Preparation and Characterization of Silica Gels Catalysts Containing Undecatungstocobaltoindic Heteropoly Acid

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Abstract Silica gels catalysts containing undecatungstocobaltoindic heteropoly acid were prepared by means of sol-gel method. Infrared spectra revealed that the Keggin structure characteristic of $InCoW_{11}O_{39}^{7-}$ anion was present in the silica gel skeleton. The regularity of the change of the characteristic peaks in the infrared spectra was investigated.

Introduction

Heteropoly acids (HPAs) are a fascinating kind of inorganic metal-oxygen cluster compounds. They play very important roles in catalysis, biology, electrochemistry and materials science as a consequence of their nanoscale size, simple composition, unique structures and tunable electronic and physical properties [1-5]. However, the demerits of HPAs, such as weak thermal stability, high sensitivity to atmospheric moisture and the difficulty in machining impeded their potential application [6]. For this reason, the design and synthesis of HPA derivatives have attracted researchers' attention.

The sol-gel syntheses offer new possibilities in the field of solid state ionics by increasing the stability and conductivity of various inorganic materials on gel matrices. The gel materials prepared using the sol-gel method, which are evidently "solid", contains a large number of micropores and mesopores filled with "liquid" which can be utilized for fast proton transport [7].

In the present paper, we report the preparation of silica gels catalysts containing undecatungstocobaltoindic acid by means of sol-gel method. The silica gels catalysts were characterized by the infrared measurements.

Experimental

Synthesis

$Na_2WO_4 \cdot 2H_2O$ (36.3 g) (0.11 mol) was dissolved in 200 ml of water and the pH of the solution was adjusted to 6.3 with acetic acid. The solution was then heated to boiling and a solution of 2.5 g (0.01 mol) of $(CH_3COO)_2Co \cdot 4H_2O$ in 30ml of hot water was added dropwise with stirring. After 30 min, a solution of 3.8 g (0.01 mol) $In(SO_4)_3 \cdot 9H_2O$ in 50ml of water was added dropwise. The pH was readjusted to 5.0 and stirring was continued for 1.5 h. After cooling, blue oil was obtained by adding absolute alcohol. The oily product was extracted three times by the dissolving-cooling method. The obtained oil was dissolved in 80 ml of water and the solution was passed on an Amberlite IR-120 cation-exchange column in H^+ form until pH<1. Finally the solid HPA had been separated by the cooling method. The final yield was about 60% [8].

Tetraethoxysilane [$Si(OEt)_4$:TEOS] was diluted with EtOH and hydrolyzed with H_2O containing appropriate amounts of $H_7InCoW_{11}O_{39} \cdot 14H_2O$. The molar ratio of TEOS/EtOH/H_2O=1/3/10. And the mixture was stirred for about 2h. A homogeneous, transparent sol was obtained. Then the sol was kept at 40℃ until it was transferred to gelation.

Three compositions of gels were prepared: 50, 60, and 80wt%.

Experimental Technique

IR spectra were recorded on a Nicolet Nexus 470 spectrometer in the range 400-4000 cm^{-1} using KBr pellets.

Results and Discussion

Preparation of Silica Gels Containing Undecatungstocobaltoindic Acid

A hydrolysis catalyst like HCl or HNO_3 is usually used in the preparation of silica gels. But we found that no catalyst was required in the preparation of silica gels doped with undecatungstocobaltoindic heteropoly acid, probably because undecatungstocobaltoindic acid can work as a hydrolysis catalyst. Between silica gels containing undecatungstocobaltoindic acid with catalysts and without catalysts, there was no marked difference in gelation time, appearance of gel products etc.

Infrared Spectra

Fig.1 compares the infrared (IR) spectra of the gels of each composition and the $H_7InCoW_{11}O_{39}{\cdot}14H_2O$ crystal.

Generally, in the range from 700 to 1200 cm^{-1}, pure silica gel exhibits three characteristic peaks at around 1130, 950 and 790cm^{-1}. The peak at about 1130cm^{-1} is a broad shoulder peak, which is actually composed of two peaks. The peak at about 1130cm^{-1} is assigned to the Si-O stretching, the peaks at about 950 and 790cm^{-1} are assigned to the Si-OH stretching. In the spectra of silica gels doped with undecatungstocobaltoindic acid, only one characteristic peak at about 1130cm^{-1} of silica gel was observed. The other two were hidden by the more intense peaks of Keggin anion. Because of the influence of undecatungstocobaltoindic acid, with the decrease of the undecatungstocobaltoindic acid content, the characteristic peak of Si-O stretching vibration is split.

