STABILITY AND REGENERABILITY OF COPPER-EXCHANGED ZEOLITE CATALYSTS FOR THE CYCLODIMERIZATION OF BUTADIENE

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A study has been made of the stability and regenerability of monovalent copper-containing zeolite Y catalysts for the selective cyclodimerization of butadiene to 4-vinylcyclohexene. It is shown that the stability of catalysts prepared by reduction of divalent copper-exchanged zeolites can be considerably enhanced when ammonia is used as the reducing agent and the activation conditions are chosen such that ammonia remains selectively chemisorbed on acidic sites. In addition such catalysts, in contrast to those prepared by direct exchange with monovalent copper, are fully regenerable.

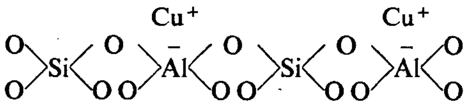
Introduction

Copper-exchanged zeolites, particularly those having the faujasite structure (*i.e.* zeolites X and Y), have been shown to be highly active and selective catalysts for the cyclodimerization of butadiene to vinylcyclohexene [1—3]. In the active form of the catalyst the copper is in the monovalent state. The active form can be prepared in the following two ways:

(1) by direct ion exchange of the parent sodium form of the zeolite with a solution containing monovalent copper in the absence of air (denoted Cu^+-zeolite catalysts);

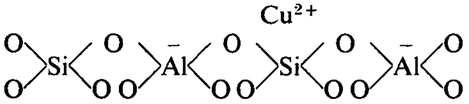
(2) by ion exchange of the parent zeolite with a solution containing divalent copper, followed by mild *in situ* reduction to the monovalent form (denoted Cu^{2+}-zeolite catalysts).

In the first case the stoichiometric structure is quite simple, with each Cu^+ ion balancing the negative charge associated with one tetrahedrally coordinated aluminium in the zeolite framework:



However, in the second case, the stoichiometric structure prior to reduction is such that each Cu^{2+} ion balances the negative charges on two framework aluminium ions:

i.e.



Hence, on reduction of divalent copper to the monovalent form a charge imbalance arises between the zeolite framework and the exchangeable cations.

Previous kinetic studies [4] on the reduction of divalent-copper-exchanged zeolites X and Y with mild reducing agents, such as butadiene and ammonia, showed that the rate of reduction was second order in the copper concentration. This suggested the involvement of (divalent) oxide ions in the reduction. A mechanism was therefore proposed according to which, in the presence of zeolitic water (lower dehydration temperatures), Brönsted acid sites are formed.

In the present paper it is shown that this difference in stoichiometric structure is particularly important with regard to stability and regenerability of the catalysts used for the butadiene cyclodimerization reaction.

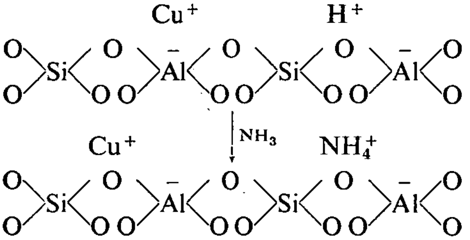
Results and discussion

Catalyst stability

Although monovalent copper-containing zeolites are highly selective catalysts for the dimerization of butadiene to 4-vinylcyclohexene, catalyst stability is often quite low. The deactivation is almost certainly caused by the deposition of polymers of butadiene on the surface of the catalyst.

In agreement with previous observations [3] we have also found that catalysts prepared by direct exchange with monovalent copper ions are more stable than those prepared by reduction (in this case using butadiene feed as reducing agent) of divalent-copper-exchanged zeolites (see Fig. 1). This is readily understood in terms of the differences in stoichiometry which, as previously discussed, lead to the formation of Brönsted acid sites in the latter case. Thus the surface acidity introduced into reduced Cu^{2+}-zeolite Y leads to a higher rate of deposition of butadiene polymer on the surface of the catalyst and hence a faster rate of deactivation.

However, as previously demonstrated [3, 4], ammonia is also a very effective reducing agent for the preparation of monovalent copper from Cu^{2+}-zeolites. In this case excess ammonia could conceivably react with the acid sites generated during reduction to form ammonium ions which should be stable under the rather mild reaction conditions (90—100 °C), *i.e.*



This points to a possible method of neutralizing the surface acidity and thereby increasing the catalyst stability. However, this requires activation (nitrogen stripping) conditions such that excess ammonia is removed from the dimerization sites (*i.e.* monovalent copper) but remains chemisorbed on the acid sites. In general, the decomposition of ammonium ions on zeolites takes place at temperatures above 300 °C [5], indicating that, with the correct choice of catalyst activation temperature, ammonia neutralization of acid sites should be feasible.

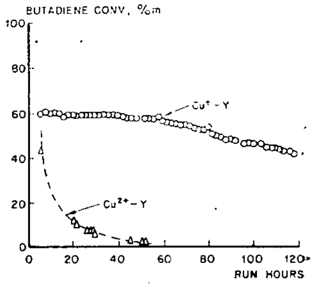


Fig. 1. Comparison of catalytic stabilities of Cu^+-Y (butadiene-reduced) and Cu^{2+}-Y catalysts, N_2 activation 300 °C, T = 100 °C, P = 25 bar, LHSV = 1 $1.1^{-1} \cdot h^{-1}$.

