

Sorption of ammonia on crystalline polyelectrolyte tantalum tungstate

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A crystalline polyelectrolyte tantalum tungstate (Ta:W:2.568:1) has been selected for the sorption of ammonia. Its BET surface area, electron micrograph and IR spectra have been reported. The sorption of ammonia at 50° and its desorption at 50° and 150°C have been carried out. Ammonia sorption may be utilized to control the pollution caused by exhaust gases of automobiles.

The synthetic inorganic ion exchange materials are being placed in an important category of materials due to their applications in separation, recovery and pre-concentration of a number of metal ions. They have been employed in nuclear establishments to separate various metals from nuclear wastes and in the treatment of industrial effluents to remove pollution causing ionic species. These materials have another salient feature i.e. thermal stability and good resistance towards radiation.

The selectivity and sorption characteristics of synthetic inorganic ion exchangers have been reviewed by Abe *et al.*¹ Recently a number of ion exchanger materials have been reported for their sorption characteristics towards cations, anions and molecules. Titanium (IV) oxide² coated on silica gel has been used to adsorb CrO_4^{2-} ions from acidic solution. The X-ray studies to measure the sorption of K^+ ions on titanium phosphate^{3,4} have been reported. Lithium ions sorption has been attained on tin-zirconium hydrogen phosphate⁵. Titanium zirconium phosphate⁶⁻⁸ in its NH_4^+ form has been studied for the sorption of Fe^{3+} , Pb^{2+} of divalent cations under the influence of various factors. Zirconium phosphate⁹ also has been reported for the sorption of Fe^{3+} , Pb^{2+} , Zn^{2+} , Cd^{2+} and Co^{2+} by using single salt aqueous solution or solution of these cations containing KNO_3 background electrolyte. The adsorption of pyridine molecules through IR study has been observed on zirconium

phosphate¹⁰. The selectivity of zirconium tungstate¹¹ has been utilized to act as catalyst in the esterification of 1-propanol and butanol with some organic acids.

Raveau *et al.*¹² have published some studies on the thermodynamics and kinetics of ion exchange on tantalum tungstate. Kumada *et al.*¹³ have proved the layered structure of $\text{HTaWO}_6 \cdot n\text{H}_2\text{O}$ through ion exchange studies of Na^+ , K^+ , Rb^+ , and Cs^+ . Gupta *et al.*¹⁴ have prepared a new crystalline phase of tantalum tungstate through hydrofluoric acid medium TaW (HF) and characterized it.

The present manuscript deals with the sorption of ammonia on tantalum tungstate¹⁴ through IR study. The BET surface area, DSC, and electron micrograph of material have also been mentioned. The sorption of ammonia has been taken for studies to use it in monitoring of environmental pollution control caused by exhaust gases of automobiles.

Experimental

A crystalline ion exchange material, tantalum tungstate¹⁴, (tantalum to tungsten mole ratio 2.568) was sieved to 50-100 mesh size particles. Differential scanning calorimetry (DSC) analysis of tantalum tungstate was recorded using Du Point 9900 DSC unit. The analysis has been performed in an inert atmosphere of N_2 and at the rate of 5°C/min. Scanning electron micrographs of tantalum tungstate were recorded at different magnifications using Stereo scanning electron microscope, Cambridge S-360 (Fig. 1). The material (50-100 mesh size) was heated to clean its surface for four hours at 150°C to remove moisture or gas molecules from the surface. Its BET surface area was determined using Pulse Chemisorb 2700 by dynamic methods. The heating/cooling rate was maintained to 3°C/min. The gas mixture (30% N_2 and 70% He) was used at the flow rate of gases 15 ml/min. The instrument reading was recorded and analysed to get surface area of tantalum tungstate.

Sorption of ammonia

One gram of TaW (HF) in H^+ form was taken in silica crucible and placed in a desiccator where 12% aqueous ammonium solution present at room temperature for 15 minutes. It was removed from



Fig. 1—SEM of tantalum tungstate

desiccator and placed in temperature controlled electric oven for one hour. Ammonia sorbed TaW (HF) (0.3 gm) was heated at 50°C and another 0.3 g of it was heated at 150° for one hour in the oven separately. IR spectra of TaW (HF) in H⁺ form, sorbed ammonia TaW (HF) heated at 50°C and 150°C were recorded by KBr disc methods.

