*Chem. Mater.* **1992,** *4,* 49–55

# *Articles*

## Rhodium Complexes with Nitrogen-Donor Ligands Anchored on Silicic Supports. 1. Synthesis and Characterization

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*Received February 5, 1991. Revised Manuscript Received June 18, 1991*

An amino-functionalized silica, $(SiO_2)O_{3/2}Si(CH_2)_3NH_2$ (I) has been synthesized by cohydrolysis of tetraethylorthosilicate (TEOS) and (3-aminopropyl)triethoxysilane (APS), following an acid-catalyzed sol–gel process. The primary amine functions of I, by reaction with diketones or pyridine-2-carboxaldehyde, create "in situ" diazabutadiene (R-DAB) or pyridinecarbiimine (R-PyCa) ligands grafted to the silicic support. By subsequent reaction of these N-donor groups with $RhCl_3·3H_2O$ or various organometallic complexes of rhodium, we have obtained anchored rhodium complexes homogeneously dispersed on the silicic support. The results obtained by this route have been compared with those obtained by forming first the rhodium complex with a ligand derivative from R-propyltriethoxysilane (R = amine, DAB, PyCa) and its subsequent copolymerization with TEOS. Some experiments with silica gel (Kieselgel-60) carried out in parallel have enabled us to study the differences between this silica matrix and that generated from TEOS. These organo-inorganic materials were characterized by elemental analysis, TEM-EDX techniques and IR, CP-MAS $^{13}C$ NMR, and XPS spectroscopy.

### Introduction

The development of materials based on modification of silica by the grafting or organosilanes or transition-metal species has been receiving increasing attention due to their potential use in different applications, mainly as chromatographic supports[1] and as solid matrices to anchor soluble catalysts.[2] In this last approach the supported catalysts combine the advantages of homogeneous and heterogeneous catalysis. The design and preparation of stable organo-inorganic systems, nanocomposites, containing functional groups, would permit changes in their topology by altering the reaction conditions and, consequently, would make it possible to obtain "new" materials, or old materials with new properties.[3]

Supports functionalized with mono- or bidentate phosphine ligands have been intensively studied;[2b] on the contrary functionalization with N-donor ligands has not been so well investigated.

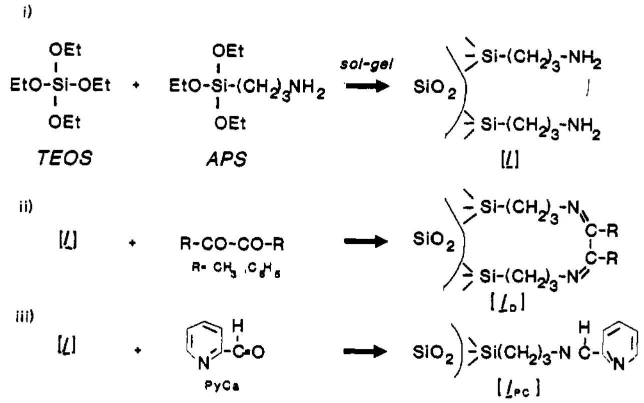
A critical problem associated with the anchoring of metal complexes is the loss (leaching) of the metal if the ligands by which the metal is attached to the support are involved in dissociation equilibria.[4] There are different ways to reduce this disadvantage in these materials: (a) The increase of the ligand concentration in the support; (b) the use of microporous matrices; (c) the use of chelating ligands.[5]

The present work is concerned with the preparation of a series of rhodium complexes anchored to silica functionalized with various chelating N-donor groups; the support in this case is robust microporous and three dimensional. We have used low metal loading in the hope of avoiding leaching when we use these materials as supported catalysts.

### Experimental Section

**Materials.** $RhCl_3·3H_2O$ (Johnson Matthey C.L.) was used without purification.

**Scheme I. Procedure for the Preparation of Silica Functionalized with N-Donor Groups: (i) —$NH_2$; (ii) —N═C—C═N—; (iii) Py—C═N—**



$[L_D]$ = Silica functionalized with diaza butadiene ligands.

$[L_{PC}]$ = Silica functionalized with pyridinecarbiimine ligands.

Organic solvents were thoroughly degassed and distilled when necessary.

(3-Aminopropyl)triethoxysilane (APS, $(EtO)_3Si(CH_2)_3NH_2$,

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* Author for correspondence.

[1] (a) Leyden, D. E., Collins, W. T., Eds. *Silylated Surfaces. Macromolecular Series*; Gordon and Breach Science Publishers: New York, 1980; Vol. 7. (b) Rosset, R. *Bull. Soc. Chim. Fr.* **1985,** 1128. (c) Pirkle, W. H.; Pochapsky, T. C.; Mahler, G. S.; Corey, D. E.; Reno, S. S.; Alessi, D. M. *J. Org. Chem.* **1986,** *51,* 4991.

[2] (a) Murrell, L. L. In *Advances in Materials in Catalysis*; Burton, J. J., Garten, R. L., Eds.; Academic Press: New York, 1977; Chapter 8. (b) Schwartz, J.; Ward, M. D. *J. Mol. Catal.* **1981,** *11,* 397. (c) Hegedus, L. L., Ed. *Catalyst Design, Progress and Perspectives*; Wiley: New York, 1987. (d) Gokak, D. T.; Ram, R. N. *J. Mol. Catal.* **1989,** *49,* 285. (e) Parish, R. V.; Habibi, D.; Mohammadi, V. *J. Organomet. Chem.* **1989,** *369,* 17.

[3] (a) Hartley, F. R. *Supported Metal Complexes*; Reidel: Dordrecht, 1984. (b) Ruiz-Hitzky, E. *Mol. Cryst. Liq. Cryst.* **1988,** *161,* 433.

[4] (a) Parish, R. V.; Vania, M. I. *J. Organomet. Chem.* **1984,** *263,* 139. (b) Jones, R. A.; Seeberger, M. H. *J. Chem. Soc., Chem. Commun.* **1985,** 373. (c) Ejike, E. N.; Parish, R. V. *J. Organomet. Chem.* **1987,** *321,* 131.

[5] Hodge, P., Sherrington, D. C., Eds. *Polymer Supported Reactions in Organic Synthesis*; Wiley: New York, 1980.

