Interaction of Hydrogen and Carbon Monoxide on Cobalt Catalysts. Part I

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This paper reports studies on the adsorption of hydrogen and carbon monoxide as well as of mixtures of them in the ratio 1 CO:1 H_2 and 1 CO:2 H_2 in the temperature range 0–100°C on a cobalt–thoria–kieselguhr catalyst. These studies reveal mutual enhancement of adsorption at higher temperatures. The analysis of the adsorbed phase suggests the formation of a –C(H)OH complex on the surface. Kinetics of the interaction of hydrogen with chemisorbed CO and the CO–H_2 complex have also been studied at different temperatures. The activation energies of these processes have been evaluated and found to be too low for either of them to figure as rate determining in hydrocarbon synthesis.

INTRODUCTION

The adsorption of reactant gas mixtures on catalysts under subreaction conditions has been the subject of numerous investigations. Typical studies include the measurement of simultaneous adsorption of hydrogen and carbon monoxide on cobalt (1) or iron (2) Fischer–Tropsch catalysts, on zinc oxide (3) and on noble metal catalysts (4), and the adsorption of hydrogen and nitrogen on iron synthetic ammonia catalysts (5). Instrumental techniques like infrared spectroscopy (6–8) and field ion mass spectroscopy (9) and experimental procedures involving the analysis of the desorbed phase (2) have been employed to deduce the composition and structure of the reactive species that is formed on the catalyst. The present work deals with the elucidation of the composition of the active complex that is formed on a promoted cobalt catalyst by the simultaneous adsorption of carbon monoxide and hydrogen from mixtures of initial compositions corresponding to 1 CO:1 H_2 and 1 CO:2 H_2. It has been established (2, 10) that carbon monoxide and hydrogen interact on the surface giving rise to (CO, H_2) complexes, which take up further quantities of hydrogen to form the final hydrocarbon products through successive stages of condensation, hydrogenation etc. It was therefore considered interesting to study the kinetics of interaction of hydrogen with the surface complex formed from a mixture of carbon monoxide and hydrogen.

EXPERIMENTAL

The adsorption measurements were carried out in a volumetric adsorption apparatus (Fig. 1), in which was incorporated a thermal conductivity meter (Cambridge Katharometer) for ascertaining the gas composition, an all-glass magnetic gas circulating pump and an Urry automatic Toepler pump.

The catalyst employed in the present study was a standard cobalt Fischer–Tropsch synthesis catalyst of composition cobalt:thoria:kieselguhr = 100:18:200, prepared as described by Sastri and Viswanathan (11) and thoroughly reduced in a stream of pure dry hydrogen at 350°C for 60 hr. The results presented here refer to adsorption by the reduced catalyst obtained from 5.2 g of the unreduced sample. After complete reduction the catalyst had a BET surface area of 42.4 m².
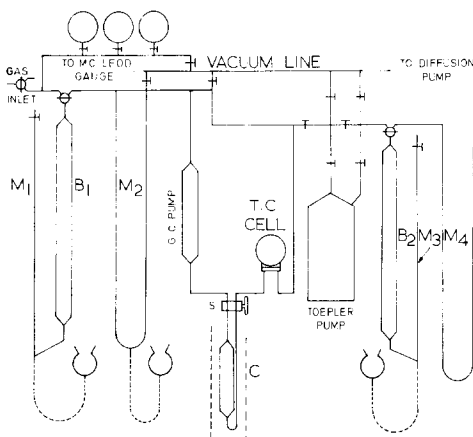
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FIG. 1. Mixed gas adsorption apparatus. B_1, B_2: Calibrated burettes; M_1, M_2, M_3, M_4: Manometers; S: 4-Way stopcock; C: Catalyst tube.

Hydrogen was obtained pure directly from an Elhygen electrolytic generator (Milton Roy Co., St. Petersburg, FL) which was provided with a Pd tube cathode. CO from formic acid was purified in the usual way (11). For the measurement of adsorption from mixtures, the evacuated catalyst kept at the selected isothermal temperature was exposed to gas mixture of known composition, approximating initially to either 1 CO:1 H₂ or 1 CO:2 H₂. The composition of the gas in equilibrium with the catalyst differed appreciably from that of the original mixture admitted. The adsorption of each gas has therefore been considered at its actual partial pressure in the system. Readings for the first point on the adsorption isotherm were taken 12 hr after admission of the gas. Readings for subsequent points were taken at intervals of 3 hr. After each adsorption experiment, the catalyst was evacuated for 2 hr at 100°, then kept in pure dry hydrogen at 250° for 2 hr and finally evacuated for 8 hr at the reduction temperature (350°). This treatment was found to give reproducible results in repeat experiments.

