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Synthesis, Characterization and Catalytic Application of Cerium(IV) Tungstosilcate

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Different samples of Cerium(IV) tungstosilcate has been synthesized by mixing solutions of Cerium(IV) ammonium nitrate, sodium tungstate and sodium silicate. The exchanger was characterized by capacity determination, effect of temperature and ionic radius on ion exchange capacity, pH titration curves, IR, TGA, DTA and XRD studies. Distribution behaviour towards 12 metal ions in different media and concentration has also been studied. On the basis of the distribution studies, some important binary separations were carried out using exchanger column. The H^+ ions contained in the structural hydroxyl groups of the exchanger are labile and hence the material can be used as a solid acid catalyst. Esterification reaction has been chosen as a model reaction wherein ethyl benzoate has been prepared.

Key Words: Ion exchange, Distribution, Solid acid catalyst.

INTRODUCTION

Inorganic ion exchangers have gained a renewed interest and a well defined position in analytical chemistry[1,2]. These ion exchange materials have a wide range of interesting properties and thus they open a land of opportunities in industrial and environmental applications[3-5]. As society becomes evermore increasingly aware of environmental issues, the major trend in the field of catalysis is to find newer catalysts, which are environment friendly. The conventional acid catalysts, although quite effective are highly corrosive, toxic, polluting and not reusable. As an alternative, solid selective and recyclable catalysts have been developed. Amongst the various solid acid catalysts used heteropolyacid salts of tetravalent metals are acquiring greater importance, owing to the fact that they are resistant to heat and radiation. These materials can be obtained in both crystalline and amorphous forms, are granular in nature and can be obtained in a range of mesh sizes. They are also found to be more resistant towards leaching and

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are reusable. The presence of exchangeable structural hydroxyl protons on the exchangers indicates good potential for acid catalysis. Use of such metal salt as solid acid catalyst has been reported earlier[6-8].

The present work describes the synthesis, characterization, ion exchange properties and the catalytic behaviour study of amorphous cerium(IV) tungstosilicate in the esterfication reaction, where in ethyl benzoate has been prepared.

EXPERIMENTAL

Cerium(IV) ammonium nitrate (Loba Chemie, India), sodium tungstate, sodium silicate (E. Merck) were used for the synthesis of the exchangers. All other reagents and chemicals used were of analytical grade.

pH measurements were made on a Systronics pH meter model MKVI, X-ray diffractogram was performed on a X-ray diffractometer (Bruker D8) with Cu-K_α radiation and FTIR spectra were recorded on a Bruker IFS 66v. Thermogravimetric analysis was performed on a thermal analyzer Netzsch STA 409C at a heating rate of 10 °C/min from room temperature to 800 ºC.

Synthesis of ion exchange material: Cerium(IV) tungstosilicate was prepared by adding a mixture of sodium tungstate and sodium silicate solution into cerium(IV) ammonium nitrate solution with constant stirring, in different volume and mole ratios. The resulting gel was kept for 24 h at room temperature and the pH was maintained at 1.0. It was then filtered, washed with deionized water and dried. The exchanger was converted into the H^+ form by treating with 1.0 M HNO_3 for 24 h with occasional shaking and intermittent changing of acid. The material was then washed with deionized water to remove the excess acid, dried and sieved to obtain particles of 60-100 mesh.

Ion exchange capacity: The ion exchange capacity of the material was determined by column method. 1.0 g of the ion exchanger in H^+ form was taken in a glass column of 1.1 cm (i.d). The H^+ ions were eluted by percolating 250 mL of NaCl solution (1 M). The effluent was collected and titrated with standard NaOH solution. The exchange capacity (meq g^{-1}) was evaluated using the formula, av/w. Where 'a' is the molarity, v is the volume of alkali used during titration and w is the weight of the exchanger taken.

