JOURNAL OF CATALYSIS 56, 336–348 (1979)

Characterization of Coprecipitated Nickel on Silica Methanation Catalysts by X-Ray Photoelectron Spectroscopy

R. B. SHALVOY AND P. J. REUCROFT*

Department of Metallurgical Engineering and Materials Science, University of Kentucky, Lexington, Kentucky, 40506

AND

B. H. DAVIS

Institute for Mining and Minerals Research, University of Kentucky, Iron Works Pike Box 13015, Lexington, Kentucky 40583

Received June 26, 1978; revised October 12, 1978

An X-ray photoemission spectroscopy study of a series of standard nickel compounds (Ni, NiO, $Ni(OH)_2$, $NiSiO_3$) and silica-supported nickel methanation catalysts has been conducted. The binding energies and spectral shapes of the standard samples provide a data base which has been used to understand the catalyst spectra.

The activity and thermal stability of coprecipitated nickel catalysts has been attributed to the metal–support interaction. This interaction has been observed in two coprecipitated nickel-on-silica catalysts. The nickel spectra closely resemble those of amorphous $NiSiO_3$. The interaction varies somewhat between the two catalysts studied as evidenced by differences in their reducibility.

INTRODUCTION

The production of pipeline quality substitute natural gas from coal requires the methanation of coal synthesis gas using metal catalysts such as nickel (*1*, *2*). These catalysts can be quickly deactivated by poisoning from sulfur in the gas stream and by sintering of the dispersed nickel particles (*1*). In general, catalysts that are more resistant to both chemical poisoning and thermal sintering while maintaining good activity are required if this process is to become economically viable in the future. In addition, a better understanding of the mechanism of methanation is highly desirable in order to develop catalysts with improved selectivity. A program has been initiated which has the broad objective of gaining a better understanding of the chemical and physical characteristics of typical methanation catalysts in order to provide a basis for designing improved catalysts. Some of the results obtained have been reported previously (*3–5*).

X-ray photoelectron spectroscopy (XPS) is a powerful tool for characterizing the chemical and physical state of surfaces (*6*). XPS has been found to be particularly useful in the study of catalyst poisoning (*7*, *8*) and changes in the chemical state occurring after reducing or oxidizing treat-

---

* To whom further correspondence should be addressed.

0021-9517/79/030336-13$02.00/0

ments (*9*). The surface sensitivity of XPS (sampling depths are less than 18 Å (*10*)) makes the technique highly appropriate for the study of fresh and treated catalysts.

In the present work, the surfaces of silica-supported coprecipitated nickel methanation catalysts have been examined using XPS with the goal of characterizing the chemical state of the catalysts. Fresh (unreduced) samples have been evaluated.

These catalysts provide a good balance of methanation activity, selectivity, thermal stability, and reducibility (*11*). Interaction of the dispersed NiO particles and the silica support during catalyst preparation has been suggested as an important factor in providing this favorable set of properties (*11*).

The spectra of the dispersed nickel and the silica support show evidence of this interaction. How the interaction is affected by specific details of the coprecipitation technique used has also been investigated. From an understanding of how the method of preparation affects the chemical state of the dispersed nickel, improvements in catalyst performance may be obtained through refined preparational techniques.

EXPERIMENTAL DETAILS

The data were acquired using a computer-controlled AEI ES200B electron spectrometer. This system used unmonochromatized Mg radiation and was operated in a variable analyzer transmission energy (of the electrons) mode giving good resolution (Au $4f_{7/2}$ full width at half maximum is 1.2 eV) and a linear (in electron kinetic energy) analyzer efficiency. Pressure in the analysis chamber was typically 5×10^{-9} Torr. The spectrometer was calibrated in the present work by setting the kinetic energy difference between the Na 1*s* and 2*p* core levels (in Na_2SO_3) at 1041.1 eV or the Cu $2p_{\frac{3}{2}}$, $3p_{\frac{3}{2}}$ core level spacing (in copper) at 857.6 eV. The spectrometer work function was determined by using the Au $4f_{7/2}$ peak (binding energy = 84.0 eV (*12*) relative to spectrometer Fermi level). The calibration was checked at least weekly and adjusted as needed. Adjustments of more than 0.2 eV were seldom necessary.

Surface charging on an insulating sample introduces an additional complication in the determination of binding energies (*13*). Sample charging of 1 to 4 eV was observed for the standard samples and the catalysts. The best way of determining the charging shifts for powdered samples is still a matter of debate. In this work the shifting of the binding energy of the contaminant C 1*s* line from its neutral value of 285.0 eV was used as a measure of the surface charging. This method gives results which are of comparable reliability to those obtained using an electron flood gun to neutralize the surface charge (*13*). However, the binding energies obtained are still considered to contain uncertainties of ±0.3 eV.

The charging corrected binding energies determined using the C 1*s* line were found to be comparable with those obtained by a Ag spotting technique (*14*). The use of the C 1*s* line also gave consistent results for the variety of sample mounting techniques used (In foil, Cu-backed adhesive tape, or pressing the powder into a shallow cavity in a Cu block). Sample charging determined varied by over 1 eV as a function of the mounting technique used.

Recent studies have shown that core level binding energies determined in different laboratories for identical samples can differ by more than 1 eV for a specified strong peak, even in the case of conductive, clean metal foils (*13, 15*). Consistency of data taken within a laboratory, however, was found to be quite good and reproducible. Variations in the techniques of spectrometer calibration appear to be primarily responsible for the systematic variation of data taken in different laboratories. Consequently, standard samples of several forms of nickel likely to appear in the catalyst samples have been examined prior to studying the catalysts. This set of binding energies and peak shapes formed a data base for interpretation of the catalyst spectra.