To study the kinetics of hydrogenation of the primary CO–H₂ complex on the surface, the catalyst was exposed to the gas mixture at the selected temperature (0, 30, 56 or 80°C) until constancy of pressure and composition were attained.

The unadsorbed and weakly bound gases were then quantitatively transferred, by means of the automatic Toepler pump, into the calibrated gas burette B₂, while keeping the catalyst at the temperature of the experiment. From the amounts and compositions of the original and recovered gas, the amounts of CO and H₂ retained on the catalyst surface were deduced by material balance. The catalyst was then warmed up *in vacuo* to the required temperature, and hydrogen admitted into the system. The absence of any pressure development in the system on heating under vacuum and of any change in the thermal conductivity meter reading during subsequent exposure to hydrogen showed that the chemisorbed complex was thermally stable at least up to 100°C. The kinetics of hydrogen interaction with the adsorbed complex could therefore be studied by merely following the change in pressure as a function of time.

For purposes of comparison, the rates of adsorption of hydrogen were determined on the bare surface, in the presence of a small amount (*ca.* 0.2 ml) of previously chemisorbed CO, and from 1 CO:1 H₂ mixture at the temperatures concerned.

By circulating synthesis gas (1 CO + 2 H₂) for several hours over the catalyst at 100°C and analyzing the gas in the system as described in a previous paper (3) (cold trapping and gas chromatography using a molecular sieve column), it was ensured that in all the experiments reported in this paper, the gas phase was free from detectable concentrations of H₂O, CO₂, CH₄ and other hydrocarbon products.

RESULTS AND DISCUSSION

Mutual Enhancement Effects in Co-adsorption

The isothermal data for the adsorption of CO and hydrogen from the respective pure gases and from their 1:1 and 1:2 mixtures are presented in Figs. 2 and 3. To facilitate comparison, the amounts adsorbed at a common (partial) pressure of 120 Torr, interpolated from the respective isotherms, are stated in Table 1.
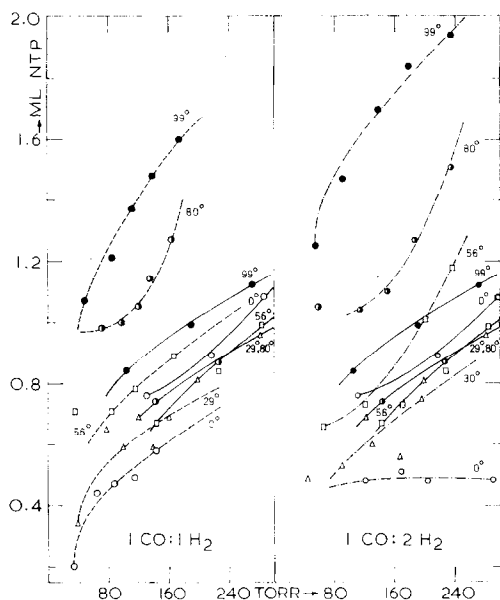
FIG. 2. Adsorption of hydrogen from pure gas and mixtures: —— pure hydrogen; – – – 1 CO:1 H₂ mixture; –·–·– 1 CO:2 H₂ mixture.

The adsorption of CO from either mixture is, at all temperatures, higher than that adsorbed from pure CO. In the case of hydrogen, however, the adsorption exceeds that from the mixture only at 56° and above; at the lower temperatures, it is slightly suppressed due to strongly biased competitive adsorption of CO at these temperatures.