Results and discussion

TaW (HF) mole ratio Ta:W :2.568:1 shows 0.40 meq/g ion exchange capacity for Na⁺ and K⁺ ions. The particular sample of tantalum tungstate polyelectrolyte has been selected for sorption studies due to its high thermal stability and better ion exchange capacity comparatively.

Differential scanning calorimetric analysis of TaW (HF) seems to be a multireaction system. The removal of water of crystallisation completes upto 73.70°C. Then the removal of coordinated water begins. Its removal starts from 101.86°C and completes at 141.37°C. The system corresponds to the nature of tungstic acid which contains three types of water:

(i) Water in the form of hydroxyl groups bonded to water;

(ii) Water molecules present as water of hydration inside the crystal lattice or in the adsorbed state and

(iii) Water in the form of hydronium ions.

The remaining small peaks represent the phase transitions in regard of crystallinity etc.

Electron micrographs of TaW (HF) at a magnification of 1130 show the presence of cylindrical

crystals. The SEM studies hint that the particle size distribution and rude surface is high. It also indicates that the final crystal growth will be excellent.

The BET surface area of TaW (HF) [50-100 mesh size] by dynamic method comes to be 1.64 m²/g. It is based on the monolayer coverage of surface by N₂ molecules at 30% N₂ and 70% He mixture. It takes place at microscopic level. Therefore, the particle size does not effect adsorption of nitrogen at surface, if it is measured with a lump of the material or fine particles. The percentage of nitrogen in the mixture is restricted upto 30% because higher percentage of nitrogen leads to multilayer absorption of nitrogen molecules over the surface. This absorption of nitrogen takes place at liquid N₂ temperature i.e. 80K or -193°C. The calculation of surface area is made by using BET equation.

In the case of solid with uniform distribution of active sites, surface area plays a main role in sorption as well as in catalytic properties of the material. Higher the surface area greater affinity will be there towards sorption and better catalytic properties will be exhibited.

IR spectra of TaW (HF) in H⁺ form, TaW (HF) after sorption of ammonia and heated at 50° and 150°C are recorded. The changes in IR spectra are more obvious. IR spectrum of TaW (HF) in H⁺ form shows the following absorptions 2850-2200 cm⁻¹ (b), water molecules and hydroxyl groups; 1700-1500 cm⁻¹ (b), structural water molecules; 1920 cm⁻¹, deformation vibration of interstitial H₂O and OH and 850-650 cm⁻¹ (b), interatomic stretching in O-Ta-O and O-W-O.

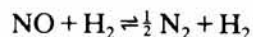
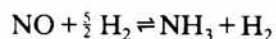
IR spectrum of TaW (HF) heated at 150°C after sorption of ammonia is similar to that heated at 50°C and the two IR spectra are very much different from that of TaW (HF) in H⁺ form. After sorption of ammonia and heating the samples at 50°C and 150°, the IR spectra of these heated samples show a number of new peaks at 2320, 1455, 910 and 605 cm⁻¹; which correspond to the absorption by NH₄⁺, bending of N-H and rocking of N-H bonds. It may be confirmed the sorption of ammonia by TaW (HF) in H⁺ form which remains absorbed there upto 150°C most probably due to its conversion into NH₄⁺.



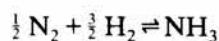
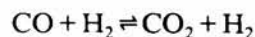
The automobiles exhaust consists of a number of gases out of which NO_x and carbon monoxide are more poisonous in nature. With the help of noble metals, base metal oxides and alloys in the presence of water, oxygen and hydrogen, these

poisonous gases are converted into N_2 , NH_3 and H_2O .

For NO the reactions which are favoured to completion are—



The reactions which play a role but are not favoured to completion are—



The above reactions show the formation of ammonia. As we have observed that tantalum tungstate absorbs ammonia. It is believed that it may be used for ammonia absorption. But the one drawback to these ion exchange materials is less BET surface area available in them. The surface area can be increased by adding supporting materials like alumina, cordierite, spodiomene, asbestos, zirconia based ceramics, pumic stone (naturally sintered silicates), silica gel and carbon (activated charcoal) in one way or the other i.e. coating, precipitation etc.

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