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Preparation and Characterization of Potential Zeolite Based Ruthenium Catalysts

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Mineral acid treatment and interaction with a chelating agent of a Ru(III)-13X zeolite brings about dealumination to the extent of 56.8% and decationisation to the extent of 44.9% in the original zeolite before calcination. After calcination further dealumination occurs for a total extent of 67.0% and decationisation remains almost unchanged (45.8%). The interacted sample before calcination shows the presence of complex ruthenium species. This sample and its calcined form have been characterized by TG, FT-IR and SEM studies and determination of N% and both exhibit thermal stability and minor changes in the crystal structure.

INTRODUCTION

The role of zeolite and molecular sieves in the field of catalysis is well known[1]. Ruthenium catalysts based on different supports including zeolites have found use in many industrial processes[2]. Deposition of ruthenium on different supports result in the formation of catalysts of considerable activity for the water-gas shift reactions[3]. Preparation and study of two X-type zeolite derivatives containing adsorbed ruthenium have been reported by this author earlier[4]. In the present study two other zeolite based ruthenium derivatives have been prepared and characterized by their TG, FT-IR and SEM data and determination of N% and other constituents like Na(I), Al(III) and Si(IV).

EXPERIMENTAL

Synthetic zeolite 13X in white powder form was obtained from Indian Petrochemicals Ltd. and characterized by thermal, XRD and FT-IR studies[5]. 3 G of this zeolite was mixed with 2 g of AnalaR ruthenium(III) chloride-trihydrate (Loba-Chemie) with minimum 39% ruthenium and 2 g of AnalaR Titriplex IV (E. Merck, Germany), a complexone 1, 2-diaminocyclohexane NNN′N′-tetra-acetic acid-monohydrate, containing polymethylene groups, in warm AnalaR hydrochloric acid of specific gravity 1.18 with constant stirring. A dark violet derivative was separated from the resultant viscous fluid by neutralising the acid with aqueous ammonia of specific gravity 0.91. The filtered, washed and air-dried sample was dark violet in colour (sample A). A part of this sample was heated in muffle furnace at red heat for 3 h when an ash-grey derivative was obtained (sample B). Both these samples were investigated by FT-IR spectroscopy between 4000–450 cm^{-1} in KBr pellets using Perkin Elmer FT-IR spectrophotometer, scanning electron microscopy using Cambridge Stereoscan 180 at different magnifications and thermogravimetric analysis upto 950°C at a heating rate of

15°C min^{-1} in N_2 atmosphere using Perkin Elmer TG balance. Percentages of N% and other constituents like Na(I), Al(III) and Si(IV) were determined using Coleman N-analyzer 29 and by usual methods[6]. Relvcant data are reproduced in Tables 1 and 2 and Scanning Electron micrographs of samples A and B are shown.

TABLE-1
THERMAL DATA

Sample	Wt. loss (%) and temp. range (°C)	Rate of Wt. loss (% min^{-1})	Ratio of 1st and 2nd steps rate of loss
Zeolite 13X	17.87 upto 183.27; and	1.64	9.65
	8.62 between 183.27 and 936.42	0.17	
Sample A	23.53 upto 219.74; and	1.77	11.8
(Dark violet)	6.91 between 219.74 and 913.95	0.15	
Sample B	11.47 upto 204.98; and	0.93	10.3
(Ash-grey)	4.47 between 204.98 and 936.69	0.09	

TABLE-2
FT-IR AND COMPOSITION ANALYSIS DATA

Sample	Na%	Al%	Si%	Si/Al	Na/Al	N%	FT-IR bands (cm^{-1}) with assignments
Zeolite 13X	10.89+	12.78+	15.63+	1.22	0.85	—	3500 ν(OH), 1640δ(OH), 1070 (asymm. str. external link), 960 (asymm. T-O), 740 (symm. str. external link), 655ν(symm. T-O), 550 (double ring), 450 δ(T-O bend).
Sample A (Dark violet)	6.00	5.52	15.63	2.83	1.09	4.79	Between 3928 and 3425 ν(OH), 2329 (org. species), 1633 δ(OH), 1401 δ(NH_2), 1326 δ(NH_2), 1048 (asymm. str. external link), 595 sh (double ring), 464 δ(T-O bend)
Sample B (Ash-grey)	5.90	4.21	15.63	3.71	1.40	0.155	Between 3926 and 3384 ν(OH), 2931–2344 (H-bonding), 1632 δ(OH), 1081 (asymm. str. external link), 788 (dealumination), 568 (double ring).

+ Calculated from known composition $Na_{86}[(AlO_2)_{86}(SiO_2)_{106}] \cdot 264H_2O$; T = (Si, Al)$O_4$.

