similarly, the formation of methane and water in the Fischer-Tropsch process can be explained by the analogous stepwise hydrogenation of the carbon and oxygen atoms formed upon dissociation.

Given the existence of the species C^*, CH^*, CH_2^*, CH_3^*, H^* and OH^* as intermediates in the Fischer-Tropsch reaction, simple *addition* reactions can account for the observed products of higher molecular weight. A number of authors (*1, 36, 37*) have explained the formation of methane, higher hydrocarbons and oxygenated

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TABLE 1

Associative Adsorption of Carbon Monoxide and Nitrogen

Gas	Metal	Temperature (°K)	Technique used	Authors
CO	Fe powder	195–433	Isotope exchange	Webb & Eischens (*6*)
CO	Supported Fe	298	ir spectroscopy	Eischens & Pliskin (*7*)
CO	Supported Fe	293–473	ir spectroscopy	Blyholder & Neff (*8*)
CO	Supported Fe	90–195	Adsorption	Brunauer & Emmett (*9*)
CO	Fe films	80–190	XPES, UPES	Kishi & Roberts (*4*)
CO	Fe promoted	77–195	Temp prog. desorption	Amenomiya & Pleizier (*10*)
CO	Co film	170	ir spectroscopy	Baker *et al.* (*11*)
CO	Ni, single crystal	<450	AES, LEED	Madden *et al.* (*12*)
CO	Ni powder	298	Isotope exchange	Yates (*13*)
CO	Ni film	295	XPES, UPES	Joyner & Roberts (*3*)
CO	Fe, Co, Ni films	113–295 (high coverage)	ir spectroscopy	Bradshaw & Pritchard (*14*)
CO	Pt, Pd, Ni, supported	298	ir spectroscopy	Eischens *et al.* (*15*)
CO	Supported Ru bulk Ru	423	ir spectroscopy	Kobayashi & Shirasaki (*16*)
CO	Ru	300	Field ion spectroscopy	Kraemer & Menzel (*17*)
CO	Ru	80–295	ir spectroscopy	Lynds (*18*)
CO	Pt, Ir, Rh, Pd films	323	ir spectroscopy	Harrod *et al.* (*19*)
CO	Mn films	78–295	Adsorption	Bickley *et al.* (*20*)
CO	Mo film	77	XPES, UPES	Atkinson *et al.* (*21*)
CO	W film	336	Flash filament desorption	Ehrlich (*22*)
N_2	Fe	76–673	Field ion emission spectroscopy	Brill *et al.* (*23*)
N_2	Fe powder	<573	Adsorption	Huang & Emmett (*24*)
N_2	Fe powder	623	Isotope mixing	Morikawa & Ozaki (*25*)
N_2	Fe supported	298–573 (high coverage)	Adsorption/desorption	Scholten *et al.* (*26*)
N_2	Fe promoted	<623	Adsorption	Takezawa & Emmett (*5*)
N_2	Ni promoted	295	ir spectroscopy Isotope labeling	Eischens & Jacknow (*27*)
N_2	Mo film	77	Adsorption/desorption	Pasternak (*28*)
N_2	W film	77–300 (γ, β, type)	Flash desorption Isotope exchange	Yates & Madey (*29*)

hydrocarbons by invoking the intermediate M(CH)OH, formed by the reaction between associatively adsorbed carbon monoxide and adsorbed hydrogen atoms. Some evidence for the intermediate has been found from kinetic (*38*), desorption (*39*), and infrared spectroscopic measurements (*40*). Such an intermediate could be formed via the dissociative adsorption of carbon monoxide proposed here, by various addition reactions.

Another alternative whereby higher-molecular-weight reaction products could be obtained is by direct insertion reactions analogous to those found for singlet biradical species in the gas and liquid phases (*41*). Species which may undergo such reactions are CH^*, CH_2^* and O^*. The proximity of the para- or ferromagnetic catalyst may be expected to align unpaired spins, producing triplet species having essentially free radical character. It is of interest, however, that insertions into bonds of Group VIII coordination complexes have been reported (*42*).

Analogous reactions to produce products of higher molecular weight in the Haber process are thermochemically unfavored, e.g.,

$$N_2 + 2H_2 \rightarrow N_2H_4 \quad \Delta H^0 = 95.4 \text{ kJ mole}^{-1}.$$

In both Fischer-Tropsch and Haber processes the most active catalysts are the group VIII metals (*1*, *2*). We can understand the commonality between catalysts for these processes on the basis of the above mechanisms. These metals are now known to dissociate not only nitrogen but also carbon monoxide at the respective temperatures involved.

