

Carbon Monoxide Adsorption as a Chemical Probe of Supported Nickel Catalysts: The Role of Carbonyl Formation and Support Effects

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Quantitative CO chemisorption measurements were made on nickel catalysts supported on SiO₂, Nb₂O₅, and Nb₂O₅-SiO₂ to investigate the nature and stoichiometry of CO adsorption. A close look at conventional methods of performing CO adsorption isotherms revealed that for supported nickel catalysts, the results are quite sensitive to a number of experimental parameters including CO pressure, adsorption temperature, and time of equilibration. The formation of Ni(CO)₄ was observed even at subambient adsorption temperature. Erroneous adsorption uptakes and unrealistic CO/Ni_s stoichiometries are likely to result if this tendency for carbonyl formation is not recognized and properly taken into account. The extent of carbonyl formation and the effect of the experimental variables just mentioned are support-sensitive. Consequently CO chemisorption data may be used to evaluate the degree of interaction between nickel and the support. © 1985 Academic Press, Inc.

INTRODUCTION

The selective chemisorption of gaseous molecules has long been recognized as an important method for characterization of the crystallite size of supported metal catalysts (1-5). This technique may even be used in conjunction with single-crystal adsorption data to provide information about the relative abundance of different crystal planes on supported metals (6). There are, however, a number of concerns which must be addressed before the full significance of the adsorption data may be understood. These include the close study of experimental parameters such as gas pressure, adsorption temperature, and time of equilibration, all of which can affect the amount of chemisorption uptake on supported catalysts.

In addition, another serious concern arises when the adsorbate actually reacts with the adsorbent. One such example is the adsorption of carbon monoxide on a

supported nickel catalyst. The formation of gaseous tetracarbonyl nickel may occur under a wide range of pressures and temperatures (7). As well as being a highly toxic substance, tetracarbonyl nickel is undesirable because its formation causes nickel to be stripped from the catalyst surface, and can also lead to erroneous adsorption results when uptakes are measured volumetrically or gravimetrically.

The purpose of this study was to investigate the adsorption of carbon monoxide on a series of differently supported nickel catalysts. The experimental parameters of CO pressure, adsorption temperature, and time of equilibration were studied to help determine the nature and stoichiometry of CO adsorption, and the conditions for and extent of carbonyl formation, all as a function of the support for this series of nickel catalysts.

EXPERIMENTAL

Nickel catalysts were supported on SiO₂, Nb₂O₅, and Nb₂O₅-SiO₂. The Ni/SiO₂ catalysts were prepared by incipient wetness impregnation and by precipitation of nickel hydroxide from a nickel hexammine solu-

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tion as described elsewhere (8). The support used in both of these preparations was Davison 952 SiO₂, a wide-pore silica with a BET surface area of 300 m²/g.

The Nb₂O₅ support was prepared by adding ammonium hydroxide to a methanolic solution of niobium(V) chloride. The resulting precipitate was filtered, repeatedly washed with distilled water, and calcined in flowing oxygen to obtain a crystalline Nb₂O₅ phase (9). The Nb₂O₅-SiO₂ support was prepared by impregnating SiO₂ (Davison 952) to incipient wetness with a hexane solution of niobium(V) ethoxide. After the solvent was evaporated in a vacuum oven, the support was heated in flowing nitrogen at 673 K for 2 h, then calcined in flowing oxygen at 773 K for 2 h. This procedure successfully deposited Nb₂O₅ as a homogeneous surface phase oxide onto SiO₂, as verified by X-ray diffraction studies and analytical transmission electron microscopy (10). The amount of Nb₂O₅ for a monolayer coverage corresponds to about 30 wt%. Nickel catalysts on Nb₂O₅ and Nb₂O₅-SiO₂ were prepared by the incipient wetness impregnation of an aqueous solution of nickel nitrate hexahydrate.

All catalysts were dried overnight at 383 K following preparation. Samples were reduced in hydrogen at either 773 or 1050 K and evacuated under 10⁻⁶ Torr at 773 K prior to chemisorption measurements. Information about sample weight loading, reduction treatment, and metal crystallite size is given in Table 1.

