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SNL-1 - CERAMIC CATALYST MATERIALS: HYDROUS METAL OXIDE ION-EXCHANGE SUPPORTS FOR DIRECT COAL LIQUEFACTION

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ABSTRACT

This presentation describes studies aimed at understanding how the activity of a catalyst is related to the concentration and dispersion of active metals on the catalyst supports. Such information is critical to designing materials having optimum catalytic properties. We have developed synthetic techniques for controlling both the concentration and dispersion of nickel on hydrous sodium titanate catalyst supports. The techniques require an understanding of the solution chemistry of both the support material and dissolved metal species. Characterization of the material and catalytic properties of Ni-loaded hydrous titanates will be presented. In addition, studies of the local molecular structure by Raman and solid-state ^{17}O NMR spectroscopies will be described.

INTRODUCTION

Coal is our most abundant fossil fuel energy source. However, it requires extensive chemical treatment and processing to convert it from a hydrogen-poor "dirty" solid to a "clean" premium liquid fuel such as gasoline. One of the missions of the Department of Energy's AR&TD research is to permit expanded use of coal-based systems by providing a focus for the exploration of ideas pertaining to coal science, conversion and utilization. This project seeks to accomplish that mission by exploring the synthesis and evaluation of new ceramic catalytic materials for efficient, direct conversion of coal to clean liquid fuels. Because the recoverable U.S. supplies of coal are 50 to 100 times that of crude oil, development of new catalysts for efficient conversion of coal to environmentally acceptable liquid fuels would have an enormous impact on extending our useable energy reserves.

As an AR&TD project, the focus of this program is to conduct research and development on catalytic materials for fossil energy applications. In this way, we are obtaining a better understanding of these materials that will impact the long-term,

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generic needs of various fossil fuel technologies. However, sufficient testing of the hydrous metal oxide ion-exchange catalysts with coal and coal-derived feeds has been accomplished to demonstrate that they show great promise for end-use process applications.[1]

The specific materials under study in this AR&TD project are from a group of hydrous oxide ion-exchange compounds of Ti, Zr, Nb, and Ta developed at Sandia National Laboratories. These compounds have been used to prepare catalysts by a novel synthesis route involving the incorporation of active metals by ion exchange.[2] Hydrous oxide ion-exchange compounds were originally developed at Sandia for use in the decontamination of aqueous nuclear waste and as precursors for ceramic materials.[3] The use of these compounds as ceramic catalyst supports arises from the unique properties which these systems exhibit: 1) any metal, or mixture of metals, can be incorporated into the materials over a wide concentration range by a simple process; 2) the materials have high surface area which displays a unique temperature dependence (increasing with increasing T); 3) they exhibit good chemical stability; 4) solution chemistry or more conventional high temperature reactions can be used to provide control of the active metal oxidation state; 5) acidity and basicity of the substrate can be modified by ion exchange; and 6) the catalysts can be prepared on transition metal-oxide supports (Ti, Nb, and Ta) known to undergo a so-called "strong metal-support interaction" (SMSI).

The hydrous metal oxides investigated in this study belong to a group of inorganic ion-exchange compounds that can be represented by the empirical formula $M(M'_xO_yH_z)_n$, where M is an exchangable cation and M' is Ti, Nb, Zr, or Ta. When added to a solution of aqueous metal cations, these powdered materials will react to form amorphous precipitates containing the dissolved metal which has replaced the exchangable cation, M. Catalytic activity has been measured at Sandia for materials synthesized in this manner.[1,4] For example, catalysts prepared using the hydrous titania ion exchangers, even at low active metal loadings of 1%, are equally effective for conversion of coal to low molecular weight products as a commercial Ni-Mo/alumina catalyst containing 15% by weight active metals.[1]

One possible reason for the improved performance of the catalysts prepared from the hydrous titanate materials may be that active metals are dispersed more completely via the ion-exchange process than when loaded by traditional incipient wetness techniques. As such, these materials offer a method to prepare greatly improved heterogeneous catalysts for many applications, provided we understand the important variables in the synthesis.

Our goal is to develop a fundamental understanding of the preparation and properties of these unique materials. Specifically, we have been investigating the following areas:

1) molecular and extended macroscopic structure of the hydrous titanate;
2) mechanism of incorporation of catalytic metals; and
3) catalytic and reactivity studies of the metal-loaded catalysts.

Having developed this basic understanding, we envision being able to tailor catalyst properties for specific applications, as well as providing a foundation for further catalyst development. This report summarizes recent work on this project and represents much of our current understanding and developments of the hydrous titanate materials.

DISCUSSION OF CURRENT ACTIVITIES

Results and Discussion

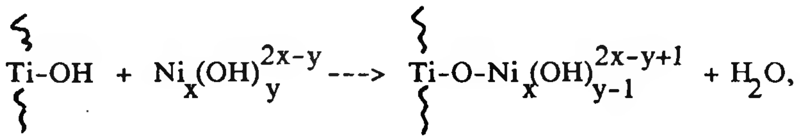
To optimize the use of the amorphous sodium titanate powders as catalyst substrates, it is important to fully characterize the ion-exchange properties of the material. Further, the solution properties of the active metal to be loaded onto the support will be an important parameter in the control of the adsorption process. For example, exposure of sodium titanate to a nickel salt solution does not guarantee that nickel will be loaded onto the sodium titanate, or that the nickel, if loaded, will be dispersed on an atomic level. Sodium titanate only behaves as a cation exchange material under certain pH conditions. The solution pH also influences the hydrolysis and speciation of dissolved nickel ions,[5] which can form large polymeric clusters or colloidal particles which are not adsorbed by the sodium titanate via a simple ion-exchange process. Thus, in order to control the mechanism by which nickel is loaded onto sodium titanate and to control the degree of nickel dispersion, we need to understand the ion-exchange properties of the sodium titanate support, the hydrolysis chemistry of the dissolved nickel, and how the different nickel species are expected to interact with the titanate support. These studies are described first, followed by comparative reactivity and characterization measurements on Ni-loaded catalysts. Finally, we discuss spectroscopic determination of the local molecular structure of the ion-exchange sites on the hydrous titanates. The experimental procedures to prepare and characterize the hydrous titanate-supported catalysts have been described elsewhere.[4,6-12]