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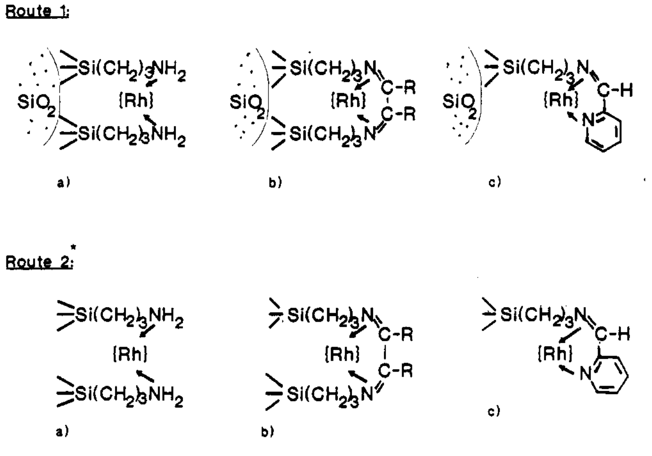
**Scheme II. Rhodium Complexes Anchored on Silica Functionalized with N-Donor Groups**[a]



*With subsequent addition of TEOS, partially hydrolysed.

[a] {Rh}, means the various Rh compounds studied: $RhCl_3.3H_2O$, $[RhCl(CO)_2]_2$, $[RhCl(COD)]_2$, and $RhClCO(PEt_3)_2$.

Aldrich, 98%) was freshly distilled before use; tetraethylorthosilicate $(EtO)_4Si$ (TEOS, Merck), benzil $(C_6H_5CO)_2$ (B, Fluka, >98%), diacetyl $(CH_3CO)_2$ (D, Carlo Erba, 99%) and pyridine-2-carboxaldehyde $NC_5H_4CHO$ (PyCa, Aldrich, 99%) were used as commercially supplied.

Silicagel was from Merck (Kieselgel-60; specific surface area (BET, $N_2$) 450 $m^2/g$, pore volume 0.7 $cm^3/g$).

**Syntheses. (1) Preparation of Functionalized Silica by Grafting of N-Donor Groups (Scheme I). (i) Compound I (silica functionalized with aminopropyl groups):**[6] A solution of 28 mL of EtOH (analytical grade) and 29 mL of water with one or two drops of concentrated hydrochloric acid as catalyst was placed in a round bottom flask; 38 mL of TEOS was slowly added while the solution was continuously stirred. The system was maintained at 25 °C under stirring for 50 min, followed by the addition of 10 mL of APS in 5 mL of EtOH. This mixture, after a few minutes, gave a white gel which was dried in a rotary evaporator at 60 °C extracted in a Soxhlet apparatus with water and heated at 110 °C for 24 h, under reduced pressure. Elemental analysis: exp 10.7% C, 3.2% H, 3.8% N; calc (supposing complete hydrolysis and subsequent condensation of TEOS and APS compounds in a 4/1 molar ratio) 10.3% C, 2.3% H, 4.0% N.

**(ii) Compounds $I_D$ (silica functionalized with diazabutadiene ligands)**: To a suspension of compound I in MeOH (0.35 g/25 mL), a solution of diacetyl or benzil in MeOH was added in a 2/1.2 molar ratio to form the diimine. The mixture was continuously stirred for 24 h at 25 °C. The solid was extracted in a Soxhlet apparatus with $CH_2Cl_2$ and dried at 110 °C. It was stored in a $N_2$ atmosphere. The color of the product was pale yellow.

**(iii) Compound $I_{pc}$ (silica functionalized with pyridine-2-carbiimine ligands)**: A solution of pyridine-2-carboxaldehyde (PyCa) was added to I in a 1.2/1 molar ratio in methanol. The reaction conditions were the same as before, and the resulting product was off-white.

**(iv) Compound $S_{NH_2}$ (Kieselgel-60 functionalized with aminopropyl groups)**: Kieselgel-60 was heated at 140 °C at reduced pressure for 3 h. After this treatment, the silica was left in toluene (100 mL) for 2 h; the suspension was continuously stirred and APS was added by drops; the molar ratio $APS/SiO_2$ was 0.4/1. Stirring was maintained for 24 h, the solid was extracted in a Soxhlet apparatus with water and vacuum dried at room temperature. The subsequent reaction with diketones (RCOCOR) or pyridine-2-carboxaldehyde $(NC_5H_4CHO)$ used in the same conditions as described for reactions with TEOS.

**(2) Formation of Supported Rh Complexes on the Functionalized Silica (Scheme II, Route 1). (a) Reaction of I with $RhCl_3 \cdot 3H_2O$**: $RhCl_3 \cdot 3H_2O$ (0.03 g) in methanol was added to a suspension of I in MeOH (0.050 g/25 mL), and the mixture was stirred at 25 °C for 3 days. The resulting orange-red solid was filtered, carefully washed with MeOH to eliminate the excess uncomplexed rhodium chloride, and vacuum dried at room temperature.

**(b) Reaction of I with other Rh complexes**: In a manner similar to that described above, compound I was treated with the following Rh complexes: $[RhCl(CO)_2]_2$ prepared by heating $RhCl_3 \cdot 3H_2O$ in a CO stream;[7] $[RhCl(COD)]_2$ obtained by reaction of $RhCl_3 \cdot 3H_2O$ with COD (cyclooctadiene) in EtOH and heated to reflux for 3 h in a $N_2$ atmosphere;[8] $RhClCO(PEt_3)_2$ prepared by reaction of $[RhCl(CO)_2]_2$ with $PEt_3$ in toluene.

**(c,d) Reaction of $I_D$ and $I_{pc}$ with $RhCl_3 \cdot 3H_2O$ and $[RhCl(COD)]_2$**: The procedure was the same as described above in (a) and (b), respectively.

In all cases the reaction period of the support with the complex was 3 days (at 25 °C) and the stoichiometric ratio N/Rh was always in the range 1–2 (N calculated from elemental analysis of the functionalized support).

**(3) Formation of Rhodium Complexes ({Rh}) with Triethoxysilyl Ligands (Scheme II, Route 2).** {Rh} means the various Rh compounds studied: $RhCl_3 \cdot 3H_2O$, $[RhCl(CO)_2]_2$, $[RhCl(COD)]_2$, and $RhClCO(PEt_3)_2$.

**(a) Reaction of APS with {Rh} and TEOS.** APS (4 mmol) was treated with {Rh} (1–4 mmol) in ethanol and stirred at room temperature for 4 h. The jelled product was treated with a partially hydrolyzed solution of TEOS; the mixture was stirred for 2 days, extracted in a Soxhlet apparatus with $CH_2Cl_2$, and dried at 70 °C for 2 h. The resulting solid was orange.