Characterization of the exchanger

Chemical composition: Chemical composition of the exchanger was determined by dissolving 0.10 g of the substance in 10 mL of conc. HNO_3 and then it was diluted to 100 mL with deionized water and cerium was estimated volumetrically[9a] with ferrous ammonium sulphate and tungstate, silicate was determined gravimetrically[9b-c].

The chemical resistivity of the sample was assessed in mineral acids like HCl, HNO_3 and H_2SO_4, bases like NaOH and KOH and organic solvents like acetic acid, acetone, ethanol and diethyl ether. For this 500 mg of the sample was soaked in 50 mL of different solvents kept for 24 h and changes in colour, nature and weight of the sample were noted.

Ion exchange capacity: The ion exchange capacity of the material for alkali and alkaline earth metal ions was determined using column method by eluting H^+ ions from the exchanger with solutions of different metal ions.

Effect of temperature: The effect of temperature on ion exchange capacity was studied by heating several 1.0 g samples of the exchanger at different temperatures for 1 h in a muffle furnace and the Na^+ ion exchange capacity in meq g^{-1} was determined by the column method after cooling them to room temperature.

pH Titrations: Topp and Pepper[10] method was used for pH titrations using NaOH-NaCl and KOH-KCl, $Ba(OH)_2$-$BaCl_2$ systems. 0.5 g of exchanger was equilibrated with varying amounts of metal chloride and metal hydroxide solutions. After equilibrium, the pH of the solutions was measured and plotted against the milliequivalents of OH^- added.

Distribution coefficient (K_d): Distribution studies were carried out for various metal ions in demineralized water by batch process[11]. In this method, 0.1 g of the exchanger (60-100 mesh) was equilibrated with 20 mL of the metal ion solution for 24 h at room temperature. The metal ion concentration before and after sorption was determined by titration against standard EDTA and the K_d values were calculated.

$$K_d = \frac{1-F}{F} \times \frac{V}{W}$$

where I is the initial volume of EDTA used, F the final volume of EDTA used, V is the volume of the metal ion solution (mL) and W is the weight of the exchanger.

Effect of electrolyte concentration on the K_d values of metal ions was studied by equilibrating known amount of exchanger with metal ion solution in different electrolyte media and concentrations: 0.001, 0.01, 0.1 M nitric acid and ammonium nitrate.

Separation of metal ions: For separation studies, 5 g of the exchanger in H^+ form was taken in a glass column (30 cm × 1.1 cm). The column was washed thoroughly with demineralized water and the mixture of metal ions to be separated was loaded on it. The mixture was recycled 2-3 times through the column to ensure complete sorption. The metal ions were then eluted separately using suitable eluents selected on the basis of K_d values obtained. The flow rate was maintained at *ca.* 0.5 mL min^{-1} throughout the elution process. The amount of metal ions in the effluent were determined quantitatively. Various binary separations were carried out on the column following this procedure.

Acid catalysis: The catalytic behaviour of cerium(IV) tungstosilicate has been explored by studying esterification as a model reaction wherein ethyl benzoate has been prepared. A mixture of benzoic acid (100 mmol), ethyl alcohol (100 mmol) and the exchanger were taken in a round bottom flask fitted with a reflux condenser. The mixture was refluxed for 4 h. After cooling the reaction mixture, the product was analyzed on gas chromatograph. The esterification reactions have been carried out by varying the amount of catalyst and the mole ratio of alcohol to acid.

Identification of the products was done by GC analysis, which were performed on GC-MS of hp-series.

RESULTS AND DISCUSSION

Cerium(IV) tungstosilicate was obtained as orange shining, hard solid and was stable in mineral acids such as HCl (10.0 N), HNO_3 (8.0 N) and H_2SO_4 (8.0 N), but was found to unstable in alkalis such as NaOH and KOH above *ca.* 0.1 M concentration. It was also found to be stable in ethanol, acetic acid and diethyl ether. Table-1 describes the preparation and properties of ion exchange material.

