JOURNAL OF CATALYSIS 61, 485–492 (1980)

Copper-Exchanged Zeolite Catalysts for the Cyclodimerization of Butadiene

I. Catalyst Stability and Regenerability

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Received January 16, 1978; revised October 24, 1978

The stability and regenerability of monovalent copper-containing zeolite-Y catalysts for the selective cyclodimerization of butadiene to 4-vinylcyclohexene have been studied. 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 acid sites. In addition, this type of catalyst is shown to be thermally stable up to 850°C and is therefore able to withstand a regeneration procedure which involves a polymer burnoff at 550°C. By contrast, catalysts prepared by direct exchange with monovalent copper form cupric oxide irreversibly when heated above 330°C.

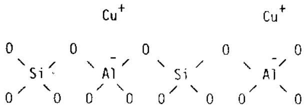
I. INTRODUCTION

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:

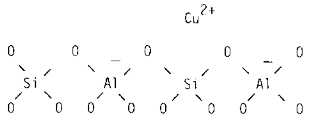
(1) by direct ion exchange of the parent sodium form of the zeolite with a solution containing monovalent copper in the absence of air (denoted Cu^+-zeolite catalyst);

(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 aluminum 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 aluminum ions;



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

Previous mechanistic (*4*) and kinetic studies (*5*) on the reduction of divalent-copper-exchanged zeolites X and Y with

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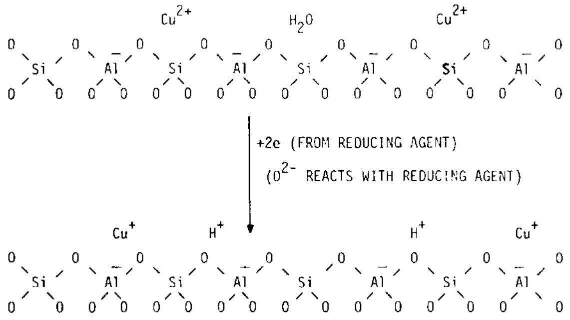
mild reducing agents, such as butadiene and ammonia, showed that the rate of reduction was second order in the copper concentration. This suggested the involvement of (divalent) oxide ions in the reduction. Also, the rate of reduction was found to be markedly dependent on the dehydration temperature adopted prior to reduction. A mechanism was therefore proposed which, in the presence of zeolitic water (lower dehydration temperatures) or protons from the reducing agent, leads to the formation of Brønsted acid sites.



This marked difference in stoichiometric structure might be expected to play an important role in the catalytic behavior of these compounds. In the present paper this is indeed shown to be the case, particularly with regard to stability and regenerability of the catalysts applied to the butadiene cyclodimerization reaction. The following paper (Part II) deals with catalyst structure and the role of the catalyst support.

II. EXPERIMENTAL

A. Catalyst Preparation

(*i*) *Direct monovalent-copper-exchanged zeolite* (Cu^+-*Y*). Monovalent-copper-exchanged zeolites were prepared according to the method of Ref. (*3*). In order to exclude oxygen rigorously from the preparations the apparatus depicted in Fig. 1 was used. The apparatus was first assembled without the horizontal tube A and purged with nitrogen, while a portion of sodium zeolite Y was dehydrated in tube A, under a nitrogen stream at 300°C. Dried cuprous iodide was introduced into the round-bottom flask, tube A fitted without interrupting the nitrogen stream, and ammonia distilled from a cylinder into the flask. By rotation about the joint indicated, tube A could be raised so as to introduce the zeolite into the cuprous iodide solution. After stirring for 5 h to allow the exchange to take place, the liquid ammonia was withdrawn through the filter with mild suction while a slight positive nitrogen pressure was maintained in the exchange vessel, after which the catalyst was washed by condensing more ammonia into the flask, stirring, and filtering again, and finally dried in a stream of nitrogen. Analysis of the catalyst showed it to contain 6.6% (w/w) copper, which for monovalent copper corresponds to about 28% exchange of sodium ions. The iodine content of the catalyst was found to be 0.07% (w/w), which corresponds to an I/Cu ratio of 0.005, indicating that the degree of salt occlusion is very small.

The source of the zeolite Y was Union Carbide SK 40 (powder, binder free) which was pressed into pellets and crushed to mesh size 14–35, suitable for testing in the microreactor.