Chemisorption measurements were made in a conventional glass adsorption system including a differential precision pressure gauge (Texas Instruments) and a known dosing volume of about 20 cm³. The reference side of the gauge was evacuated continuously to 10⁻⁶ Torr. Hydrogen chemisorption experiments were begun by dosing the reduced and evacuated sample with a known amount of hydrogen at ambient temperature such that the equilibration pressure was about 100 Torr. The first dose was allowed to equilibrate about 15 h. Each subsequent dose required about 1 h equilibration time. Only one isotherm was recorded for each sample since literature results (11) and our own studies have shown negligible adsorption of hydrogen on any of the supports used.

CO chemisorption experiments were per-

TABLE I
Preparation and Characterization Data for Supported Ni Catalysts

Sample	Support	Preparation method	% Ni ^a	Reduction ^b treatment time (h)/T(K)	Crystallite size (nm)		
					H ₂ Chem.	XRD	Magnetic
A	SiO ₂	iw ^c	8	4/773	6.0	6.0	4.5 ^e
B	SiO ₂	p ^d	20	4/773	2.5 ^f	<3.0 ^g	2.5
C	SiO ₂	p	20	15/1050	6.0	4.5	4.0
D	Nb ₂ O ₅	iw	10	1/773	200 ^h	9.0	8.5 ^e
E	Nb ₂ O ₅ -SiO ₂	iw	9	1/773	13.5	6.0	4.5 ^e

^a Determined by atomic absorption spectroscopy.

^b Reduction in 3 liters/h H₂ flow.

^c Incipient wetness impregnation.

^d Precipitation.

^e These samples exhibited slightly nonsuperparamagnetic behavior due to the presence of some large (>10 nm) crystallites.

^f Calculated after taking into account 70% reduction of metal. All other samples are 100% reduced as determined by volumetric oxygen treatment at 673 K.

^g Crystallite size smaller than detection limit for Mo X-ray source.

^h Hydrogen uptake severely suppressed on this sample.

formed either at 273 or 195 K. In most experiments, desorption rather than adsorption isotherms were recorded. In these experiments, a large quantity of CO was initially dosed onto the catalyst surface, and for each subsequent data point CO was removed from rather than added to the known volume. A second isotherm was performed on each sample to account for the large amount of CO weakly held on the surface at the low temperatures used. An evacuation time of at least 1 h was required between the two isotherms.

The time of equilibration of each point on the isotherm varied with samples and with conditions, but in all cases attempts were made to establish that equilibrium had been reached (no further change of CO pressure with time) before recording the data. The initial point of the first isotherm was equilibrated at least 15 h for each sample. Isotherms performed at 273 K appeared to require longer equilibration times, taking even up to several days to complete two isotherms on some SiO₂-supported samples. Desorption isotherms of CO chemisorption on the blank supports were completed for each support, and all results reported here are corrected for this adsorption.

Infrared spectra were recorded on a Digilab FTS-15C spectrometer. Samples were reduced, evacuated, and contacted with small doses of CO at ambient temperature.

TABLE 2
CO Chemisorption on SiO₂-Supported Ni

Sample	Isotherm Type/temp. (K)	CO dosing pressure (Torr)	Isotherm slope	CO/H ratio
A	Adsorption/273	700	^a	14
B	Adsorption/273	600	^a	12
A	Desorption/195	1000	Positive	1.6
B	Desorption/195	1000	Positive	1.8
C	Desorption/195	900	Positive	0.6
A	Desorption/195	500	Positive	0.9
B	Desorption/195	500	Positive	1.4
C	Desorption/195	500	Positive	0.5

^a Isotherm performed in adsorption mode.