Ion-Exchange Behavior of Sodium Titanate

The ion-exchange characteristics of sodium titanate supports are summarized in Fig. 1.[4] In the figure, proton (H^+) consumption is plotted by the solid line as the $Na_{0.5}Ti$ is titrated from a basic pH (≃12) with HCl. Na+ (+) loss from and Cl^- (-) adsorption onto the support are followed by analysis of the solutions by ICP. At pH values above the isoelectric point (iep) of sodium titanate (pH 5), the surfaces of the sodium titanate particles are covered with anionic surface sites that are charge compensated by cations such as sodium. Above pH 5, the titanate support can function as a cation exchanger. For example if Ca(II) ions are added to a sodium titanate slurry, solution analyses indicate that one calcium ion is adsorbed by the support for every two sodium ions released into solution. Below pH 5, surface sites on the titanate support are primarily cationic, and the support behaves as an anion rather than a cation exchanger. In the above example, neither Ca(II) or Na(I) ions are adsorbed by the titanate powder when the solution pH is highly acidic (below pH 4). Therefore, the solution chemistry of sodium titanate suggests that if the powder is exposed to Ni(II), and if the Ni(II) is to be loaded via an ion-exchange process, no Ni(II) adsorption is to be expected below pH 5. Also apparent in Fig. 1 (note the two regimes of H^+ consumption at nearly constant pH of about 8 and 12) and in surface charge measurements as a function of pH[10] is the presence of at least two anionic surface sites above pH 5. The distribution of these two sites is controllable during the synthesis of the sodium titanate powder as will be shown by our spectroscopic studies to be described below. It should be noted here that these latter studies will also show that the view of the titanate surface sites as strictly anionic above and cationic below the iep is naive.

Ni(II) Hydrolysis Chemistry and Loading Studies

Although Ni(II) exists in solution as a simple aquated cation in acidic solutions, increases in the solution pH can lead to the deprotonation of bound water molecules, leading to hydrolysis and condensation of Ni(II) to form polymeric clusters. The calculated hydrolysis diagram[5] for Ni(II), shows that for a 3×10^{-2} M nickel nitrate solution, hydrolysis and condensation should commence at a pH of approximately 6.5. Further increases in pH lead to the formation of larger insoluble polymeric species with Ni becoming less and less soluble as the pH is raised to pH 10. The hydrolysis diagram suggests that Ni(II) can only be loaded by a simple ion-exchange process at pH values below 6.5 where hydrolysis is negligible. Above pH 6.5, polymeric nickel clusters will be present which can either condense with surface sites on the titanate support via reactions such as:



$$\mathrm{Ti{-}OH} + \mathrm{Ni_x(OH)_y^{2x-y}} \;\text{--->}\; \mathrm{Ti{-}O{-}Ni_x(OH)_{y-1}^{2x-y+1}} + \mathrm{H_2O}, \qquad (1)$$

or can condense with each other to form larger colloidal particles of nickel hydroxide. The relative amounts of nickel which are adsorbed as small clusters and as colloidal particles should be influenced by the relative availability of reactive sites on the support vs. the other clusters present in solution. In any case, the hydrolysis diagram predicts that above pH 6.5, Ni(II) adsorption should occur via hydrolysis and condensation rather than by ion exchange.

Combining the information obtained in our studies of the ion-exchange properties of sodium titanate with what is known concerning the hydrolysis characteristics of Ni(II), we would predict that below pH 4, Ni(II) is not adsorbed by sodium titanate, between pH 4 and pH 6.5, Ni(II) is adsorbed as a monomeric cation via an ion-exchange process, and that above pH 6.5, Ni(II) should be adsorbed as polymeric clusters and colloids via hydrolysis and condensation mechanisms. To check the above hypothesis, we have titrated acidic nickel nitrate solutions with sodium hydroxide in the absence and in the presence of sodium titanate and analyzed solution aliquots for Ni(II) as a function of pH (Fig. 2). The results obtained for nickel nitrate alone show that the hydrolysis of nickel leading to the formation of insoluble nickel hydroxide occurs between pH 7.5 and 8 (slightly higher than the pH of 6.5 predicted from simple hydrolysis diagrams, Ref. 5). Results obtained in the presence of sodium titanate suggest that as predicted, little Ni(II) is adsorbed by the sodium titanate below pH 4. Between pH 4 and pH 7.5, Ni(II) is removed from solution via ion exchange, with more Ni(II) being adsorbed as the solution pH increases. Above pH 7.5, the precipitous drop in the dissolved Ni(II) concentration indicates that Ni(II) hydrolysis occurs at about the same pH in the presence of sodium titanate as in its absence. In this basic pH regime, Ni(II) adsorption should no longer occur via an ion-exchange reaction. Also plotted in Fig. 2 is a titration of a $Ni(NO_3)_2$ solution in the presence of a commercial TiO_2 powder (Degussa P-25). In this case, the behavior is very similar to that obtained without any powder demonstrating the lack of ion-exchange sites on this material.

Characterization and Reactivity Studies of Nickel-Loaded Catalysts

Because results from earlier catalytic studies[1,4] suggested that we have good metal dispersion even at high metal loadings (> 5%) on the sodium titanates relative to materials prepared by traditional methods, we investigated how the degree of nickel dispersion depends on the loading conditions. In this study, we compare two nickel-loaded catalysts prepared by ion exchange on the titanate powders or by impregnation on Degussa P-25 TiO_2. We have previously described characterization and reactivity studies of two very different Ni catalysts prepared on the titanates in which it was demonstrated that the ion-exchanged material showed characteristics of being highly dispersed, even at metal loadings of 5% or more.[9,10]

A good test of the dispersion of the active metal is the activity and selectivity for the hydrogenolysis of n-butane. For example, it has been reported that highly dispersed Ir catalysts are particularly selective for ethane by preferential scission of the central C-C bond in n-butane.[13] Fig. 3 displays the results obtained for the selectivity for C_1, C_2

and C_3 paraffin hydrocarbons as a function of temperature on the two catalysts described above. It can be seen that the catalyst prepared by ion exchange on the hydrous titanate powders is very selective for C_2 hydrocarbons (ethane) at temperatures below 540 K. At higher temperatures (> 550 K), methane is the predominant product. In the case of the catalyst prepared by impregnation of TiO_2, methane and propane are the primary products for most temperatures studied. These results suggest that larger metal particles are present in the impregnated catalyst.