(*ii*) *Divalent-copper-exchanged zeolite* (Cu^{2+}-*Y*). Divalent-copper-exchanged zeolites were prepared by means of a simple exchange reaction between the parent (sodium form) of zeolite Y (as above) and an aqueous solution containing cupric acetate (0.36 *M*). The exchange reaction was repeated five times with fresh solution and intermediate washing steps. The final catalyst was dried at 120°C, then pressed into pellets and crushed as above. Analysis showed that the final catalyst contained 8.4% copper, which for divalent copper is equivalent to 75% exchange of the parent sodium ions.

B. Catalyst Performance Evaluation

A fixed-bed microreactor (316 stainless steel, 330 mm × 10 mm i.d., fitted with

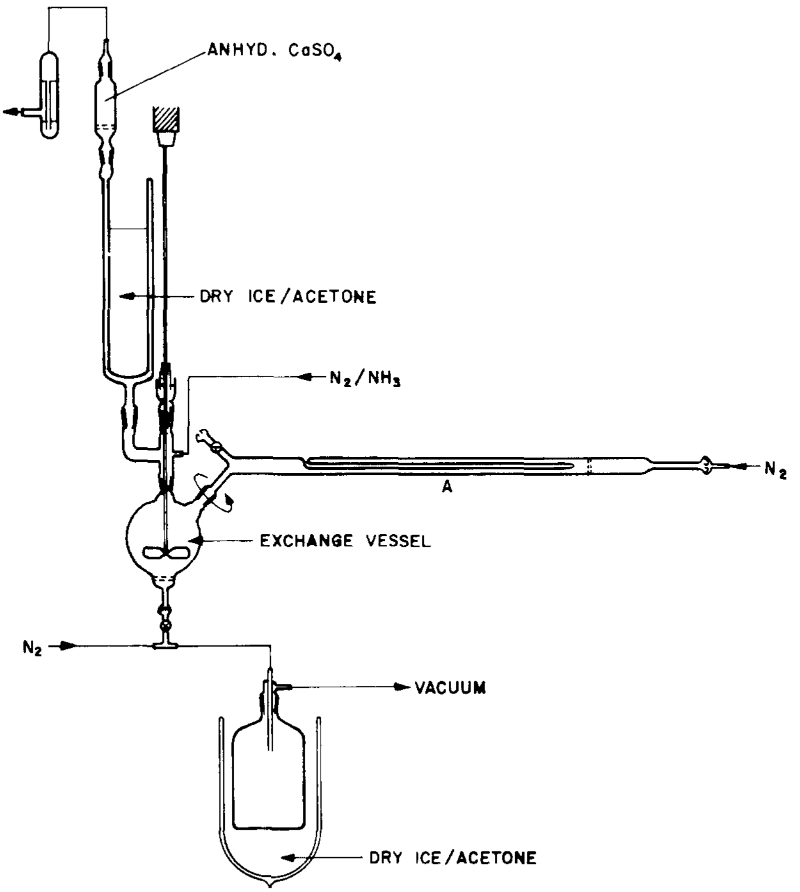


FIG. 1. Apparatus for ion exchange in liquid ammonia solvent.

a 5-mm central thermowell) was employed for catalyst testing. Portions of catalyst (17 ml), with mesh size 14–35, were placed in the reactor (in a nitrogen-filled, polyethylene glove bag in the case of Cu$^+$-Y catalysts). The feed was supplied, in upflow operation, at a pressure sufficient to maintain it in the liquid phase (25 bar). Before use the butadiene was distilled to free it from traces of gum polymer or inhibitor, which might poison the catalysts. The normal catalyst activation and operation conditions were as follows:

Catalyst activation	100–300°C for 16 h in nitrogen stream (2 nl h^{-1})
Operating temperature	95°C
Total pressure	25 bar
LHSV	1 liter liter^{-1} h^{-1}
Feed	Butadiene, 40% (v/v) in *n*-pentane

The reactor effluent was automatically sampled and analyzed at 2-h intervals using two glc columns. The butadiene and pentane were determined by means of an 18-m column of 30% dimethylsulfolane (DMS) on Sil-o-Cel at 30°C. The C$_8$ products were analyzed using a 24-ft column of 5% Carbowax 5000 on Chromosorb G, AWDMCS, 60–80 mesh, at 80°C. The marker was the pentane solvent.