The partial hydrolysis of TEOS was carried out in a separate reaction flask for 4 h in a mixture of 1.4 mL of TEOS, 30 mL of ethanol, 1 mL of $H_2O$, and a drop of HCl.

**(b) Reaction of APS with Diacetyl, {Rh}, and TEOS.** APS (4 mmol) was allowed to react with diacetile (2 mmol) in toluene during 18 h of stirring. The resulting $\alpha$-diimine ligand was made to react with the rhodium compound at room temperature for 4 h with stirring. As the ethoxy groups of APS hydrolyze more quickly than TEOS, a partially hydrolyzed solution of the latter was added to an ethanolic suspension of the rhodium R-DAB complex (R = triethoxysilyl). The process follows as previously described.

**(c) Reaction of APS with Benzil, {Rh}, and TEOS.** APS (4 mmol) was made to react with benzil (2 mmol) in toluene, with stirring for 18 h. This APS, functionalized with the benzildiazadiene ligand and dissolved in 30 mL of ethanol, was allowed to react with the rhodium compound as before; partially hydrolyzed TEOS was added, as above, to give an off-white product.

**(d) Reaction of APS with Pyridine-2-carboxaldehyde, {Rh}, and TEOS.** A solution of pyridine-2-carboxaldehyde in benzene was added to an APS solution in the same solvent. The molar ratio of reactants was 1/1. The reaction mixture was kept at 0 °C with stirring. After 1 h the reaction was complete, and the jelled product was filtered off, washed with acetonitrile, and vacuum dried. The metal loading was as described before and finally treated with partially hydrolyzed TEOS.

**Techniques.** Microanalyses were performed on a Perkin-Elmer Model 240C elemental analyzer for C, H, and N. Rhodium was determined by atomic absorption in a PYE UNICAM spectrophotometer after decomposition of the sample with $HF:HNO_3$ (2:1).

IR spectra were recorded in the range 4000–250 $cm^{-1}$, using KBr disks, fluorolube, or Nujol mulls, on a Perkin-Elmer 580B spectrophotometer, coupled to a M-3500 data station.

The $^{13}C$ solid-state NMR spectra were obtained at room temperature on a Brucker Model MSL 400 spectrometer operating at 10.62 MHz equipped with a 3000 Aspect computer with Fourier transform. The instrument settings were as follows: 90° pulse width for $^{13}C$ and $^1H$, $3 \times 10^{-3}$ s; spectra width 10 kHz; acquisition time 0.05 s; proton decoupling power 20 G; sample spinning speed 2.1 kHz; contact time $10^{-3}$ s; time delay between scans, 3 s.

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[6] (a) Klein, L. C. *Annu. Rev. Mater. Sci.* **1985**, *15*, 227. (b) Scherer, G. W. *Yogyo-Kyokai-Shi* **1987**, *95*, 21. (c) Khatib, I. S.; Parish, R. V. *J. Organomet. Chem.* **1989**, *269*, 9.

[7] Lipson, L. G.; Maddox, M. L.; Herbert, D. *Inorg. Synth.* **1966**, *8*, 211.

[8] Cocevar, C.; Mestroni, G.; Camus, A. *J. Organomet. Chem.* **1972**, *35*, 389.

**Table I. Analytical Data of the Compounds Obtained by Reaction of I[a] or $I_D$[b] with Different Rhodium Compounds (Scheme II, Route 1)**

| | | elem anal. | | | | | |
|---|---|---|---|---|---|---|---|
| compound | color | % C | % H | % N | % Rh | C/N[c] | N/Rh |
| I | white | 10.71 | 3.19 | 3.78 | | 3.3 (3) | |
| 1, I + $RhCl_3 \cdot 3H_2O$ | orange | 10.60 | 2.76 | 3.18 | 3.45 | 3.8 (3) | 6.8 |
| 2, $I_D$[d] + $RhCl_3 \cdot 3H_2O$ | orange | 10.97 | 2.67 | 3.39 | 2.44 | 3.8 (5) | 10.2 |
| 3, $I_D$[e] + $RhCl_3 \cdot 3H_2O$ | orange | 15.05 | 3.97 | 3.20 | 2.74 | 5.5 (10) | 8.6 |
| 4, I + $RhClCO(PEt_3)_2$ | pale yellow | 14.19 | 3.32 | 3.37 | 3.11 | 4.9 | 8.0 |
| 5, I + $[RhCl(COD)]_2$ | pale yellow | 12.13 | 2.97 | 3.09 | 3.92 | 4.6 | 5.8 |
| 6, I + $[RhCl(CO)_2]_2$ | cream | 12.25 | 2.89 | 3.27 | 6.18 | 4.4 | 3.9 |

[a] I = $(SiO_2)O_{3/2}Si(CH_2)_3NH_2$. [b] Silica functionalized with diazadiene groups. [c] Experimental (calculated). [d] I + diacetyl. [e] I + benzil.

XPS measurements were carried out on a Leybold Heraeus LHS10 spectrometer, employing Mg K$\alpha$ ($h\nu$ = 1253.6 eV) nonmonochromated radiation. All reported binding energies (BE) are referred to the carbon signal $C_{1s}$ (284.6 eV).

The morphology of the samples was determined by direct transmission electron microscopy (TEM), on a Siemens Elmiscop 102. The chemical homogeneity of the particles was observed with a Philips EM 420 microscope with an energy-dispersive X-ray spectrophotometer and an EDAX 9100 analyzer computer system.

The specific surface area (BET, $N_2$) of compound I (silica functionalized with aminopropyl groups) was determined on a Carlo Erba Strumentazione Sorptomatic 1800 instrument, using a Milestone 100 program.

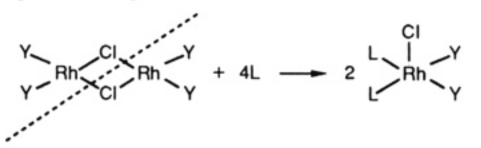
## Results and Discussion

The preparation of a silica matrix containing $NH_2$ functions (I) was carried out by cohydrolysis of tetraethylorthosilicate (TEOS) and (3-aminopropyl)triethoxysilane (APS) following a conventional acid-catalyzed sol–gel process[6] (Scheme Ii) from a molar proportion of TEOS:APS:EtOH:$H_2O$ of 4:1:16:32.[6a] The gel obtained after drying at 110 °C has a content of 2.7 mmol of aminopropyl groups/g of substrate as estimated from the elemental analysis. It exhibits good homogeneity in the shape and size of the particles, which are present as connected spheres of about 20-nm diameter, as evidenced by electron microscopy (Figure 1A). The specific surface area (BET, $N_2$) and pore volume are 107 $m^2/g$ and 0.43 $cm^3/g$, respectively.

