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# Activated Adsorption of $H_2$ on Cobalt and Effects of Support Thereon

## INTRODUCTION

The technique of temperature programmed desorption (TPD) has been demonstrated (*1–6*) to provide useful qualitative and quantitative information relative to the types of catalytic sites, binding energies, and orders of desorption of adsorbates from both unsupported and supported metal catalysts. Most quantitative information from TPD is obtained as a result of measuring the response of the desorbing species to changes in (i) the temperature ramp or (ii) the initial coverage of the adsorbate on the catalyst. This note describes the effects of varying a third TPD parameter, the temperature at which adsorption takes place, on the desorption of $H_2$ from unsupported, alumina-supported and silica-supported cobalt catalysts. These results provide evidence of activated adsorption of $H_2$ on cobalt metal, the nature of which is dramatically affected by supporting cobalt on alumina or silica.

## EXPERIMENTAL

Alumina-supported and silica-supported catalysts containing 3, 10, and 15 wt% cobalt were prepared by successive impregnations with aqueous cobalt nitrate solutions of finely divided $\gamma$-$Al_2O_3$ (Dispal M from Conoco) and silica (Cab-O-Sil Grade M-5 from Cabot Corp.) accompanied by several hours of drying in air at 100°C. An unsupported cobalt catalyst was prepared by decomposition of cobalt nitrate in air at 200°C. All catalysts were reduced at 400°C for 16 h in flowing hydrogen (99.999%) that had been passed over a molecular sieve and a Pt/Pd deoxo catalyst. The carrier gas was Argon (99.999%) which was purified by passing it through a molecular sieve trap and a Matheson Gas Filter deoxo unit. Total hydrogen uptakes from static adsorption measurements, extents of reduction and percentage dispersions (percentage exposed) determined in a companion study (*7*) are listed in Table 1.

Catalyst samples, typically weighing between 50 and 100 mg (depending on loading) were housed in a 0.635-cm o.d. quartz tube which was surrounded by a 1.27-cm o.d. quartz tube/nichrome wire furnace. Temperature was controlled by an in-house-built programmer capable of delivering ramps from 100 to 1°C/min, and temperature was monitored by a chromel–alumel thermocouple which was inserted directly in the catalyst bed.

Adsorbate gas was introduced into the carrier stream by a six-port Carle sampling valve (#5618) equipped with a 0.1-$cm^3$ sample loop while desorbing species were detected by a Hewlett–Packard Chromatograph (Model 5730A) with thermal conductivity detector from which the column had been removed. All gas flows were monitored by Matheson rotameters or bubble flow meters. Carrier gas flow rates were fixed during each run in the range of 30 to 40 $cm^3$ per min.

The absence of both inter- and intraparticle diffusional limitations in the TPD runs was verified by calculations based on recently reported criteria (*4, 8*). Concentration gradients in the relatively thin beds (2–10 mm) were small as indicated by a lower than unity value ($<10^{-2}$) of the rate of $H_2$ desorption relative to the rate of flow leaving the cell. Further evidence of small axial

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TABLE 1

Total Hydrogen Uptakes, Percent Reductions, and Percent Dispersions for Unsupported and Silica- and Alumina-Supported Cobalt Catalysts (From Ref. *7*)

| Catalyst | Total $H_2$ uptake[a] ($\mu$ moles/g) | % Reduction[b] | % D[c] |
|---|---|---|---|
| Unsupported | 22.3 | 100 | 0.26 |
| 3% $Co/SiO_2$ | 20.4 | 75 | 11 |
| 10% $Co/SiO_2$ | 82.2 | 92 | 10 |
| 15% $Co/SiO_2$ | — | — | — |
| 3% $Co/Al_2O_3$ | 5.6 | 22 | 10 |
| 10% $Co/Al_2O_3$ | 29.5 | 34 | 9.9 |
| 15% $Co/Al_2O_3$ | 37.1 | 44 | 6.6 |

[a] Measured by the static adsorption method at the temperature of maximum uptake. Includes reversible and irreversible adsorption and has been corrected for chemical and physical adsorption on the support.