The standard samples were obtained from commercial sources and were examined as powders mounted on copper backed adhesive tape or on In foil. The nickel silicate sample was prepared by precipitation from $Ni(NO_3)_2$ and Na_2SiO_3 solution followed by calcination in air at 400°C for 20 hr (*16*). The catalyst samples were furnished by United Catalysts, Inc. of Louisville, Kentucky. The C150-1-01 catalyst was obtained by precipitation a complex carbonate from a nickel nitrate solution which contained SiO_2 as a slurry. After aging for 1 hr at 82°C, the precipitate was filtered, washed, dried, and calcined for 8 to 16 hr at 371°C. The material was ground to a fine mesh, mixed with graphite (2–3%), and pressed into $\frac{1}{8}''$ or $\frac{3}{16}''$ tablets. The sample was then calcined further to remove any remaining water. The C150-1-02 catalyst was prepared in a similar manner except that in this case the complex carbonate precipitate was obtained from an aqueous solution which contained nickel nitrate and sodium silicate. These preparations gave catalysts of good activity and small catalyst particle size (*11*). Physical properties of these materials are summarized in Table 1. Methanation activity studies have been described previously (*11*).

TABLE 1

Physical Properties of Catalysts

	C150-1-01	C150-1-02
Percent Ni (by weight)	51.7	46.6
Percent C	2.9	2.1
Total surface area ($m^2\ g^{-1}$)	183	235
Metal surface area $(m^2\ g)^{-1}$ (Reduced 450°C)	76	59
Pore volume ($cm^3\ g^{-1}$)	0.34	0.58
NiO crystallite size (Å)	20.4	22
Density ($g\ cm^{-3}$)	1.05	0.88

TABLE 2

Standard Sample Binding Energies[a]

Sample	Ni $2p_{3/2}$	Ni satellite splitting	O $1s_{1/2}$	Si $2p$
Ni	852.8			
NiO	856.0	7.0	529.6	
	854.6			
Ni_2O_3[b]	855.8	5.6	531.4	
$Ni(OH)_2$	855.5	5.8	531.0	
$NiSiO_3$	856.7	6.0	532.5	103.5
SiO_2			532.6	103.4

[a] In electron volts.
[b] Ref. (*19*).

RESULTS

The work was divided into two parts: measurements on the standard samples and studies on the catalysts. The experimental details were unchanged between the two runs.

(*a*) *Standard Samples*

Powdered samples of high purity Ni, NiO, NiO–Ni_2O_3, $Ni(OH)_2$, and $NiSiO_3$ were examined. The $2p_{3/2}$ peak in the nickel spectrum was used to characterize the chemical state of nickel. It has the largest cross section in nickel (*17*) and has been studied extensively in other laboratories (*18–29*). A summary of the binding energies of the core levels is given in Table 2. All energies are given in electron volts and have been corrected for sample charging.

It is observed that the binding energies of nickel $2p_{3/2}$ level in many of the different forms of nickel are similar if the uncertainty in the energies is recalled. To make an unambiguous identification of a particular compound, other core levels must