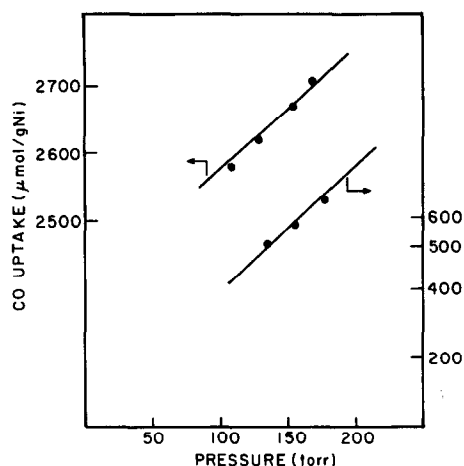


FIG. 1. Desorption CO isotherms for Sample A, Ni/SiO₂. Adsorption temperature: 195 K. Upper curve, first CO isotherm on bare surface. Lower curve, second CO isotherm; CO uptake after 1 h evacuation following first isotherm.

In addition to crystallite size determination from hydrogen chemisorption measurements, crystallite sizes were also measured by X-ray diffraction using a Rigaku D-Max diffractometer and MoK α radiation. In some cases crystallite sizes and size distributions were also measured by magnetic methods using a Cahn magnetic susceptibility instrument. Metal weight loadings were confirmed by atomic absorption spectroscopy.

RESULTS

Silica-Supported Ni

Table 2 gives details of CO chemisorption results for SiO₂-supported nickel catalysts under a variety of conditions. A typical isotherm is shown in Fig. 1. It can be seen from these data that the experimental conditions can have a tremendous effect on the results. In particular, the temperature of adsorption of CO on supported Ni has a marked influence on the data. It appears from the CO uptakes measured that adsorption at 273 K is an order of magnitude greater than that at 195 K, leading to unrealistically large CO/H ratios of greater than 10.

Since it is sterically highly unlikely that

such a large number of CO molecules may be in intimate contact with each surface nickel atom, the uptake of CO from the gas phase must be due to another phenomenon. The formation of gaseous tetracarbonyl nickel requires four gaseous CO molecules to form one gaseous $\text{Ni}(\text{CO})_4$ molecule. Hence, the formation of this species would manifest itself in chemisorption measurements as a decrease in CO pressure, and could be erroneously interpreted as being due to CO uptake on the surface. Carbonyl formation on nickel surfaces is commonly known but has not been considered a very fast process at temperatures as low as 273 K (11).

Metal weight loadings of some samples were determined both before and after these CO chemisorption experiments. For Sample B a nearly 30% nickel weight loss was found after CO chemisorption at 273 K as just described. This is strong evidence that adsorption of CO at 273 K can lead quite readily to substantial volatilization of nickel through $\text{Ni}(\text{CO})_4$ formation.

In order to better account for the possibility of carbonyl formation during chemisorption experiments, the remainder of the experiments were performed using desorption rather than adsorption isotherms. The experiment started at high pressure and proceeded toward lower pressure to obtain a relationship between pressure and amount of CO adsorbed. In a system where the adsorption-desorption equilibrium is the only process occurring, a decrease in pressure above the sample causes a decrease in the amount of adsorbate as the system reaches a new equilibrium. This produces a conventional isotherm with a positive slope when the number of molecules adsorbed is plotted against the equilibrium pressure of the system. If $\text{Ni}(\text{CO})_4$ is being formed in addition to the CO adsorption-desorption process, the experimental result is a decrease in the number of gas-phase molecules since there are four CO molecules in each single tetracarbonyl nickel molecule. Since the total system

pressure is measured rather than the partial pressures of each type of gas-phase molecule, this carbonyl formation would lower the total pressure and create the impression that the amount of gas-phase CO adsorbed on the surface has actually increased. An apparent increase in adsorption with a decrease in pressure is inconsistent with an equilibrium adsorption-desorption process; hence, the use of desorption isotherms can help detect the formation of $\text{Ni}(\text{CO})_4$ which might have been erroneously attributed to enhanced CO adsorption if conventional adsorption isotherms had been performed. Figures 2 and 1 show desorption isotherms for systems in which carbonyl formation is and is not a dominant factor, respectively.