Mutual enhancement of the adsorption of hydrogen and CO could be attributed to two causes: (i) a "cooperative work function effect" and (ii) complex formation between the adsorbed species. In the former case, the oppositely oriented chemisorbed dipoles (12) of $H^{\delta+}$ and $CO^{\delta-}$ will affect the
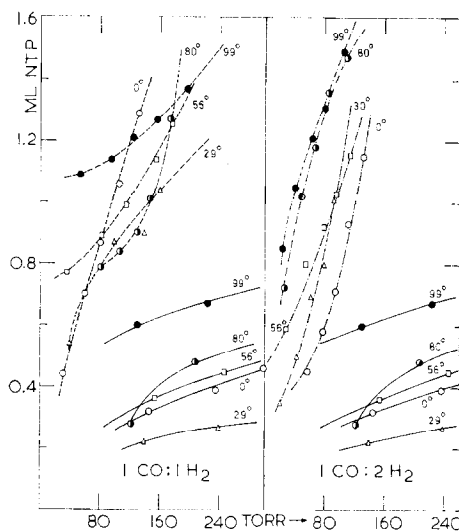

FIG. 3. Adsorption of CO from pure gas and from mixtures: —— pure CO; – – – 1 CO:1 H₂ mixture; –·–·– 1 CO:2 H₂ mixture.

work function of the metal in opposite ways; the increase caused by one will be partly offset by the decrease caused by the other, thereby raising the limiting adsorptions of both species $(3, 5, 13–15)$. However, the fact that mutual enhancement is observed only at higher temperatures ($>56°$) undermines the importance of the work function effect which should operate at all temperatures.

The quick response of the thermal conductivity meter and the efficiency of gas circulation enabled the kinetics of hydrogen adsorption from the mixtures to be followed effectively. The rate curves for adsorption from pure H₂ and 1 CO:1 H₂ mixture at 56, 80 and 99° are shown in Fig. 4. It is seen that the rate of uptake of hydrogen from

TABLE 1

ADSORPTION OF CARBON MONOXIDE AND HYDROGEN FROM THE PURE GASES AND FROM MIXTURES AT $P = 120$ TORR

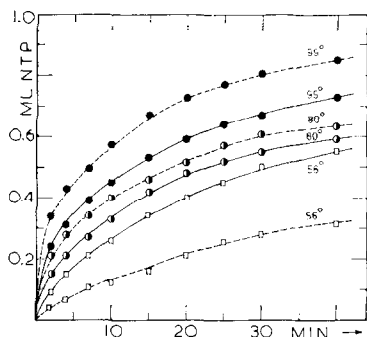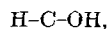| Temp °C	Hydrogen			Carbon monoxide		
	Pure gas	1 CO:1 H₂	1 CO:2 H₂	Pure gas	1 CO:1 H₂	1 CO:2 H₂
0	0.73	0.57	0.44	0.29	1.20	0.98
29	0.68	0.70	0.60	0.21	0.91	1.34
56	0.74	0.80	0.67	0.35	1.05	1.20
80	0.62	1.05	1.03	0.29	0.88	1.56
99	0.87	1.40	1.61	0.58	1.20	1.60

Fig. 4. Kinetics of hydrogen adsorption from pure gas and 1:1 mixture: —— from pure hydrogen (initial pressure = 350 Torr). ——— from 1 CO:1 H₂ mixture (initial total pressure = 300 Torr).

the mixture which is lower than that from pure gas at 56° rapidly increases with temperature, so that it nearly equals the pure gas rate at 80° and surpasses the latter at 99°. This is strongly indicative of a chemical interaction process which increases with temperature.
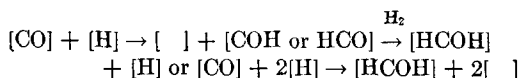
Composition of the Adsorbed Phase

The compositions of the residual adsorbed phase formed at the various temperatures from the two $CO-H_2$ mixtures and retained after Toepler-pumping are presented in Table 2. At the three higher temperatures, the surface composition approximates closely to 1 CO + 1 H₂, regardless of the parent gas composition. This

suggests strongly the formation of a chemisorbed entity of the composition COH_2, presumably

$$H-C-OH,$$

as shown below:

$$[CO] + [H] \rightarrow [\ \ ] + [COH\ or\ HCO] \xrightarrow{H_2} [HCOH]$$
$$+ [H]\ or\ [CO] + 2[H] \rightarrow [HCOH] + 2[\ \ ]$$

where [ ] denotes a vacant surface site and [X] a chemisorbed species X. The sites released as a result of complex formation become available for adsorption of further quantities of CO and H₂. A surface composition of COH_2 was found on iron catalysts also by Kölbel *et al.* (*2*) by employing a "desorption technique" with mass spectral analysis of the desorbed gas mixture. The higher CO content of the adsorbed phase formed at lower temperatures (Table 2, 0 and 30°) is in all probability due to the presence of "free" chemisorbed CO, besides COH_2 complexes.

