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Effect of metal ion exchange on the polymerization initiation activity of molecular sieves

Mukul Biswas and Narayan C. Maity
Department of Chemistry, Indian Institute of Technology, Kharagpur 721302, *India*

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Recent studies[1-3] by Biswas and Maity have revealed that 13X molecular sieves are much less potent than SK-500 in initiating the cationic polymerization of *N*-vinylcarbazole (NVC), isobutyl vinyl ether (IBVE) and styrene. This observation on styrene–13X system sharply contradicts the findings of Barson *et al.*[4] who reported a very high molecular weight polymerization of styrene by clay free 13X sieves. It has now been observed that the catalytic efficiency of these sieves may be modified after exchange with transition metal ions. This paper highlights some interesting observations on the effect of cupric ion exchange of 13X molecular sieves in respect of the polymerization of NVC and IBVE.

EXPERIMENTAL

Materials

IBVE and NVC (BASF, West Germany) were purified by procedures described earlier[2,3]. Solvents, all of analytical grade, were purified and fractionated by standard methods. Linde 13X (Union Carbide) supplied as a white powder containing no clay binder was activated at 500°C for 2 h just before the experiment.

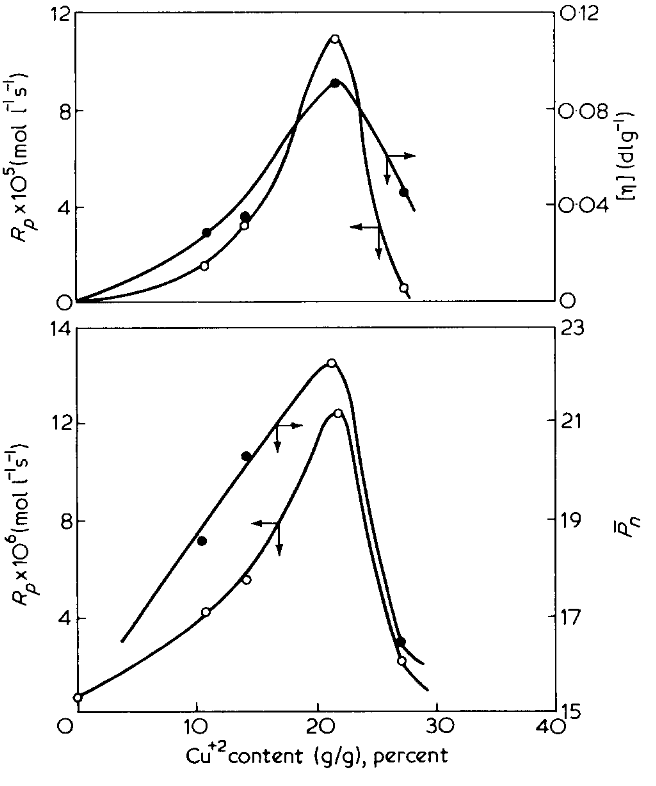

Figure 1 (a), Dependence of R_p and $\bar{P}_n$ on % Cu^{+2} content in the 13X sieve for the polymerization of NVC in benzene at 25°C. [NVC] = 0.1 mol l^{-1}; weight of Cu^{+2} – 13X sieve = 0.150 g.
(b), Dependence of R_p and [η] on % Cu^{+2} content in the 13X sieve for the polymerization of IBVE in benzene at 25°C. [IBVE] = 5.0 mol l^{-1}; weight of Cu^{+2} – 13X sieve = 0.150 g

The ion exchange of sodium ions by cupric ions was performed by stirring an aqueous suspension of 13X zeolite in dilute solution of cupric chloride at 60°C. pH was maintained around 5 during the exchange process. High exchange species were obtained by repeating the treatment several times. After the final exchange, the material was collected by filtration, washed till free of Cl$^-$, heated to 100°C for 3 h, cooled to room temperature in a dry box and powdered to 100 mesh size. Finally, before each experiment, the catalyst was activated at 500°C for 2 h. The degree of ion exchange was determined by chemical analysis[5].

