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Characterization of Nickel Complexes on Oxide Supports by Secondary Ion Mass Spectrometry

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The nickel complexes $Ni[P(OR)_3]_4$, where R = Me or Et, $Ni(PR_3)_2Cl_2$, where R = Et, *n*-Bu, or Ph, and $(\eta^5\text{-}C_5H_5)Ni(PPh_3)Cl$ supported on silica and alumina have been detected using secondary ion mass spectrometry (SIMS). When solutions of these complexes are deposited directly onto the oxide material, a method commonly used in catalyst preparation, these complexes can be identified by NiL_n^+ ions, where L is the phosphine ligand, in the corresponding SIMS analysis. On the other hand, the SIMS of materials emanating from the reactions between solutions of these complexes and suspensions of the oxides produced only ions characteristic of the phosphine ligands. These results can be explained in terms of a stronger complex–support interaction relative to that obtained by the incipient wetness impregnation method. Supporting $(\eta^5\text{-}C_5H_5)_2Ni$ on silica, however, produced only Ni^+ in the SIMS analysis, a result which may reflect, in this case, the presence of oxide supported nickel.

INTRODUCTION

Transition metal complexes supported on insoluble materials have received attention as an important new class of catalysts (*1–5*). These materials combine the advantages of selectivity and controllability associated with homogeneous catalysts with the ease of product separation of the heterogeneous catalyst due to its insoluble nature. This procedure has also been used to advantage to prevent the occurrence of reactions such as oligomerization which often compete with desired catalytic reactions and can eventually spend the catalyst (*6*). In addition, there can be an increase in catalytic activity and selectivity of supported complexes over their homogeneous counterparts (*7, 8*).

Transition metal complexes may be bound to polymeric materials (*9–11*) or supported on oxidic materials such as silica, alumina, or zeolites (i) by direct diffusion into the porous structure, (ii) through binding to reactive surface hydroxyl groups, or (iii) via attachment to an intermediate functionality such as a phosphino linkage (*3, 12*). Such complex systems, though, can be difficult to adequately characterize using conventional analysis methods. However, a variety of developing spectroscopic methods are appropriate for the study of surface complexes (*5, 13, 14*). Secondary ion mass spectrometry (SIMS) in particular has the advantage of high surface sensitivity coupled with the ability to detect molecular complexes via a mass analysis. The technique has been applied extensively to the analysis of metal surfaces (*15*) and adsorbate species (*16*). Much effort has gone into the characterization of nonmetallic materials, particularly silica and its derivatives, due to the interest in their semiconducting properties (*17–19*). Dopants and impurities in these systems have also been successfully analyzed by SIMS (*20*). The results of a SIMS study on a series of impregnated cobalt–alumina catalysts demonstrated the effect of percent metal loading and calcination temperature on surface composition (*21*). SIMS has been successfully applied to molecular compounds (*22, 23*), including transition metal complexes (*24, 25*), and this technique, in principle, should also be

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able to identify a supported metal complex present on a surface and yield information concerning the nature of the complex–support interaction through the appearance of diagnostic fragment ions in the SIMS spectrum.

Nickel complexes in general, are quite widely used as homogeneous catalysts for a variety of processes (*26*). Several of these complexes have been supported on insoluble polymeric and oxidic materials and were found to be catalytically active (*27–29*). Employing similar procedures, silica and alumina have been impregnated with nickel phosphine and phosphite complexes and SIMS has been used to ascertain the presence of the complex on the support material. The SIMS spectra of these complexes analyzed off silver foil are also presented for comparison purposes.

EXPERIMENTAL

Materials

The nickel complexes $Ni[P(OR)_3]_4$, where R = Me or Et, $Ni(PR_3)_2Cl_2$, where R = Et, *n*-Bu, or Ph, $(\eta^5\text{-}C_5H_5)Ni(PPh_3)Cl$, and $(\eta^5\text{-}C_5H_5)_2Ni$ were prepared according to established methods (*30–33*).