The presence of free primary amine functions will allow their subsequent reaction with dicarbonyl compounds, (RCOCOR, R = $CH_3$, $C_6H_5$; Scheme Iii) and with pyridine-2-carboxaldehyde ($NC_5H_4CHO$, Scheme Iiii) in order to create heterodiazabutadiene (R-DAB, —N=C—C=N—), and pyridine-2-carbiimine (R-PyCa, 2-$C_5H_4$NC(H)=N—) functions, respectively. The three types of N-donor functions, –$NH_2$, –DAB, and –PyCa, should be able to coordinate to rhodium compounds to give surface-anchored complexes (Scheme II).

Two alternative routes have been followed: route 1, anchoring of the soluble Rh compound ({Rh}) to the functionalized silica; route 2, formation of the rhodium complex containing N-donor ligand attached to a triethoxisilyl function, followed by cohydrolysis with TEOS.

**Route 1.** For the preparation of rhodium-supported complexes, three different procedures have been followed. In Table I we have chosen some representative examples: (i) direct reaction of the halide (compounds 1–3), (ii) displacement of a ligand of the soluble complex for the N-donor ligand attached to the silica (compound 4, elimination of phosphine); (iii) bridge cleavage of a dimer such as $[RhCl(CO)_2]_2$ and $[RhCl(COD)]_2$ (compounds 5 and 6), according to the equation



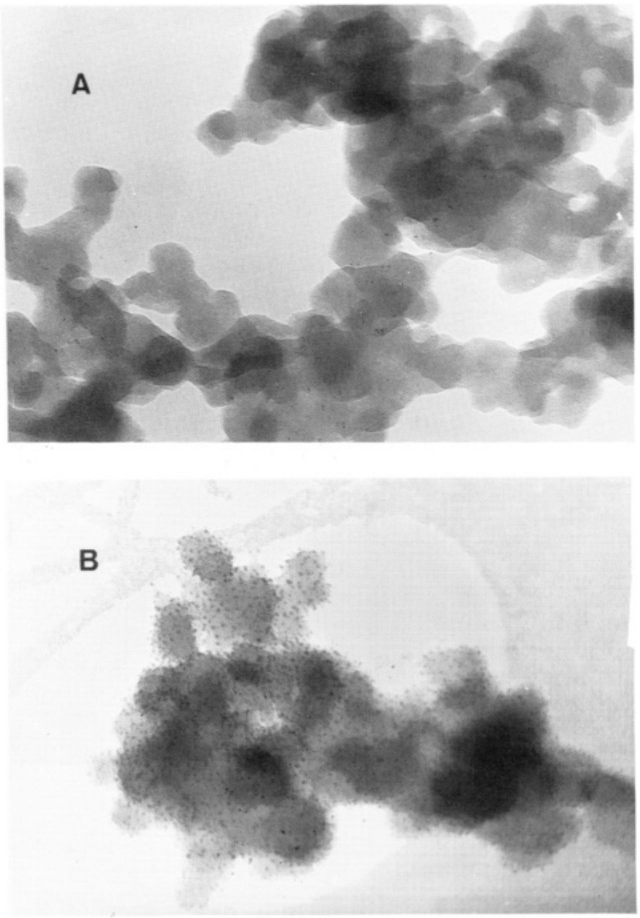


**Figure 1.** TEM photomicrographs: (A) silica functionalized with $NH_2$ groups (I, ×300 000); (B) I after anchoring $[RhCl(CO)_2]_2$ (×370 000).

where L represents a monodentate grafted N function on the silica (–$NH_2$), and LL the chelating functions DAB and PyCa; Y and YY represent CO and COD, respectively.

The loading of rhodium was carried out in methanol or toluene at 25 °C, with stirring for 3 days.[9] In the resulting compounds, the metal is well dispersed on the functionalized support as is revealed by the homogeneous dotting shown in the photomicrograph B (Figure 1) of sample 6 (I + $[RhCl(CO)_2]_2$, rhodium, as $Rh^+$, content 6.18; Table I), which has been selected as an illustrative example. Spots and average TEM-EDX analyses realized on randomly selected particles show good homogeneity of rhodium distribution.

To be sure that rhodium coordinates to the N-donor functions and that attachment to the silanol groups of the silica does not take place, we have tested the reaction of

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[9] Allum, K. G.; Hancock, R. D.; Howell, I. V.; McKenzie, S.; Pitkethly, R. C.; Robinson, P. J. *J. Organomet. Chem.* **1975**, *87*, 203.

**Table II. Influence of the Solvent on the Reaction Products**

| compound | color | elem anal. | | | | | |
|---|---|---|---|---|---|---|---|
| | | % C | % H | % N | % Rh | C/N$^a$ | N/Rh |
| 1, I + $RhCl_3 \cdot H_2O$ (alcohol) | orange | 10.60 | 2.76 | 3.18 | 3.45 | 3.8 (3) | 6.8 |
| 1′, I + $RhCl_3 \cdot 3H_2O$ (water) | mauve-gray | 7.80 | 2.33 | 2.91 | 4.82 | 3.1 (3) | 4.4 |

[a] Experimental (calculated).

silica gel with rhodium compounds under the same reaction conditions (3 days, room temperature). The sample was washed with methanol, and a white silica and orange solution was obtained. No rhodium was detected in the silica (by atomic absorption or fluorescence analyses).

Experiments at different N/Rh ratios in the interval 1–2 have shown that the effective loading is lower than the theoretical value proposed in Scheme II (a ratio of 2N/Rh); to increase the amount of rhodium fixed on the sample, a higher initial concentration of rhodium, higher temperature, and longer periods of reaction would have been necessary, but we have intentionally followed very mild reaction conditions to be sure that the coordination around the metal is the same as in solution.[2a,9] In this first part of our work, we have not tried to get a maximum metal loading[6c] because we are proposing to try these materials as catalysts, with a surface loading of metal of 1–2 Rh/100 Å$^2$, well dispersed and firmly attached to the support.