To confirm the highly dispersed nature of the ion-exchanged hydrous titanate supported Ni catalyst, we have obtained Ni K-edge EXAFS and XANES spectra of this catalyst in collaboration with Dr. Farrel Lytle of Boeing. The Ni K-edge EXAFS spectrum of the catalysts after H_2 reduction is shown in Figure 4 where the spectrum of a Ni foil is also shown for comparison. Significantly, there is a complete absence of the second, third and fourth nearest neighbor Ni peaks (at approximately 3.9, 4.5 and 5.2 Å, respectively) in the HTO-supported catalyst. There is a strong feature at approximately 4.8 Å which is unprecedented in supported-Ni catalysts. At the present time, we are not sure what this peak represents. However, a second nearest neighbor of Ni (or O) at such a long distance is very strong evidence that the Ni is highly dispersed.

Raman and ^{17}O NMR Spectroscopic Studies

In this section, we focus on ongoing studies of the local molecular structure of the hydrous titanate materials. As discussed above, the loading of active metals on sodium titanate supports by ion exchange leads to much more active and selective catalysts than can be obtained by other loading procedures. In addition, from the above ion-exchange studies it appears that the concentrations and ion-exchange characteristics of active sites on the titanate supports are controlled by the coordination geometry of oxygens in the structure. We have utilized Raman spectroscopy and solid state NMR spectroscopy on ^{17}O labeled samples to determine the distribution of oxygen types and ion-exchange sites in amorphous titanates.

Crystalline titanates reported in the literature[14-18] exhibit a wide range of local structural environments. The titanium (IV) ions in the structures can be coordinated by either 4, 5, or 6 oxygens (designated Ti(4), Ti(5), and Ti(6)). The oxygens can be bonded to 1, 2, 3, or 4 titanium ions (designated O(1), O(2), O(3), and O(4)). To make definitive NMR peak assignments, we therefore prepared ^{17}O labeled crystalline compounds having as many possible combinations of O and Ti coordinations as possible to derive standards relating structure to the observed ^{17}O chemical shifts and Raman bands. The chemical shift information obtained for all model compounds is summarized in Fig. 5. (All chemical shifts are reported in ppm, with $H_2{}^{17}O$ serving as the 0 ppm reference.) While each type of oxygen does not always produce an NMR signal at exactly the same chemical shift, it appears that the chemical shifts tend to fall in the following ranges as illustrated in Fig. 5: O(4) = 600-700 ppm, O(3) = 400-600 ppm, O(2) = 330-450 ppm, and O(1) = 180-420 ppm. While the peaks associated with O(4) and O(3) are well separated from other ranges of chemical shift, there is considerable overlap in the ranges for O(2) and O(1). For an unknown compound, such as our amorphous titanates, peaks observed below 400 ppm could be attributed to either oxygen type. Fortunately, the presence of O(1) is easy to detect using Raman spectroscopy (see below), so we are confident that relative amounts of O(2) and O(1) can be obtained by combining NMR and Raman results.

The primary factor influencing the ^{17}O NMR chemical shift appears to be the electron density on the oxygen. One way to characterize the electron density on the oxygen is to use simple formal charge arguments (Fig. 6). For example, if Ti(IV) is bonded to six oxygens, the net charge which the titanium donates per oxygen is $+4/6 = +0.67$. The formal charge on oxygen is taken to be equal to -2. Therefore, if the oxygen is bonded to two Ti(6) ions, the net charge on the oxygen in this hypothetical structure is $-2 + 2(0.67) = -0.67$. Fig. 6 illustrates that similar arguments can be made to rationalize neutral and positively charged oxygen sites. We have demonstrated that there is a good correlation between the net charge on the oxygen and the observed chemical shift.[11,12]

Raman spectra have also been obtained for all model compounds investigated via NMR. The crystalline titanates exhibit rich Raman spectra below 1000 cm^{-1} associated with stretching and bending modes of different Ti-O bonding configurations. Definitive assignment of all modes is complicated and is not yet complete. However, one important spectral region has been identified, and that is the region associated with non-bridging oxygens (nbo's). All compounds containing non-bridging oxygens exhibit a strong band (or bands) in the 700-900 cm^{-1} region of the Raman spectrum. Compounds which do not have non-bridging oxygens exhibit weak bands in this region, probably associated with impurities. Therefore, in those instances where the NMR results are ambiguous with regard to the presence of non-bridging oxygens, the Raman spectra can provide unambiguous proof that nbo's are present.

In our recent spectroscopic studies, we have also focussed on 1) the effect of altering the Na/Ti stoichiometry in the amorphous powders, and 2) the effect of ion-exchange reactions in acid solution on the distribution of ion-exchange sites in the material.

Varying Na/Ti Stoichiometry. In the synthesis of the sodium hydrous titanate powders, the Na to Ti stoichiometry is easily controlled by varying the amount of NaOH used. This leads to altered ion-exchange properties as indicated by pH titrations and surface charge measurements.[19] From both the Raman and ^{17}O NMR spectra shown in

Fig. 7, such altered properties can be rationalized. For example, the ^{17}O NMR spectra of $Na_{0.25}Ti$ and $Na_{0.5}Ti$ are both dominated by two features near 350 and 500 ppm that we assign to two-fold and three-fold oxygens respectively. However, the spectrum of $Na_{0.5}Ti$ also shows a peak at approximately 240 ppm, in the region expected for non-bridging oxygens. This assignment is reinforced by the Raman spectra of these two materials also shown in the figure. In this case, the spectrum of the $Na_{0.5}Ti$ powder contains a large scattering feature near 900 cm^{-1} while the $Na_{0.25}Ti$ sample shows little intensity in this region. On the basis of the formal charge arguments described earlier, we expect that the charged ion-exchange sites in the hydrous titanate materials will be the non-bridging and doubly-bridged oxygen sites. Such sites in the structure will be formally negative and charge-compensated by the Na cations. Thus, these results demonstrate that both the type and number of ion-exchange sites can be manipulated in a simple manner during the preparation of these materials.