The selectivity of 4-vinylcyclohexene

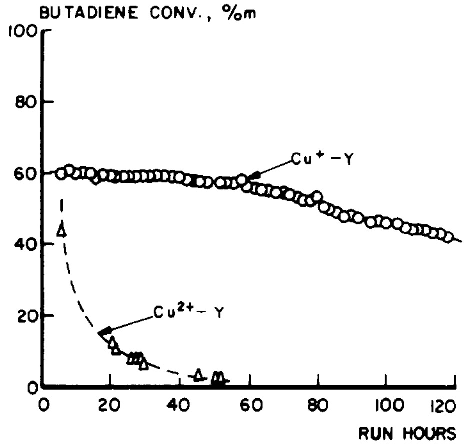


FIG. 2. Comparison of stabilities of Cu^+-Y (butadiene-reduced) and Cu^{2+}-Y catalysts. N_2 activation 300°C; T = 100°C; P = 25 bar; LHSV = 1 liter $liter^{-1}$ h^{-1}.

obtained with these catalysts was practically quantitative, by-products and heavy ends amounting to not more than 1%.

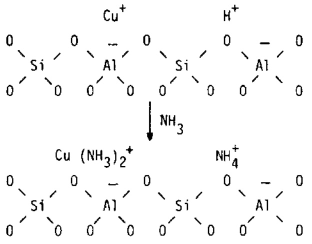
III. RESULTS AND DISCUSSION

A. 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. 2). This is readily understood in terms in the differences in stoichiometry which, as previously discussed, lead to the formation of Brønsted and/or Lewis 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*, *5*), 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 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 (*6*), indicating that, with the correct choice of catalyst activation temperature, ammonia neutralization of acid sites should be feasible.

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. 3. Clearly, the results fully confirm predictions in that the lower activation temperature results in a catalyst with a lower

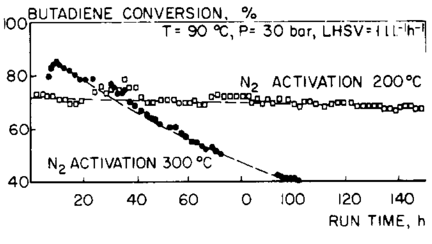


FIG. 3. Butadiene dimerization over Cu^{2+}-Y catalyst.

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. 2).

Further evidence in support of the above conclusions is obtained from thermogravimetric and mass spectrometric data (see Fig. 4) of a spent Cu^{2+}-Y catalyst. Mass spectrometric analysis of the 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 (*6*). Quantitative analysis of ammonia on Cu^{2+}-Y catalyst after activation at 200 and 300°C gave N/Cu ratios of 1.69 and 0.60, respectively. In the ideal situation each Brønsted acid site would be just neutralized by an ammonia molecule leading to an N/Cu ratio of unity. The observed values bracket this ideal value, indicating that some ammonia also probably remains adsorbed on Cu^+ ions following activation at 200°C (consistent with the slightly lower initial activity), while ammonia is probably removed from Brønsted acid sites following activation at 300°C (consistent with the lower catalyst stability). The residual ammonia present even after activation at 300°C most probably accounts for the higher stability of this catalyst compared to the comparable butadiene-reduced catalyst which is activated at the same temperature (cf. Figs. 2 and 3).

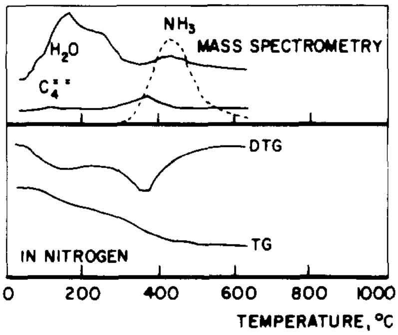


FIG. 4. Thermogravimetry (TG) and differential thermogravimetry (DTG) (with effluent gas mass spectrometry) of spent Cu^{2+}-Y catalyst.

B. 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. A regeneration step would involve a high-temperature polymer burn-off; it therefore seemed worthwhile to study the thermal stabilities of the catalysts.