Although we have chosen 3 days as the standard reaction time at room temperature, we have studied the effect that the increasing time of reaction up to 40 days has on the oxidation state of the metal if the solvent is an alcohol, (either ethanol or methanol, able to act as reducing agent on $Rh^{3+}$ (Figure 2); the reduction $Rh^{3+} \rightarrow Rh^{+} \rightarrow Rh^{0}$ is accompanied by a progressive change in color from orange to dark gray. The increasing amount of reduced rhodium has been confirmed by XPS spectroscopy (Figure 2). The XPS data reported in the literature for the different oxidation states of Rh for the level $3d_{3/2}$ and $3d_{5/2}$ are $Rh^0$ = 312.1 and 307.2 eV, $Rh^+$ = 312.5 and 307.8 eV, $Rh^{3+}$ = 315 and 310.3 eV.[10] According to our results, the $Rh^{3+}$ of the $RhCl_3 \cdot 3H_2O$ is reduced by the alcohol to $Rh^+$, which is the predominant species in the reaction product, but prolonged contact with the alcohol produces some $Rh^0$ in the batch. This fact is consistent with the color of the sample and the appearance of a shoulder in the XPS spectra on the side of lower binding energy (samples b and c).

When the experimental C/N ratio is higher than the theoretical one, it is attributed to the presence of methoxy or ethoxy groups, either not hydrolyzed or incorporated from the alcoholic medium (see compound I, Table I). The percentage of C in a compound allows us to determine the number of C atoms attached to the functional group, and the experimental C/N ratio compared with the theoretical one tells us whether or not the reaction of amine groups with the diketone (diacetyl or benzil) or the aldehyde (pyridine-2-carboxaldehyde) has been completed (compounds 2 and 3, Table I).

In these systems, it is necessary to define rigorously the reaction conditions as the variation of any one of them may change considerably the nature of the reaction product. See, for example, Table II, where we have compared the results obtained using an aqueous solution with those obtained in an alcoholic one. In an aqueous medium, the amount of rhodium fixed is higher than in alcohol. When the reaction takes place in water, a loss of ligands occurs, possibly due to the removal of soluble oligomeric siloxanes,[6] that are formed by self-condensation reactions. As a consequence of this an easier fixation of rhodium and a lower N/Rh ratio occur.

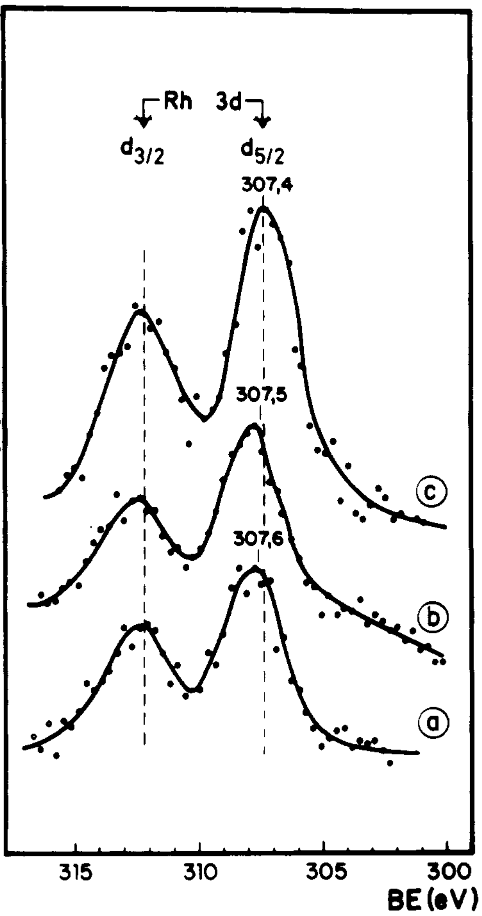

**Figure 2.** Binding energy for $Rh_{3d}$ levels after increasing periods of reaction. I + $RhCl_3 \cdot 3H_2O$: (a) 3 days, (b) 6 days, (c) 10 days.

**Route 2.** This alternative route consists in first obtaining the various N-donor ligands bonded to (aminopropyl)triethoxysilane which have been made to react with the {Rh} to form a complex subsequently anchored to the silicic support proceeding from hydrolyzed $Si(OEt)_4$.

The formation of R-DAB or R-PyCa ligands has been monitored by IR and NMR spectroscopies. By IR spectroscopy (Figure 3) we can easily follow the reaction of the amine groups from APS ($\nu$(N–H) 3372 and 2292 cm$^{-1}$) with the ketone or aldehyde functions of diacetyl, benzil, or pyridine-2-carboxaldehyde, respectively, to give the imine signals at 1636 (diacetyl), 1627 (benzil), and 1653 cm$^{-1}$ (pyridine-2-carboxaldehyde). Simultaneously, the very intense C=O stretching bands of the carbonyl compounds, in the 1680–1665-cm$^{-1}$ region, diminish their intensity and practically disappear. The remaining $\nu$(C=O) band in the case of benzil can be assigned to $\equiv Si(CH_2)_3N{=}C(R)(R){-}C{=}O$ grafted groups. Other bands ($\nu_{C-H}$, $\nu_{C-C}$, etc.) of alkyl, phenyl, or pyridine are unchanged after the reaction. Negligible changes in the characteristic $\nu$(N=C) absorption

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(10) (a) Okamoto, Y.; Ishida, N.; Imanaka, T.; Teranishi, S. *J. Catal.* **1979**, *58*, 82. (b) Furlani, C.; Mattogno, G.; Polzonetti, G.; Braca, G.; Valentini, G. *Inorg. Chim. Acta* **1983**, *69*, 199. (c) Zanoni, R.; Boschi, T.; Licoccia, S.; Paolesse, R.; Tagliatesta, P. *Inorg. Chim. Acta* **1988**, *145*, 175.

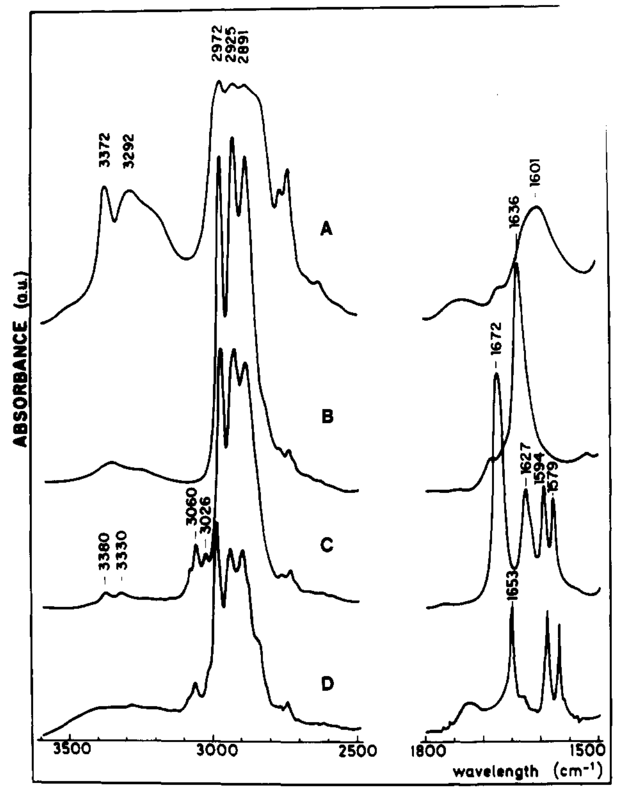

**Figure 3.** Infrared spectra of the silane APS $(EtO)_3Si(CH_2)_3NH_2$ (A) and its reaction products with diacetyl (B), benzil (C), and 2-pyridinecarboxaldehyde (D).