TABLE-1
CONDITIONS OF SYNTHESIS AND PROPERTIES OF CERIUM(IV) TUNGSTOSILICATE

Sample no.	Molar concentration			Volume ratio	pH	Appearance	Ion exchange capacity (meq g^{-1} for Na^+)
	Ce^{4+}	WO_4^{2-}	SiO_4^{2-}				
1	0.10	0.10	0.10	1: 1: 1	1	Yellow orange	0.60
2	0.10	0.10	0.10	2: 1: 1	1	Orange	1.00
3	0.05	0.05	0.05	1: 2: 2	1	Yellow orange	0.54
4	0.05	0.10	0.10	1: 1: 1	1	Orange shining	1.28
5	0.10	0.05	0.05	1: 1: 1	1	Orange	0.51

Chemical analysis of the material indicates the ratio Ce:W:Si to be 1:1:3. Thermogram of cerium(IV) tungstosilicate indicates a 7.34 % weight loss up to 200 °C corresponding to the loss of water molecules, after which a slow change in weight was observed till 500 °C. The FTIR spectra of the material shows broad bands in the 3400 cm^{-1} region, attributed to asymmetric and symmetric hydroxo -OH and aquo -OH stretches. A sharp medium band at 1620 cm^{-1} is attributed to aquo (H-OH) bending. In the X-ray diffractogram, absence of any characteristic peak, confirms the non-crystalline nature of the exchanger.

The thermal stability of the exchanger was also studied by determining the Na^+ ion exchange capacity of the exchanger subjected to different temperatures between 30-500 °C. It was observed that the exchange capacity decreases slightly from 1.28 at 30 °C to 1.02 at 200 °C. After that a sharp change in capacity was observed. This confirms that the exchanger is fairly stable and functions normally up to 200 °C. The ion exchange capacity in meq g^{-1} (dry basis) for Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+} and Ba^{2+} was found to be 1.19, 1.28, 1.34, 1.22, 1.35 and 2.04, respectively. The ion exchange capacity increases with the decrease in hydrated radii of ions.

The pH titration curves (Fig. 1) obtained under equilibrium conditions for NaCl/NaOH, KCl/KOH and $BaCl_2/Ba(OH)_2$ systems show first disso-cia-tion in acidic medium and the second dissociation in basic medium indicates bifunctional behaviour of the exchanger. The bifunctional behaviour becomes prominent in the case of H^+-Na^+ and H^+-K^+ exchange, but less prominent in the case of H^+-Ba^{2+} exchange.

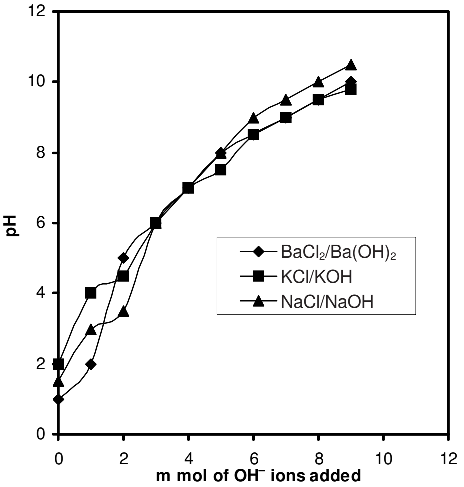

Fig. 1. pH Titration curve of cerium(IV) tungstosilicate

The distribution studies (Table-2) indicate that the material is selective for Bi(III) in comparison with other metal ions studied. The decreasing order of K_d values for various metal ions in distilled water, 0.1 M, 0.001 M and 0.001 M HNO_3 and NH_4NO_3 is given as follows: Bi(III) > Cd (II) > Pb(II) > Ca(II) > Cu(II) > Zn(II) > Al(III) > Co(II) > Mg(II) > Th(IV) > Ni(II) > Hg(II). Results of important binary separations such as Cu(II)-Bi(III), Hg(II)-Cd(II), Hg(II)-Pb(II), Ni(II)-Pb(II) and Ni(II)-Cd(II) are given in Table-3. The results were found to be quite precise and reproducible.