Structural Rearrangement During Ion-Exchange Reactions. Previously, we showed that the ion-exchange properties of a $Na_{0.5}Ti$ powder can be irreversibly altered upon proton for sodium exchange in acidic solutions.[6] On the basis of Raman spectra, we suggested[8] that this might arise from a reaction between doubly protonated non-bridging oxygens (O(1)'s) and doubly-bridged oxygens (O(2)'s) in the material. More recently, we have obtained ^{17}O NMR spectra of the $Na_{0.5}Ti$ starting material, and after it had been contacted with pH 7 and pH 2 solutions. The results, shown in Fig. 8, suggest that our previous conclusions were incomplete. Again the spectrum of the starting material (labeled pH 12 in the figure) shows spectral features at about 240, 350 and 500 ppm assigned above to nbo, O(2) and O(3) structural units, respectively. In agreement with the Raman results,[12] we find that the nbo peak disappears at low pH. However, in addition to seeing changes in the relative populations of O(1), O(2), and O(3), we see a new NMR peak at about 600 ppm indicative of the presence of O(4). It now appears that network repolymerization at low pH is more complex than originally thought, involving formation of both O(3) and O(4) units from condensation reactions. The occurance of reactions which convert mixtures of O(1), O(2), and O(3) into mixtures of O(2), O(3), and O(4) not only eliminates anionic oxygen sites available for cation exchange, but creates positively charged O(4) sites which are potential anion exchange sites (see Fig. 6). Notice that these sites begin to appear even at pH 7, above the isoelectric point (iep) of the sodium hydrous titanate material.[9,10] The generation of sites available for ion-exchange of anions from solution (cationic sites) in this pH regime may explain why anions such as solvated Mo and V species adsorb onto the hydrous titanates above pH 5 (the iep). (These results will be reported in an upcoming semiannual report.) Similarly, that formally negatively charged O(2) sites persist at low pH may explain cation exchange (Ni(II) adsorption[9,10]) below the iep.

Summary and Conclusions

We have prepared and studied the properties of a sodium hydrous titanium ion-exchange material which have shown great promise for use as a heterogeneous catalyst support. In these studies we have identified the solution conditions (e.g., pH) in which the sodium titanates contain sites for the adsorption of either metal cations or anions. For the exchange of Na for Ni(II) cations, solutions with a pH of 4-5 or more are required. However, Ni(II) undergoes extensive hydrolysis and condensation reactions above a pH of about 7-8 which competes with ion-exchange onto the support when both are present in solution. We have prepared several Ni-loaded hydrous titanates under different solution conditions to compare their material and catalytic properties. The catalysts were characterized by solution analyses, TEM, hydrogen chemisorption, BET surface area measurements, EXAFS, and the activity and selectivity of the n-butane hydrogenolysis reaction. The catalyst prepared via ion exchange displayed a high degree of selectivity for ethane from scission of the central C-C bond in n-butane indicative of highly dispersed metal even at the loading of 5% used in this study. EXAFS measurements verify the high degree of metal dispersion in this case. The ability to obtain high metal dispersions in catalysts prepared by ion exchange onto the hydrous titanate supports may well explain the high activity (on a per gram of metal basis) of these catalysts relative to catalysts prepared by more conventional methods.[1,4]

By utilizing results obtained from model crystalline titanate compounds, we have been able to make Raman and ^{17}O NMR assignments for spectra obtained from amorphous hydrous sodium titanate powders. In this way, we have discovered that the type and distribution of ion-exchange sites can be manipulated by the synthesis of these materials. In addition, spectra of a $Na_{0.5}Ti$ powder which had been ion exchanged for protons in acidic solutions suggest that anionic non-bridging oxygen sites are converted to cationic 4-fold oxygen sites by reaction with triply-bridged oxygens in the structure. The new sites formed under such conditions may well account for the ability of the hydrous titanates to function as anion exchangers at lower pH.