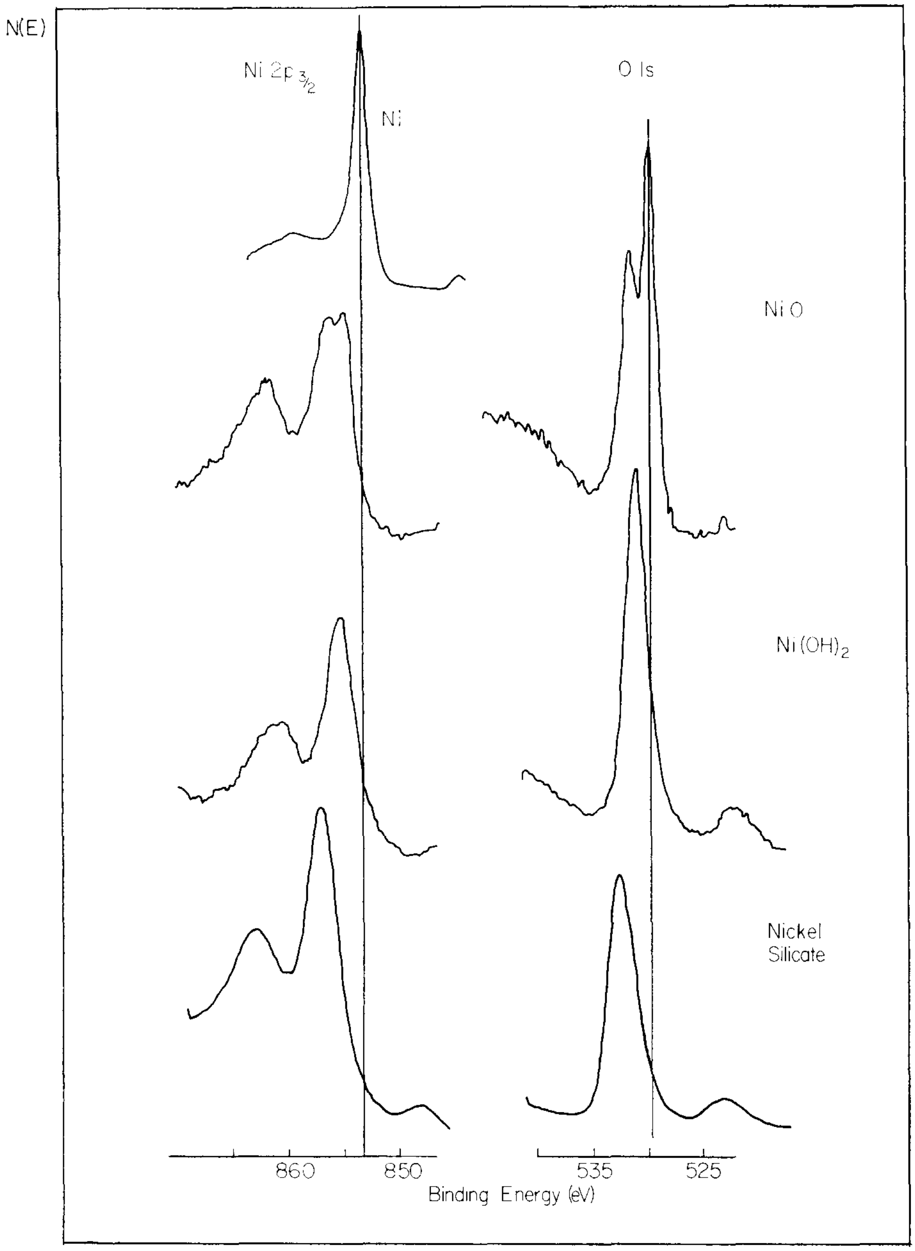

FIG. 1. Principal core level peaks (Ni $2p_{3/2}$, O 1s) for standard samples. All binding energies are corrected for charging (C 1s reference—285.0 eV).

be examined, particularly the oxygen 1s level. The shape of the peaks also contains information. For example, the separation and intensity of the shakeup satellite of the Ni 2p level can be helpful in identifying a particular species. The spectra of the elements of interest are shown in Figs. 1 and 2 in the various standard compounds.

The chemical forms of nickel have certain characteristics which serve to identify their presence. These charac-

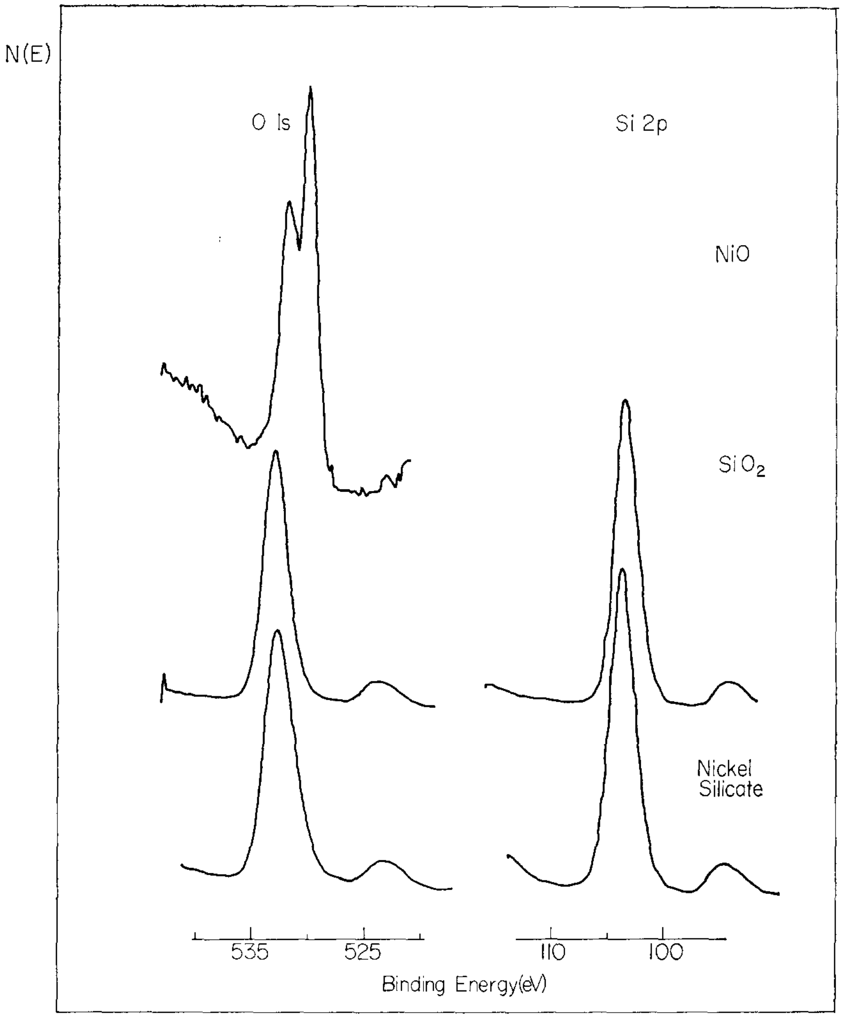

FIG. 2. O 1*s* and Si 2*p* core level peaks for NiO, SiO_2, and $NiSiO_3$.

teristics are summarized in Table 3. NiO has a unique doublet structure for the nickel $2p_{\frac{3}{2}}$ level as well as having the smallest binding energy for the oxygen 1*s* level. Conversely, the spacing of the Ni and O levels is larger than for the other standard compounds examined. Ni_2O_3 is similar spectrally to $Ni(OH)_2$. It appears to be present in the surface regions of most NiO samples, being evidenced by the higher binding energy oxygen peak typically observed in the spectrum of commercially obtained NiO samples and oxidized Ni foils (*18, 19, 21, 25–29*). It is not commonly found as a bulk material, however. This material has been described rather as a gross defect structure of NiO (*18, 19*). $Ni(OH)_2$ has binding energies which are relatively distinct from both NiO and $NiSiO_3$. It is also relatively difficult to reduce the Ni^{+2} to Ni^0 by argon ion etching of this compound. Other compounds such as NiO and $NiSiO_3$ have been observed to be reduced by the argon ion etching process usually used to clean the sample surfaces *in situ*.