Figure 5 shows moving-film Guinier diffractograms of a sample of Cu^+-Y catalyst as measured at various temperatures in air. These show clearly that at about 330°C, CuO is formed as a separate crystalline phase. The concentration does not increase above 400°C and remains constant until the zeolite structure collapses at 750°C, after which a further increase in the CuO concentration is observed. Above 800°C the CuO crystal structure also collapses. Quantitative measurements have been carried out which show that the amount of CuO formed at temperatures between 400 and 750°C (3.2% w/w) is equivalent to half the amount of copper present in the zeolite. After collapse of the zeolite structure all the copper is found in the CuO phase.

In contrast to the above, no CuO for-

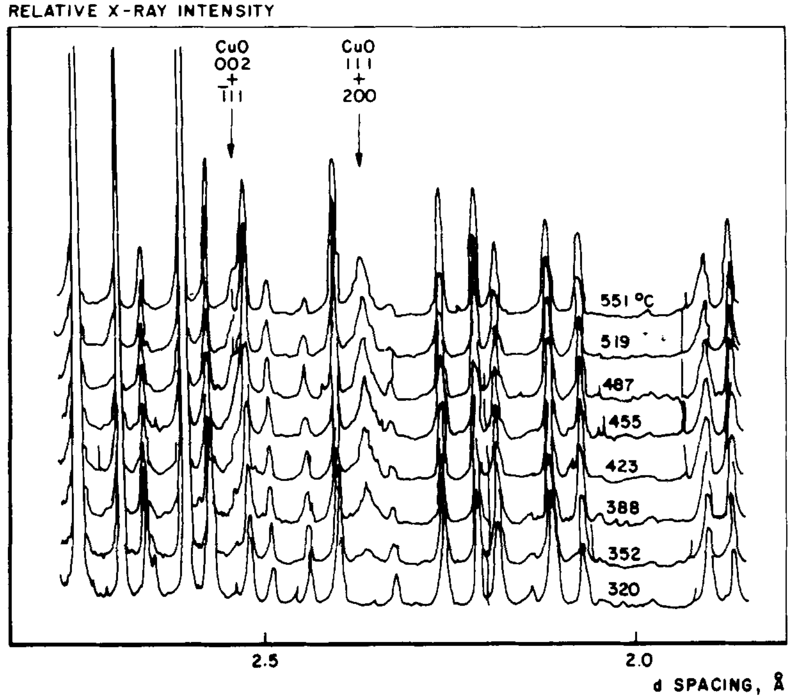
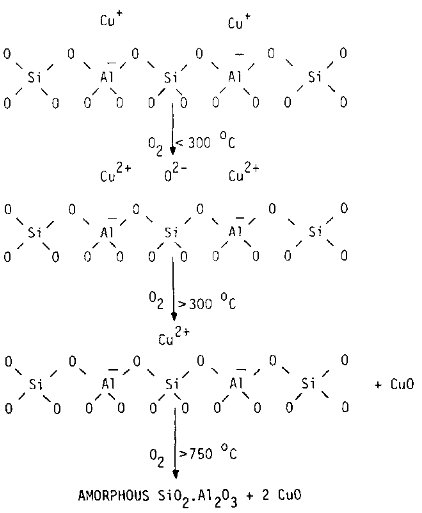


FIG. 5. Moving-film Guinier diffractograms of Cu^+-Y at various temperatures in air. (1 Å = 10^{-1} nm.).

mation was detected in a sample of Cu^{2+}-Y zeolite (with approximately the same Cu content) on heating in air until the zeolite structure collapsed at ~800°C. This confirms that CuO formation at higher temperatures is specific for the Cu^+-Y system.

A possible explanation for the observed phenomena is that in the low-temperature oxidized form of Cu^+-Y, Cu^{2+} and O^{2-} ions are formed in the zeolite pores, which on heating migrate to the external surface of the zeolite and agglomerate to form discrete CuO crystals (measured average diameter from X-ray line broadening is approximately 20 nm). This may be visualized as follows:



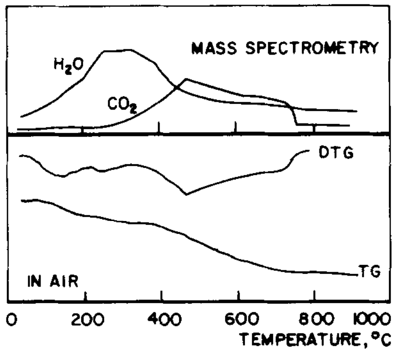


FIG. 6. Thermogravimetry (TG) and differential thermogravimetry (DTG) (with effluent gas mass spectrometry) of spent Cu^{2+}-Y catalyst.

