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The Catalytic Synthesis of Hydrocarbons from H_2/CO Mixtures over the Group VIII Metals

V. The Catalytic Behavior of Silica-Supported Metals

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The catalytic behavior of silica-supported Group VIII metals in the CO/H_2 synthesis reaction has been determined and compared to that of alumina-supported metals. A wider range of specific activities is observed over the silica-supported metals when based upon either adsorbed CO or adsorbed hydrogen to determine metal surface sites. Inclusion of a Cu/SiO_2 catalyst has established the left-hand portion of the volcano plot that was predicted from an earlier study. The most recent values for CO heats of adsorption on these metal surfaces were utilized to obtain this volcano plot and verify the correlation between activity and $\Delta H_{(ad)}$ observed earlier with alumina-supported metals.

INTRODUCTION

Earlier studies by the author have indicated that the support can have a noticeable effect upon the catalytic behavior of Group VIII metals in CO hydrogenation reactions (*1*). Significant differences in specific activity were found between Pd/Al_2O_3 and Pd/SiO_2 catalysts, while the catalytic behavior of Pt appeared to be relatively independent of the support. The specific activities determined for a series of nickel catalysts varied by less than one order of magnitude, and no trend was apparent between activity and the type of support utilized (*2*). The major influence of the support seemed to be reflected in the product selectivity; however, these were not major differences in selectivity, although they were readily detectable. From these studies the conclusion could be reached that the support can influence the overall catalytic behavior of a metal-support system in CO/H_2 synthesis reactions.

Since the Al_2O_3-supported Group VIII metals had been studied earlier, a basis existed to which a series of SiO_2-supported metals could be compared (*3*). With the alumina-supported metals, a correlation was found between the specific activity for CO hydrogenation (or methanation) and the CO heat of adsorption. The most active metals had the lowest heat of adsorption, based upon values which existed at that time in the open literature. Since that study, many new $\Delta H_{(ad)}$ values, obtained under ultra-high-vacuum conditions, have been reported for CO on all the Group VIII metals except cobalt and osmium. One might suppose that SiO_2-supported metals would approximate un-

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supported metal surfaces better than Al_2O_3-supported metals; for instance, with silica, surface spinel structures are avoided and metals are more easily reduced than those dispersed on alumina. This present study was of interest, then, to determine specific activities of SiO_2-supported metals for CO hydrogenation to learn if the correlation between activity and CO heats of adsorption still existed using these recent $\Delta H_{(ad)}$ values obtained on metal films and single crystal surfaces. In addition, by comparing the catalytic behavior of silica-supported metals to alumina-supported metals, differences in catalytic properties could be observed, should they exist, which might be attributable to the support.

EXPERIMENTAL METHODS

All catalysts were compared at 103 kPa (1 atm) of total pressure of $H_2 + CO$ in a glass differential flow reactor. Unless otherwise specified, H_2/CO ratios of 3 were used. Catalyst samples required were typically 0.5 g or less. Product analyses were determined using subambient, temperature-programmed gas chromatography. Chromosorb 102 columns gave good separation of inorganics, olefins, and paraffins up to carbon numbers of eight or nine. Normally, total CO conversions to all hydrocarbon products were maintained at 5% or less to eliminate heat and mass transfer effects. However, higher conversions were obtained in some cases which provided more accurate product distributions. The reactor has been described in more detail elsewhere (*4*).

Both hydrogen and CO chemisorption measurements were made on all used catalyst samples and most fresh, reduced catalysts also. A glass, mercury-free, high-vacuum ($\sim 10^{-7}$ Torr) adsorption unit incorporating a quartz spiral Bourdon tube was used for these measurements. The zero-pressure intercept was used as the hydrogen monolayer coverage value, while the irreversible CO uptake was obtained as the difference between an initial CO isotherm and that obtained after a 2-min evacuation following the first CO exposure. Greater detail on both the adsorption unit and the experimental procedure has been provided earlier (*4*).

