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

M. V. C. SASTRI,* R. BALAJI GUPTA, AND B. VISWANATHAN

Department of Chemistry, Indian Institute of Technology, Madras-600036, India

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The simultaneous adsorption of CO and H_2 from their 1:1 mixture on a cobalt Fischer-Tropsch catalyst has been studied by kinetic and quasi-static measurements in the temperature range 0–132°C. Mutual enhancements indicating interactive adsorption have been observed in both rates and amounts of adsorption.

Breaks appear in the Elovich equation plots for the rates of adsorption of both gases from the mixture. The ratios of the post-break slopes of these plots check fairly closely with the H_2/CO ratios in the mixed adsorbed phase found under quasi-static conditions. Both types of measurements indicate the formation of a surface compound of the composition H_2CO in the temperature interval 85–95°C. The kinetics of interaction of hydrogen with the composite adsorbate formed at various temperatures have also been studied.

INTRODUCTION

In the previous paper (*1*), we reported quasi-static measurements of the adsorption of carbon monoxide and hydrogen from their binary mixtures at various temperatures on a cobalt–thoria–kieselguhr catalyst. From the amounts of carbon monoxide and hydrogen retained on the catalyst after prolonged exposure to the CO–H_2 mixtures and removal of unadsorbed and weakly adsorbed gases by Toepler-pumping the composition of the adsorbed phase could be deduced. It was found that the amounts of CO and hydrogen retained at the higher temperatures (80 and 99°C) were nearly in 1:1 ratio, thereby suggesting the formation of a surface complex of the composition H_2CO (presumably HCOH) at these temperatures as a precursor to Fischer-Tropsch synthesis.

In a recent review (*2*), Aharoni and Tompkins have discussed the possibilities of obtaining useful information relative to interaction between the components of a binary mixture on a catalyst surface through application of the Elovich equation to the kinetics of mixed adsorption. In particular, they have studied (*3*) the kinetics of adsorption of CO and hydrogen on zinc oxide and observed "breaks" in the plots of q versus log time for both the gases. From the equality of the slopes of these plots after the break, they have concluded that a surface compound of the empirical formula H_2CO was formed. This has prompted us to study the kinetics of individual adsorptions of CO and hydrogen from their binary mixtures on cobalt Fischer-Tropsch catalysts and to see if by application of the Elovich equation, information regarding interaction between the chemisorbed CO and H species could be obtained. In the present paper, such kinetic studies have been reported on the adsorption of CO and hydrogen from their 1:1 mixture on a cobalt–thoria–magnesia–kieselguhr catalyst. This catalyst has been found to possess greater stability of activity on repeated high temperature regeneration than the cobalt–thoria–kieselguhr catalyst that was used in the previous studies (*1*).

For comparison, quasi-static measurements also have been made of adsorption

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* To whom all inquiries should be addressed.

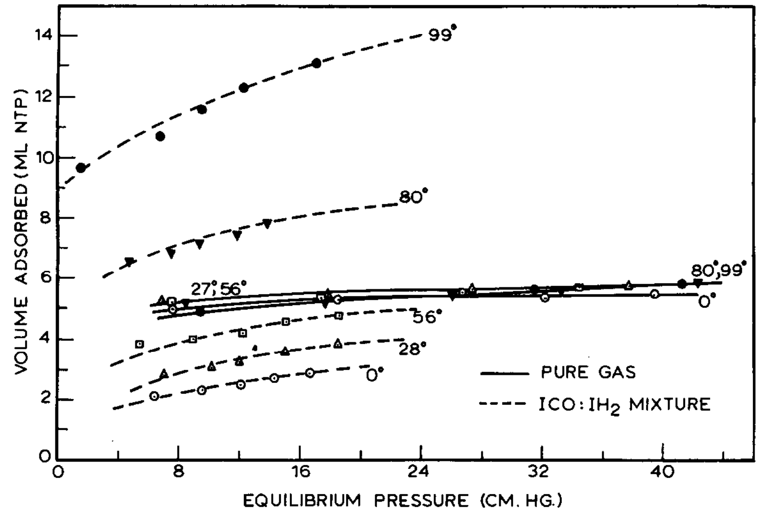

FIG. 1. Adsorption of hydrogen from pure gas and $1CO:1H_2$ mixture: (—) pure hydrogen; (- -)$1CO:1H_2$ mixture.

of CO and hydrogen from the same mixture and of the composition of the chemisorbed composite adsorbed phase. The interaction of the latter with hydrogen has also been studied.