Sample Preparation

The nickel complexes were first analyzed from an ammonium chloride matrix with an approximate 1 : 10 ratio of sample to NH_4Cl on silver foil, a procedure established from previous SIMS studies of transition metal complexes (*24, 25*). Use of this matrix material was found to enhance secondary ion yields. Second, these complexes were analyzed after pipetting a small volume of a dilute dichloromethane solution of the sample onto the support material. The amount of complex to be deposited was predetermined to achieve approximate average monolayer coverage (10^{15} molecules/cm^2); for example, 0.0046 g of $Ni[P(OMe)_3]_4$ was dissolved in 25 ml of CH_2Cl_2 and 5 μl of solution was deposited onto a 1-cm^2 aluminum-backed oxide plate. The solvent was allowed to evaporate in air. Aluminum-backed plates of silica (precoated TLC sheets, EM Reagents) and alumina (prepared from Al_2O_3 60 G Neutral (type E), EM Reagents) were utilized for this purpose. Third, the complexes were analyzed as oxide "supported" complexes prepared via the direct reaction of solutions of the metal complex with suspensions of the oxide. The nickel complexes were added to a stirred suspension of silica gel (Davison Grade 923, mesh 100–200) or alumina (Fisher Scientific Company) in dichloromethane to give ca. 5% of complex by weight. The mixture was stirred for approximately two hours. The resulting solid was then filtered off, washed with three portions (10 ml each) of dichloromethane and allowed to air dry. This powder was burnished directly onto a silver foil for SIMS analysis. A very thin layer (with deliberate exposure of underlying silver) was used to compensate for charge buildup which might occur during argon ion bombardment due to the insulating nature of the support material.

Physical Measurements

SIMS spectra were obtained on a commercial Riber instrument (Model SQ 156L) in the positive ion mode using an energy selector, a quadrupole mass filter, a Channeltron electron multiplier, and pulse counting electronics. A 4-keV argon ion beam was used unless otherwise specified and ion currents were typically on the order of 1×10^{-10} A/mm^2. Main chamber pressure during analysis was 1×10^{-8} Torr or less. No charge compensation was used.

RESULTS AND DISCUSSION

The SIMS spectra of the nickel phosphite complexes $Ni[P(OR)_3]_4$, where R = Me or Et, analyzed from an ammonium chloride matrix off silver foil, are characteristic of the analyte although no molecular ion is observed. The loss of a single phosphite ligand (L) yields NiL_3^+ as the highest mass ion observed; NiL_2^+ and NiL^+ are also observed as shown in Fig. 1 for the methyl

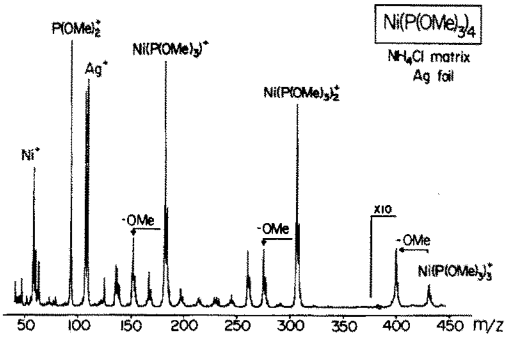

FIG. 1. SIMS spectrum of $Ni[P(OMe)_3]_4$ from an ammonium chloride matrix on silver foil.

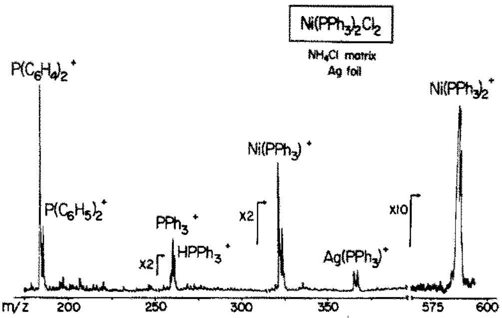

FIG. 2. SIMS spectrum of $Ni(PPh_3)_2Cl_2$ on silver foil.