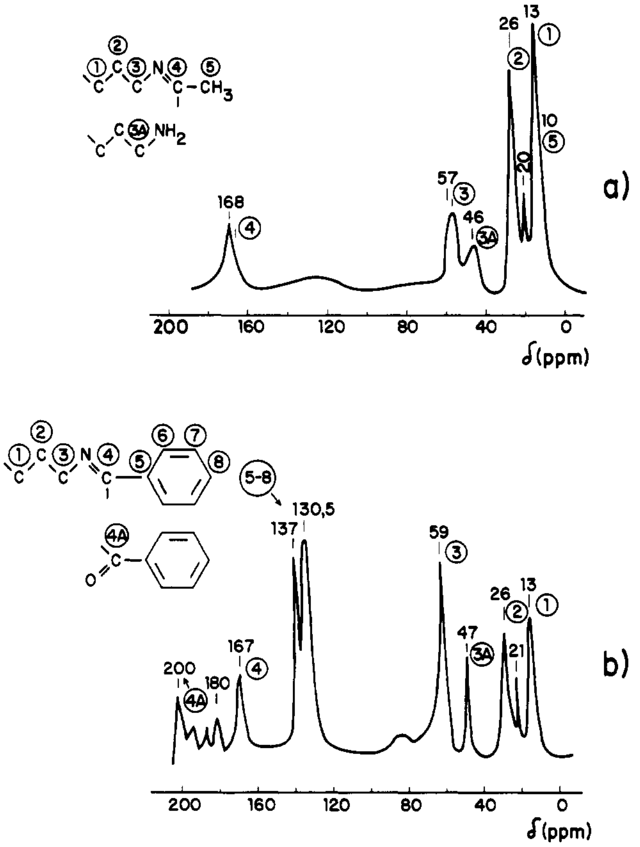

**Figure 4.** CP-MAS $^{13}C$ NMR spectra: (a) APS + D, i.e., $(EtO)_3Si(CH_2)_3NH_2$ + $CH_3COCOCH_3$; (b) APS + B, i.e., $(EtO)_3Si(CH_2)_3NH_2$ + $C_6H_5COCOC_6H_5$.

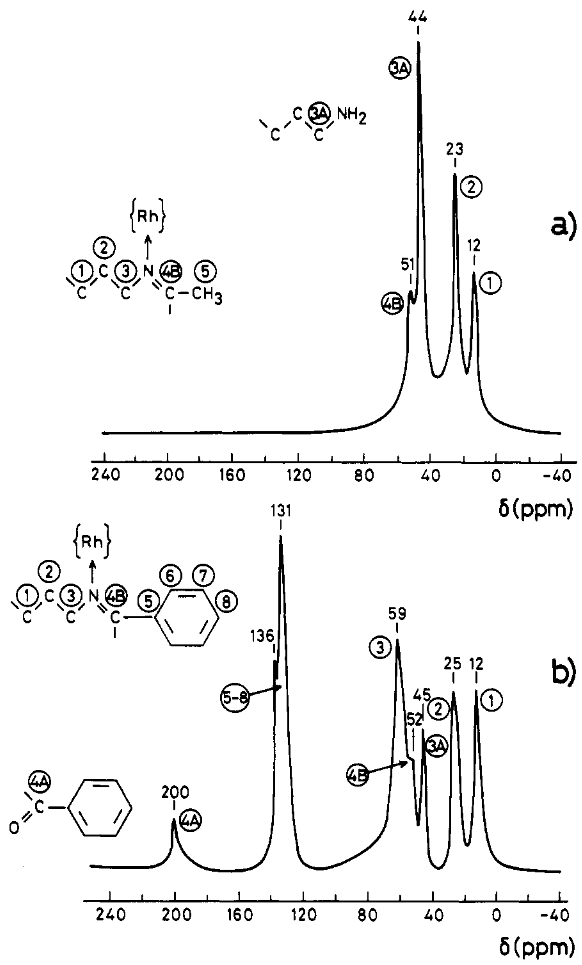

**Figure 5.** CP-MAS $^{13}C$ NMR spectra: (a) APS + D + $RhCl_3$, i.e., $(EtO)_3Si(CH_2)_3NH_2$ + $CH_3COCOCH_3$ + $RhCl_3$; (b) APS + B + $RhCl_3$, i.e., $(EtO)_3Si(CH_2)_3NH_2$ + $C_6H_5COCOC_6H_5$ + $RhCl_3$.

bands of R-DAB or R-PyCa ligands are observed when the corresponding silica derivatives are treated with the {Rh} rhodium compounds. Besides, it is known that the ν(N=C) stretching bands are not very sensitive to any modification in either frequency or intensity when electronic environment changes affecting these imino bonds take place.[11]

In Figures 4 and 5, it can be seen that high-resolution $^{13}C$ solid-state CP-MAS NMR spectroscopy provides useful information on the reaction of APS with diketones, as well as on the formation of the complexes with rhodium species. One can observe the presence of the methylene groups of the propyl chain ($C_1$–$C_3$) which appear at 12–13, 23–26 and 57–59 ppm, respectively.[12] The signals at 167 and 168 ppm can be assigned to the imine carbons ($C_4$). The phenyl groups in the benzil derivative show signals in the 130–140 ppm range, whereas the remaining CO groups in these compounds are identified by the signal at 200 ppm ($C_{4A}$). The unreacted $NH_2$ groups ($C_{3A}$) give peaks at 46–47 ppm, indicating the presence of some free primary diketones. Low-intensity signals at 20–21 ppm can be attributed to nonhydrolyzed ethoxy groups remaining in the support.

