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Preparation of Rhodium(III)-13X Zeolite from Hydrochloric Acid Medium and Thermogravimetric and FTIR Studies of its Reprecipitated and Calcined Forms

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A yellow and an ash-grey derivatives of 13X zeolite have been prepared with $RhCl_3$ from HCl medium after reprecipitating with ammonia followed by calcination. The yellow form contains 3.55% nitrogen and gives a weight loss of 28.99% upto 945°C on TG analysis. The calcined form shows total absence of nitrogen and only 0.6% weight loss. Both these forms clearly indicate the presence of Rh–H type species identified by FTIR band at 2300 cm^{-1}.

INTRODUCTION

A new method has been used for preparing Rh(III) derivative of 13X synthetic zeolite for use as catalyst. The method consists of dissolving the synthetic zeolite in powder form and rhodium(III) chloride in AnalaR hydrochloric acid and precipitating the interacted sample by neutralising the acid with liquor ammonia. The resultant waxy solid, yellow in colour, has been calcined in a muffle furnace at red heat when an ash-grey derivative was obtained. Both the derivatives differ in their FTIR and thermal characteristics as well as composition. However, a stable hydride complex of rhodium is indicated in both the samples with potential catalytic applications.

EXPERIMENTAL

3 Gm of 13X zeolite in powder form, supplied by Indian Petrochemicals Corporation Ltd., was dissolved in AnalaR hydrochloric acid (sp. gravity = 1.18; 35% by weight) alongside 250 mg of an AnalaR sample of rhodium (III) chloride (Fluka Chemie, AG). The dark red solution was changed to yellow as soon as liquor ammonia (sp. gravity=0.888; 32.5% by weight) was added to it with gradual separation of gelatinised solid. On filtration, repeated washing with hot distilled water and air-drying a yellow waxy sample was obtained together with a colourless supernate confirming complete precipitation of the rhodium derivative. A portion of this yellow derivative was heated in a muffle furnace at red heat resulting in an ash-grey residue with evidence of sintering[1]. Both the yellow and ash-grey samples were analyzed using a TG balance (Perkin-Elmer) at the heating rate of 15°C min^{-1} upto 945°C in air, a FTIR spectrophotometer (Perkin-Elmer) between 400 cm^{-1} and 4000 cm^{-1} and determining N% with a

Coleman N-Analyzer 29. Figs. 1 and 2 reproduce the TG and FTIR plots of the two derivatives identifying the yellow sample by 1 and the calcined ash-grey sample by 2.

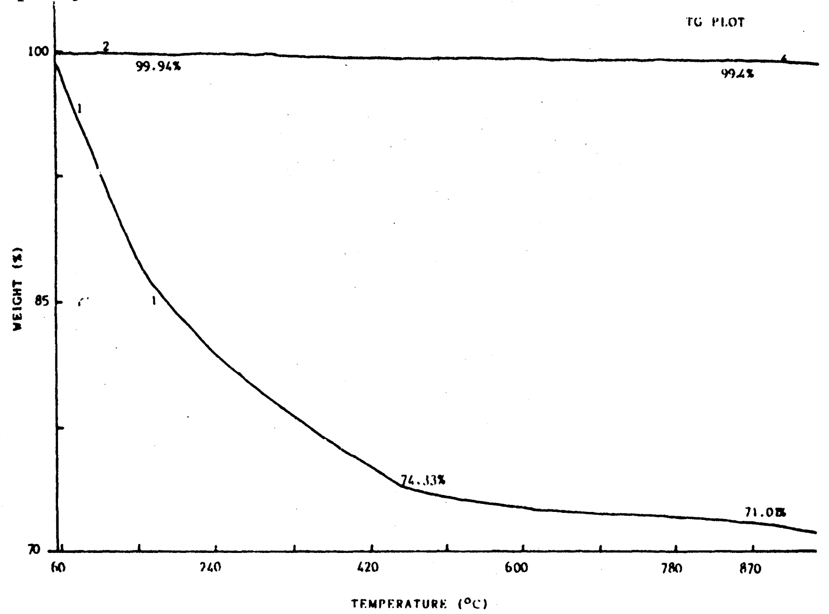

Fig. 1. TG plots of (1) yellow reprecipitated derivative, and (2) ash-grey calcined derivative.