Interaction of H_2 with Presorbed CO and COH_2 Complex

The kinetic data relating to the sorption of hydrogen in presence of CO and $CO-H_2$ complex previously chemisorbed on the surface and, for comparison, on the bare surface also, are given in Table 3. At each temperature of rate determination (T_2), the rate of uptake of hydrogen increased

TABLE 2

COMPOSITION OF ADSORBED PHASE FROM CO-H₂ MIXTURES

Temperature (°C)	Initial composition of the mixture	Composition of residual adsorbed phase		
		V_{CO} ads (ml NTP)	V_{H_2} ads (ml NTP)	CO:H₂ ratio
0	1 CO:1 H₂	1.08	0.79	1:0.73
	1 CO:2 H₂	1.13	0.60	1:0.53
29	1 CO:1 H₂	1.02	0.76	1:0.75
30	1 CO:2 H₂	0.98	0.69	1:0.70
56	1 CO:1 H₂	1.16	1.05	1:0.91
	1 CO:2 H₂	1.19	1.12	1:0.94
80	1 CO:1 H₂	1.32	1.24	1:0.94
	1 CO:2 H₂	1.37	1.49	1:1.09
99	1 CO:1 H₂	1.34	1.54	1:1.15
	1 CO:2 H₂	1.50	1.94	1:1.29

TABLE 3

KINETICS OF INTERACTION OF H_2 WITH PRESORBED CO AND $(CO + H_2)$

Amounts CO/H_2 preadsorbed (ml NTP) and temperature (T_1°C) of preadsorption			CO/H_2 ratio	Uptake of hydrogen (ml NTP) at initial P_{H_2} = 350 Torr								Activation energy (E_a) kcal mole^{-1}
				$T_2 = 30°$		56°		80°		99°		
T_1	CO	H_2		4 min	30 min	4 min	30 min	4 min	30 min	4 min	30 min	
—	bare		—	—	—	0.15	0.50	0.21	0.55	0.31	0.67	5.4
0	0.19	0	—	0.08	0.33	0.19	0.55	0.24	0.62	0.42	0.76	6.7
0	0.52	0.30	1.73	0.18	0.45	0.36	0.84	0.53	0.98	0.75	1.22	4.7
30	0.70	0.55	1.27	0.19	0.41	0.27	0.63	0.35	0.74	0.46	0.89	3.6
56	0.75	0.68	1.10	—	—	0.21	0.50	0.30	0.68	0.36	0.78	3.0
80	0.93	0.94	0.99	—	—	—	—	0.25	0.58	0.31	0.67	2.6

consistently in the following order of surface condition: Bare surface < with CO only < CO + H_2 preadsorbed at 0° and then decreased with increasing temperature (T_1) of preadsorption of CO + H_2. The latter was evidently due to increasing surface coverage by the presorbed gases.

For each surface condition, the rate of sorption of hydrogen increased with temperature and the data fitted well into Arrhenius plots (Fig. 5), from which the activation energies (E_a) given in Table 3 (last column) have been evaluated. The trend of increasing E_a with decreasing temperature (T_1) of CO–H_2 presorption should be correlated with increasing ratio of CO/H_2. Presumably, the adsorbed phase formed at lower temperatures contained free [CO] species in addition to the [COH$_2$] com-

plexes. The higher activation energy found for H_2 interaction with chemisorbed CO (6.7 kcal) would account for the observed trend. It is also discerned that the E_a tends to attain a constant minimum value (ca. 3 kcal/mole) at the higher temperatures of initial mixed adsorption. This value may be taken as the E_a for the hydrogenation of the intermediate surface complex, –C(H)OH, as the composition of the adsorbed phase at these temperatures corresponds closely to the required stoichiometry.

The overall activation energy for the Fischer–Tropsch synthesis on Co–ThO$_2$–Kgr catalyst has been found to be 25 kcal/mole (16). Obviously, the initial hydrogenation step cannot be anywhere near rate determining in the synthesis of higher hydrocarbons. It is doubtful if it would be rate determining even in a simple methanation reaction, as suggested by McKee (4), as the E_a found by him for this reaction even on the most active hydrogenation catalyst (Ru) is 9 kcal/mole.

FIG. 5. Arrhenius plots for the interaction of hydrogen: —— with [CO, H$_2$] complex; – – – with presorbed CO.

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