The initial CO dosing pressure is also seen to have an effect on the CO chemisorption results. Consider Samples A and B in Table 2. Two different sets of desorption experiments were performed at 195 K on these samples. The first set used a CO dosing pressure of around 1000 Torr and the second set a 500-Torr dosing pressure. While isotherms performed at 195 K appear to avoid the problem of extensive carbonyl formation observed at 273 K, the CO pressure to which the sample is exposed at this temperature appears to influence the CO uptake, and hence the CO/H ratio. On Sam-

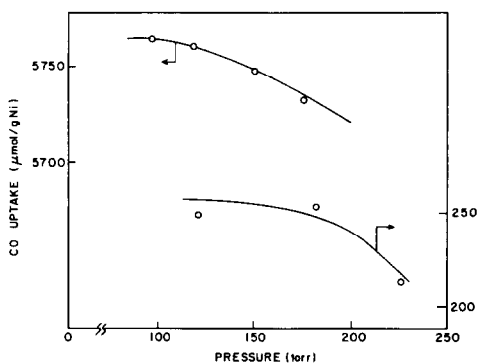


FIG. 2. Desorption isotherms for Sample E, $\text{Ni}/\text{Nb}_2\text{O}_5\text{-SiO}_2$. Adsorption temperature: 273 K. Upper curve, first isotherm of CO uptake on bare surface. Lower curve, second isotherm; CO uptake after 1 h evacuation at 273 K following first isotherm.

ple A, the higher CO dosing pressure led to a higher CO/H ratio of 1.6 compared to 0.9 for the lower dosing pressure. The ratio changed from 1.8 to 1.4 with the decrease in CO pressure for Sample B. Carbonyl formation did not seem to be significant in these experiments since the desorption isotherms exhibited positive slopes.

In contrast to Samples A and B, Sample C appeared to be less affected by the CO dosing pressure. Sample C was prepared by the same method as Sample B, but was reduced at a higher temperature to produce a catalyst with a crystallite size similar to that of Sample A. The trend in CO/H ratio for the three samples does not appear to correlate with either method of preparation or with crystallite size. For Sample C, a CO/H ratio of about 0.5 resulted for both 1000- and 500-Torr CO dosing pressures. Again, the well-behaved positive slopes of the desorption isotherms implied minimal carbonyl formation in the time frame of the experiment.

Ni on Other Supports

Isotherms were also completed on nickel supported on Nb₂O₅ and Nb₂O₅-SiO₂. Metals supported on Nb₂O₅ have been shown (8) to exhibit strong metal-support interactions (SMSI). The one monolayer Nb₂O₅-SiO₂ combines characteristics of both the relatively inert SiO₂ and the highly interacting Nb₂O₅, and its behavior has

been shown to be intermediate between the two types of supports (10). Comparison of metal crystallite sizes from X-ray diffraction and hydrogen chemisorption results (Table 1) for Samples D and E indicates severe suppression of hydrogen adsorption for the Nb₂O₅-supported nickel and less severe suppression for the Nb₂O₅-SiO₂-supported nickel. It has been established that such a suppression is not due to the poor reducibility of nickel on these supports (9, 10).

Details of CO desorption isotherm experiments are summarized in Table 3. As in the case of SiO₂-supported nickel, experiments were completed at two temperatures, 273 and 195 K. CO dosing pressures were kept near 500 Torr for all samples.

Isotherms performed at 195 K for Samples D and E indicate minimal carbonyl formation, as shown by the low CO uptakes and by the positive slopes of the desorption isotherms. A CO/H ratio is not very meaningful for the Nb₂O₅-supported Sample D because of the extremely low hydrogen uptake. A CO/Ni_s ratio derived using the X-ray diffraction crystallite size also indicates significant suppression of CO chemisorption. For Sample E, however, the small suppression of hydrogen chemisorption observed allows calculation of a reasonable CO/H ratio of 1.2. This value decreases to 0.6 if a CO/Ni_s ratio based on X-ray diffraction results is used. In the following discus-