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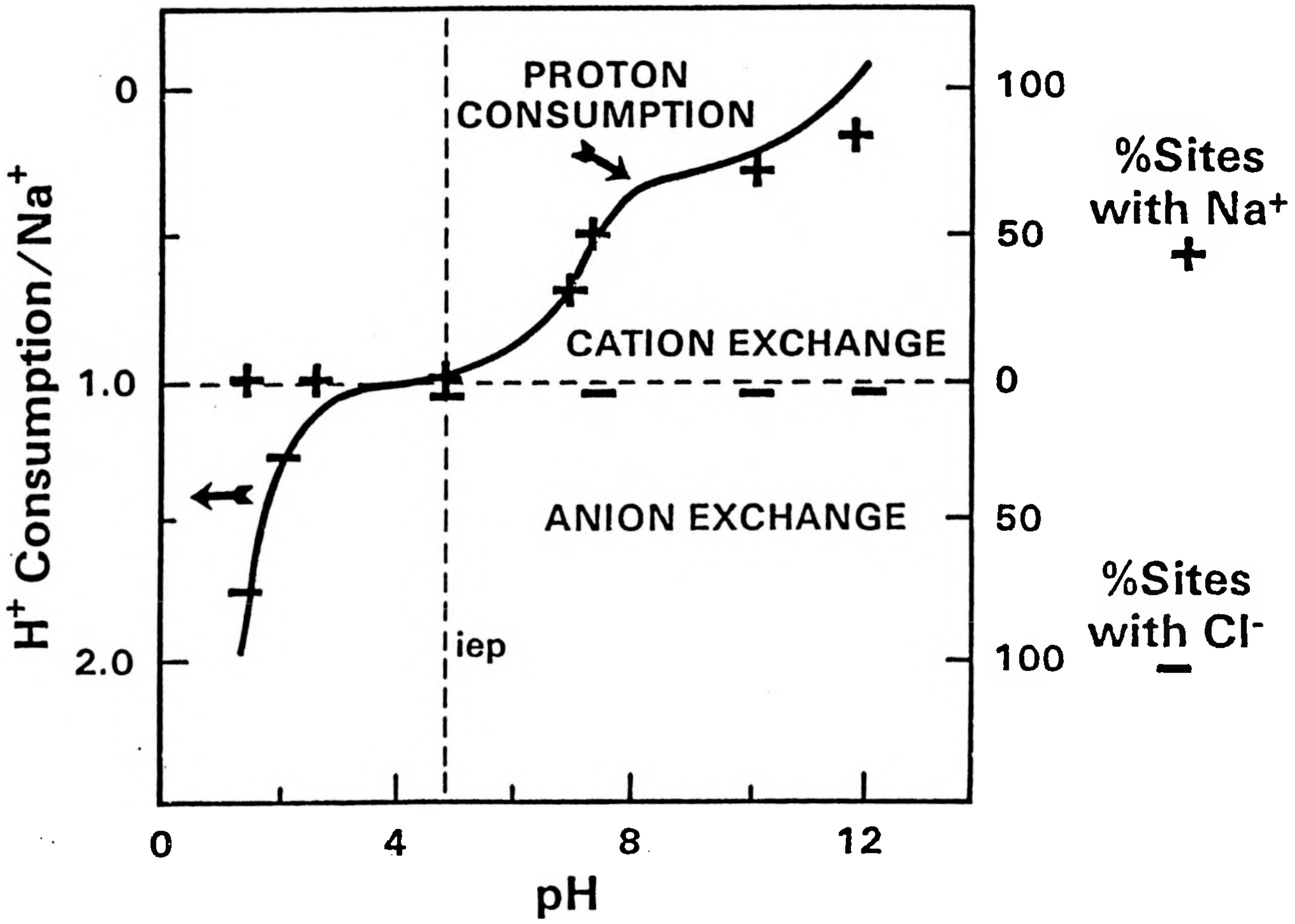
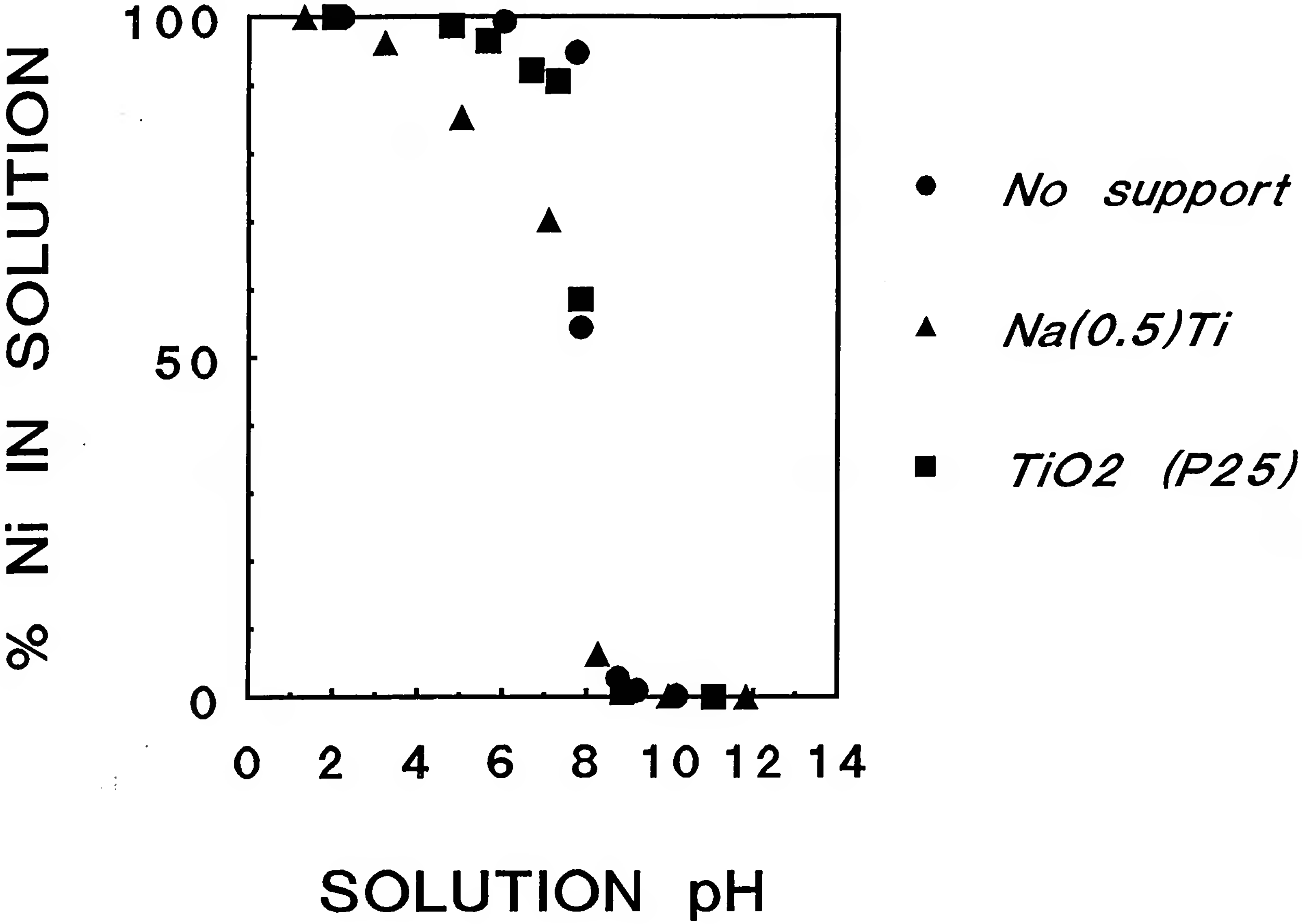
FIGURE CAPTIONS

Figure 1:	Plot of the H^+ (solid line) and Cl^- (-) consumption from solution, and Na^+ (+) depletion from a $Na_{0.5}Ti$ during titration with HCl (starting pH = 12).[2]
Figure 2:	Plot of the amount of Ni in a 0.25M $Ni(NO_3)_2$ solution as a function of pH both in the presence and absence of a $Na_{0.5}Ti$ powder.
Figure 3:	Selectivity for C_1 (CH_4), C_2 (C_2H_6), and C_3 (C_3H_8) hydrocarbon formation from the hydrogenolysis of n-butane over Ni/HTO and Ni/TiO_2 catalysts.
Figure 4:	Ni EXAF spectra for a reduced HTO-supported Ni catalyst prepared by ion exchange. A spectrum of Ni foil is also shown for comparison.
Figure 5:	Approximate ranges observed for the ^{17}O chemical shifts of crystalline titanates as a function of oxygen coordination.
Figure 6:	Three examples of Ti-O coordination geometries which can give rise to variably charged sites in a titanate structure.
Figure 7:	^{17}O solid state NMR and Raman spectra of $Na_{0.25}Ti$ and $Na_{0.5}Ti$ amorphous hydrous titanate powders.
Figure 8:	^{17}O solid state NMR spectra of $Na_{0.5}Ti$ amorphous hydrous titanate powder as a function of solution pH.