The coordination between N-donor groups and $Rh^{3+}$ can be inferred from the shifts detected in the $^{13}C$ NMR signals corresponding to C(4) nuclei, both before and after formation of the supported complexes. Figure 5 shows, as an example, the corresponding spectra of compounds (APS

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(11) Brisdom, B. J.; Watts, A. M. *J. Chem. Soc., Dalton Trans.* **1985**, 2191.

(12) (a) Chiang, C.-H.; Liu, N.-I.; Koenig, J. L. *J. Colloid Interface Sci.* **1982**, *86*, 26. (b) Sudhölter, E.; Huis, R.; Hays, G. R.; Alma, N. *J. Colloid Interface Sci.* **1985**, *103*, 554.

**Table III. Analytical Data of Some of the Compounds Formed before and after Being Supported According to Route 2**

| compound | elem anal. % C | % H | % N | % Rh | C/N[a] | N/Rh |
|---|---|---|---|---|---|---|
| 7, APS[b] + B[c] | 50.46 | 6.02 | 6.08 | | 9.7 (10) | |
| 8, 7 + TEOS[d] | 37.35 | 5.19 | 4.15 | | 10.5 (10) | |
| 9, 8 + $RhCl_3 \cdot 3H_2O$ | 32.94 | 4.19 | 3.82 | 3.65 | 10.1 (10) | 7.7 |
| 10, APS + B + $RhCl_3 \cdot 3H_2O$ | 44.45 | 4.87 | 5.01 | 10.03 | 10.3 (10) | 3.7 |
| 11, APS + D[e] + TEOS | 35.50 | 6.50 | 8.40 | | 4.9 (5) | |
| 12, 11 + $RhCl_3 \cdot 3H_2O$ | 34.60 | 5.80 | 7.90 | 0.26 | 5.1 (5) | 199 |

[a] Experimental (calculated). [b] APS = (3-aminopropyl)triethoxysilane. [c] B = benzil ($C_6H_5COCO_6H_5$). [d] TEOS = tetraethylorthosilicate ($(OEt)_4Si$). [e] D = diacetyl ($CH_3COCOCH_3$).

**Table IV. Example of the Different Composition Obtained According to the Route Followed**

| compound | elem anal. % C | % H | % N | % Rh | C/N | N/Rh |
|---|---|---|---|---|---|---|
| 3, I + B + $RhCl_3 \cdot 3H_2O$ | 15.05 | 3.97 | 3.20 | 2.74 | 5.5 (10) | 8.6 |
| 9, APS + B + TEOS + $RhCl_3 \cdot 3H_2O$ | 32.94 | 4.19 | 3.82 | 3.65 | 10.1 (10) | 7.7 |

**Table V. Values of the Binding Energies (eV) of Some of the Complexes Investigated**

| compound | $C_{1s}$ | $O_{1s}$ | $Si_{2p}$ | $N_{1s}$ | $Cl_{2p}$ | $Rh_{3d}$ $d_{3/2}$ | $d_{5/2}$ |
|---|---|---|---|---|---|---|---|
| APS + D[a] | 284.6 | 531.7 | 101.9 | 398.4 | | | |
| APS + B[b] (7)[c] | 284.6 | 531.9 | 102.9 | 398.6 | | | |
| APS + $RhCl_3$ | 284.6 | 530.0 | 102.1 | 399.6 | 197.6 | 313.5 | 308.6 |
| APS + D + $RhCl_3$ | 284.6 | 531.5 | 101.9 | 399.6 | 197.7 | 313.9 | 309.0 |
| APS + B + $RhCl_3$ (10)[c] | 284.6 | 532.5 | 102.4 | 399.5 | 198.4 | 313.7 | 308.8 |
| APS + D + TEOS + $RhCl_3$ (12)[c] | 284.6 | 532.6 | 102.5 | 400.1 | 199.4 | 315.3 | 309.9 |
| APS + B + TEOS + $RhCl_3$ (9)[c] | 284.6 | 529.9 | 102.7 | 399.7 | 198.9 | 314.8<br>314.2 | 309.9<br>308.9 (sh) |

[a] Diacetyl. [b] Benzil. [c] The numbers in parentheses correspond to compounds of Table III.

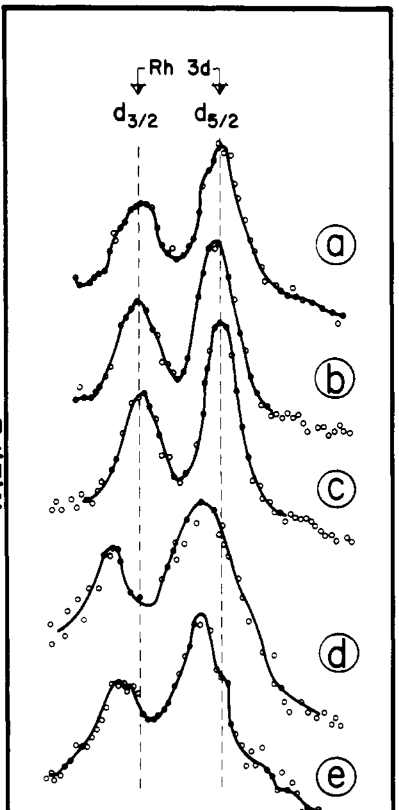

Figure 6. Binding energy for $Rh_{3d}$ of compounds (a) APS + $RhCl_3$, (b) APS + D + $RhCl_3$, (c) APS + B + $RhCl_3$, (d) APS + D + TEOS + $RhCl_3$, (e) APS + B + TEOS + $RhCl_3$.

+ diacetyl + $RhCl_3$, Figure 5a) and (APS + benzil + $RhCl_3$, Figure 5b). The signals corresponding to C atoms involved in C=N bonds ($C_4$) at 168 and 167 ppm showed in Figure 4 disappear after treatment with $RhCl_3$, which can be explained by a decrease of the double-bonding character of the imino groups to almost a single C–N bond, and this will produce new signals in the higher field; in this way, the new signals appearing at 51 and 52 ppm can be tentatively assigned to C nuclei of $—C\overset{-}{\cdot\cdot}N\cdots Rh^{3+}$ species ($C_{4B}$ in Figure 5).

Some analytical results of the partial reactions are presented in Table III. Depending on the route followed (1 or 2, Scheme II) equivalent compounds have different percentage compositions (see, for example, compounds 3 (route 1) and 9 (route 2), Table IV). As expected, the C/N ratio is almost equal to the theoretical one when the ligand is obtained previously. When the ligand is obtained before being anchored to the support, there is no possibility of $-NH_2$ functions from free APS.