RESULTS AND DISCUSSION

The complexone, Titriplex IV, contains two carbon atoms in the N, N′ chain which are connected by a polymethylene chain. The complexes with this ligand are more stable than EDTA complexes mainly due to the increased basicity of the ligand evident only in strong alkaline solution. However, in the presence of strong HCl the complex formed cannot be stable, but the complexone can aid solubilization of the metal by complexation. Addition of ammonia to the complex mixture raises the pH to only 6.73 when the dark violet sample separated out. Because of the complexity of ruthenium chemistry and its tendency to form both aquo and amine complexes it is equally possible that a complex of the type

$NH_4[Ru(Titriplex\ IV—H)Cl]\cdot xH_2O$ is formed on ammoniation from the viscous fluid in HCl. Kerr[7] had eliminated aluminium directly from a synthetic Y type zeolite with EDTA as a chelating agent. It has also been established in the case of Y zeolite that removal of upto 50% of the framework aluminium results in the formation of highly crystalline zeolite with improved thermal stability[8]. Calcination of the $NH_4(I)$—exchanged zeolite Y at elevated temperatures in the presence

Fig. 1 SEM of Sample A: Ru(III)-13X titriplex IV before calcination

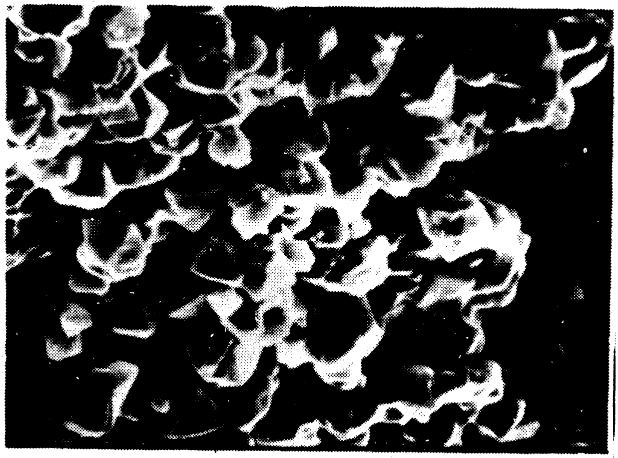

Fig. 2 SEM of Sample B: Calcined Ru(III)-13X titriplex IV

of steam results in the migration of the part of the framework aluminium into non-framework positions[9]. Narayanan[10] has reported that a sample of ruthenium in zeolites like L, Y and mordenite on calcination in air prior to reduction has a decreased ruthenium area due to the formation of large crystallites. The results obtained for samples A and B conform to such reported behaviours in similar studies.

Against the theoretical values for the main constituents of 13X zeolite $Na_{86}[(AlO_2)_{86}(SiO_2)_{106}]\cdot 264H_2O$ the samples A and B prepared show evidence of decationisation to the maximum extent of 45.8% and dealumination to the maximum extent of 67.0%, while the silicon contents in both remain unchanged. Weight loss of 26.49% recorded on TG analysis of 13X zeolite agrees well with the expected value corresponding to 264 moles of H_2O. The resultant increase due to dealumination of samples A and B for Si/Al ratios is about 130% and 200% respectively (Table-2) while the change in Na/Al ratio for the two samples compared to 13X is from 0.85 to 1.09 and 1.40 respectively. The high value of N% for sample A can be equated to 6.16% NH_4(I) or 0.623 mol Titriplex IV. These get reduced to 0.20% and 0.020 due to heating in the muffle furnace indicating more than 96% reduction in these components present in samples A and B. Like 13X both samples A and B show two-step weight losses on TG analysis. Between the original 13X and samples A and B the difference noted in weight loss sequence is that upto about 200°C sample A shows 5.66% more loss compared to the original zeolite and 12.06% more loss than sample B. This is due to the presence of NH_4(I) and the water molecules in greater quantity compared to 13X and sample B. At higher temperature the weight losses are recorded in decreasing order from 13X (8.62%) to sample A (6.91%) to sample B (4.47%) showing the extent of mostly dehydroxylation. Compared to the expected FT-IR data for 13X zeolite[11] samples A and B show typical behaviours brought about by Ru(III)-Titriplex IV-interaction and subsequent heating. Apart from strong bands around 3400 cm^{-1} for lower frequency OH groups protons-bonded to framework oxygen there are 4 bands between 3928 cm^{-1} and 3425 cm^{-1} for sample A due to higher frequency surface OH group and 8 bands between 3926 cm^{-1} and 3384 cm^{-1} for sample B for the same. Sample A shows two additional IR bands at 1410 cm^{-1} and 1326 cm^{-1} for $\delta(NH_2)$ which disappear due to almost 96% deammoniation in the spectrum of sample B. A band at 2329 cm^{-1} for sample A can be attributed to the organic species and bands between 2931 cm^{-1} and 2344 cm^{-1} in the case of sample B is attributed to H-bonding resulting from calcination. An additional band at 788 cm^{-1} for sample B is due to further dealumination due to heating. SEM profiles of both samples A and B as reproduced at X5500 magnification show mixed solid forms and only partial crystal structure collapse.

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