TABLE 3
CO Chemisorption on Ni on Supports Other Than SiO₂^{a,b}

Sample	Support	Isotherm temp. (K)	Sense of slope	% Dispersion		Adsorption stoichiometry		
				CO Uptake	XRD	CO/H	H/Ni _s ^c	CO/Ni _s ^c
D	Nb ₂ O ₅	195	Positive	1.2	9.2	4.2	0.03	0.13
E	Nb ₂ O ₅ -SiO ₂	195	Positive	8.5	13.8	1.2	0.5	0.6
D	Nb ₂ O ₅	273	Negative	3.2	9.2	11	0.03	0.35
E	Nb ₂ O ₅ -SiO ₂	273	Negative	32.0	13.8	5.2	0.5	2.4

^a All isotherms are desorption isotherms.

^b All CO uptakes are corrected for adsorption on the support.

^c Ni_s determined from crystallite size measurements by X-ray diffraction.

sion, CO/Ni_s ratios will be used to characterize the CO uptake measurements for these interacting supports rather than the CO/H ratios used for SiO₂-supported nickel.

Desorption CO isotherms recorded at 273 K on Samples D and E give very different results. On the Nb₂O₅-supported Sample D, CO adsorption at 273 K is a factor of three greater than it is at 195 K. This adsorption, however, still represents a suppression of CO adsorption over what one should expect for a noninteracting sample: a CO/Ni_s ratio based on X-ray diffraction data is about 0.35. Inspection of the desorption isotherms reveal that the slopes are negative. This indicates either that carbonyl formation is occurring or that the adsorption process had not reached equilibrium at each point before the data were recorded. If the latter is the case, it implies that a slow chemisorption process is occurring at 273 K that is suppressed at lower temperatures.

CO desorption isotherms at 273 K on Sample E, the Ni/Nb₂O₅-SiO₂ sample, show that the CO uptake is four times greater than that obtained at 195 K. Here, also, negative slopes of desorption isotherm curves indicate either the possibility of carbonyl formation or of a slower adsorption process that had not equilibrated in the time allowed for each isotherm point. In the case of Sample E, however, the very large CO uptakes and large CO/Ni_s ratio of 2.4 strongly imply the formation of Ni(CO)₄.

The intermediate behavior of the Nb₂O₅-SiO₂ support is demonstrated by the results of CO chemisorption at 273 K: the SiO₂-supported samples exhibit relatively extensive carbonyl formation at 273 K, resulting in CO/H or CO/Ni_s ratios of greater than 10 (see Table 2); the interacting Nb₂O₅ supported samples exhibit a suppression of CO chemisorption at 273 K (with a CO/Ni_s ratio of 0.35); and the intermediate Nb₂O₅-SiO₂ supported samples exhibit an intermediate amount of carbonyl formation as evidenced by the CO/Ni_s ratio of 2.4. The hydrogen

adsorption isotherms also illustrate this trend. Hydrogen uptake per gram nickel was greatest for catalysts supported on SiO₂, suppressed by a factor of 2 on Nb₂O₅-SiO₂, and was severely suppressed on Nb₂O₅-supported nickel.

CO adsorption was also studied by IR spectroscopy for Samples D and E. The CO spectrum for Ni/Nb₂O₅-SiO₂, Sample E, is shown in Fig. 3. The striking observation which these studies yielded is that no peaks for adsorbed CO of any type was detected on Samples D and E. At CO pressures of less than 10 Torr, no peaks were detected at all in the CO region. As the CO pressure was increased, peaks for gaseous CO could be detected above 2100 cm⁻¹, and finally a sharp peak near 2055 cm⁻¹ began to appear. This peak corresponds to the frequency for gaseous Ni(CO)₄. The spectra for CO in contact with Sample D had a much higher noise level due to the higher electron density of the Nb₂O₅ support. However, the results show the same trend noted for Sample E in Fig. 3.