Figure 1

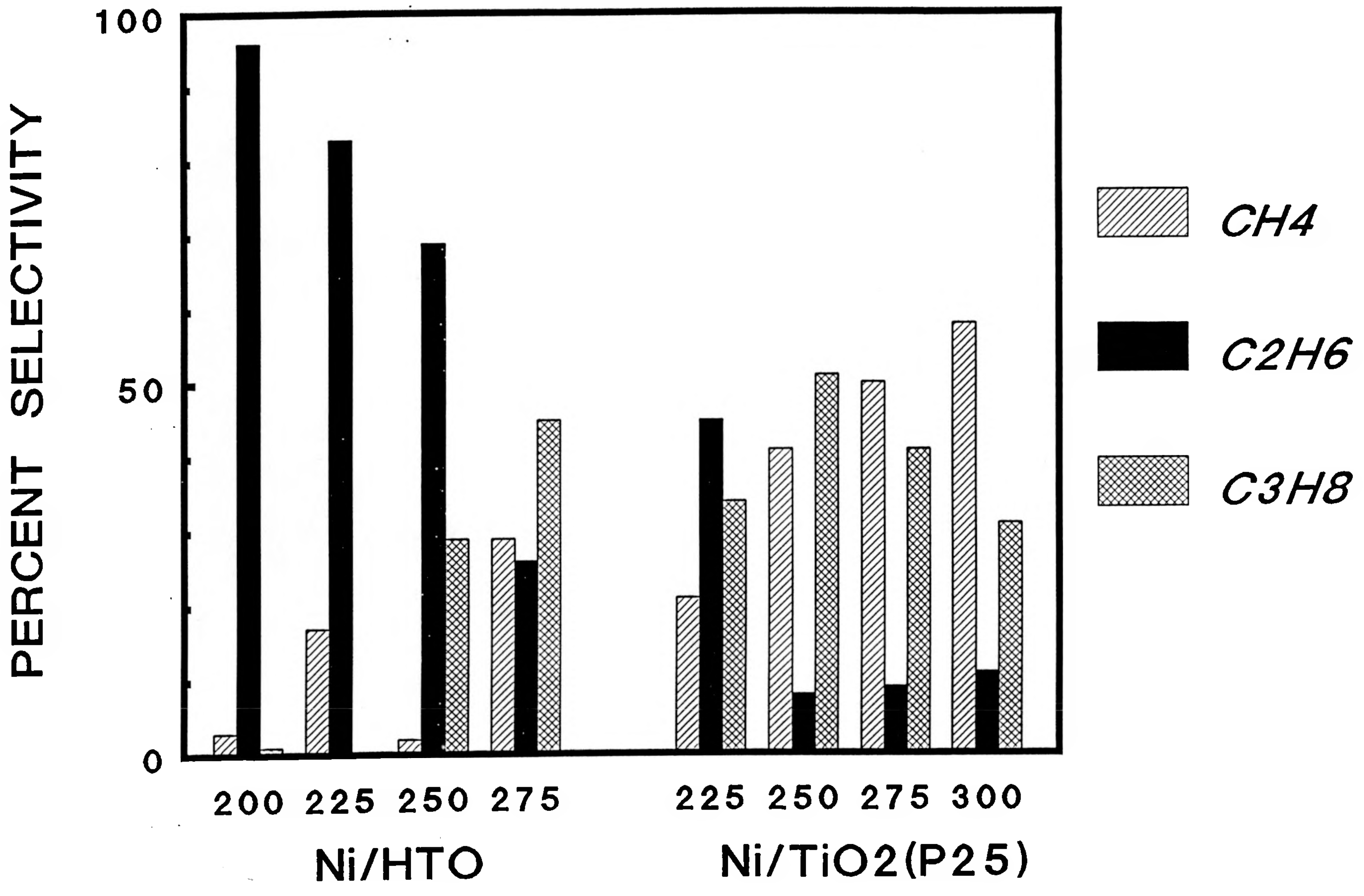
Equilibrium Titration of $Na_{0.5}$ Ti





PERCENT Ni DISSOLVED VERSUS pH

Figure 2



N-BUTANE HYDROGENOLYSIS SELECTIVITY

Figure 3

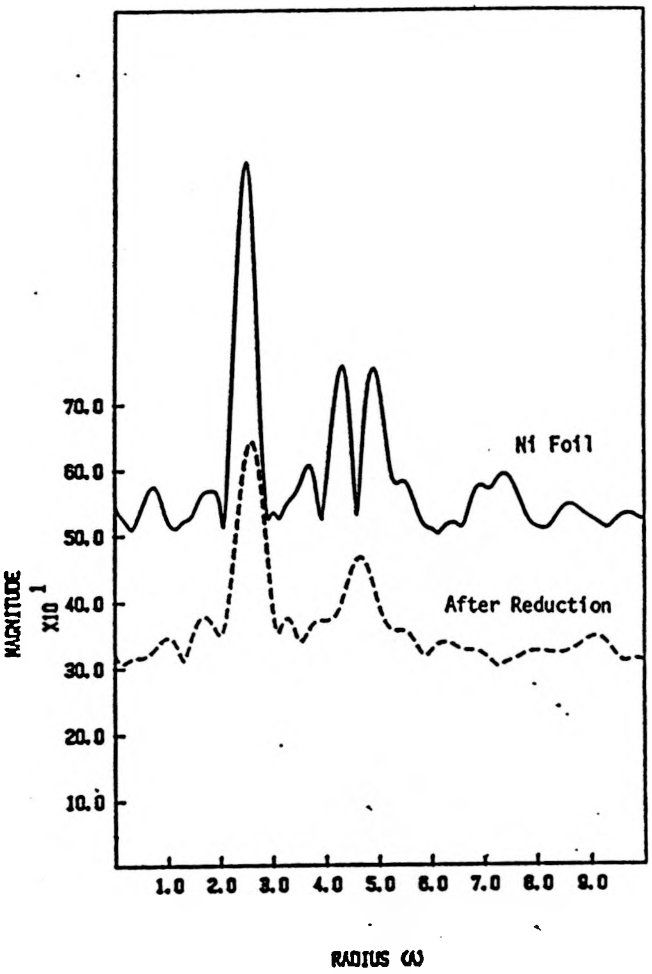

70.0
60.0
50.0
40.0
30.0
20.0
10.0
MAGNITUDE
X10 1
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
RADIUS (A)
Ni Foil
After Reduction