$NiSiO_3$ is observed to have high Ni and O binding energies. The nickel core level, as

TABLE 3

Summary of Distinguishing NiX Characteristics

Material	Characteristics
Ni metal	Ni $2p$ peak narrow, weak satellite structure. No charging, no chemical shift.
NiO	Ni $2p$ peak is doublet, large O $1s$ chemical shift.
Ni_2O_3	Singlet Ni $2p$ peak of intermediate binding energy, reduced by Ar^+ etching.
$Ni(OH)_2$	Intermediate Ni $2p$ binding energy, stable against Ar^+ ion induced reduction.
$NiSiO_3$	High Ni $2p$ binding energy, High O $1s$ binding energy.

seen in Fig. 1, is distinct in shape from both Ni metal and NiO. The oxygen peak (Fig. 2) is similar to that observed in SiO_2 and again is quite distinct from that seen in NiO. The silicon $2p$ peak is similar to that for SiO_2, reflecting a similar chemical environment for silicon in these two materials.

The nickel in this sample can be reduced by argon ion etching although not as readily as the nickel in pure NiO. This material does not appear to be the $NiSiO_3$ spinel which is very difficult to reduce, however (*11*).

(*b*) *Fresh* (*Unreduced*) *Catalysts*

The fresh catalysts were examined as supplied (no pretreatment other than a light roughing up of the surface immediately prior to study). As coprecipitated catalysts display better performance than conventionally prepared catalysts (*11*) it was of interest to see how the two coprecipitation methods of preparation affect the chemical state, reducibility, and thermal stability of the nickel dispersion. The simplest spectrum would be a superposition of those of NiO and SiO_2. The relative signal intensities would be modulated by the NiO particle sizes (*3, 30*) and the physical character of the support itself, especially the pore size (*31*). The spectral characteristics of NiO as given in Table 3 would nonetheless be present. As nickel silicate has been observed to form under certain coprecipitation conditions (*11*), it would not be surprising to find some interaction between the NiO and SiO_2 which would affect the catalyst's properties.

The two catalyst samples (C150-1-01 and C150-1-02, referred to as 1-01 and 1-02 henceforth) have quite similar spectra (Figs. 3 and 4). These spectra are quite distinct in both peak binding energy and spectral shape from those of NiO. The spectra resemble (in shape and binding energy) those of the $NiSiO_3$ standard sample most closely although the matchup is not perfect. The variation in peak widths also suggests that the systems being examined are not necessarily simple compounds of one type, specifically that the catalysts are not solely composed of $NiSiO_3$. Nonetheless, the agreement between the catalyst's spectra and the spectra of the $NiSiO_3$ sample is quite good, particularly when the uncertainty in the binding energies is considered. It may be definitely said that NiO, as characterized by the Ni $2p_{\frac{3}{2}}$ doublet peak, is not present in the surface regions.

An argon ion etching study was performed additionally on each sample. According to previous reports (*18, 19*), some forms of nickel are reduced by the bombardment of the surface with charged energetic argon ions (Ar^+) as used in the etching process. The primary purpose of etching is to clean the surface by removing the exposed atoms on the surface thereby

TABLE 4

Catalyst Binding Energies and FWHM[a]

Sample	Ni $2p_{3/2}$	Ni satellite splitting	O $1s_{1/2}$	Si $2p$
C150-1-01	857.0 (3.3)	6.0	532.5 (2.8)	103.5 (2.1
C150-1-02	856.9 (3.1)	5.9	532.5 (2.6)	103.2 (2.1)
$NiSiO_3$	856.7 (3.8)	6.0	532.5 (3.1)	103.5 (2.4)

[a] In electron volts.

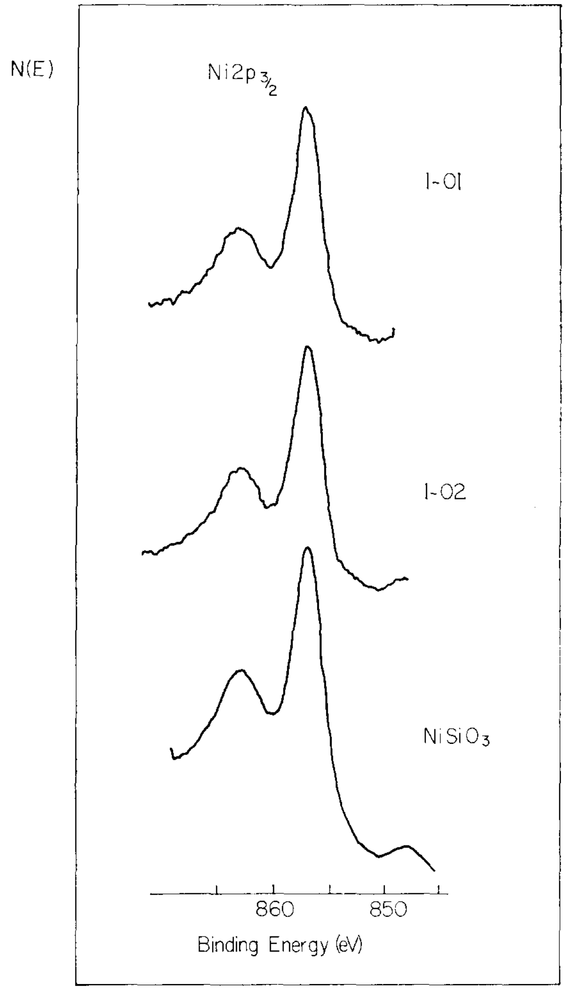

FIG. 3. The Ni $2p_{\frac{3}{2}}$ core level peak for the fresh (unreduced) catalysts and nickel silicate.

exposing the underlying material. However, nickel is reduced only for materials with a heat of formation of less than about 60 kcal/mole (*20*). This process may be used to further characterize the surface regions when the XPS spectra of two different chemical states of an atom are similar but where only one of the forms is reducible by argon ion etching.