EXPERIMENTAL METHODS

The catalyst, comprising $Co\text{–}ThO_2\text{–}MgO$–kieselguhr in the proportion 100:6:12:200 by weight, was prepared as described by Sastri and Srinivasan (*4*) and reduced by passing pure dry hydrogen at 350°C for 60 hr until no more water could be detected in the exit-hydrogen stream. The BET surface area of the reduced catalyst (determined with nitrogen at −195.6°C) was 35 m^2/g, 48% of which was metal as estimated by low temperature CO-chemisorption (*5*). The preparation and purification of the gases, the apparatus used, the method of evaluation of the amounts of CO and H_2 adsorbed from the mixture and the experimental procedures relative to obtaining the data pre-

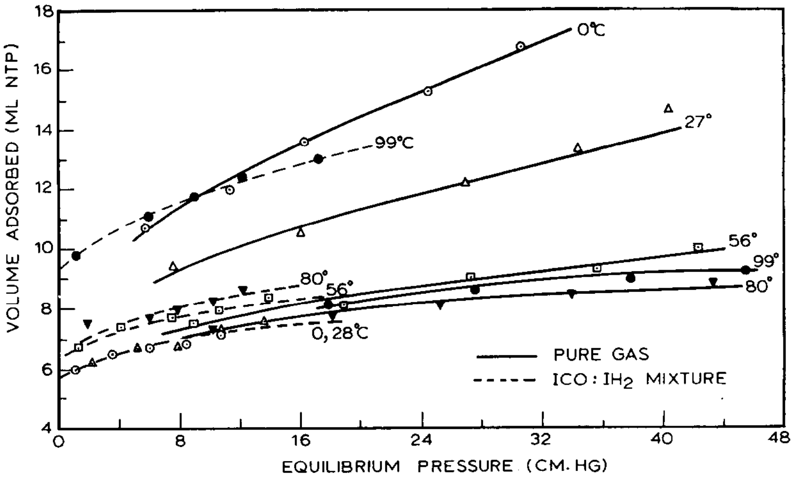

FIG. 2. Adsorption of a carbon monoxide from pure gas and $1CO:1H_2$ mixture: (—) pure CO; (- -) $1CO:1H_2$ mixture.

TABLE 1
COMPOSITION OF ADSORBED PHASE FORMED FROM 1 CO:1 H_2 MIXTURE

Temp (°C)	Composition of adsorbed phase		
	$V_{CO(ads.)}$ (ml NTP)	$V_{H(ads.)}$ (ml NTP)	V_H/V_{CO}
0	6.85	2.79	0.41
28	7.31	3.31	0.46
56	7.83	4.59	0.59
80	8.24	7.46	0.91
99	12.26	12.52	1.02
118	16.80	17.80	1.06
132	20.50	22.50	1.10

sented in Figs. 1 and 2 and Tables 1 and 3 have been described in the previous paper (*1*). The adsorption measurements were carried out from 1 CO + 1 H_2 mixture at temperatures up to 132°C, since mass spectrometric analysis (with Varian-MAT-CH 7 mass spectrometer) confirmed the complete absence of H_2O, CO_2 and hydrocarbons in the mixture left in contact with the catalyst at temperatures up to 150°C for over 6 hr and in the gas desorbed from the catalyst at the same temperature with the automatic Toepler pump.

After each adsorption experiment, the catalyst was regenerated by evacuation at 150°C and 10^{-5} Torr for 3 hr, followed by soaking in hydrogen at atmospheric pressure and 250°C for 2 hr and a final evacuation for 8 hr at 350°C and 10^{-5} Torr.