[b] Determined by oxygen titration of the reduced catalyst at 400°C assuming formation of $Co_3O_4$ based on the work of Chin and Hercules (Ref. *28*).

[c] Percentage dispersion (percentage exposed) calculated from total $H_2$ uptake and percent reduction based on $\% D = 1.179\, X/Wf$ where $X$ is the total $H_2$ uptake, $W$ is the weight percent cobalt, and $f$ is the fraction reduced to the metal.

concentration gradients was that the peak temperature was independent of flow rate within experimental error under the conditions of this study.

## RESULTS AND DISCUSSION

In the TPD runs, hydrogen was pulsed over the catalyst surface at a given temperature after which the "charged" catalyst was cooled to room temperature before applying a uniform temperature ramp (30°C/min). Figures 1–3 show the family of desorption spectra obtained for each catalyst (except 3% $Co/Al_2O_3$) by varying the adsorption temperature. It is evident that for each catalyst, maximum hydrogen uptake does not occur at room temperature but rather at an elevated temperature. Not only is maximum adsorption a function of adsorption temperature but also of metal loading on the support. Table 2 lists the optimal adsorption temperature, the ratio of adsorption area at the temperature of maximum adsorption to that at room temperature, and the amount adsorbed under optimum conditions (selected catalysts). Note that on the supported catalysts the amount adsorbed at higher temperature relative to room temperature and the optimal temperature for adsorption increase as metal loading decreases suggesting effects of metal–support interactions (MSI). In fact, the amount of $H_2$ adsorbed on 3% $Co/SiO_2$ at 150°C is 34 times the amount adsorbed at 25°C compared to only 2.8 times greater adsorption on 10% $Co/SiO_2$ at 100°C relative to 25°C. This effect is even more pronounced in the $Co/Al_2O_3$ system; indeed, the adsorption of $H_2$ on 10% and 15% $Co/Al_2O_3$ at 25°C is negligible, and, in the case of 3% $Co/Al_2O_3$ no measurable adsorption occurs at any temperature (using the pulse-flow method). The fact that $H_2$ adsorption is more highly activated on the alumina-supported catalysts relative to the silica-supported catalysts is strong evidence of a support effect.

Further evidence that hydrogen adsorption is highly activated and that the degree of activation is affected by support or promoter was obtained in recent companion

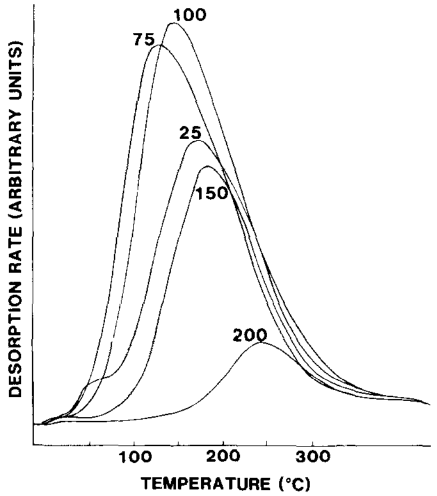

FIG. 1. Temperature programmed desorption spectra of $H_2$ from unsupported cobalt as a function of adsorption temperature.