The silica used as the support in all cases was Cab-O-Sil, obtained from the Cabot Corp. The preparation of the Pt/SiO_2, Pd/SiO_2, and Ni/SiO_2 catalysts is described in Refs. (*1*) and (*2*). The Co/SiO_2, Fe/SiO_2, Ru/SiO_2, Rh/SiO_2, Ir/SiO_2, and Cu/SiO_2 catalysts were prepared by impregnating silica with aqueous solutions of $Co(NO_3)_2$, $Fe(NO_3)_3$, $RuCl_3$, $RhCl_3$, $H_2IrCl_6 \cdot 6H_2O$, and $Cu(NO_3)_2$, respectively. The catalysts were then dried overnight at 120°C. The final metal loadings were determined by typical wet chemistry analytical techniques.

For the fresh catalysts, a standard pretreatment procedure was used which has been employed in this laboratory before (*4*). This same pretreatment was used prior to either chemisorption measurements or kinetic studies and, in brief, consisted of a stepwise reduction in flowing H_2 which concluded with a 1-hr reduction period at 450°C. If an adsorption run were planned, the sample was evacuated at ca. 425°C, whereas the sample was cooled to the desired temperature in flowing H_2 if a kinetic study were desired. One additional pretreatment was employed with the 5% Fe/SiO_2 (16 hr) catalyst. In this case, an overnight reduction of 16 hr at 450°C was also used to determine the effect of reduction time on both adsorption and catalytic properties of the 5% Fe/SiO_2 catalyst. As in the earlier studies, a procedure similar to that used by Sinfelt (*5*) was employed to maintain catalytic activity as total time on-stream increased. This consisted of cyclic 20-min purges in pure H_2 between 20-min H_2/CO exposures. Samples were taken for analysis after the latter exposure (*4*).

RESULTS AND DISCUSSION

Measurements of CO and H_2 Uptakes

The uptake data for these catalysts are given in Table 1. The original data for the Pt, Pd, and Ni catalysts are given in Refs. (*1*) and (*2*). Reasonable agreement between H_2 and CO uptakes occurs on the fresh reduced samples; however, significant differences are apparent for the re-reduced used samples. For highly dispersed metals on SiO_2, H/M ratios significantly greater than unity are commonly observed. There are various possibilities to explain this behavior, such as hydrogen spillover (*6*), but, regardless of the reason, this behavior is indicative of a highly dispersed metal system. The assumption of a dispersion of 100% for Ir, Rh, and Pt is supported by CO/M ratios near unity on these fresh catalysts.

The uptake data on the used samples are more difficult to interpret. Perhaps the best explanation to account for generally higher H_2 uptakes and lower CO uptakes, compared to the fresh samples, is residual carbon or carbonaceous material on the metal surface, even after a 450°C exposure to hydrogen. Hydrogen can migrate from the metal surface onto the carbonaceous material (*7*), whereas these sites would conceivably be blocked for CO adsorption. Because of this complication, the H/M values for Rh/SiO_2 and Ru/SiO_2 might be suspected to be anomalously high. Despite this behavior, with the exception of Ru and Rh, the relative trend of metal dispersion is similar when either the CO/M ratio or the H/M ratio is chosen as the basis of comparison. Therefore, the comparison of relative specific activities, based upon either adsorbed CO or adsorbed H to define the number of sites, should be consistent even though there may be some uncertainty about the absolute magnitudes of the turnover numbers calculated. Hydrogen adsorption data on the fresh samples can be used to determine the initial reduced metal surface areas. If serious sintering is assumed not to occur under these relatively mild reaction conditions, turnover numbers based on initial surface area can be cal-

TABLE 1

CO and H_2 Adsorption on SiO_2-Supported Metals

Catalyst	CO uptake (μmol/g)			H_2 uptake (μmol/g)		
	Fresh	Used	CO/M^a	Fresh	Used	H/M^a
5% Fe/SiO_2 (1 hr)	4.6	4.8	0.005	5.6	14	0.03
5% Fe/SiO_2 (16 hr)	—	2.8	0.003	—	14	0.03
1% Ru/SiO_2	68	12	0.12	20	40	0.81
5% Ru/SiO_2	102	55	0.11	110	174	0.70
4% Co/SiO_2	—	12	0.018	26	73	0.21
1.4% Rh/SiO_2	88.7	10	0.074	210	58	0.86
2% Ir/SiO_2	84	35.9	0.34	150	110	2.1
8.3% Cu/SiO_2	—	5.4	0.0041	—	23	0.035
2% Pt/SiO_2 (I)	—	23	0.23	(63% D)[b]	15	0.30
2% Pt/SiO_2 (E)	—	35	—	(100% D)	38	0.74
4.75% Pd/SiO_2 (A)	—	84.8	0.38	(46% D)	58[c]	0.26
4.75% Pd/SiO_2 (B)	—	51	0.23	(46% D)	—	—
16.7% Ni/SiO_2 (27)	—	456	0.16	384	121	0.085
16.7% Ni/SiO_2 (11)	—	179	0.063	157	110	0.077

[a] For the used samples, M is the total number of metal atoms per gram.