The samples (in pellet form) were etched with a 2 kV Physical Electronics gun. The normal to the sample's surface was at a 30° angle to the axis of the incoming beam. A flow of research grade Ar giving a dynamic system pressure of 2×10^{-5} Torr was established before etching was begun. An etching routine of 2 min (1 kV beam energy), 5 min (1 kV), and 28 min (1.5 kV) was performed sequentially on each sample with spectra recorded after each etch. The spectra recorded after the second and third etches are shown in Figs. 5 and 6. A repetition of the study at a later time gave similar results.

The reduction of some nickel atoms to the metallic state is clearly seen for each sample. The amount of reduction, estimated from areas under the silicate and reduced nickel peaks measured with a

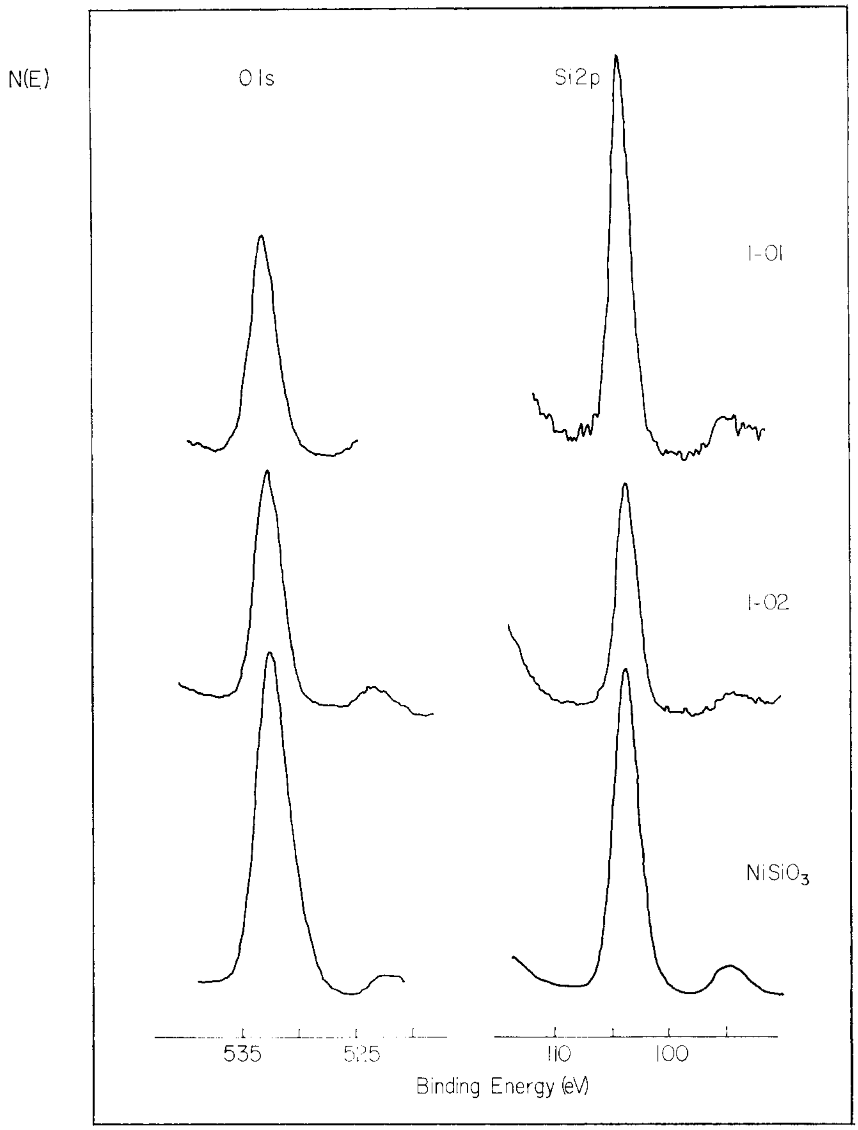

FIG. 4. The O 1*s* and Si 2*p* doublet core level peaks for the fresh catalysts and nickel silicate.

planimeter using a linear baseline correction (*3*), is 45% for the 1-01 and 25% for the 1-02 catalyst. This difference in reduction is in agreement with that observed in Thermal Gravimetric Analysis (TGA) studies of these samples (*32*). The reduction observed is less than that found for NiO when similarly treated. The occurrence of reduction for these samples is in agreement with the characterization of the surface by XPS as being primarily amorphous nickel silicate. An alternate form of nickel that could be indicated by XPS spectra, $Ni(OH)_2$, is not reduced by argon etching and hence is not the predominant form of nickel in the catalyst surfaces.