The role of carbides in the Fischer-Tropsch process has long been a contro-

TABLE 2

Dissociative Adsorption of Carbon Monoxide and Nitrogen

Gas	Metal	Temperature (°K)	Technique used	Authors
CO	Fe film	290	XPES, UPES	Kishi & Roberts (*4*)
CO	Ni sheet	573–923	Isotope exchange	Gregg & Leach (*30*)
CO	Ni film	430	XPES, UPES	Joyner & Roberts (*3*)
CO	Mn films	>350	Adsorption	Bickley *et al.* (*20*)
CO	Mo film	298	XPES, UPES	Atkinson *et al.* (*21*)
CO	W ribbon	298	Desorption spectra & electron stimulated desorption	Goymour & King (*31*)
CO	W films	400	UPES	Egelhoff *et al.* (*32*)
N_2	Fe powder	573	Adsorption	Huang & Emmett (*24*)
N_2	Fe supported	673–723	Adsorption	Brunauer & Emmett (*9*)
N_2	Fe supported	298–573 (low coverage)	Adsorption/desorption	Scholten *et al.* (*26*)
N_2	Fe promoted	473	Temp prog desorption	Amenomiya & Pleizier (*10*)
N_2	Fe promoted	623	Adsorption	Takezawa & Emmett (*5*)
N_2	Mo ribbon	225–710K	Flash filament Adsorption/desorption	Pasternak & Wiesendanger (*33*)
N_2	Mo film	300	Adsorption/desorption	Pasternak *et al.* (*28*)
N_2	W film	350	UPES	Egelhoff *et al.* (*32*)
N_2	W film	77–300 (β_2 type)	Flash desorption Isotope exchange	Yates & Madey (*29*)

versial subject (*43*). Iron carbide is a good catalyst for the reaction and yet it has been shown (*44*) that bulk carbides are not formed under reaction conditions. The mechanism we report here resolves this controversy since the carbide species formed by dissociative adsorption would be expected (*45*) to be readily hydrogenated.

Electron-donating species and in particular potassium compounds promote both Fischer-Tropsch and Haber process catalysts. On the other hand, electron-withdrawing species such as chlorine and sulfur are poisons. This can be understood on the basis of the above mechanism. The bonding of carbon monoxide to Group VIII metals occurs (*46*) by electron donation from the lone pair of electrons on the carbon atom into the vacant *d* orbitals of the metal. The excess negative charge on the metal is reduced by back-donation from the filled *d* orbitals of the metal into π antibonding orbitals of the carbon monoxide, thus weakening the C–O bond relative to the bond to the metal. Various phenomena, such as frequency shifts found in infrared spectroscopic studies of carbon monoxide adsorption (*46*), can be explained by this model.

When potassium is added to an iron Fischer-Tropsch catalyst the activity is greatly increased. This can be rationalized on the basis that electron donation from potassium causes a further drift of electrons into antibonding π orbitals of carbon monoxide, thus weakening the C–O bond such that dissociation is facilitated. It has been demonstrated for instance that the work function of iron decreases (*47*, *48*) while its electron emissivity increases (*49*) when it is combined with potassium.

On the other hand when sulfur or chlorine are added to Fischer-Tropsch catalysts such as iron, the activity decreases. Here the electron-withdrawing nature of the adsorbed poison causes a drift of electrons out of the antibonding π orbitals of carbon monoxide, thus strengthening the C–O bond and retarding the dissociation. Kishi and Roberts (*4*) have demonstrated this effect using XPS and UPS, showing that dissociation of carbon monoxide was retarded when sulfur was chemisorbed on iron.

A similar explanation to the above has recently been put forward (*50*) to account for the promoter effects of potassium on ammonia synthesis catalysts and needs no further amplification here, other than to say that since dissociative adsorption takes place in both reactions as we suggest, the promotor and poisoning effects should be similar.

The dissociative adsorption mechanism has implications for the development of new, perhaps more active, catalysts for the Fischer-Tropsch process. Metals which have been shown to be effective for the dissociation of carbon monoxide, such as Mn, Mo and W, might be considered as catalysts. Previously, these have shown little activity for the Fischer-Tropsch process. However, it is possible that they bond carbon, oxygen and nitrogen atoms too strongly for them to be effective reaction intermediates. It may be possible to reduce the catalyst/atom bond strength by the addition of electron-withdrawing species. Thus, sulfided or fluorided Mn, Mo and W may prove to be effective catalysts for the Fischer-Tropsch process.

It is significant that $LaNi_5$ has recently been shown (*51*) to have high activity for both ammonia and methane synthesis. Moreover, earlier work (*52*) demonstrated that both ammonia and hydrocarbon syntheses could proceed simultaneously on doubly promoted Fe catalysts.

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