Figure 4

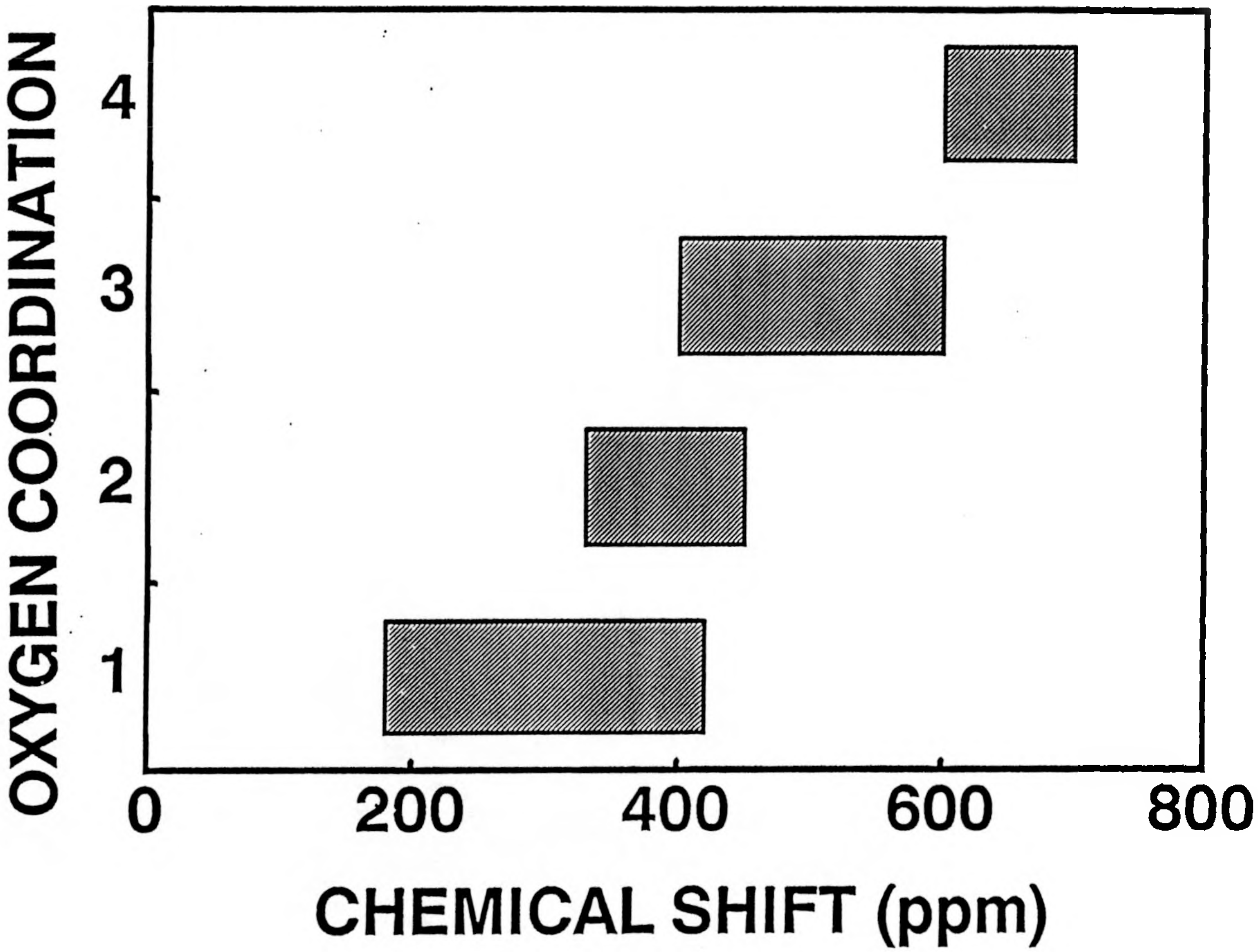

OXYGEN COORDINATION
4
3
2
1
0
200
400
600
800
CHEMICAL SHIFT (ppm)