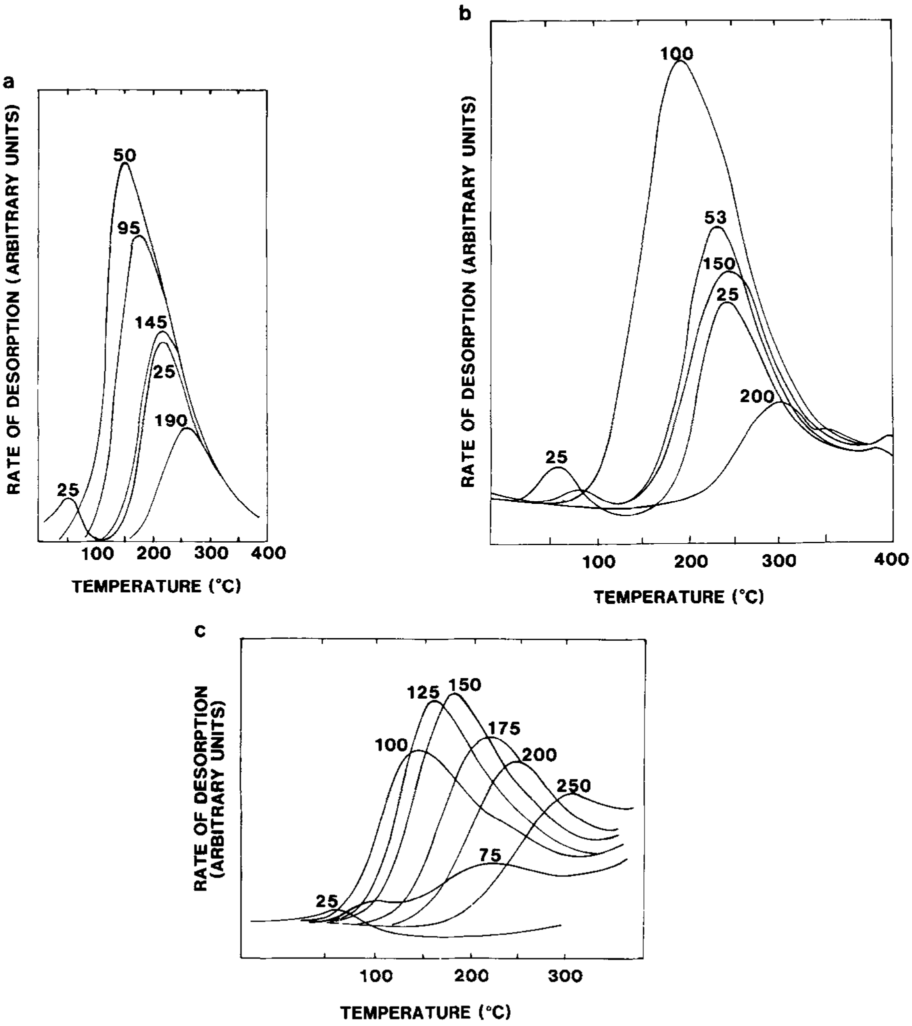

FIG. 2. Temperature programmed desorption spectra of $H_2$ from silica-supported cobalt as a function of adsorption temperature. (a) 15% Co/$SiO_2$; (b) 10% Co/$SiO_2$; (c) 3% Co/$SiO_2$.

studies of $H_2$ adsorption on cobalt catalysts using static, volumetric adsorption techniques (*7, 9–10*). For example, the adsorption of $H_2$ on 3% Co/$SiO_2$ and Co/$Al_2O_3$ catalysts was found to be 1.3 and 1.4 times greater at 125°C compared to 25°C (*7*). In the case of 3–9% Co/ZSM-5 the $H_2$ uptakes at 100°C were 10–100 times greater than those measured at 25°C. Adsorption of $H_2$ on boron-promoted cobalt is also significantly more activated than on unpromoted cobalt (*10*).

Comparison of the optimum hydrogen uptakes for unsupported cobalt, 10% Co/$SiO_2$ and 10% Co/$Al_2O_3$ measured by static-volumetric and pulse-flow techniques (Tables 1 and 2) reveals another interesting fact. The hydrogen uptakes measured in this study by pulse-flow techniques are 35–75% lower. This difference is undoubtedly due to reversible $H_2$ adsorption, i.e., using the pulse flow method, only irreversibly adsorbed $H_2$ is measured while static techniques are capable of measuring total (reversible and irreversible) uptake. Data from a companion study (*7*) reveals that the degree of reversibility of $H_2$ adsorption on cobalt varies from 15 to 90% of the total ad-

