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Sol-gel synthesis of Ru(II) complex of 3-4,5-dihydroimidazol-1-yl-propyltriethoxysilane aerogels and xerogels

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ABSTRACT

The preparation and the measurement of some properties of Ruthenium (II) coordinated 3-4,5-dihyroimidazol-1-yl-propyltriethoxysilane have been achieved. The organosilicon precursor chosen for this study was N-aminoethyl-3-aminopropyltriethoxysilane converted to 3-4,5-dihydroimidazol-1-yl-propyltriethoxysilane that was then coordinated with ruthenium (II). FT-IR spectroscopy, DTA and TGA analysis were used to characterize the bond formation during gelation, aging and drying of gels. The prepared aerogels are low-density 0.19-0.30 g/cm^3 amorphous materials with surface areas of 405 to 530 m^2/g. The resulting aerogel catalysts exhibited unique structural and chemical properties.

1. INTRODUCTION

The gel route to glasses and ceramics has attracted increasing scientific and technological interest because of their diverse utilities. Since the sol-gel chemistry is based on inorganic polymerization reactions, a macromolecular oxide network is obtained *via* hydroxylation-condensation reactions. Owing to the fact that the chemical synthesis of sols is performed in organic solutions at low temperatures, major efforts have been directed toward to the development of new sol-gel materials that effectively combine the advantages of both organic and inorganic systems. For this reason, the sol-gel route is increasingly extended to prepare organically modified materials by using organically substituted alkoxides of the type $(RO)_3Si(CH_2)nA$. Materials with interesting physical and chemical properties were obtained if the organic groups capable of coordinating metal ions. Groups A suitable for coordinating metal ions are for example, NH_2, $NHCH_2CH_2NH_2$, CN, or CH $(COMe)_2$ (1-5). The low synthesis temperatures often result in the formation of oxides with amorphous or metastable phases that are impossible to prepare by other synthetic routes. The sol-gel method is also suitable for preparing catalytic materials. The preset paper describes a new synthetic approach for sol-gel derived materials whereby Ruthenium (II) bonds are present. Recently, preparative and catalytic studies on cyclic diaminocarbene and N-3 bound 2-imidazoline complexes that were effective catalysis for the intramolecular cyclization of (Z)-3-methylpent-2-en-4-yn-1-ol into 2,3-dimethylfuran containing η-arene moiety have been

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carried out because of their catalytic potential (6). Tris (2,2'-diimine) ruthenium (II) complexes as water-insoluble freestanding films of partially quaternized poly (1-vinylimidazole) ruthenium (II) complexes were applied as photoinduced hydrogen generation in aqueous solution (7-9). The synthesis and characterization of a series of metallopolymers of poly (4-vinylpyridine) and poly (N-vinylimidazole) containing $(OC)_3RuCl_2$- and (2,2'-bipyridine)$_2$Ru moieties have recently been described (10) .We previously reported preliminary results on preparation of (η-arene) ruthenium (II) complexes containing pyridine ligands with pendant vinyl groups to anchor these complexes on a matrix by sol-gel processing *via* hydrolysis of a γ-methacryloxy propyltriethoxy silane and a metallic alkoxide of the type Si $(OR)_4$, $Ti(OR)_4$, Zr $(OR)_4$ and $Al(OR)_3$ (11).

Here, we have explored the possibility to employing 3-4,5-dihydroimidazol-1-yl-propyltriethoxysilane group as a coordinating chelate with (η-arene) ruthenium (II) complexes. In this work stable sols were produced by complexing the precursor alkoxide with (η-arene) ruthenium (II). In our approach, 3-4,5-dihydroimidazol-1-yl-propyltriethoxysilane was synthesized and coordinated with ruthenium(II) complex. Trialkoxysilyl functional group that were hydrolyzed and co-condensed with silicon tetraalkoxides to afford a molecular composite SiO_2 glass containing active metal group in pores. The resulting aerogel catalyst exhibited a unique chemical properties evidenced by catalytic activity in the step-growth hydrosilation copolymerization.