phosphite derivative. Loss of small radicals such as OR from NiL_n^+, where $n = 1–3$, is readily observed for these complexes. The nickel phosphine complexes $Ni(PR_3)_2Cl_2$, where R = Et, *n*-Bu, or Ph, also yield SIMS spectra devoid of the molecular ion, and ions characteristic of the ligand dominate the spectra. The protonated ligand $(R_3PH)^+$ is the base peak in the spectra of alkyl phosphines and the fragment ion $[P(C_6H_4)_2]^+$ is the base peak for the phenyl derivative. Both the triethyl and the tri-*n*-butyl phosphine derivatives give $Ni(PR_3)_2^+$ as the only nickel containing species observed; the triphenylphosphine derivative is characterized by both $Ni(PPh_3)^+$ and $Ni(PPh_3)_2^+$ as shown in Fig. 2. Attachment of silver from the support to the free ligand to give $(Ag + PR_3)^+$ also readily occurs in each case. Such results are consistent with a previous report on alkyl and aryl phosphine complexes of molybdenum and rhenium (*34*) except for the appearance of metal containing ions in the nickel system. No rhenium or molybdenum containing ions were observed for any compound studied (*34*). The organometallic complex $(\eta^5\text{-}C_5H_5)Ni(PPh_3)Cl$ can be characterized by metal containing species such as $Ni(PPh_3)^+$, $(\eta^5\text{-}C_5H_5)Ni(PPh_3)^+$, and $(Ag + PPh_3)^+$, in addition to ions characteristic of the triphenylphosphine ligand, i.e., $[P(C_6H_4)_2]^+$, $[P(C_6H_5)_2]^+$, $[P(C_6H_5)_3 + H]^+$, and $[P(C_6H_5)_3 - H]^+$.

Each of the complexes was also analyzed from graphite following deposition of the complex from a CH_2Cl_2 solution onto graphite foil. These measurements were carried out in an attempt to minimize fragmentation by using a potentially less interactive surface (i.e., graphite vs silver). The resulting spectra, however, are virtually identical in each case to that obtained from analysis off silver foil except, of course, for the absence of silver containing ions. The spectrum of $(\eta^5\text{-}C_5H_5)Ni(PPh_3)Cl$ on graphite is given in Fig. 3. For each of these complexes, the SIMS spectrum did not contain the molecular ion and these species were characterized by fragments due to ligand loss from the molecular species, i.e., NiL_n^+ ions, as well as ions corresponding to the phosphine and phosphite ligands themselves.

The SIMS spectra of the untreated SiO_2/Al and Al_2O_3/Al plates produced Si^+ and Al^+ ions, respectively, indicative of the

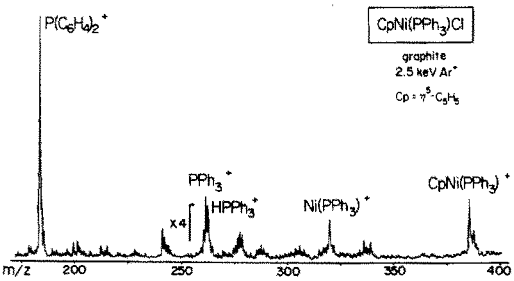

FIG. 3. SIMS spectrum of $(\eta^5\text{-}C_5H_5)Ni(PPh_3)Cl$ deposited from CH_2Cl_2 onto graphite foil.

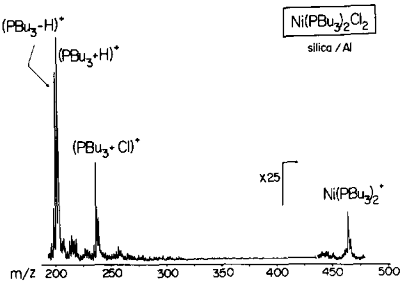

FIG. 4. The SIMS spectrum of Ni(P-*n*-Bu$_3$)$_2$Cl$_2$ deposited from a dilute CH$_2$Cl$_2$ solution onto an aluminum-backed silica plate.

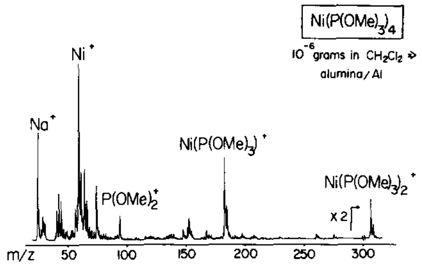

FIG. 5. SIMS spectrum of Ni[P(OMe)$_3$]$_4$ deposited from a dilute CH$_2$Cl$_2$ solution onto an aluminum-backed alumina plate.