DISCUSSION

Silica-Supported Ni

Metal crystallite sizes are given in Table 1 for SiO₂-supported nickel catalysts as determined by hydrogen adsorption data, X-ray diffraction, and magnetic measure-

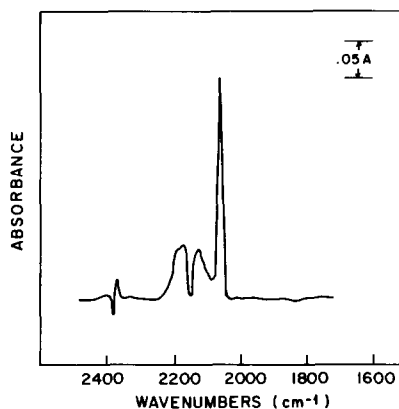


FIG. 3. IR spectrum of CO in contact with Sample E, Ni/Nb₂O₅-SiO₂, at 25 Torr and ambient temperature.

ments. The good agreement between results for these three methods confirms that the assumption of an H : Ni_s of 1 : 1 is a good one for these catalysts, as has been well established for SiO₂- and Al₂O₃-supported nickel (11). Hence CO and H₂ adsorption data may be compared in order to determine the number of CO molecules adsorbed per surface nickel atom. In the following discussion of CO chemisorption, CO/H ratios for different samples and different conditions help to characterize the chemisorption of CO on SiO₂-supported nickel. For SiO₂-supported Ni, CO/H and CO/Ni_s ratios can be used interchangeably.

The results for SiO₂-supported Ni reported here indicate that the formation of tetracarbonyl nickel on these catalysts is still quite significant at temperatures as low as 273 K, under the conditions employed in these chemisorption experiments. There appears to be a delicate balance between equilibration of adsorption processes on the surface and formation of gaseous carbonyl from the adsorbed surface species. It appears from our experiments that it is only when the temperature of adsorption is lowered to 195 K that the process of carbonyl formation becomes insignificant in the time frame required for equilibration of the adsorption process.

This ease of carbonyl formation even under conditions previously considered to be "safe" for CO adsorption on supported nickel (11) indicates the care which must be taken in carrying out these experiments. If CO chemisorption on Ni/SiO₂ is monitored in the adsorption mode, with insufficient time allowed between each data point to establish that equilibrium had been attained, misleading results might be reported, and/or the formation of carbonyl might be overlooked or mistakenly considered as uptake on the surface. The relative rates of carbonyl formation and CO adsorption are unknown, and hence it is impossible to separate the two. If CO adsorption is fast compared to carbonyl formation, then perhaps short equilibration times can

lead to valid CO adsorption isotherms. However, results from our laboratory indicate that even short equilibration times can lead to desorption isotherms with negative slopes and consequently large CO/H ratios. In any case, if the isotherms are performed by desorption of CO from the system at each data point, the questions of equilibration and carbonyl formation can be settled simply by checking the sense of the slope of the isotherm. Bartholomew and Pannell (11) have suggested that desorption isotherms provide the optimal way to measure CO chemisorption on supported nickel, and the results of our study fully support this conclusion, with the added emphasis on the importance of checking for carbonyl formation.

In the absence of carbonyl formation, CO/Ni_s ratios of greater than 1 imply some degree of surface subcarbonyl formation, the adsorption of two or three CO molecules on a single Ni surface atom. It has been conjectured (12, 13) that this stoichiometry may be more prevalent for catalysts with small crystallite sizes (ca. 2.5 nm). The results of this study show that Sample B does indeed exhibit CO/H ratios greater than unity for both higher and lower CO dosing pressures. The small crystallite size of Sample B supports the argument that multiple adsorption of CO on a single surface nickel atom occurs easily on small crystallites.

Examination of the chemisorption data for Ni/SiO₂ samples indicate, however, that factors other than crystallite size influence the CO/H ratio of a sample. The dosing pressure of CO used in these desorption isotherm experiments was seen to influence the amount of CO adsorbed on the surface for Samples A and B. Higher CO pressure led to a higher CO/H ratio. Extensive carbonyl formation was ruled out since the desorption isotherm slope was positive, and the CO/H ratio was not unreasonably high. Instead, this change in stoichiometry of CO adsorption with CO pressure might indicate that there is an adsorption process which

can occur at this low temperature only under a high CO pressure. Pannell *et al.* (14) have also reported that the stoichiometry of CO adsorption on Ni depends on temperature, equilibration time, and equilibration pressure.