After all the experiments with the catalyst were completed its reduced weight was determined by sealing off and weighing the catalyst tube and then breaking the latter and weighing the glass pieces after emptying out the catalyst. All the results reported in this paper relate to 2.62 g of the reduced catalyst.

RESULTS

a. Quasi-static Measurements

The isotherms for the adsorption of hydrogen and carbon monoxide from the respective pure gases and from their 1:1 mixture are presented in Figs. 1 and 2. These have been plotted with values taken when the adsorption had become very slow or quasi-static and are not claimed to represent true equilibrium values. As in the case of the Co–ThO_2–kieselguhr catalyst (*1*), the adsorption of either gas from the mixture above 56°C is markedly higher than that from the pure gas at the same partial pressure.

Table 1 shows the compositions of the adsorbed phase retained by the catalyst at various temperatures after 12 hr exposure to the CO–H_2 mixture at 600–700 Torr total pressure and removal of residual and weakly held gases by Toepler-pumping without increasing the temperature.

b. Kinetics of Adsorption

The rates of adsorption of CO and H_2 from the single gases and their 1:1 mixture were determined at 56, 80, 99, 118 and 132°C. The initial pressure of the gas was 300 Torr in the case of adsorption from the single gases and 600 Torr (total) in the case of the 1:1 mixture. For purposes of analysis of the kinetic data, the Elovich equation [see Ref. (*2*), Eq. (3)]

$$q = (2.3/b)\log(ab) + (2.3/b)\log(t + t_0)$$

is simplified to

$$q = C + k \log_{10} t,$$

since $t_0 = 1/ab \ll t$, and we are presently concerned with the relative rates of adsorption of CO and H_2 and hence with the slopes given by $k = dq/d \log t$. The Elovich plots for 80 and 99°C are shown in Figs. 3 and 4. The plots for 56°C are similar to those for 80°C and those for 118 and 132°C are similar to those for 99°C. A marked change in the trend of the plots is noticed in passing from 80 to 99°C. In each of the plots for adsorption from the mixture a distinct break occurs at log $t = 1.0$ to 1.2 (t = 10–16 min), demarcating two stages in the adsorption of each component from the mixture, which may be identified by the slopes k_1 and k_2. No breaks are discernible in the plots for the pure components. The slopes of the Elovich plots and other pertinent data of the kinetics experiments are presented in Table 2.

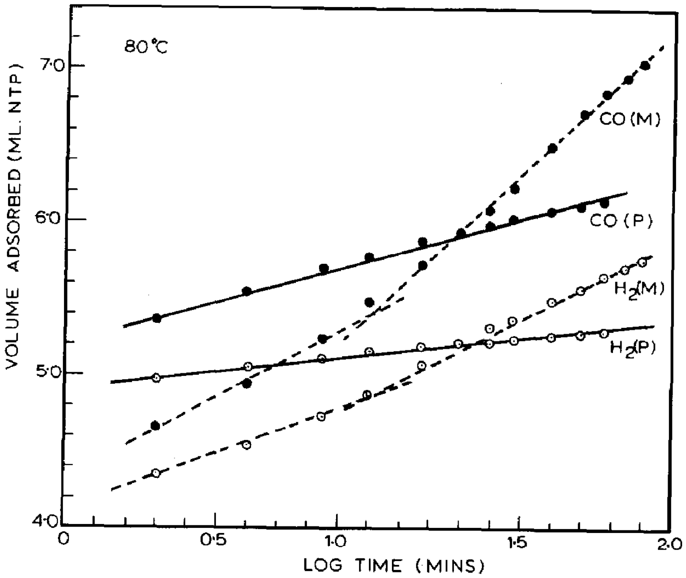

FIG. 3. Elovich equation plots for simultaneous CO–H_2 adsorption at 80°C.