The results obtained by reducing a Cu^{2+}-Y zeolite catalyst with ammonia at 200 °C (6 h at 3 Nl/h) and then stripping it with N_2 (16 h at 3 Nl/h) at temperatures of 200 and 300 °C are shown in Fig. 2a. Clearly, the results fully confirm predictions in that the lower activation temperatures results in a catalyst with a lower initial activity but a considerably higher stability (*i.e.* 0.06 and 0.45 conversion percentage points loss per hour for 200 and 300 °C, respectively). In fact, the stability following activation at 200 °C is now comparable with that attained using Cu^+-Y catalysts (see Fig. 1).

Further evidence in support of the above conclusions is obtained from thermogravimetric and mass spectrometric data (see Fig. 3a) of a spent Cu^{2+}-Y catalyst. Mass spectrometric analysis of effluent gas during programmed heating in a nitrogen atmosphere clearly indicates that residual ammonia is present on the spent catalyst and is only removed at 450 °C. Such a temperature is consistent with the decomposition of ammonia bound to strong acid sites [5].

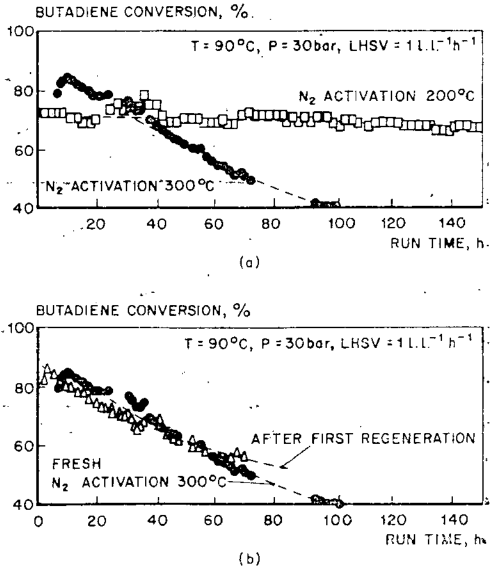
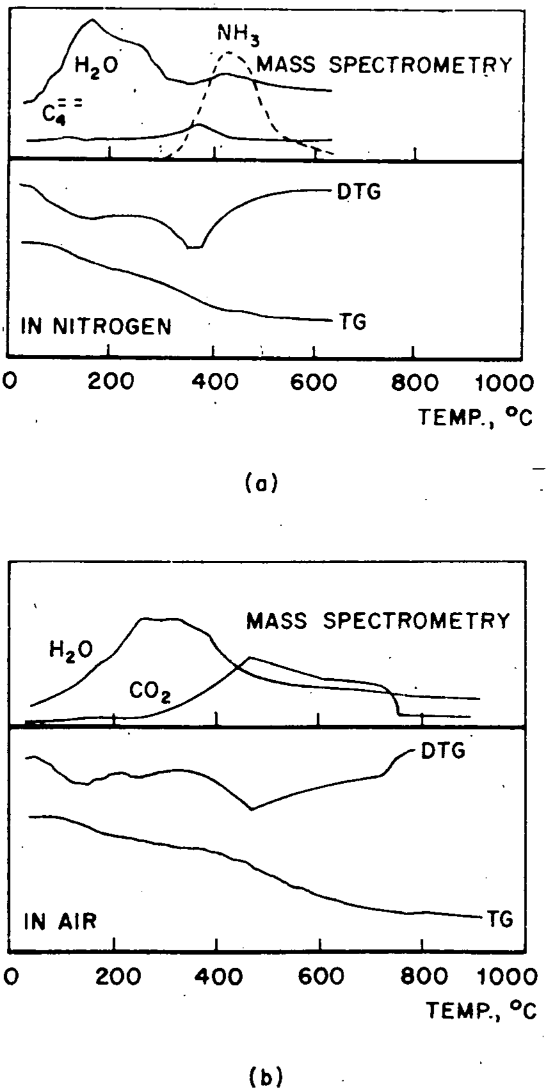


Fig. 2. Butadiene dimerization over Cu^{2+}-Y catalyst

Catalyst regenerability

In the previous section it has been shown that by the appropriate choice of reducing agent and activation conditions Cu^{2+}-Y catalysts can be prepared which are comparable in stability to those prepared by direct exchange with monovalent copper *i.e.* Cu^+-Y catalysts. However, even at this level of stability (*i.e.* approximately 0.05 conversion percentage points loss per hour) long-term continuous operation will necessitate periodic restoration of the original catalytic activity. Since rejuvenation of the catalyst would be preferable to replacement, we have investigated the relative merits of Cu^+-Y and Cu^{2+}-Y catalysts with regard to regenerability. Powder X-ray diffraction studies showed that on heating Cu^+-Y in air, above 330 °C, CuO is formed irreversibly as a separate crystalline phase. This is not the case for Cu^{2+}-Y which displays good thermal stability up to 800 °C and is therefore a promising candidate



(a)

(b)

Fig. 3. Thermogravimetry (TG) and differential thermogravimetry (DTG) (with effluent gas mass spectrometry) of spent Cu^{2+}-Y catalyst

for regeneration. Thermal analysis data, obtained in air, for a spent Cu^{2+}-Y catalyst (see Fig. 3b) show that even under continuous temperature programming all carbonaceous residues are removed at 760 °C and that the zeolite structure remains intact up to 850 °C (consistent with the X-ray data).

A polymer burn-off was accordingly carried out on a spent Cu^{2+}-Y catalyst which, over a 100 h operating period, had declined in activity from 85 to 40% butadiene conversion (see Fig. 2b). As shown in Fig. 2b, the initial activity and the rate of decline in activity of the regenerated catalyst are, within experimental error, the same as those of the fresh catalyst.

References

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