support material. Other ions were observed in the low mass region ($m/z < 100$) in each case due to hydrocarbon background and sodium ion impurity. Dispensing Ni[P(OMe)$_3$]$_4$ from a dichloromethane solution onto a SiO$_2$/Al plate resulted in the identification of this complex by the appearance of the ions NiL$^+$ and NiL$_2^+$ in the corresponding SIMS spectrum. There was no direct evidence for complex/support interaction as ions containing fragments of support + metal complex were not observed. The support itself contributed the same low mass ions such as Si$^+$ that were observed for untreated SiO$_2$/Al. In a similar fashion, impregnation of supported silica with Ni(PR$_3$)$_2$Cl$_2$, where R = Et, *n*-Bu, or Ph, and (η^5-C$_5$H$_5$)Ni(PPh$_3$)Cl also resulted in SIMS spectra analogous to those obtained from a silver support except for an overall decrease in secondary ion abundance due to the decreased amount of analyte material. The SIMS spectrum of Ni(P-*n*-Bu$_3$)$_2$Cl$_2$ from an aluminum backed silica plate is given in Fig. 4. Similar results were obtained for each of these complexes when analyzed from Al$_2$O$_3$/Al plates. This is illustrated for Ni[P(OMe)$_3$]$_4$ in Fig. 5.

Although approximately 10^{15} molecules of sample were deposited on 1 cm^2 of oxide-coated surface in the above experiments to yield an approximate average monolayer, complete uniform dispersion free of molecular "stacking" or aggregation cannot be assured using this sample preparation technique.[2] While the bulk of the analyte will undoubtedly be in contact with the oxide support, it seems likely that the ions observed in these SIMS analyses are those derived from molecules which are not influenced by strong complex–support interactions, i.e., those which are subject to molecular aggregation. Indeed, visual examination of these materials provided clear evidence for some degree of aggregation. Unfortunately, the relative abundance of Si$^+$ or Al$^+$ in the SIMS of these materials, relative to the untreated SiO$_2$/Al and Al$_2$O$_3$/Al plates, is not an adequate indication of the extent of coverage because of the strong dependence of these abundances on sample position, primary ion current, and time.

The product of the reaction between a dichloromethane solution of Ni[P(OMe)$_3$]$_4$ and a suspension of an oxide material in bulk form (see Experimental section) produced no evidence in the SIMS analysis for the adherence of this complex to the oxide support. However, treating a dichloromethane solution of (η^5-C$_5$H$_5$)Ni(PPh$_3$)Cl in a similar manner, with either silica gel or alu-

[2] From studies of molybdena–alumina by W. K. Hall and co-workers (see Wang, L., and Hall, W. K., *J. Catal.*, **77**, 232 (1982) and references cited therein) the problems associated with aggregation of Mo^{+6} for samples made by the incipient wetness method have been carefully delineated. Such a situation most likely pertains to the nickel complexes on the SiO$_2$/Al and Al$_2$O$_3$/Al plates that we have prepared by such a method.

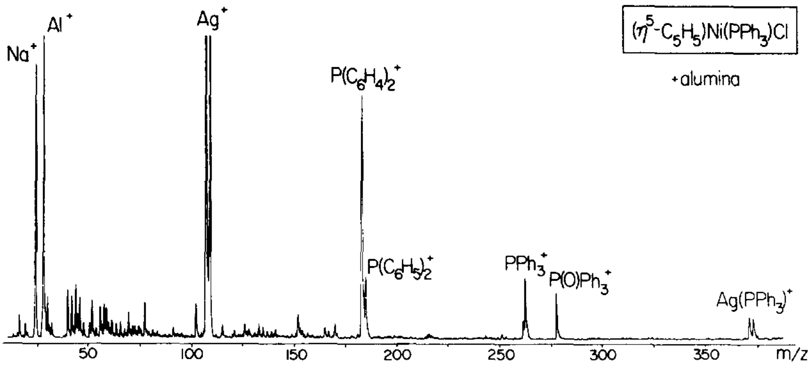

FIG. 6. SIMS spectrum of the product of the reaction between $(\eta^5\text{-}C_5H_5)Ni(PPh_3)Cl$ and alumina in CH_2Cl_2 burnished on Ag foil.

mina, produced a sample that gave ions that were characteristic of the phosphine ligand (see Fig. 6). No nickel containing ions were detected. Note that there was visual evidence for the adherence of this complex to the support material in that the product possessed the characteristic red color of the nickel complex. An additional ion due to the oxidation of the phosphine ligand was also observed (*m/z* 279). This oxygenated species was not observed in the SIMS spectrum of $(\eta^5\text{-}C_5H_5)Ni(PPh_3)Cl$ off silver foil and is most likely the result of oxidation of the phosphine ligand by oxygen on the oxide support material. Whether this reaction occurred during the sample preparation or is beam induced cannot be discerned from this experiment. Reaction of the $Ni(PR_3)_2Cl_2$ complexes with silica or alumina in solution also produced materials whose SIMS spectra gave only ions indicative of the phosphine ligands. The lack of nickel containing ions may be due to the existence of relatively strong metal–support interactions; as a result, cleavage of the nickel–phosphine bonds rather than the support–complex bonds occurs upon argon ion impact.