[b] D = Surface metal atoms/total metal atoms.

[c] Uptake at 1 Torr and 70°C.

TABLE 2

Catalytic Behavior of SiO_2-Supported Metals

Catalyst	$N_{CH_4} \times 10^3$ at 275°C (sec^{-1})			$N_{CO} \times 10^3$ at 275°C (sec^{-1})		E_{CH_4} (kJ/mol)	E_{CO} (kJ/mol)
	I[a]	II[b]	III[c]	I[a]	II[b]		
5% Fe/SiO_2 (1 hr)	28	5.2	12	54	10	29	37
5% Fe/SiO_2 (16 hr)	160	16	34	770	77	76.6	118
1% Ru/SiO_2	230	36	72	270	42	111	90.4
5% Ru/SiO_2	270	43	68	360	57	113	91.7
4% Co/SiO_2	870	72	200	1300 (est.)	100 (est.)	133	95.4
1.4% Rh/SiO_2	7.3	0.63	0.54	11.7	1.0	110	120
2% Ir/SiO_2	0.79	0.27	0.27	0.91	0.31	70.3	70
8.3% Cu/SiO_2	0.015	0.0018	—	0.015	0.0018	63.6	63.6
2% Pt/SiO_2 (I)	1.6	1.2	0.57	—	—	—	—
2% Pt/SiO_2 (E)	1.6	0.74	0.55	—	—	—	—
4.75% Pd/SiO_2 (A)	0.32	0.23	0.13	0.32	0.23	113	113
4.75% Pd/SiO_2 (B)	0.26	—	0.06	0.26	—	—	—
16.7% Ni/SiO_2 (27)	18	34	11	25	47	127	130
16.7% Ni/SiO_2 (11)	55	45	32	76	62	116	111

[a] Based on CO uptake on used sample.

[b] Based on H_2 uptake on used sample.

[c] Based on initial metal dispersion determined by H_2 adsorption on fresh, reduced sample.

culated to provide a good check on the values obtained using adsorption data on the used samples.

Catalytic Behavior

Three sets of turnover numbers, based on CO and H_2 uptakes on the used samples and also on the initial metal dispersions, are listed in Table 2 along with activation energies for both methane formation and overall CO conversion to hydrocarbon products. The activation energies for the SiO_2-supported metals are quite similar to those reported earlier for Al_2O_3-supported metals, with the exception of the 5% Fe/SiO_2 (1 hr) catalyst. Reduction of this catalyst for only 1 hr at 450°C does not appear sufficient to give the behavior expected from a completely reduced iron catalyst, and the different behavior of this sample is attributed to incomplete reduction.

The range of specific activities over the SiO_2-supported Group VIII metals listed in Table 2 is wider than that observed over these metals when supported on alumina. Nearly three orders of magnitude separate the least active Group VIII metal, palladium, from the most active metal, cobalt, regardless of the basis chosen to count active sites. This spread in turnover numbers is very similar to that for the unsupported metals (*8*). As expected, the specific activity of Cu is lowest of all the metals.

With the exception of cobalt and palladium, the turnover numbers based on adsorbed CO agree within a factor of 2 compared to the alumina-supported metals reported earlier (*4*). The variation in specific activity for Pd was discussed in Ref. (*1*). The ordering of relative specific activities is somewhat different for the silica-supported metals since Pd is now the least active and cobalt is one of the most active Group VIII metals for methanation and CO conversion. The other metals retain their relative order. The exact cause

TABLE 3

Comparison of Methanation Turnover Numbers on Ru Catalysts at 275°C, $P_{\text{total}} = 103$ kPa, and $H_2/CO = 3$

Catalyst	$N_{CH_4} \times 10^3$ (sec^{-1})[a]	Reference
1% Ru/SiO_2	68	(*9*)
1% Ru/SiO_2	72	This study
5% Ru/SiO_2	68	This study
5% Ru/Al_2O_3	147	(*4*)
1.5 and 5% Ru/Al_2O_3	26	(*10*)

[a] Based on initial dispersion.

for the higher activity for Co/SiO_2 compared to Co/Al_2O_3 is not known at this time. One of the most reasonable explanations is that the cobalt dispersed on SiO_2 was more completely reduced than the cobalt on alumina.