Polymerization

All polymerizations were conducted in a pyrex flask (100 ml capacity) under nitrogen atmosphere with constant stirring. The polymers were collected and conditioned following the standard procedures reported elsewhere[2,3].

The degree of polymerization ($\bar{P}_n$) for NVC and intrinsic viscosity ([η]) for IBVE were determined cryoscopically and viscometrically respectively in benzene and toluene.

The i.r. spectra of the sieves were recorded on a Perkin Elmer 237B infrared spectrophotometer in nujol.

RESULTS AND DISCUSSION

Figure 1*a* presents the variation of the rate of polymerization (R_p) and $\bar{P}_n$ with the Cu^{+2} content in the 13X zeolite for the polymerization of NVC (0.1 mol l^{-1}) in benzene at 25°C. It is observed that the activity of 13X increases as the degree of exchange of Cu^{+2} is increased and after a threshold uptake (21.72%) of Cu^{+2}, the same falls to a very low value. A similar trend is observed for $\bar{P}_n$ with the variation of Cu^{+2} content in the sieve.

Figure 1*b* reveals the variation of R_p and [η] with Cu^{+2} content of the sieve for the polymerization of IBVE (5.0 mol l^{-1}). In this system 13X (no exchange) fails to initiate the polymerization reaction whereas R_p increases sharply as the Cu^{+2} content increases up to a threshold uptake, falling thereafter. The variation of [η] follows the same trend.

The results above indicate that metal ion exchange appreciably modifies the zeolite. It has been observed that after exchange, the zeolite contains chlorine as Cl$^-$. This may be taken to imply that exchange occurs in the form of CuCl$^+$. The enhanced catalytic activity may be due to the

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formation of Bronsted acid sites through the liberation of HCl, according to the reaction.

$$CuCl^+ + H_2O \rightarrow Cu(OH)^+ + HCl$$

$$CuOH^+ + CuCl^+ \rightarrow Cu^{2+} + CuO + HCl$$

A similar mechanism was proposed by Tsutsumi *et al.*[6] to explain the effect of Cu^{+2} exchange on cumene cracking activity of zeolite catalysts (Faujasite type). Ward' also has pointed out such hydrolytic fission of adsorbed water on the zeolite surface in presence of various metal ions. In the present system, occurrence of i.r. absorption bands (*Figure* 3) at 3550, 3625 and 3740 cm^{-1} are perfectly consistent with data of Ward on the i.r. absorption of Cu^{+2} exchanged zeolites endorsing the above mechanism.

The polymerization observed in the present systems occurs not only through Bronsted acid sites but also through polarization[3] of the vinyl double bond by the increased electrostatic field associated with the Cu^{+2} ion.

The exact reason as to why the rate and $\bar{P}_n$ fall at high exchange levels is obscured. It is felt that the growing chains undergo increased transfer reactions with the Cl^- or other entities likely to be formed at this stage due to possible break down of the zeolite structure by HCl under these conditions. HCl is reported[6] to facilitate the decomposition of zeolite structures during Cu^{+2} ion exchange. the zeolite turning black with heating at 300°C. In the present instance such a change of colour was also observed.

To ascertain whether the Cu^{+2} exchanged sieve (21.7% exchange) might be rendered more catalytically active through water co-catalysis, some experiments were also performed with this sieve along with increasing amounts of added water. Results in *Figure 2* indicate that the activity of the sieve is consistently depressed with increasing water concentration. Interestingly, with unmodified SK-500 sieve or with H-mordenite and H-faujasite as polymerization (NVC, IBVE and n-BVE) catalysts water has been observed[2,3,8] to exhibit typical co-catalystic effects up to a certain optimum concentration.