In the high wavenumber region, each spectrum of the gels and undecatungstocobaltoindic acid crystal exhibits two other peaks at around 3500cm^{-1} and 1630cm^{-1}. These are assigned to the stretching vibration of O-H bonds and the bending vibration of H-O-H bonds, respectively. The wavenumbers of both peaks of pure undecatungstocobaltoindic acid crystal are lower than that of doped silica gels.

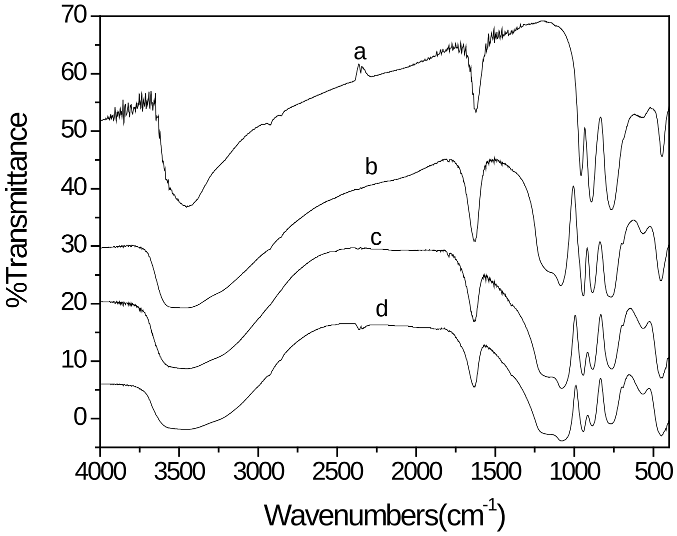

Fig.1. IR spectra: a. pure HPA; b. doped silica 80wt% HPA; c. 60wt%; d. 50wt%.

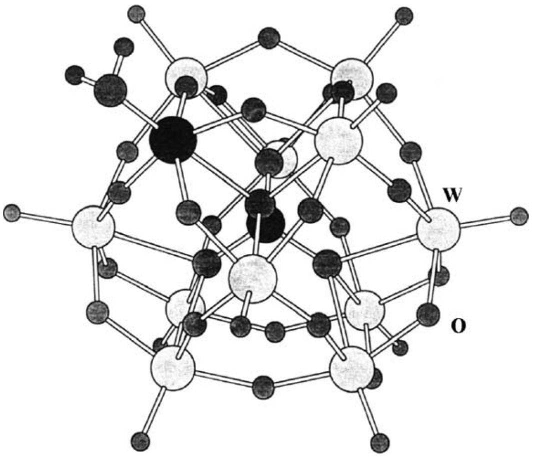

Fig. 2. Structure of $InCoW_{11}O_{39}^{7-}$. The In(III) ion, which is in the upper left-hand corner, is depicted as a darker sphere with a terminally coordinated H2O molecule. The Co(II) heteroatom resides in a central pseudo-tetrahedral hole of the structure and it is the dark central atom.