The agreement in CH_4 turnover numbers reported for nickel catalysts has been discussed in Ref. (*2*). Recently, Bond and Turnham have reported specific activities for SiO_2-supported ruthenium where turnover numbers were based upon initial dispersion (*9*). On that basis, the agreement in N_{CH_4} for Ru/SiO_2 catalysts is excellent, as shown in Table 3. If N_{CH_4} values from earlier studies for Ru/Al_2O_3 catalysts are also included, where again initial dispersions are used to calculate specific activities, the value reported by this author agrees within a factor of 2, while that reported by Dalla Betta *et al.* is one-third the value reported for Ru/SiO_2 (*10*). All values in Table 3 have been adjusted to the same temperature and pressure using the kinetic parameters determined by each set of investigators. The utility of specific activities allows us to make these direct comparisons of rates measured in three different laboratories.

Recently, many new values have been reported for the heats of adsorption of CO on various metals between 0 and 300°C. All these values have been obtained on clean metal surfaces under conditions of ultrahigh vacuum, and those obtained at low coverages are listed in Table 4 along with the references from which the data were obtained. Although some of these heats of adsorption have been measured on only one single crystal surface, whereas others have been measured on a number of single crystal surfaces or on films, they probably represent the most accurate values to date. Using these $\Delta H_{(\text{ad})}$ values for CO, a correlation between the turnover numbers for methanation and CO heat of adsorption is obtained, as shown in Fig. 1, which was predicted earlier (*3*). A similar plot for total CO conversion also exists, as shown in Fig. 2. One of the biggest differences between these $\Delta H_{(\text{ad})}$ values and those reported earlier is the contraction in the spread of heats of adsorption. As predicted, when the CO–metal bond strength is weakened too much, a sharp decline in specific activity occurs as shown by Cu. This plot, then, contains the second half of the expected volcano-shaped plot which can be predicted by simple arguments. It was assumed in this

TABLE 4

Heats of Adsorption of CO on Clean Metal Surfaces

Metal	Crystal face	$\Delta H_{(\text{ad})}$ (kJ/mol)	Reference
Ni	Film	105–125	(*11*)
Ni	(111)	111	(*12*)
Ru	(001)	121	(*13*)
Fe	Bulk	125	(*14*)
Fe	Film	125–146	(*15*)
Pt	(111)	126	(*16*)
Pt	(110)	134	(*16*)
Ir	(111)	147	(*16*)
Ir	(111)	138–142	(*17*)
Rh	Foil	140 (est.)	(*18*)
Pd	(111)	142	(*19*)
Pd	(100)	153	(*19*)
Pd	(110)	167	(*19*)
Pd	(210)	147	(*19*)
Pd	(311)	149	(*19*)
Cu	(111)	69	(*20*)
Cu	(100)	77	(*20*)
Cu	(110)	82	(*20*)

plot, for lack of data, that the heat of adsorption of CO on a clean Co surface would lie between the values measured for Ni and Fe, due to the position of cobalt in the periodic table. The availability of these data in the future will test the validity of this assumption. Plots very similar to those in Figs. 1 and 2 are obtained when the dispersion of the fresh catalyst is chosen as the basis for turnover number calculations, as shown in Fig. 3. This provides excellent support for the correlation based on adsorbed CO even though some differences exist in the absolute values of the turnover number. Even if the H_2 uptakes on the used samples are used to calculate turnover numbers. the patterns shown in Figs. 1–3 are obtained; however, greater scatter in the data point occurs.