DISCUSSION

The standard samples have sufficient characteristics (Table 3) to permit the

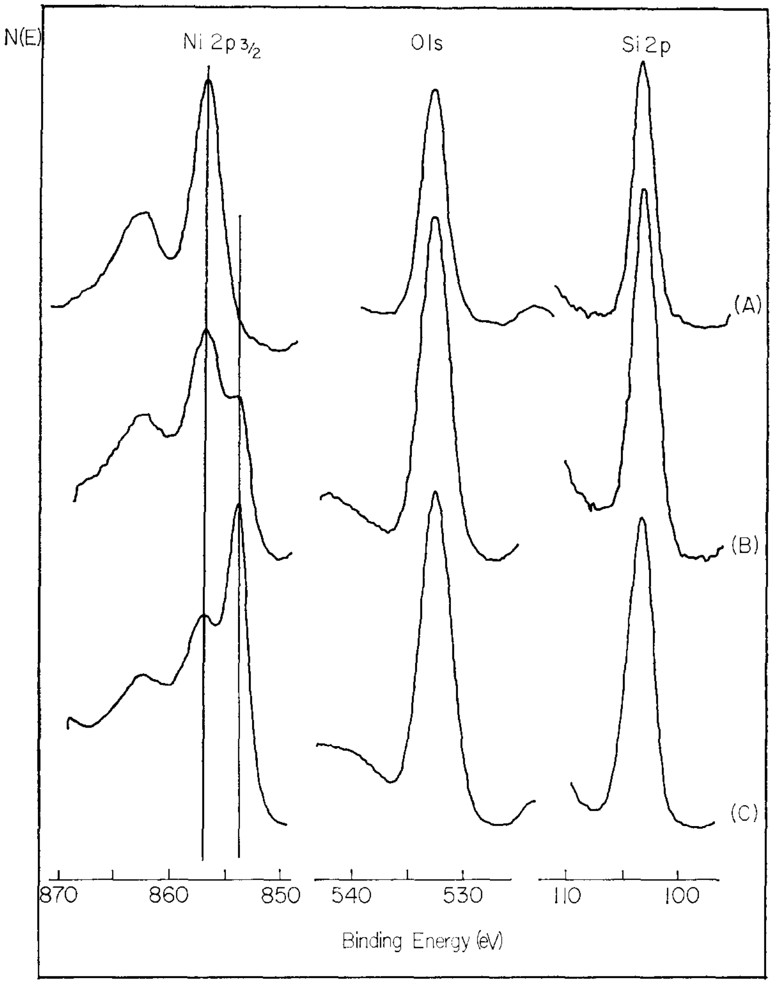

FIG. 5. The spectra for the C150-1-01 catalyst (unreduced). (a) Unetched, (b) etched 7 min (total time) at 1-keV beam energy, (c) etched an additional 28 min at 1.5-keV beam energy.

different chemical forms of nickel to be distinguished. The fingerprint of NiO is of particular concern in this study. In other studies (*18–19*) of the nickel oxide system, two special features have been observed. The principal Ni $2p_{\frac{3}{2}}$ peak displays an unique doublet structure (splitting: 1.8 eV). No completely satisfactory explanation of this structure is known (*29*). This does not lessen its usefulness as an identifier of NiO. The O 1*s* spectrum is commonly found (*18, 19, 21, 23–28*) to consist of two peaks as shown in Figs. 1 and 2. Stoichiometric NiO has just the lower binding energy peak of the O 1*s* doublet (*18, 19*). The higher binding energy peak has been attributed to $Ni(OH)_2$ (*27*) and Ni_2O_3 (*18, 19, 26*). Both peaks of the doublet have similar depth profiles (*26*) indicating that the higher binding energy peak is not just a surface contaminant. This suggests that the higher binding energy peak is due to the presence of Ni_2O_3 at the surface of most commercially prepared samples in NiO. Care would need to be taken to eliminate the possible presence of $Ni(OH)_2$ when characterizing an unknown sample. This could be done

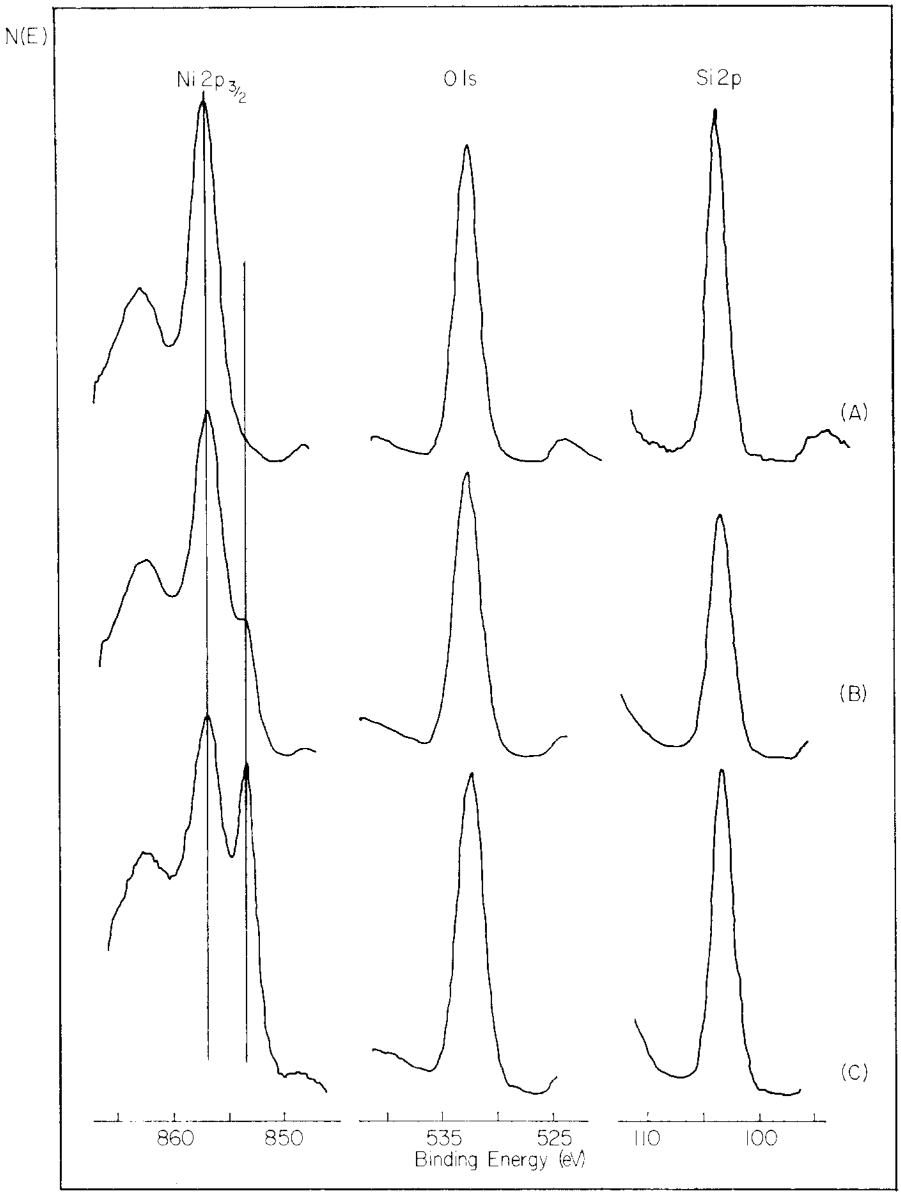

FIG. 6. The spectra for the C150-1-02 catalyst (unreduced). (a) Unetched, (b) etched 7 min (total time) at 1-keV beam energy, (c) etched an additional 28 min at 1.5-keV beam energy.