TABLE-2
DISTRIBUTION STUDIES OF VARIOUS METAL IONS ON CERIUM(IV)TUNGSTOSILICATE

Distribution studies in DMW		Effect of electrolyte concentration on K_d values					
Metal ion	K_d value (mL/g)	0.1 M HNO_3	0.01 M HNO_3	0.001 M HNO_3	0.1 M NH_4NO_3	0.01 M NH_4NO_3	0.001 M NH_4NO_3
Hg(II)	NS	NS	NS	NS	NS	NS	NS
Zn(II)	16.30	NS	NS	14.32	NS	6.83	15.65
Mg(II)	10.90	3.22	7.85	8.90	3.20	8.90	10.72
Ca(II)	28.92	6.95	13.82	27.20	6.50	12.92	26.80
Cd(II)	189.80	111.01	145.25	175.55	110.49	156.15	188.21
Co(II)	11.20	3.21	5.22	11.00	2.59	4.85	11.40
Cu(II)	28.06	NS	14.00	25.50	NS	16.30	26.20
Ni(II)	3.00	NS	NS	NS	NS	NS	NS
Pb(II)	171.61	10.02	68.85	168.99	49.41	84.14	170.20
Al(III)	13.54	NS	NS	13.00	NS	8.15	12.84
Bi(III)	237.55	42.36	98.42	118.53	150.24	191.04	210.33
Th(IV)	8.60	NS	NS	NS	NS	NS	5.25

NS = No sorption.

TABLE-3
BINARY SEPARATION OF METAL IONS ON CERIUM(IV) TUNGSTOSILICATE

Separation achieved	$\alpha = \frac{k_{d_1}}{k_{d_2}}$	Eluant	Metal ion (mg)		Efficiency (%)
			Loaded	Eluated	
Cu(II)-Bi(III)	8.32	0.1M NH_4NO_3 (Cu) 0.5 M HNO_3 (Bi)	2.00 3.50	1.97 3.40	98.50 97.14
Hg(II)-Cd(II)	189.80	DMW (Hg) 0.2 M HNO_3 + 0.2M NH_4NO_3 (Cd)	2.50 2.00	2.47 1.96	98.80 98.00
Hg(II)-Pb(II)	171.60	DMW(Hg) 0.1 M HNO_3 + 0.2M NH_4NO_3 (Pb)	2.50 2.50	2.49 2.44	99.60 97.60
Ni(II)-Pb(II)	57.20	0.001M NH_4NO_3 (Ni) 0.1 M HNO_3 + 0.2M NH_4NO_3 (Pb)	1.98 2.50	1.94 2.42	97.98 96.80
Ni(II)-Cd(II)	63.27	0.001MNH_4NO_3 (Ni) 0.2 M HNO_3 + 0.2M NH_4NO_3 (Cd)	1.98 2.00	1.93 1.98	97.47 99.50

DMW = Demineralized water.

The results of esterification reactions are summarized in Table-4. The reactions were carried out varying the amount of catalyst and the mole ratio of alcohol to acid. As can be observed from the Table-4, the best yields were obtained when alcohol to acid mole ratio was 1:2. The esterification reaction is an equilibrium reaction with a low value of K_{eq}. Therefore, as in any equilibrium reaction, the reaction may be driven to the product side by controlling the concentration of one of the products or reactants, in accordance with Le Chatlier's principle. When concentration of one of the two reactants relative to the other is increased, the reaction is driven to the product side. As expected, on decreasing the amount of catalyst, the yield decreases.

TABLE 4
ESTERIFICATION OF ETHYL ALCOHOL CATALYZED BY CERIUM(IV) TUNGSTOSILICATE

Sample	Catalyst (g)	Ration of alcohol:acid	Yield of ethyl benzoate (%)
1	1.0	1:1	26
2	1.0	1:2	37
3	1.0	2:1	20
4	2.0	1:1	33
5	2.0	1:2	56
6	2.0	2:1	27

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