Samples obtained by route 2 have been analyzed by XPS. The values of the binding energy[13] of the complexes investigated are reported in Table V: emissions of $C_{1s}$, $O_{1s}$, $Si_{2p}$, $N_{1s}$, $Cl_{2p}$, and $Rh_{3d}$ were registered (0–1500 eV). When the metal coordinates to the N-donor ligand, the $N_{1s}$ emission at around 398.5 shifts about 1 eV to higher binding energy (399.5–400.1 eV). We have not been able to distinguish by XPS when the linkage of rhodium is to a N-amine or to a N-imine function, as the shifts apparently are of same order of magnitude. The $Rh_{3d}$ spectra are shown in Figure 6, and the values of the binding energies for $3d_{3/2}$ and $3d_{5/2}$ are summarized in Table V. The emission at around 310 eV has been assigned to $Rh^{3+}$ species (samples d and e); emission in the range of

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[13] Briggs, D., Seach, M. P., Eds. *Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*; Wiley: New York, 1983.

**Table VI. Quantification of Surface Atomic Ratios**

| compound | Si/N | N/Rh | Cl/Rh | Si/Rh |
|---|---|---|---|---|
| APS + $RhCl_3$ | 1.24 | 4.34 | 1.60 | 5.40 |
| APS + D + $RhCl_3$ | 1.31 | 2.92 | 2.81 | 3.82 |
| APS + B + $RhCl_3$ (10)[a] | 1.34 | 3.92 | 3.31 | 5.26 |
| APS + D + TEOS + $RhCl_3$ (12)[a] | 4.88 | 3.12 | 3.02 | 15.21 |
| APS + B + TEOS + $RhCl_3$ (9)[a] | 12.66 | 0.85 | 3.09 | 10.71 |

[a] The numbers in parentheses correspond to compounds of Table III.

308.6–309.0 (about 1 eV lower) can be assigned to $Rh^+$ compounds (samples a–c); some of the samples (a, d, and e) show the presence of both oxidation states ($Rh^{3+}$ and $Rh^+$), in agreement with the values given in the literature.[10]

The quantification of the surface atomic ratios (Table VI) agrees in some aspects with those calculated from the elemental analysis. Thus the N/Rh ratio in the samples of nonsupported complexes are quite similar (2.9 from XPS and 2.6 from elemental analysis in sample (APS + D + $RhCl_3$); 3.9 from XPS and 3.7 from elemental analysis in samples (APS + B + $RhCl_3$). Nevertheless, when the N functions are supported on hydrolyzed TEOS, the addition of $RhCl_3$ leaves the metal located mainly on the surface, and consequently the N/Rh ratio is lower (3.12 against 199, in sample 12, or 0.85 against 7.7, in sample 9). The Cl/Rh ratio varies in the range 1–3 in relation to the oxidation state of the metal.

**Acknowledgment.** This work was partially supported by the Comisión Interministerial de Ciencia y Tecnología, Spain (CICYT, project MAT88-0179C02-02) and by the Fundación Ramón Areces. We express our appreciation to Dr. J. L. Fierro for his help in the XPS studies. Grateful acknowledgement is also due to Dr. J. Sanz for the $^{13}C$ NMR spectra and to Dr. B. Casal for a critical reading of the manuscript.

**Registry No.** $(EtO)_4Si$, 78-10-4; $(EtO)_3Si(CH_2)_3NH_2$, 919-30-2; $PrNH_2$, 107-10-8; PhCOCOPh, 134-81-6; $CH_3COCOCH_3$, 431-03-8; $NC_5H_4CHO$, 1121-60-4; $PrN{=}C(CH_3)C(CH_3){=}NPr$, 78788-23-5; $PrN{=}C(Ph)C(Ph){=}NPr$, 136838-86-3; $PrN{=}CH$-2-py, 4206-52-4; $SiO_2$, 7631-86-9; $[RhCl(CO)_2]_2$, 14523-22-9; $[RhCl(COD)]_2$, 12092-47-6; $RhClCO(PEt_3)_2$, 14871-47-7.

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# Molecular Dynamics Simulation of the Temperature-Dependent Ionic Conductivity in Sodium(I)-β''-Alumina

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*Received February 22, 1991. Revised Manuscript Received September 20, 1991*

Molecular dynamics (MD) simulation has been applied to a study of structure, ion motion, and superlattice formation in the fast ion conductor, sodium(I)-β''-alumina. The results reproduce, in a general way, the curved variation of ionic conductivity with temperature observed in an Arrhenius-type plot of single-crystal conductivity data for the compound. The curvature in the conductivity plot may be explained as resulting from an evolution in the conduction mechanism from a vacancy mechanism at high temperatures to highly correlated superlattice motion at lower temperatures. A correlation is seen between the location of Mg(II) ions in the spinel blocks and the ion/vacancy arrangement in the conduction layers.

## Introduction

Developing the ability to design materials with specified properties is an intriguing goal, one which may become more attainable with the growing accessibility of fast computers. To achieve this goal, however, computer models must be developed which accurately reproduce experimentally observed properties of known materials before they can be trusted as design tools. β''-Alumina is a particularly good material for testing such models. Well-known for its ability to undergo ion exchange with a variety of mono-, di-, and trivalent cations, β''-alumina exhibits varied optical, structural, and transport properties depending on its mobile cation composition. It represents a good beginning challenge for simulation, since its composition and properties can be varied extensively without altering its structural framework. A reasonable computer model for β''-alumina should be able to reproduce the properties of its isomorphs.

This paper presents a study of the temperature-dependent ionic conductivity of pure sodium(I)-β''-alumina using molecular dynamics (MD) simulation. Prior studies of Na(I)-β''-alumina have shown that MD is effective as a structural probe, but its transport properties have not been accurately simulated for reasons both particular to the MD technique and to the structure of β''-alumina. For example, Wolf et al.[1] encountered the limitations of the MD technique in their study of Na(I)-β''-alumina. The MD technique enforces periodic boundaries on the system being simulated to avoid edge effects and more accurately represent long-range interatomic forces. Therefore, if the system under study has a tendency to order, as do the mobile ions in Na(I)-β''-alumina, the periodicity imposed by the MD technique must match the periodicity of the ordering under consideration. Otherwise, the MD-enforced periodicity will predominate over the system periodicity, and the atoms will never achieve an equilibrium configuration. As Wolf et al. noted in their work, their choice of MD "box" size, that is, the total number of unit cells explicitly included in the simulation, obstructed the mobile

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(1) Wolf, M. L.; Walker, J. R.; Catlow, C. R. A. *Solid State Ionics* 1984, *13*, 33.