The silica gels doped with undecatungstocobaltoindic acid exhibit four characteristic peaks of Keggin anion, which are also observed in the spectrum of the pure undecatungstocobaltoindic acid crystal. The $InCoW_{11}O_{39}^{7-}$ structure (Keggin structure) consists of one GoO_4 tetrahedron surrounded by three W_3O_{13} sets and one InW_2O_{13} formed by three edge-sharing octahedrons. The W_3O_{13} and InW_2O_{13} sets are linked together through oxygen atoms. Thus there are four kinds of oxygen atoms in $InCoW_{11}O_{39}^{7-}$, four Co-Oa in which oxygen atom connects with heteroatom, twelve W-O_b-W oxygen-bridges (corner-sharing oxygen-bridge between different W_3O_{13} sets and InW_2O_{13} set), twelve W-Oc-W oxygen-bridges (edge-sharing oxygen-bridge within W_3O_{13} sets and InW_2O_{13} set) and eleven W-Od terminal oxygen atoms. In the IR spectrum of pure undecatungstocobaltoindic acid crystal, there are four characteristic bands : 942.91cm^{-1}， νas (W-Od)； 884.01cm^{-1}， νas (W-Ob-W)； 763.74cm^{-1}， νas (W-Oc-W)； 452.27cm^{-1}， νas (Co-Oa)或δ(O-Co-O). Generally, the W-Od stretching can be considered as pure vibration and is an increase function of the anion-anion interaction. The W-Od asymmetrical stretching frequency of the silica gels decreases from 943.61cm^{-1} to 943.11cm^{-1}with the decrease of undecatungstocobaltoindic acid wt% from 80% to 50%. This is attributed to the weakening of anion-anion interactions of the electrostatic type. We assumed that due to the influence of silica such as lengthening the anion-anion distances, the anion-anion interactions are weakened. The stretchings involving Ob or Oc atoms are different from W-Od stretching and they present some bend character. This can be assumed from geometrical considerations. Because W-Ob-W and W-Oc-W vibrations are not pure and can not be free from bending character, there is a competition of the opposite effects. The electrostatic anion-anion interactions lead to an increase in the stretching frequencies, but they lead to a decrease in the bending vibrations. Moreover, perturbations due to water molecules and anion-cation interactions lead to a decrease in the frequencies of vibrations and can strengthen the decreasing effect of anion-anion interactions. In the competition of the opposite effects, the decreasing effect is stronger than the increasing one. So W-Ob-W and W-Oc-W asymmetrical stretching frequencies are decrease functions of anion-anion interaction. With the decrease of dopant wt% from 80% to 50%, the W-Ob-W and W-Oc-W asymmetrical stretching frequencies increase from 884.88cm^{-1} to 885.83cm^{-1} and 765.91cm^{-1} to 769.03cm^{-1}, respectively. Because the CoO_4 tetrahedron is assumed to vibrate almost independently, the Co-Oa stretching vibration and O-Co-O bending vibration show no relation with the dopant wt%.

Conclusion

Silica gels doped with undecatungstocobaltoindic acid were prepared by means of the sol-gel method. Their IR spectra confirm the existence of Keggin anions in the silica gels. The regularity of the change of the characteristic peaks in the infrared spectra was investigated.

Acknowledgements

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References

[1] H.Y. Zang, J.J. Chen, D.L. Long, L. Cronin, H. Miras, Assembly of thiometalate-based {Mo_{16}} and {Mo_{36}} composite clusters combining $[Mo_2O_2S_{2]}^{2+}$ cations and selenite anions, Adv. Mater. 25 (2013) 6245–6249.

[2] X.F.Wu, X. Tong, Q.Y.Wu, H. Ding,W.F. Yan, Reversible phase transformation-type electrolyte based on layered shape polyoxometalate, J. Mater. Chem. A. 2 (2014) 5780–5784.

[3] M. Armand, F. Endres, D.R. MacFarlane, H. Ohno, B. Scrosati, Ionic-liquid materials for the electrochemical challenges of the future, Nat. Mater. 8 (2009) 621–629.

[4] T.P. Huang, N.Q. Tian, Q.Y. Wu, W.F. Yan, Keggin-type polyoxometalate-based ionic liquid gels, Soft Matter 11 (2015) 4481–4486.

[5] E. Rafiee, N. Nobakht, Keggin type heteropoly acid, encapsulated in metal-organic framework:A hererogeneous and recyclable nanocatalyst for selective oxidation of sulfides and deep desulfurization of model fuels, J.Mol.Catal.A-Chem. 398 (2015) 17–25.

[6] P.E. Car, M.Guttentag, K.K. Baldridge, R. Alberto, G.R. Patzke, Synthesis and characterization of open and sandwich-type polyoxometalates reveals visible-light-driven water oxidation via POM-photosensitizer complexes, Green. Chem. 14 (2012) 1680–1688.

[7] X. F. Wu, W. Wu, X.Y. Qian, Q.Y. Wu, W. F. Yan, Proton-conducting materials based on heteropoly acid and matrixes, J. Non-Cryst. Solids 426 (2015) 88–91.

[8] Q.Y. Wu, X.G. Sang, F. Shao, W. Q. Pang, Synthesis and conductivity of undercatungstocobaltoindic heteropoly acid, Mater. Chem. Phys. 92 (2005) 16–20.