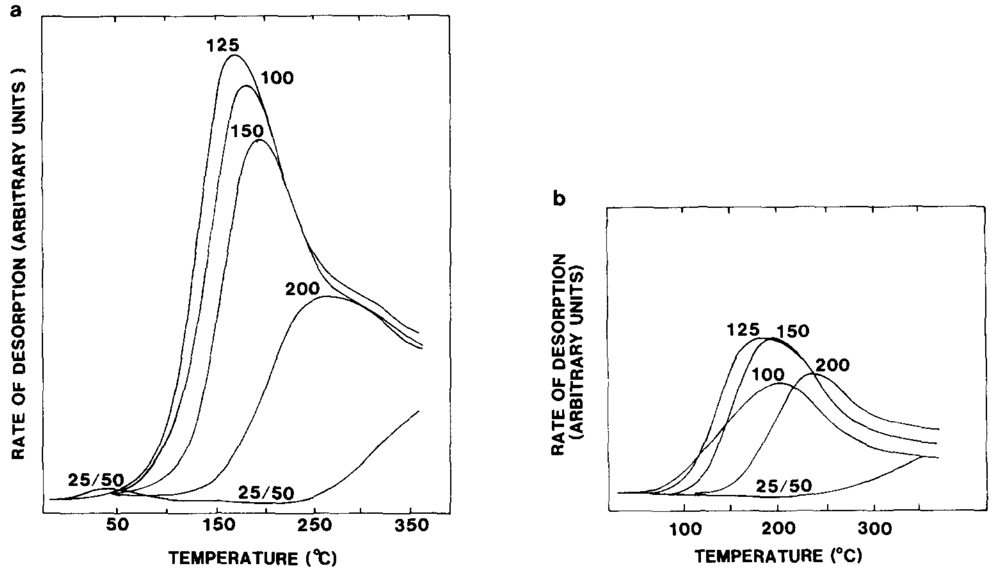

FIG. 3. Temperature programmed desorption spectra of $H_2$ from alumina-supported cobalt as a function of adsorption temperature. (a) 15% $Co/Al_2O_3$; (b) 10% $Co/Al_2O_3$.

sorbed depending upon support, metal loading, and preparation.

The nature of hydrogen adsorption on and desorption from cobalt is not well documented in previous literature. Indeed there are only three previously reported TPD studies of $H_2$ desorption from cobalt (*11–13*) and only three rarely cited papers (*11, 14, 15*) which mention that $H_2$ adsorption on cobalt is activated. Matsumara *et al.* (*14*) observed that $H_2$ uptake on potassium-promoted cobalt was maximum at 200°C, while Sastri and Srinivason (*15*) observed maximum adsorption on Co/Kieselguhr catalysts at 50°C. Dollimore and Harrison (*11*) observed negligible $H_2$ adsorption on $Co/TiO_2$ at 25°C, although a significant amount was adsorbed at 300°C. In other words, there were significant variations in the maximum adsorption temperature observed for these catalysts containing different supports and promoters. The data of this study provide a basis for explaining these differences, i.e., *the extent of activation is a function of the extent of interaction of cobalt metal with a support or promoter.*

The concept of activated adsorption was introduced by Taylor over five decades ago (*16*). Since that time workers have generally assumed that activation energies for $H_2$ adsorption on Group VIII metals were sufficiently small to enable equilibrium monolayer coverages to be obtained at room temperature (*17*). However, recent data

TABLE 2

Temperatures for Maximum Adsorption of $H_2$ on Cobalt Catalysts and Amounts Adsorbed by Pulse-Flow Method

| Catalyst | Optimal adsorption temp. (°C)[a] | Area max[b] /area 25°C | $H_2$ Uptake[c] ($\mu$ mol/g) |
|---|---|---|---|
| Unsupported | 100 | 1.3 | 5.8 |
| 3% $Co/SiO_2$ | 150 | 33.5 | — |
| 10% $Co/SiO_2$ | 100 | 2.8 | 27.5 |
| 15% $Co/SiO_2$ | 50 | 2.1 | — |
| 3% $Co/Al_2O_3$[d] | — | — | — |
| 10% $Co/Al_2O_3$ | 125 | ∞ | 19.1 |
| 15% $Co/Al_2O_3$ | 125 | ∞ | — |

[a] Temperature at which the maximum amount of $H_2$ was adsorbed.