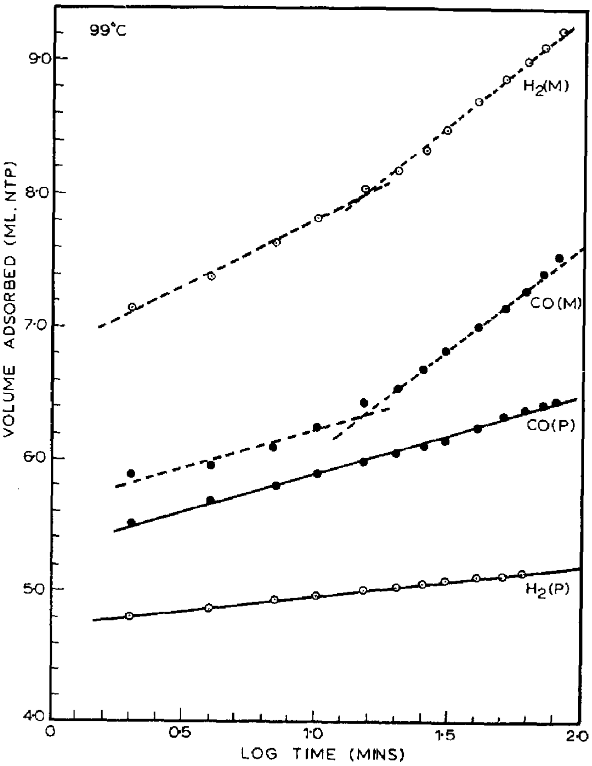

FIG. 4. Elovich equation plots for simultaneous CO–H_2 adsorption at 99°C.

TABLE 2

DATA OF ELOVICH EQUATION PLOTS OF CO, H_2 ADSORPTION

Temp (°C)	Pure gas				Adsorption from mixture									
					First stage					Second stage				
	V_H (ml)	V_{CO} (ml)	k_H	k_{CO}	$V_{1(H)}$ (ml)	$V_{1(CO)}$ (ml)	$k_1(H)$	$k_1(CO)$	$k_1(H)/k_1(CO)$	$V_{2(H)}$ (ml)	$V_{2(CO)}$ (ml)	$k_2(H)$	$k_2(CO)$	$k_2(H)/k_2(CO)$
56	4.93	5.80	0.27	0.69	3.39	4.65	0.32	1.03	0.31	3.65	5.46	0.91	1.97	0.47
80	4.97	5.36	0.23	0.58	4.35	4.66	0.68	1.05	0.65	4.87	5.39	1.02	1.84	0.56
99	4.80	5.50	0.20	0.60	7.12	5.83	0.89	0.60	1.47	8.02	6.35	1.66	1.61	1.03
118	4.94	5.94	0.27	0.40	5.32	3.82	0.59	0.39	1.52	5.85	4.18	2.30	2.08	1.10
132	4.76	5.63	0.29	0.35	6.65	6.13	1.11	1.12	0.99	7.43	6.93	2.11	1.76	1.18

V_H and V_{CO}: Initial amounts of H_2, CO adsorbed from pure gas at 2 min from start.

$V_{1(H)}$ and $V_{2(CO)}$: Amounts of H_2, CO adsorbed from mixtures at the start of first stage (i.e., at 2 min from start).

$V_{2(H)}$ and $V_{2(CO)}$: Amounts of H_2, CO adsorbed from mixtures at the break.

TABLE 3

ACTIVATION ENERGY VALUES FOR THE INTERACTION OF HYDROGEN WITH [CO, H_2] COMPLEXES FORMED AT DIFFERENT TEMPERATURES

T_1 (°C)	Composition of adsorbed phase V_{CO} (ml NTP)	 V_H (ml NTP)	 H_2/CO	T_2 (°C)	E_a (kcal/mole)
0	1.20	—	—	0, 25, 56, 80	7.4
0	5.59	2.04	0.36	0, 30, 56, 80, 99	6.2
30	5.81	3.26	0.56	30, 56, 80, 99	5.4
56	5.55	4.47	0.81	56, 80, 99	4.3
80	5.97	5.43	0.91	80, 99	3.3

T_1 = temperature of initial [CO, H_2] complex formation; T_2 = temperature of H_2 interaction kinetic measurements.