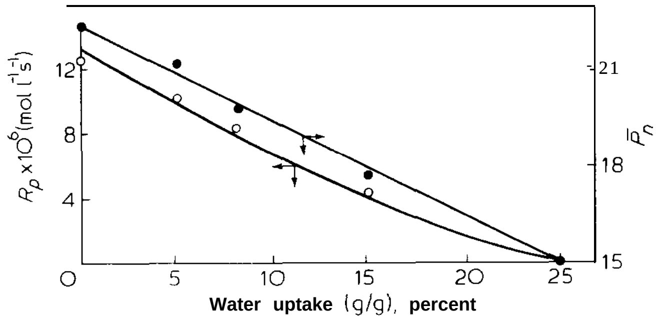

Figure 2 **Effect of water content of the zeolite on R_p and $\bar{P}_n$** *for* **the polymerization of NVC by Cu^{+2}– 13X zeolite in benzene at 25°C. [NVC] = 0.1 mol l^{-1}; weight of Cu^{+2}– 13X = 0.150 g; Cu^{+2} content in the 13X = 2 1.7% by weight**

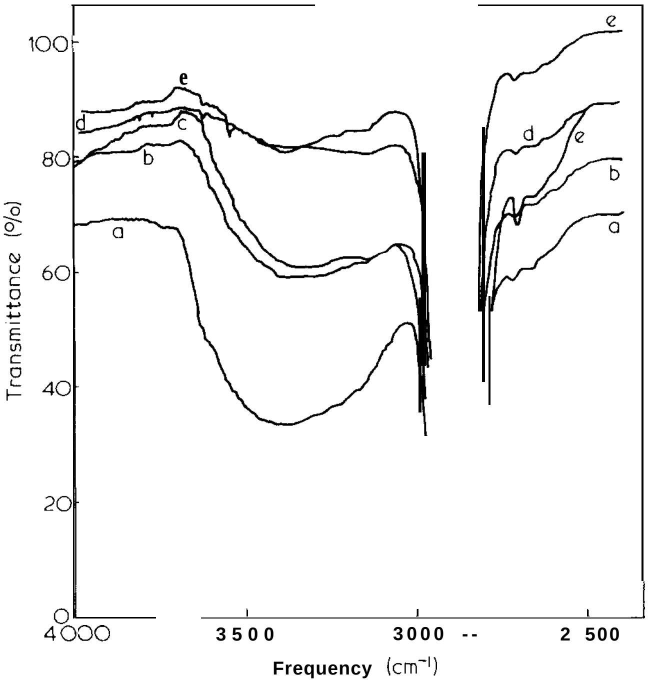

Figure 3 Infra-red spectra of Cu^{+2}– 13X after activation at 500°C for 2 h. % Cu^{+2} content by weight: (A) zero; (B) 10.86; (C) 21.72 with 5% water; (D) 21.72; (E) 14.12

In this instance the gradual decrease of the rate with added water may be consistent with the fact that hydrated Cu^{+2} ions are very stable[6] and are therefore reluctant to form fresh Bronsted centres through the dissociation

$$Cu(OH_2)^{+2} = Cu(OH)^+ + H^+$$

so that the rate should fall. Significantly, the zeolite colour changes to light blue (at room temperature) following the addition of water, then to green (100°C) and finally becomes brown at 500°C. This latter change is reversible and the colour turns to light blue after rehydration. The i.r. spectrum *(Figure* 3) of Cu^{+2}-13X sieve containing 5% water reveals the reappearance of the broad band 3700–3000 cm^{-1} which gradually disappeared with increasing Cu^{+2} uptake, a water bending vibration at 1625 cm-' and a sharp OH chelating frequency at 2700 cm ^{1} In addition to the above mechanism, it is also possible that excess amounts of water block the intracrystalline sites* and the monomer–zeolite interfaces and thus lower the rate further.

The parallel fall in $\bar{P}_n$ implies that termination and transfer reactions of growing chains with water are also important under these conditions.

In conclusion, exchange of 13X sieve with Cu^{+2} enhances the rate and degree of polymerization of NVC and IBVE up to a certain exchange limit.

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