[b] Ratio of peak area at temperature of maximum adsorption to the area at 25°C.

[c] $H_2$ uptake at temperature of maximum adsorption using the pulse flow adsorption method. Determined by TPD.

[d] No detectable $H_2$ uptake at any temperature using pulse-flow technique.

obtained in this laboratory indicate that strongly activated adsorption of $H_2$ on Group VIII metals due to metal–support or metal–promoter interactions may be a general phenomenon. In a recent companion TPD study in our laboratory (*18*) "activated" adsorption of $H_2$ was observed for $Ru/SiO_2$ but was not observed in either the case of silica-supported Ni or Fe catalysts. That is, the amounts of $H_2$ adsorbed on $Ni/SiO_2$ or $Fe/SiO_2$ diminished with increasing adsorption temperature. Nevertheless, $H_2$ adsorption on $Ni/Al_2O_3$ was found to be moderately activated (*19*) while $H_2$ adsorption on Fe/zeolites was strongly activated (*20*).

The observation in this study of "activated" and highly reversible $H_2$ adsorption on cobalt has important implications with regard to previous investigations and current experimental practice in catalytic science. It is convention to use $H_2$ adsorption at room temperature to estimate metal dispersion and metal particle size (*17, 21–23*). $H_2$ adsorption at 25°C is also used as the basis for calculating specific activities in the form of turnover frequencies, examples of which are recent determinations of specific activities of cobalt catalysts in CO hydrogenation (*21–23*). Thus, with the exception of Butt *et al.* (*24*), it appears that a number of investigators are not aware that $H_2$ adsorption on cobalt is highly activated. However, the data of this study and companion studies (*7, 10*) show that significantly greater quantities (in some cases 10–100 times greater) of $H_2$ chemisorb on cobalt catalysts at 50–150°C compared to 25°C and that this effect is more important at low cobalt loadings. In addition, our data show that the pulse-flow method results in less than monolayer adsorption because of kinetic limitations and because $H_2$ adsorption on cobalt is highly reversible. Accordingly previously reported dispersions (*21–24*) based on room temperature $H_2$ uptakes and/or those measured by pulse-flow techniques are probably erroneously low while turnover numbers (*21–24*) based on these $H_2$ uptakes are probably erroneously high, particularly those measured for 3–5% $Co/SiO_2$ (*22, 24*). This could explain, at least in part, the order-of-magnitude higher turnover numbers reported for 3–5% $Co/SiO_2$ (*22, 24*) based on $H_2$ adsorption compared to those for 2% $Co/Al_2O_3$ based on CO adsorption (*21*) and 23–48% $Co/ThO_2/Al_2O_3$ (*23*) based on $H_2$ adsorption. Furthermore, the results of this study explain the unexpectedly low $H_2$ uptake of 1 $\mu$mol/g reported by Vannice for 2% $Co/Al_2O_3$ (*21*). Indeed, strongly activated adsorption might explain, at least in part, the suppression of $H_2$ adsorption on titania-supported metals, attributed to strong metal support interactions (*25, 26*). Moreover, since generally accepted techniques for determining kinetics of desorption (*1–3*) assume nonactivated adsorption, more sophisticated methods need to be applied in the case of hydrogen desorption from cobalt. Finally, the kinetics reported in earlier TPD studies (*11–13*) may also need to be reevaluated. The quantitative aspects of hydrogen adsorption and desorption kinetics involving cobalt will be discussed in a later publication (*27*).

In summary then, the data of this study provide evidence that the conditions for measuring $H_2$ adsorption on cobalt catalysts and any previously reported data based on $H_2$ adsorption at 25°C need careful reevaluation. There is clearly a need to determine the conditions under which monolayer adsorption of $H_2$ is obtained on cobalt using static, volumetric techniques. We are currently undertaking additional studies in our laboratory to accomplish these objectives, one of which has been recently submitted for publication (*7*).

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