c. Kinetics of Interaction of Hydrogen with Presorbed [CO, H_2] Complex

Composite adsorbed phases of different CO–H_2 compositions were obtained by exposing the catalyst to the 1:1 CO–H_2 mixtures at various temperatures, T_1^0 = 0, 30, 56 and 80°C, as described in the previous paper (*1*), and exposed to pure hydrogen at 350 Torr and temperatures $T_2 \geqslant T_1$. The rates of uptake of hydrogen showed a temperature dependence that gave perfectly linear Arrhenius plots. The data relating to these experiments and the activation energies calculated therefrom are given in Table 3. The activation energy decreases with increasing hydrogen content of the presorbed composite reactant and the latter increases with increasing temperature (T_1) of CO–H_2 adsorption. These are in close agreement with the results of similar experiments previously reported (*1*) with the Co–ThO_2–kieselguhr and can be explained similarly on the basis of free (uncombined) CO molecules being present in the CO-rich adsorbed composites formed at the lower temperatures and the relatively high activation energy (7.4 kcal/mole on the present catalyst) required for the interaction of hydrogen with chemisorbed CO.

DISCUSSION

1. Mutual Enhancement Effects

The results of the quasi-static and kinetic experiments presented in Figs. 1 to 4 and Tables 1 and 2, all show that, particularly at temperatures above 56°C, the amounts and rates of adsorption of both CO and hydrogen are higher from the mixture than from the single gases. This means that the mutual retardation effect of competitive adsorption is more than off set by mutual enhancement effects such as the following:

i. Increased activity of the catalyst surface per se due to a cooperative work function effect arising from the chemisorbed CO and H species forming oppositely charged dipoles ($CO^{\delta-}$ and $H^{\delta+}$) on the surface, thereby altering the work function of the metal in opposite ways and reducing the electronic barriers to the adsorption of both the gases.

ii. Attractive interaction between the chemisorbed CO and H dipoles, without complex formation. This would also give the effect of enhanced activity of the surface for the adsorption of either gas.

iii. Chemical interaction on the catalyst surface between chemisorbed CO and H species (Langmuir-Hinshelwood type) or between chemisorbed CO and gaseous hydrogen or vice versa (Rideal type) leading to the formation of chemisorbed surface complexes, such as HCO or COH.

iv. Chemical interaction of the primary surface complex (HCO or COH) with chemisorbed or gaseous hydrogen to give rise progressively to HCOH and H_2COH complexes. This would account mainly for enhancement of hydrogen adsorption.

2. Kinetics of Mixed Adsorption

The occurrence of the break in the Elovich plots for adsorption of CO and hydrogen from the mixture may be explained as follows: The initial stage of mixed adsorption is subject to the opposing effects of mutual retardation, due to competition and repulsive interaction, and the various types of mutual enhancement effects referred to in the preceding section. Besides, the extents of surface coverage due to initial rapid adsorption of CO and hydrogen in the first 1 or 2 min and the temperature will also affect the individual rates of adsorption during the succeeding period of the first stage. With the apparent exception of CO-adsorption at 99 and 118°C, the rate of adsorption of either gas from the mixture exceeds its rate of adsorption from pure gas at the same temperature even in the first stage (i.e., $k_1(\mathrm{H}), k_1(\mathrm{CO}) > k(\mathrm{H}), k(\mathrm{CO})$, respectively) indicating that enhancement effects prevail over mutual suppression effects even in this stage. However, as the coverage of the surface advances, the competition effects decline, because of a diminishing number of sites to compete for, and ultimately become negligible, leaving the adsorption rate to be controlled almost wholly by the factors contributing to enhancement. Presumably, this is what happens after the "break" in the Elovich plots. It is noteworthy that at each temperature the break in the Elovich plot occurs at the same value of log t for both the constituents, suggesting that it marks the same event for both of them, presumably, the termination of the mutual retardation effect of competitive adsorption.