Clearly, these results indicate that, due to the irreversible formation of CuO above 330°C, Cu^{+}-Y zeolites will not be regenerable.

However, as previously mentioned, Cu^{2+}-Y zeolite displays good thermal stability and is therefore a promising candidate for regeneration. Thermal analysis data, obtained in air, for a spent Cu^{2+}-Y catalyst (see Fig. 6) 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). Further, the shape of the CO_2 evolution curve indicates that carbon burn-off should be effective at about 600°C.

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. 7). (This catalyst had been deliberately activated at 300°C so as to give a higher deactivation rate, suitable for comparison of the new with the regenerated catalyst.) The oxidation was carried out by means of an air/nitrogen mixture (10 nl/h) in which the oxygen concentration was slowly increased from 0 to 2.5%. The temperature was also gradually increased to 550°C and maintained at this level until the CO_2 production became negligible. The catalyst was then cooled and reduced back to the monovalent copper form with ammonia as previously described. This was followed by an activation treatment under nitrogen at 300°C. As shown in Fig. 7, the initial activity and rate of decline in activity of the regenerated catalyst are, within experimental error, the same as those of the fresh catalyst. After five regeneration cycles some catalyst deterioration was in fact observed (20% loss in initial activity). This was shown to be accompanied by a partial loss of zeolite crystallinity. Since the structure is thermally stable to 850°C, hot spots occurring during the burn-off operation are thought to be responsible for this partial structure breakdown.

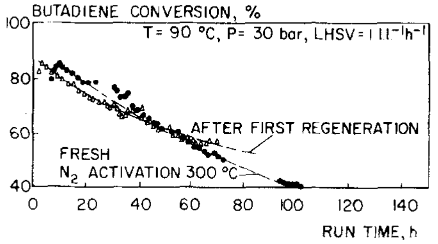


FIG. 7. Butadiene dimerization over Cu^{2+}-Y catalyst.

IV. CONCLUSIONS

It has been shown that differences in stoichiometric structure between Cu^{+}-Y and Cu^{2+}-Y zeolites lead to substantial differences in their catalytic properties with regard to the cyclodimerization of butadiene to 4-vinylcyclohexene. We have confirmed that Cu^{2+}-Y catalysts reduced with butadiene are deactivated at a considerably faster rate than Cu^{+}-Y catalysts (*2*).

The results of the present study lead to the following conclusions:

(1) The marked difference between the catalytic stabilities of Cu^{+}-Y and Cu^{2+}-Y is probably related to a faster rate of deposition of butadiene polymer on the surface of the Cu^{2+}-Y catalyst.

(2) Acid sites formed during the reduction of Cu^{2+}-Y to the catalytically active monovalent form are responsible for the faster rate of polymer deposition.

(3) Reduction of Cu^{2+}-Y with ammonia yields significantly more stable catalysts than reduction by butadiene.

(4) Ammonia-reduced Cu^{2+}-Y catalysts may be further stabilized by the appropriate choice of activation conditions such that ammonia remains bound to the acid sites formed during the reduction step.

(5) On heating Cu^{+}-Y in air above 330°C half of the copper ions, originally present in ion-exchangeable sites, migrate to the outer surfaces of the zeolite particles

to form a separate phase of discrete crystalline particles of CuO. On collapse of the framework structure at 750°C, the remaining zeolitic copper ions combine to form a CuO phase.

(7) CuO formation does not occur on heating Cu^{2+}-Y, even after structure breakdown at 800°C.

(8) The thermal stability of Cu^{2+}-Y is such that, following a polymer burn-off (550°C) and reduction cycle, the original catalytic activity and stability are restored, i.e., the catalyst is completely regenerable.

ACKNOWLEDGMENTS

The assistance of the following co-workers is gratefully acknowledged: Messrs. H. B. M. Wolters and C. T. J. Mensch for the X-ray diffraction measurements; Mr. P. Rietveld for experimental work with the microflow reactor; and Mr. J. van Amstel for the thermal analyses.

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