2. EXPERIMENTAL

Unless otherwise stated, all reactions were performed under an oxygen-free nitrogen atmosphere using predried solvents and standard Schlenk techniques. The complexes $[RuCl_2(p\text{-}MeC_6H_4CHMe_2)]_2$ were prepared according to literature methods (11).
Infrared spectra were recorded as KBr pellets in the range 4000 - 400 cm^{-1} on an ATI UNICAM systems 2000 Fourier transform spectrometer. ^1H NMR spectra (300 MHz) ^{13}C NMR spectra (80 MHz) on a Bruker AM 300 WB FT spectrometer with δ referenced to residual solvent $CDCl_3$. Microanalyses were performed by the TÜBİTAK (Ankara). The identification of Si $(OH)_3$ was made using a multichannel Raman Spectrometer (DILOR xy) equipped with a CCD detector. The band position was accurate to ±1 cm^{-1}. All spectra were taken at 20-40 mW on the sample. Thermal analysis was performed on Shimadzu system 60 in air. Surface area, pore size, pore volume, and adsorption-desorption isotherm measurements were done on a Micrometrics ASAP 2010 Chemi system. Prior to nitrogen physisorption experiments the samples were degassed at 473 K for 2h. 3-4,5-dihydroimidazol-1-yl-propyltriethoxysilane (IMEO) was prepared starting from N-aminoethyl-3-aminopropyl-triethoxysilane by acetal methods. IMEO was fractionally distilled before use.

Preparation of Precursors, (2).

A solution of 3-4,5-dihyroimidazol-1-yl-proyltriethoxysilane (1.10g, 4mmol) in toluene (40mL) and $[RuCl_2(p\text{-}Me_2CHC_6H_4Me)]_2$ (1.25g, 2 mmol) were heated for 2h under reflux. Hexane (20mL) was added to the solution while it is warm. The product **2** was filtered off, and washed with n-hexane (2x20 mL) and dried in vacuum. Recrystallization from CH_2Cl_2/Et_2O at -25°C, gave orange crystals of **2** (yield 89% m.p. 104-105°C).

Anal. calc. for $C_{22}H_{40}N_2RuSiO_3Cl_2$: C: 45.52; H: 6.89; N: 4.83. Found: C : 45.56; H : 6.80; N : 4.75 %. ^{1}H NMR (300 MHz, $CDCl_3$, 297 K, δ) 7.28 (s, 1H, C**2**-*H*), 3.49
(t, 2H, C**4**-H_2, *J* = 10. 3 Hz), 4.12 (t, 2H, C**5**-H_2, *J* = 10. 3 Hz],
3.13 [t, 2H, $CH_2CH_2CH_2Si(OCH_2CH_3)$, *J* = 7.3 Hz],
1.61 [pent., 2H, $CH_2CH_2CH_2Si(OCH_2CH_3)$, *J* = 7.4 Hz],
1.62 0.56 [t, 2H, $CH_2CH_2CH_2Si(OCH_2CH_3)$, *J* = 7.8 Hz],
3.81 [q, 2H, $CH_2CH_2CH_2Si(OCH_2CH_3)$, *J* = 7.0 Hz],
1.23 [t, 3H, $CH_2CH_2CH_2Si(OCH_2CH_3)$, *J* = 7.0 Hz],
5.23 and 5.39 [d, 4H, $Me_2CHC_6H_4Me$-*p*), *J*= 6.0 Hz],
3.02 [sept, 1H, $Me_2CHC_6H_4Me$-*p*), *J* = 6.9 Hz],
1.31 [d, 6H, $(CH_3)_2CHC_6H_4Me$-*p*), *J* = 7.0 Hz],
2.24 [s, 3H, $Me_2CHC_6H_4(CH_3)$-*p*), *J*= 6.0 Hz].
^{13}C{H} NMR (75. MHz, $CDCl_3$, 297 K, δ) : 161.73 (s, *C***2**-H),
57.9 (s, *C***4**-H_2), 48.97 (s, *C***5**-H_2), 50.67 [s, $CH_2CH_2CH_2Si(OCH_2CH_3)$],
22.41 [s, $CH_2CH_2CH_2Si(OCH_2CH_3)$], 8.05 [s, $CH_2CH_2CH_2Si(OCH_2CH_3)$],
59.09 [s, $CH_2CH_2CH_2Si(OCH_2CH_3)$], 18.96 [s, $CH_2CH_2CH_2Si(OCH_2CH_3)$],
81.74, 82.35, 97.18 and 102.59 [s, $Me_2CHC_6H_4Me$-*p*)],
31.34 [s, $Me_2CHC_6H_4Me$-*p*)], 22.88 [s, $(CH_3)_2CHC_6H_4Me$-*p*)],
19.30 [s, $Me_2CHC_6H_4(CH_3)$-*p*), *J*= 6.0 Hz].