This high-pressure adsorption process does not seem to affect Sample C. This sample was prepared by the same precipitation technique as the small-crystallite-size Sample B, but was reduced under more rigorous conditions to obtain a catalyst with a crystallite size similar to Sample A, which was prepared by impregnation. Hence it is seen that neither crystallite size nor preparation method alone can fully explain the effect of CO pressure on CO adsorption for these catalysts.

Recent infrared spectroscopic results of CO adsorption for this same catalyst series help to explain this set of data (15). Although a direct comparison is difficult since all IR data were recorded at ambient temperature at pressures two orders of magnitude lower to avoid carbonyl formation, it is possible to elicit trends that may be helpful in the interpretation of the nature of the CO adsorption. IR spectra of CO adsorption on Samples A, B, and C differ mainly in the relative ratio of two peaks in the linear region, a high-frequency (HF) peak at 2080 cm^{-1} and a low-frequency peak (LF) at 2040 cm^{-1} . It has been suggested (13) that the HF peak is related to the presence of subcarbonyl species on nickel. Sample B, the 2.5-nm precipitated catalyst, has the highest HF/LF ratio. Sample C, the 6.0-nm catalyst prepared by the same method but a more severe pretreatment, exhibits a much smaller HF/LF ratio, while Sample A lies intermediate between the two. This trend for increasing HF/LF ratio follows the same trend as was found for increasing CO/H ratio. Small crystallite size does indeed appear to promote multiple CO adsorption, but larger crystallite size does not in itself appear to be sufficient to inhibit multiple adsorption under some conditions.

Samples A and C, with similar crystallite

sizes, differ in preparation method and in conditions of activation. The difference in their CO/H ratios may be attributed to differences in the surface structure of the nickel crystallites of each catalyst. The rigorous reduction treatment to which Sample C was subjected may have brought about a "smoothing" or annealing of the nickel surface. Consequently Sample C is expected to have less surface defects than either Sample A or B. Sample A in turn may have less defects than Sample B due simply to its larger crystallite size. The trend already noted in these three samples for increasing CO/H ratios and HF/LF infrared absorption can also be assigned to increasing amounts of defect sites or decreasing smoothness of the nickel surface. The trend reported in the literature for increasing formation of subcarbonyl species might therefore be more rigorously attributed to decreasing surface smoothness rather than simply to decreasing crystallite size. It also appears likely that the formation of subcarbonyl species is the adsorption process which is sensitive to the dosing pressure of CO.

Ni on Other Supports

The results for CO chemisorption on Nb_2O_5 and $\text{Nb}_2\text{O}_5\text{-SiO}_2$ supported nickel show a trend similar to SiO_2 -supported nickel for the effect of the temperature of adsorption. On Nb_2O_5 , CO adsorption at 195 K is severely suppressed, as is expected from such a strongly interacting catalyst (9). On $\text{Nb}_2\text{O}_5\text{-SiO}_2$, neither CO chemisorption at 195 K nor hydrogen chemisorption at ambient temperature appear to be significantly suppressed. In fact, it was pointed out that the CO/Ni_s ratio for Sample E is quite similar to that of the SiO_2 -supported Sample A prepared by the same method.

When CO chemisorption takes place at 273 K, both Samples D and E show significant increases in amount of adsorption as well as negative slopes in the desorption isotherms. For Sample D, even this large

increase amounts to a suppression of CO chemisorption over that found for SiO₂-supported nickel. The question remains, then, as to whether this increase is due to formation of carbonyl or to the adsorption of CO on some surface sites which, while proceeding too slowly to be detected at 195 K, at 273 K it proceeds more rapidly but requires a much longer time for equilibration. Either of these postulates could be used to explain the negative desorption isotherm slopes.