An alternative explanation for the absence of nickel containing ions is that the amount of complex actually on the support is too small to permit the ready detection of these ions. However, this is unlikely to be the case since the relative intensities of phosphine containing ions versus those containing nickel (e.g., $(R_3PH)^+$ vs $Ni(PR_3)_2^+$, for R = Et or *n*-Bu, and $(Ph_3P)^+$ vs $Ni(PPh_3)^+$) are known from measurements of these complexes on supports (silver, graphite, and SiO_2/Al and Al_2O_3/Al plates) that give rise to only *very weak* complex–support interactions (e.g., see Figs. 2 and 3). Based upon the measured intensities of the phosphine containing ions for the samples of the complexes supported on bulk silica and alumina, we would have expected to detect quite easily ions such as $Ni(PR_3)_2^+$ and $Ni(PPh_3)^+$. Since they are absent in the SIMS analysis, we conclude that these materials differ from those in which the complexes are deposited on SiO_2/Al and Al_2O_3/Al plates.

The SIMS spectrum of nickelocene could not be obtained from silver or graphite foils due to its volatile nature. Also, depositing this complex from solution onto silica or alumina plates produced materials which failed to give ions indicative of the analyte upon SIMS analysis. However, by supporting $(\eta^5\text{-}C_5H_5)_2Ni$ on silica through the reaction between a tetrahydrofuran solution of this complex and the bulk oxide, Ni^+ was detected in low abundance in the SIMS spectrum; ions derived from the cyclopentadienyl groups were not observed. Heating a sample of $(\eta^5\text{-}C_5H_5)_2Ni$ supported on silica to 120°C, as described by Ichikawa in a study of the catalytic activity of this supported complex (*27*), again produced a material in which Ni^+ was observed in the subsequent SIMS analysis. This is consistent with the report (*27*) that stoichiometric amounts of cyclopentadiene are lost upon heating, resulting in the dispersion of nickel on silica. Apparently, loss of cyclopentadiene also occurs to some extent under the vacuum conditions of the SIMS instrument even without heating, since, as mentioned above, Ni^+ was also observed for the unheated sample.

CONCLUSIONS

The work outlined here on oxide supported nickel phosphine and phosphite complexes illustrates that the SIMS technique can be used to (1) identify molecular species in low concentrations in complex matrices such as oxide materials, and (2) detect the presence of metal complexes supported on a bulk oxide. The characteristic secondary ions observed in the SIMS spectra of complexes deposited from solution onto aluminum-backed silica and alumina plates is identical to that obtained from burnishing the complex onto silver foil. However, no metal containing ions were observed in the SIMS analysis of materials prepared by the reaction of solutions of the complexes with suspensions of the oxide support although secondary ions corresponding to the phosphine ligands were detected. This result can be explained in terms of a strong interaction between the oxide and the metal center in the latter case, perhaps leading to Si–O–Ni linkages, resulting in cleavage of the Ni–P bonds upon argon ion bombardment rather than the metal–support (Ni–O?) bonds. The appearance of Ni^+ in low abundance in the SIMS analysis of $(\eta^5\text{-}C_5H_5)_2Ni$ supported on bulk silica is not inconsistent with this suggestion. In this case, the loss of the cyclopentadienyl groups upon heating (or under vacuum) results in oxide supported nickel. In such an event, the metal itself is exposed to primary ion bombardment and is consequently observed in the SIMS analysis.

It appears that in the SIMS spectra of the materials containing strong complex–oxide (support) interactions, the Ni–P bonds are cleaved rather than the Ni–support bonds, thereby explaining the absence of Ni containing ions in such instances. This explanation is given support by recent work on the EI mass spectra of transition metal supported polymers (*35*). Studies of $RuCl_2(PPh_3)_3$, $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$, and $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ on functionalized polystyrene supports showed (*35*) the absence of any fragments whatsoever associated with the transition metal and attest to the strength of the metal complex–support bond.

The present study is the first that has been devoted to the SIMS of oxide supported transition metal complexes. It is hoped that this work will prompt further studies on the use of SIMS to characterize heterogenized homogeneous catalysts.

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