The maximum activity occurs around a $\Delta H_{(\mathrm{ad})}$ value of 30 kcal/mol. Therefore, for bulk, unsupported metals whose surfaces have heats of adsorption near 30 kcal/mol, a weakening of the CO–metal bond strength caused by any effect would not be expected to enhance activity significantly and could even reduce activity. The behavior of nickel catalysts is consistent with this reasoning (*2*), and the specific activity on

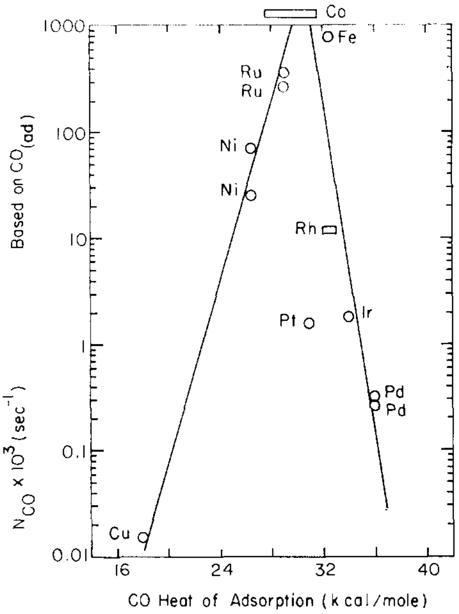

FIG. 2. CO hydrogenation over silica-supported metals.

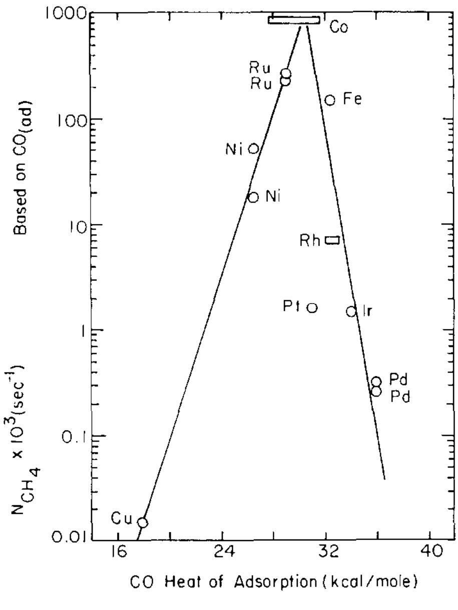

FIG. 1. Methanation activity over silica-supported metals.

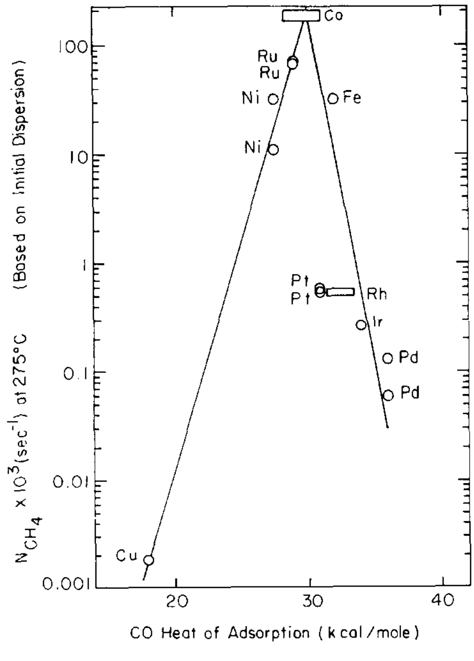

FIG. 3. Methanation over silica-supported metals.

TABLE 5

Product Distributions for SiO_2-Supported Metals with $H_2/CO = 3$ and $P = 103$ kPa

Catalyst	Temperature (°C)	Conversion (% CO)	Hydrocarbon product (mol%)							
			C_1	$C_2^=$	C_2	$C_3^=$	C_3	$C_4^=$	C_4	C_5^+
4% Co/SiO_2	203	3.8	67.1	0.7	7.1	5.6	2.5	2.3	5.4	9.2
4% Co/SiO_2	220	7.4	72.5	0.5	8.0	3.8	3.5	1.4	4.1	6.1
5% Ru/SiO_2	219	7.1	72.1	0	8.6	1.8	3.3	0.3	6.9	7.0
1% Ru/SiO_2	218	2.0	80.6	1.2	7.4	5.5	1.5	1.2	1.7	1.0
5% Fe/SiO_2 (16 hr)	247	3.7	60.2	3.7	11.4	13.1		7.9		3.8
(16 hr)	224	1.7	72.8	4.2	10.5	8.5		3.0		1.0
(1 hr)	245	1.1	75.1	4.4	16.8	1.7		2.0		—
16.7% Ni/SiO_2 (27) and (11)	220	3.3	92	tr	3	tr	3	1		0
1.4% Rh/SiO_2	271	0.63	85.5	4.7	9.9	—	—	—	—	—
2% Pt/SiO_2	274	0.22	100	0	0	0	0	—	—	—
2% Ir/SiO_2	265	0.84	83.4	0	16.6	0	0	—	—	—
4.75% Pd/SiO_2	275	~0.4	100	0	0	0	0	—	—	—
8.3% Cu/SiO_2	400	0.04	100	0	0	—	—	—	—	—

Ru has been reported to be independent of the crystallite size (*10*).