using the Ni Auger spectrum (*18, 19*). Some of the ambiguity in characterization may be removed by the additional information obtained from argon ion etch-induced reduction of the samples. NiO and the $NiSiO_3$ sample are reduced by etching while $Ni(OH)_2$ is difficult to reduce. Hence, if a nickel compound (as in the catalysts) can be easily reduced by etching, it is unlikely that that compound is hydroxide. This capability has been used to clarify the characterization of the catalysts.

Some differences have been observed in the properties of the two catalysts that may be attributed to the different precipitation methods used to prepare them. The 1-02 catalyst is a "true" coprecipitated catalyst. The 1-01 catalyst, which was prepared with SiO_2 in a slurry with $Ni(NO_3)_2$, is not a coprecipitated catalyst in the same sense, but rather may be called a precipitated catalyst. The 1-01 catalyst preparation is thus an intermediate type between coprecipitation and impregnation. Its properties (Table 1) and activity *(11)* are similar to those of the 1-02 catalyst, however.

The XPS spectra of the two catalysts indicate a similar chemical state (see below). The 1-01 sample charges up less than the 1-02 (2 vs 3.5 eV). The 1-01 sample is more readily reduced by argon etching than the 1-02. Bulk NiO reduces more readily than either, however. These reduction findings are paralleled in the TGA studies *(32)*. It was also observed from analysis of the X-ray diffraction lines of NiO that the 1-01 catalyst sinters more rapidly than the 1-02 catalyst *(5, 32)*. These results suggest that the nickel in the 1-01 catalyst is in a chemically more available form while the nickel in the 1-02 catalyst appears to be more stable regarding reduction and sintering. The coprecipitation method appears to lead to a catalyst in which more nickel has interacted with the support forming a more stable phase. The precipitation method used to prepare the 1-01 sample does, however, also lead to some nickel–silica interaction as indicated by the fraction of nickel not reduced at 400° (35% as compared with 60% for 1-02 and 0% for NiO). As it is possible to prepare an unreducible coprecipitated catalyst [due to the formation of the $NiSiO_3$ spinel *(11)*] it is reasonable to find a greater nickel–silica interaction in the 1-02 catalyst. That more than 80% of nickel in the catalysts could ultimately be reduced (at 500°C) shows that the interaction has not led to the formation of the $NiSiO_3$ spinel, however. This interaction, while hindering the reducibility of the nickel does give good stability and dispersion to the catalysts. The reducibility problem can be overcome by the higher metal content of the coprecipitated catalysts.

The reduction and sintering studies point toward a $NiO–SiO_2$ interaction of varying degrees of completeness in these two catalysts. The XPS spectra (Figs. 3 and 4) support this finding. The Ni $2p_{\frac{3}{2}}$ and O 1*s* spectra do not indicate NiO, but rather are similar to those for the $NiSiO_3$ sample both in binding energy and spectral shape. As the samples are pellets formed from the precipitate which is expected to be of reasonably homogeneous composition, we expected (and have found) that the spectra of the pellet surface also reflects the chemical composition of the interiors of the pellets.

This interpretation is in some conflict with the X-ray diffraction (XRD) spectra used to characterize the catalyst particle size *(5)*. The diffraction spectra show lines due to NiO and none that are attributed to the $NiSiO_3$ spinel. A diffraction scan of the $NiSiO_3$ standard sample (calcined at 400°) did not show any lines at all. After being calcined at 1100°C for 20 hr lines due to NiO, SiO_2, and the $NiSiO_3$ spinel were observed. The XPS spectra of these samples before and after heating were essentially unchanged, however. This suggests that the $NiSiO_3$ present in the catalysts and the standard sample is basically amorphous in structure and that the core level XPS spectra of the $NiSiO_3$ spinel are similar to those of amorphous $NiSiO_3$, at least within the accuracy of the binding energy determinations for these samples.

However, a problem remains as to why NiO is not observed in the XPS spectra when it is readily visible in the XRD spectrum. In the reduction studies, it is found that some (30% for the 1-01 catalyst) of the nickel reduces almost immediately (at 400°C), while some (40%)

of the nickel reduces more slowly, requiring 1 hr. The remainder of the nickel can only be fully reduced at 500°C. This behavior is attributed to, respectively, the presence of easily accessible NiO, less accessible NiO, and amorphous $NiSiO_3$. Any unreducible nickel would be due to the $NiSiO_3$ spinel. While the spinel was not observed in these Ni/SiO_2 catalysts, it has been observed in another coprecipitated Ni/SiO_2 catalyst (*11*) and in coprecipitated Ni/Al_2O_3 catalysts (*33*). Hence, the NiO in the 1-01 and 1-02 catalysts is present either within pores in the SiO_2 support or is covered by an amorphous $NiSiO_3$ overlayer, as NiO in these locations would not be visible through XPS, but would be seen by XRD.

It is possible that small NiO particles dispersed on a silica support do not display the characteristic Ni $2p_{\frac{3}{2}}$ doublet structure if the doublet's origin requires a large-scale order that is not present in a small (20 Å) particle. However, we note that the spectra of a NiO on $MgSiO_3$ catalyst which was prepared similarly to the 1-01 catalyst do display the characteristic NiO spectra (*33*). As the porosity of the $MgSiO_3$ support is similar to that of the SiO_2 in the 1-01 catalysts, the appearance of the singlet Ni $2p_{\frac{3}{2}}$ peak in the one case and not the other is due to changes in the chemical form of the nickel and not to the small particle size.