Gel formation

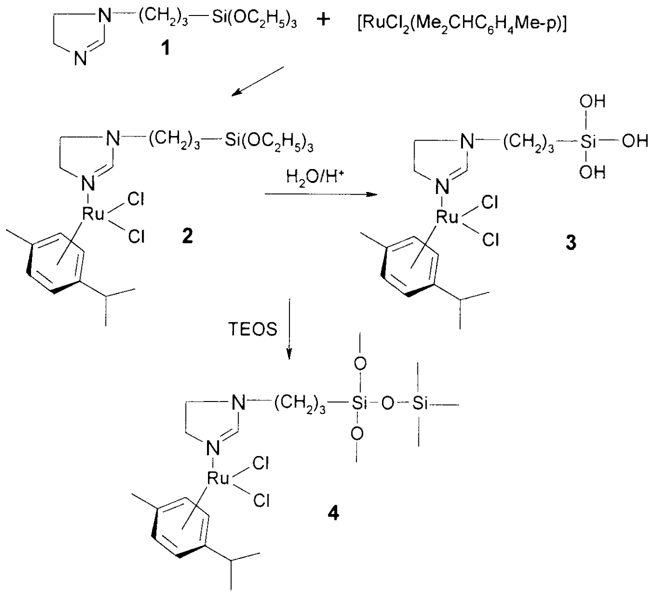
Aerogels were prepared using the compound **2**, hydrochloric acid and water. The compound **2** was dissolved in isopropyl alcohol. The isopropyl alcohol was removed through vacuum evaporation and replaced with acetonitrile. HCl and water were then added with vigorous stirring to form the final sol. The molar ratios of acetonitrile:Ru (0:1 to 40:1) and of water: Ru (0:1 to 50:1) and pH of the solution were varied in order to determine the composition range for sol formation. After co-condensation with tetraethylorthosilicate (TEOS), the gel was formed that was aged in closed containers for 3-5 weeks. In a typical preparation,
10 mmol of **2** in 440 mmol of isopropanol was mixed and stirred for 2h. After removal of isopropanol 440 mmol of acetonitrile was added with the required amount of water (1.35 mol H_2O / mol **2**) in isopropanol and HCl. pH of the solution was adjusted to 1.00, 1.35, 1.45, and 3.6 to maintain optimal condition for hydrolysis. The required amount of water, determined with Karl Fisher Coulometric Titrator, was found to be 1.15-1.47 mol per silane. The content of **2** in the matrix varied from 10 to 100 mol%. The co-condensation with tetraethylorthosilicate (TEOS) was performed in the presence of a catalyst. The results were given in Table 1.

To prepare xerogels, the sample containers were opened to air after the aging period. After 1 week of ambient drying conditions, the gels were placed in a vacuum oven at 110°C to complete the solvent removal.

3. RESULTS AND DISCUSSION

Since the divalent ruthenium cation is classified as a borderline acid that shows affinity for borderline bases such as pyridine, [(η-arene)$RuCl_2$]$_2$ is much readily reacted to give **2** with imidazol moiety of IMEO as shown in scheme 1. Preliminary studies showed that the reactions catalyzed by **2** activated by a stoichometric amount of styrene in toluene were suitable for the step-growth hydrosilation copolymerization of 4-dimethylsiloxyacetophenone, 4-dimethylsiloxybenzophenone, and 4-dimethylsiloxybenzaldehyde to yield symmetric poly(sillyl ether). The Ru content was determined by ICP analysis after digesting with HF by microwave heating. The degree of Ru incorporation in a sol-gel matrix was fixed at 0.046 g of Ru/g of SiO_2 that was required amount to maintain maximum catalytic activity.