Turning now to the second stage, Aharoni and Tompkins (*3*) have suggested that "the ratio of the rates of adsorption of components 1 and 2 from the binary mixture at this stage gives the stoichiometric ratio of the components in the surface compound," assuming that interaction between the constituents in this stage results in the formation of a surface compound. It would therefore be interesting to see how the values of $k_2(\mathrm{H})/k_2(\mathrm{CO})$ compare with the compositions of the adsorbed phase determined under quasi-static conditions at various temperatures (Table 1). This has been done in Fig. 5 in which the values of $k_2(\mathrm{H})/k_2(\mathrm{CO})$ and $V_{\mathrm{H}}/V_{\mathrm{CO}}$ are plotted against temperature. Both curves indicate rather low H_2/CO ratios ($\sim$0.5) at lower temperatures rising steeply with increase of temperature to give an inflexion at $H_2/CO \cong 1.0$ between 85 and 95°C, after which the ratio increases only moderately with temperature. Since the initial complex formation by surface interaction of CO with hydrogen requires an activation energy of nearly 7.5 kcal/mole (see Table 3), the chemisorbed CO is mostly free, i.e., uncomplexed with hydrogen, at the lower temperatures. The high CO/H_2 ratio is due to the preferential adsorption of CO at these temperatures (compare the adsorption isotherms for CO and H_2, Figs. 1 and 2). The inflexion at $H_2/CO \sim 1$ presumably corresponds to the formation of a surface complex of the formula H_2CO, which becomes hydrogenated further in a facile manner to H_2COH giving rise to $H_2/CO > 1$. For instance, a H_2/CO ratio = 1.1 would result from 80% H_2CO + 20% H_2COH. The much reduced slope of the curve from 99 to 132°C is in keeping with the modest requirement of activation energy (ca. 3 kcal/mole) for the hydrogenation of H_2CO to H_2COH (see Table 3, last row).

The catalyst appears to be less active for complex formation in the kinetics experiments than in the quasi-static experiments. This may be because the latter preceded the former and the repeated long exposures to CO–H_2 mixture and high temperature regenerations may have caused a slight but inevitable deactivation of the catalyst surface. Otherwise, it is seen that Elovich analysis of the kinetics of simultaneous adsorption leads to practically the same deductions as regards composition of the mixed adsorbed phase, occurrence of interaction and surface complex formation as quasi-static adsorption measurements and has the advantage of being experimentally simpler and faster. However, more comparisons of kinetic and quasi-static experiments are necessary to establish the absolute reliability of the kinetic method,

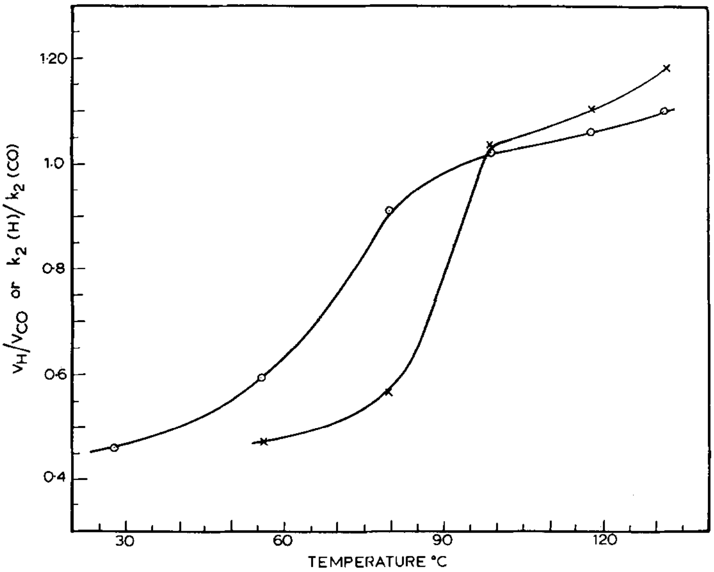

FIG. 5. Composition of the adsorbed phase deduced from quasi-static and kinetic measurements. (○) H_2/CO ratio in adsorbed phase by quasi-static method (from Table 1); (×) $k_2(H)/k_2(CO)$ of Elovich equation plots (from Table 2).

particularly as it lacks the analytical directness of the quasi-static method.

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