CONCLUSIONS

A study of the spectral shapes and binding energies of a series of nickel compounds and commercial coprecipitated nickel on silica catalysts has shown that the surface regions of the fresh (unreduced) catalysts are composed primarily, but not solely of amorphous $NiSiO_3$ with some NiO particles present either within the pores of the support or covered by a $NiSiO_3$ layer. A large fraction of the nickel present has interacted with the silica support which gives the catalysts good thermal stability and activity. The interaction is more complete in the coprecipitated 1-02 catalyst than the precipitated 1-01 catalyst, which affects the stability and reducibility of these materials accordingly.

ACKNOWLEDGMENTS

Support of this project was provided by the U.S. Department of Energy through Contract No. Ex-76C-01-2229, and the Institute for Mining and Minerals Research, University of Kentucky.

Catalyst samples and useful technical information were provided by A. L. Hausberger, W. A. Kustes, and M. Miller, United Catalysts, Inc., Louisville, Kentucky.

The assistance and helpful advice of R. J. DeAngelis, W. G. Lloyd, and T. Rebagay are also acknowledged.

REFERENCES

1. Mills, G. A., and Steffgen, F. W., *Catal Rev.* **8**, 159 (1973).
2. Lom, W. L., and Williams, A. F., "Substitute Natural Gas." Wiley, New York, 1976.
3. Shalvoy, R. B., and Reucroft, P. J., *J. Electron Spectrosc.* **12**, 351 (1977).
4. Kidron, A., DeAngelis, R. J., and Reucroft, P. J., *J. Appl. Phys.* **48**, 5296 (1977).
5. Ganesan, P., Kuo, H. K., Saavedra, A., and DeAngelis, R. J., *J. Catal.* **52**, 310 (1978).
6. Siegbahn, K., Nordling, C., Fahlman, A., Nordbert, R., Hamrin, K., Hedman, J., Johansson, G., Bergmark, T., Karlsson, S. E., Lingren, I., and Lindberg, B., ESCA: Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy, *Nova Acta Regiae Soc. Sci. Upsal.* (*IV*) **20**, Almquist and Wiksells, Uppsala (1967).
7. Delgass, W. N., Hughes, T. R., and Fadley, C. S., *Catal. Rev.* **4**, 179 (1970).
8. Brinen, J. S., *J. Electron. Spectrosc.* **5**, 377 (1974).
9. Ng, K. T., and Hercules, D. M., *J. Phys. Chem.* **80**, 2094 (1976).
10. Penn, D. R., *J. Electron Spectrosc.* **9**, 29 (1976).
11. Hausberger, A. L., Atwood, K., and Knight, C. B., *Adv. Chem. Ser.* **146**, 47 (1975).
12. Dianis, W. P., and Lester, J. E., *Anal. Chem.* **45**, 1416 (1973).
13. Madey, T. E., Wagner, C. D., and Joshi, A., *J. Electron Spectrosc.* **10**, 359 (1977).
14. Shalvoy, R. B., Fisher, G. B., and Stiles, P. J., *Phys. Rev. B* **15**, 1680 (1977).

15. Powell, C. J., personal communication.

16. Bailar, J. C., Emeleus, H. J., Nyholm, R., and Trotman-Dickinson, A. F., "Comprehensive Inorganic Chemistry." Pergamon, Oxford, 1973.

17. Scofield, J. H., *J. Electron Spectrosc.* **8**, 129 (1976).

18. Kim, K. S., and Davis, R. E., *J. Electron Spectrosc.* **1**, 251 (1972/73).

19. Kim, K. S., and Winograd, N., *Surface Sci.* **43**, 625 (1974).

20. Kim, K. S., Battinger, W. E., Amy, J. W., and Winograd, N., *J. Electron. Spectrosc.* **5**, 351 (1974).

21. Hirokawa, K., Honda, F., and Oku, J., *J. Electron Spectrosc.* **6**, 333 (1975).

22. Holm, R., *Appl. Phys.* **9**, 217 (1976).

23. Holm, R., and Storp, S., *J. Electron Spectrosc.* **8**, 139 (1976).

24. Matienzo, L. J., Yin, L. I., Grim, S. O., and Swartz, W. E., *Inorg. Chem.* **12**, 2762 (1973).

25. McIntyre, N. S., and Cook, M. G., *Anal Chem.* **47**, 2208 (1973).

26. Evans, S., Pielaszek, J., and Thomas, J. M., *Surface Sci.* **56**, 644 (1976).

27. Haber, J., Stoch, J., and Ungier, L., *J. Electron Spectrosc.* **9**, 459 (1976).

28. Wertheim, G. K., and Hufner, S., *Phys. Rev. Lett.* **28**, 1028 (1972).

29. Oku, M., and Hirokawa, K., *J. Electron Spectrosc.* **10**, 103 (1977).

30. Briggs, D., *J. Electron Spectrosc.* **9**, 487 (1976).

31. Brinen, J. S., and Schmitt, J. L., *J. Catal.* **45**, 274 (1976).

32. Reucroft, P. J., Bradley, E. B., DeAngelis, R. J., and Sargent, G. A., "Surface Structure and Mechanisms of Gasification Catalyst Deactivation," Quart. Rep. No. 5, Feb. 1, 1977 to April 30, 1977 and Quart. Rep. No. 9, Feb. 1, 1978 to April 30, 1978, DOE Contract No. EX-76-C-01-2229.

33. Shalvoy, R. B., Davis, B. H., and Reucroft, P. J., to be published.