Fig. 5

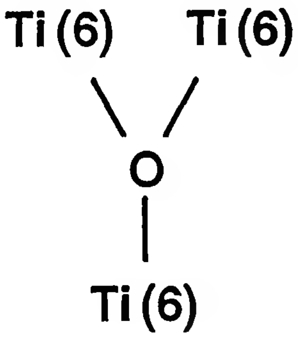
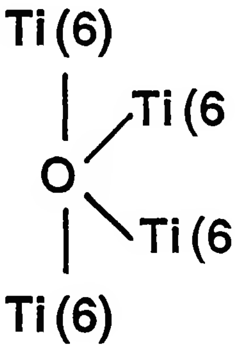
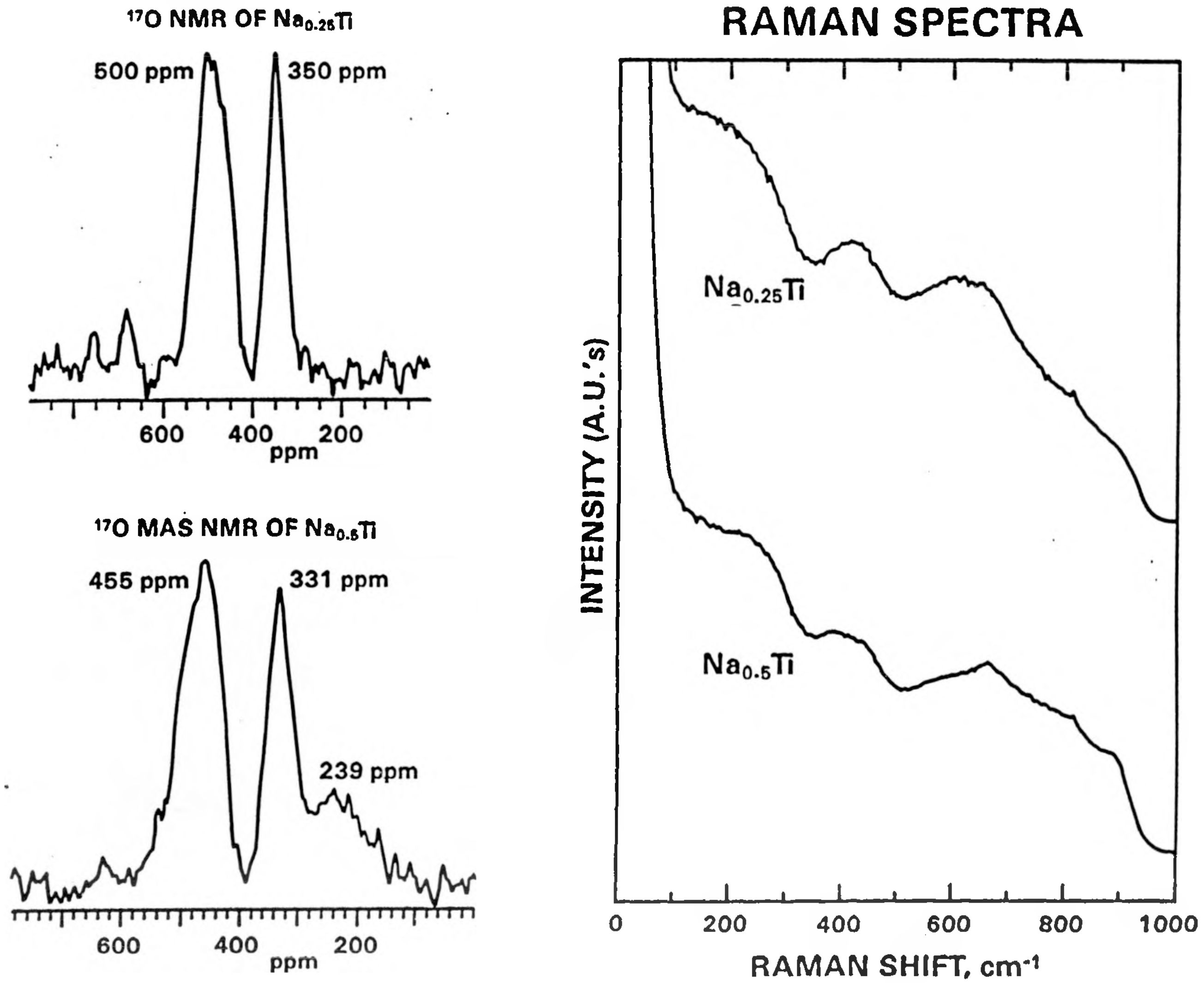
	Anionic	**Neutral**	**Cationic**
Charge	-2/3	0	+2/3
Species	Ti (6) — O — Ti (6)		
Compound	$PbTiO_3$	TiO_2	$K_2Ti_4O_9$

Fig. 9



^{17}O NMR OF $Na_{0.25}Ti$
500 ppm
350 ppm
600
400
200
ppm
^{17}O MAS NMR OF $Na_{0.5}Ti$
455 ppm
331 ppm
239 ppm
600
400
200
ppm
RAMAN SPECTRA
INTENSITY (A.U.'s)
$Na_{0.25}Ti$
$Na_{0.5}Ti$
0
200
400
600
800
1000
RAMAN SHIFT, cm^{-1}

Fig. 7

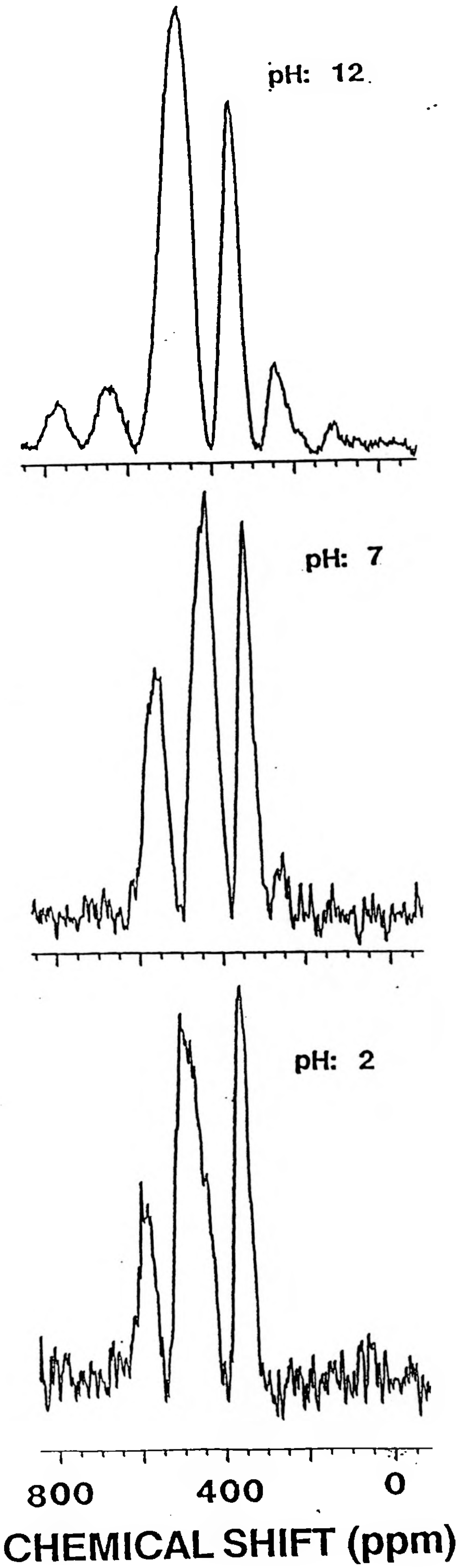


Fig. 8