We may once again turn to infrared spectroscopic studies of CO adsorption at ambient temperature to aid in the explanation of chemisorption results. Infrared studies performed on Ni/Nb₂O₅ and Ni/Nb₂O₅-SiO₂ indicate first of all that CO adsorption is indeed suppressed on this sample. Addition of much larger amounts of CO to this sample than to any SiO₂-supported nickel samples result in no visible IR bands corresponding to adsorbed CO. But even more interestingly, we have found that increased CO dosing ultimately results in observation of a peak due to gaseous Ni(CO)₄ but still no detectable adsorbed CO species of linear, bridged, or subcarbonyl forms. This could imply that the formation of Ni(CO)₄ on Nb₂O₅- and Nb₂O₅-SiO₂-supported nickel is limited by an extremely slow first step of the adsorption of one CO molecule. Experimental evidence for CO chemisorption suppression supports the idea of this very slow adsorption. The fact that no adsorbed CO was observed on Samples D and E with IR even as carbonyl formation occurred also supports the idea that the apparent uptake observed in chemisorption experiments at 273 K is due to carbonyl formation.

Previous studies on CO adsorption on Ni/TiO₂ (16, 17) also suggest that carbonyl formation occurs much more slowly on interacting supports than on SiO₂. An investigation of Ni(CO)₄ formation from nickel single crystals (18) suggested a Langmuir-Hinshelwood mechanism for carbonyl formation. This could be the case

for the Nb₂O₅-supported nickel if the steps following the initial adsorption are very fast.

CO desorption isotherms for Sample E, the Nb₂O₅-SiO₂-supported nickel, also show equilibration problems as manifested by the negative slope of the desorption isotherm. The CO/Ni_s ratio of 2.4 suggests that these equilibration problems are due to the formation of gaseous nickel carbonyl. In comparison with CO/Ni_s ratios of 12-14 for Ni/SiO₂ samples at the same adsorption temperature, the results for the Nb₂O₅-SiO₂ sample suggest again the intermediate interacting nature of this support. While the formation of carbonyl proceeds easily for nickel supported on Nb₂O₅-SiO₂, it appears to be somewhat more inhibited than it is on the relatively inert SiO₂. As just discussed, carbonyl formation is even further inhibited for nickel on the more highly interacting bulk Nb₂O₅ support. This relative strength of metal-support interaction is consistent with the trend established by other chemical probes for the same catalyst (10). As discussed elsewhere (10), the mechanism of interaction, which involves the migration of oxide species to the metal surface, is believed to be the same for both Nb₂O₅ and Nb₂O₅-SiO₂. The less interactive nature of the latter under the same pretreatment is ascribed to the lower availability of the migrating species. If the suppression of carbonyl formation is related to the presence of oxide species on the metal surface, then results in this study provide indirect evidence that the Ni/Nb₂O₅-SiO₂ surface is indeed more sparsely decorated. The observation of carbonyl formation over the Ni/Nb₂O₅ sample also suggests that the metal surface is not totally covered. Hence, CO chemisorption experiments have provided a method to detect and to order the extent of nickel-support interactions through the monitoring of carbonyl formation under specific conditions.

CONCLUSIONS

The problem of gaseous carbonyl forma-

tion on supported nickel catalysts is a significant one even at temperatures as low as 273 K. Incorrect interpretation of this carbonyl formation as CO uptake on the sample is possible unless chemisorption data are recorded in the form of desorption isotherms.

Both nickel crystallite size and surface structure are shown to influence the nature and stoichiometry of CO adsorption on SiO₂-supported nickel. Multiple adsorption of CO on single nickel surface atoms increases with decreasing crystallite size and decreasing surface smoothness.

CO adsorption on the highly interacting Nb₂O₅-supported nickel is severely suppressed. Carbonyl formation still occurs, however, on this catalyst when adsorption is carried out at 273 K. The gaseous carbonyl appears to form after very slow adsorption of CO molecules on the nickel surface.

The nature of CO chemisorption on nickel supported on Nb₂O₅-SiO₂ appears to be intermediate between that of SiO₂- and Nb₂O₅-supported nickel. Monitoring of carbonyl formation on these catalysts provides a way to order the extent of nickel-support interactions.

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