The product distributions achieved with these silica-supported metals are listed in Table 5. A range of temperature exists due to the desirability of maintaining low conversions. However, product distributions did not change markedly with temperature over a range of 20–30°C, so that useful comparisons can still be made from the data in Table 5. As one might have expected, Ru has a high fraction of C_5^+ hydrocarbons in the product stream; however, Co gave the highest fraction of C_5^+ hydrocarbon species under these experimental conditions. This behavior is consistent with the old data of the German workers which showed that waxy deposits build up on Co catalysts thereby necessitating periodic cleaning by soaking the catalyst in a solvent to dissolve most, if not all, of this paraffinic material (*21*).

Somewhat less methane was produced over silica-supported iron (60 mol% at 247°C) compared to alumina-supported iron (70% at 240°C), as reported in Ref. (*3*). This is consistent with present knowledge concerning iron catalysts which predicts that more acidic materials like alumina enhance CH_4 production, while more basic materials like K_2O decrease it (*22*). Silica is a less acidic material than alumina and would be expected to produce this shift in selectivity.

An important observation in this study was that no significant deactivation was apparent during the kinetic study, which strengthens the belief that clean, reduced metal surfaces are being studied under these experimental conditions. This is most likely due to the periodic H_2 cleaning between each measurement of activity which is a consequence of the experimental technique (*4*). However, the adsorption behavior could allow the inference that some carbonaceous material is retained on the surface after the standard pretreatment. Others have reported evidence to support this possibility (*23*). Either the coverage of the metal surface by the carbonaceous material occurs very rapidly and, once formed, does not change markedly within the time scale of these experiments or, through present, this surface carbonaceous material does not inhibit activity in a significant manner.

One reason for this study was the supposition made by the author that silica-supported metals would behave more like unsupported metals than alumina-supported metals since, for one reason, no surface spinel structures can be formed with silica. This assumption seems to have been borne out. The spread in turnover numbers is three orders of magnitude for both unsupported and silica-supported metals. In addition, the relative specific activities are very similar for unsupported and silica-supported metals (*8*).

This study provides more evidence that the support can alter the catalytic behavior of metals in an observable way although the mechanism of this metal–support interaction is not known at this time. The specific activity of cobalt supported on SiO_2 is certainly much higher than cobalt supported on alumina. It has been known for decades, however, that SiO_2 and Al_2O_3 can change the activity and selectivity of bulk Fe catalysts when they are deposited on the surface of the iron (*21*, *22*). In addition, the most active Fischer–Tropsch catalyst discovered by the Germans was cobalt supported on kieselguhr, although other promoters were present (*21*). It is perhaps amusing to note that this study confirms data obtained over 40 years ago since kieselguhr is composed primarily of silica.

CONCLUSIONS

The correlation between specific activities for methanation and CO heats of adsorption reported recently has also been observed for silica-supported metals. This correlation utilizes the most recent values for CO heats of adsorption on clean metal surfaces. As predicted earlier, a volcano-shaped plot occurs when the spread in $\Delta H_{(ad)}$ for CO is wide enough, and the $\Delta H_{(ad)}$ value giving optimum activity appears to be around 30 kcal/mol.

A greater spread in turnover numbers exists for the silica-supported Group VIII metals primarily because Pd/SiO_2 is less active than Pd/Al_2O_3 and Co/SiO_2 is more active than Co/Al_2O_3. The silica-supported metals encompass a range of three orders of magnitude compared to a factor of 100 for the alumina-supported metals.

The influence of the support was most apparent on cobalt, increasing both the specific activity and the average molecular weight of the synthesis products of cobalt on silica, compared to cobalt on alumina. A noticeable influence of the support was also observed for iron, while previous effects have already been reported for Pd (*1*). This general area of metal–support interaction is very intriguing, although not well understood, and the questions which now exist will hopefully be answered by future investigations.

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