Scheme 1. The synthetic route



The result of the structure analysis suggests that imidazol of the type $(RO)_3Si(CH_2)_nA$ with a functional group in a more distant position would be suitable to form **2**; the compound **2** was identified on the basis of elemental analysis and spectroscopic measurements. Tentative band assignment found in Raman Spectrum for **3** was as follows: The band at 430-440 cm^{-1} (s) is the Si-O-Si in plane vibration (12). The band at 490-500 cm^{-1} was attributed to the structures sketched previously (13). Si-O-Si symmetric stretching, and Si-O-Si asymmetric stretching band appeared at 800 and 1100 cm^{-1} respectively. Internal and surface silanols stretching at 910-920 and 970-985 cm^{-1} were also noted. (14-15).

Compositions and physical properties of aerogels and xerogels were given in Table 1.

The changes of structures of gels with pH were observed with DTA and FT-IR curves as shown in Figure 1 and 2. The bands at 1090 cm^{-1} assigned as Si-O-Si bond.

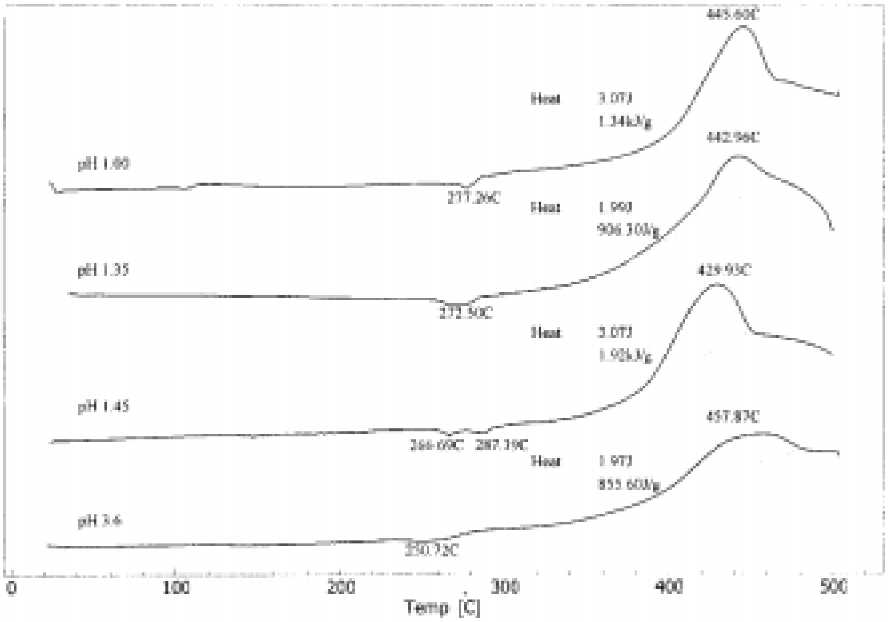


Figure 1. DTA showing thermal changes due to pH.

Table 1. Physical properties of Ru(II) Complex of 3-4,5-Dihydroimidazol-1-yl-propyltriethoxysilane Aerogels and Xerogels

Code	[HCl]/[TEOS][a]	**2** mol%	SiO_2 (wt%)[b]	Surface Area m^2/g[c]		Density (g/cm^3)[d]	
				Aerogel	Xerogel	Aerogel	Xerogel
T1	0,02	10	7 (7)	405	235	0,26	0,24
T2	0,02	10	81 (78)	509	290	0,21	0,19
T3	0.01	50	22 (20)	505	255	0,23	0,18
T4	0.01	50	78 (76)	432	202	0,29	0,24
T5	0.001	100	35 (34)	474	206	0,19	0,17
T6	0.001	100	76 (75)	531	310	0,26	0,18
T7	0.001	-	96 (96)	510	330	0,24	0,23

[a] 2.0 M HCl was added; [b] Determined by TGA at 700°C, parenthesis denotes xerogel ;
[c] ±0.05 g/cm^3; [d] ±0.10