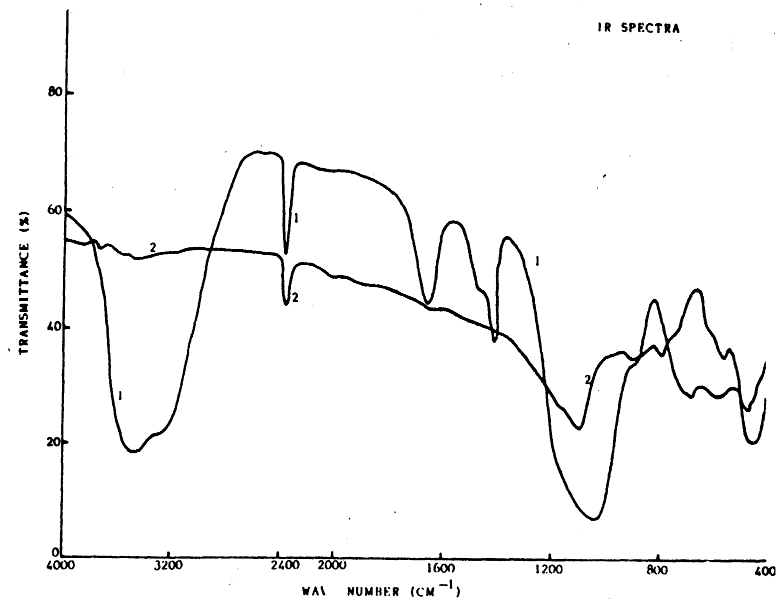

Fig. 2. FTIR plots of (1) yellow reprecipitated derivative, and (2) ash-grey calcined derivative.

RESULTS AND DISCUSSION

The FTIR plot of the yellow Rh(III)-13X derivative indicates the presence of aquo, amino and the hydride complexes of the metal. The colour of the derivative helps in the identification of these complex species. The hexamine complex is colourless while both the aquo complex (yellow) and triamine complex (yellow to red) have colours[2]. The presence of all the three species in mixture is, therefore, distinctly possible. Rh(III) complexes tend to form the hydride and carbonyl derivatives with ease[3]. FTIR band at 1400 cm^{-1} for coordinated ammonia, two bands appearing between 600 and 700 cm^{-1} due to the rocking mode of coordinated water[4] besides bands at 1640 cm^{-1} (δ_{HOH}) and 3700 cm^{-1} (ν_{OH}) and most significantly the band at 2300 cm^{-1} clearly support the presence of amine, aquo and hydride complex[5] species in the reprecipitated derivative. Mashchenko *et al.*[5] had identified a surface complex species, $[Pt–H]^+$ in Pt–Y zeolite by the Pt–H bond vibrations at 2120 cm^{-1}. Acid treatment followed by ammonia treatment produce the Bronsted acid form of 13X zeolite which favours the formation of $[Rh–H]^+$ type of species, thereby establishing the potential use of this derivative in hydrogenation processes both as a catalyst as well as hydrogen generator. This derivative loses weight initially at a fast rate upto 448°C giving 25.67% weight loss. The final slow step of weight loss, 3.31%, occurs between 448°C and 945°C. Considering the presence of 3.55% nitrogen in this derivative (corresponding to 4.32% NH_3), the initial weight loss step can be attributed to the loss of water and ammonia and the final weight loss step to dehydroxylation. Based on the unit cell contents of X-type zeolite[6], $Na_{86}[(AlO_2)_{86}(SiO_2)_{106}]\cdot 264H_2O$, the water loss expected would be 26.16%. The observed value of total weight loss on TG analysis, 28.99%, compares very well with the expected loss for dehydration and nitrogen together (29.71%).

Calcination of the yellow derivative brings about decomposition of both the aquo and the amine complexes as the FTIR bands at 1400 cm^{-1} and 1640 cm^{-1} disappear, but the hydride complex remains unaffected. This residue shows total absence of nitrogen and only 0.6% weight loss on TG analysis. A new FTIR band around 800 cm^{-1} for the calcined derivative shows the expected evidence of dealumination. While acid treatment followed by ammoniation produces the yellow derivative comprising the complex species on a decationised 13X zeolite calcination leaves only the hydride complex of rhodium on a dealuminated 13X zeolite. This derivative also has the potential for catalysis as well as hydrogenation. It has been found that heating beyond 600°C converts the Bronsted sites to Lewis sites[7].

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