The bond at 1090 cm^{-1} due to stretching vibration of the Si-O bond was almost constant, while the intensity of the band at 800 cm^{-1} is changed. The band at 1600 attributed to the C=N stretching. When the sol is aged three-dimensional network and monolithic gel were obtained. An exotherm at 445.6°C is shifted higher temperatures as the pH was increased that was confirmed by the Si-O-Si bond formation at 960 cm^{-1} in Figure 2. At higher pH, Si-O-Si bond formation leading to the network is favored. DTA shows that an exothermic reaction occurs at 445°C that corresponds well to the DTA data found in literature (16-17). A phase transformation from amorphous to orthorhombic starts at approximately 440°C and is completed by 475°C. aerogels and xerogels possessed a density between 0.19 to 0.6 It was found that the density is lower in xerogels as expected from the pore formation. The prepared aerogels are amorphous and remain amorphous up to 450°C evidenced by XRD and DTA analysis. It was observed that these materials are amorphous in state in electron diffraction studies. FT-IR spectra showing structural change due to pH (Figure 2.)Adsorption analysis of the amorphous aerogel gives a BET surface area of 400 to 530 m^2/g and a density

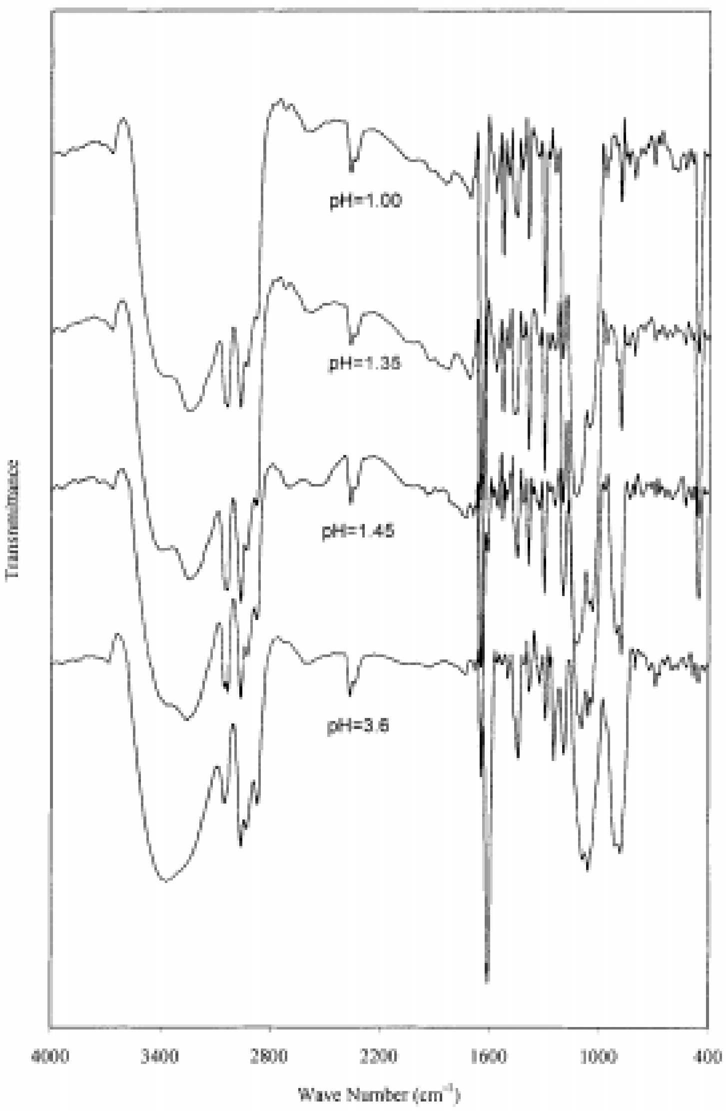


Figure 2. FT-IR spectra showing structural changes due to pH

0.19 to 0.30 g/cm^3. In contrast to the aerogels, xerogels have surface areas of 200 to 330 m^2/g and the density of 0.17 to 0.24 g/cm^3

4. CONCLUSION

Ormocer matrixes made by sol-gel method are ideal as hosts for active catalytic group for several reasons. They are chemically produced at room temperature or slightly elevated temperatures, so that catalytically active end group can be introduced in the original sol and thus they could easily be bonded within the pores of the gradually forming matrix and preserved without destruction. These virtually endless valuable properties of the sol-gel matrixes warrant and explain the large growing interest on these systems.

Preliminary results showed that, the completion of Ru catalyzed hydrosilation polymerization activated by a styrene in toluene is usually indicated by a color change associated with the Ru content of the catalyst. The reaction also generated high molecular weight copolymers in excellent chemical yield.

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