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# NOTE

# The Influence of Zeolitic Water on the Rate of Butadiene Dimerization

Zeolites find widespread usage as catalysts for a variety of chemical transformations. Frequently, the catalytically active agent is a transition metal ion located at an exchange site in contact with the zeolitic surface. Although the extraframework cation positions and relative populations can often be determined by spectroscopic methods, the influence of cation siting and adsorbed reactant induced migration under reaction conditions is less well understood. This note describes the role which water exerts on the activity of copper-exchanged zeolite Y for the dimerization of butadiene to 4-vinylcyclohexene (4-VCH).

During the dehydration of zeolite Y, metal ions initially located within the supercages migrate into inaccessible sites within the hexagonal prisms and sodalite cages (1). This process is reversible since upon exposure to water the ions migrate back to supercage sites (2). A variety of adsorbates other than water are known to induce ion migration within the zeolite lattice (3). Keane and co-workers (4) has previously remarked upon the "considerable consequences during catalysis" of adsorbate induced cation migrations. Maxwell and Drent (5) have shown that the presence of small quantities of residual zeolite water greatly enhanced the rate of reduction of Cu(II) to Cu(I) by ammonia or butadiene in an ion-exchanged X or Y zeolite. Part of this high rate of reduction may be due to ion migration and siting of the hydrated Cu(II) ions. Few previous studies have knowingly adjusted the hydration level of a zeolite catalyst as a method to produce optimum activity via cation siting. The rate of butadiene dimerization to 4-VCH over copper(I) zeolite Y is observed to be a sensitive function of the catalyst water content.

The dimerization rate constants were determined in a 300-ml stainless steel Parr reactor which was loaded in a nitrogen glove box. A typical procedure was as follows: the bomb was charged with 86.7 g of ethyl benzene containing <80 ppm water. The annular basket was loaded with the catalyst pellets (3.95 g of dry zeolite) and suspended between the thermowell and sampling tube. The reactor was sealed and degassed three times by filling with nitrogen to 440 psig and venting to atmospheric pressure. Liquid butadiene, 28.9 g (0.535 mole), was loaded into the reactor from a weigh cell. The bomb was repressurized to 440 psig with nitrogen and the temperature brought to 100°C. Samples were taken over time by injecting the contents of a sample loop into 15 ml of hexane containing a known amount of toluene as an internal standard. The rate constant (in $\mathrm{hr}^{-1}$ $\mathrm{mole}^{-1}$/3.95 g of dry zeolite) was determined for the second-order reaction by plotting 1/(mole butadiene) vs time. The slope of the straight line is the rate constant. It was found to be more accurate to determine the remaining butadiene concentration by measuring the 4-VCH formed and subtracting twice the number of moles of 4-VCH formed from the moles of butadiene initially charged. All of the determinations are linear with a correlation coefficient >0.98. The standard deviation of any rate constant determination was ±0.01 ($\mathrm{hr}^{-1}$ $\mathrm{mole}^{-1}$). All runs were made with exactly the same amount of dry zeolite which had a nominal copper content of 6–10%. While the turnover numbers for the catalysts based on total copper have been calculated—catalyst #1, 108 mole butadiene/mole copper; catalyst #2, 125 mole butadiene/mole copper; and catalyst #3, 121 mole butadiene/mole copper—these may be misleading since it was not possible to determine the amount of catalytically active copper in the catalyst.

The dimerization of butadiene to 4-VCH on Cu(I) containing zeolite catalysts was originally reported by Reimlinger *et al.* (6). Other Cu(I) containing materials were also found to catalyze this reaction (7). In none of these early works was a relationship made between the butadiene dimerization activity and the hydration level of the catalyst. During the course of our studies on Cu-exchanged Na zeolite Y (CuNaY) catalysts, a strong correlation was observed between the butadiene cyclodimerization rate and the residual water content in the reduced and catalytically active zeolite, Fig. 1. The observed influence is dramatic with an optimum hydration level being quite apparent within the range of 2–20 wt% water, especially for catalysts #2 and 3. The importance of the hydration level has also been observed for the cyclodimerization rates with CuNaY catalysts produced by impregnation with copper salts (8).

Since the active cyclodimerization species is Cu(I), one might surmise that a catalyst of maximum activity

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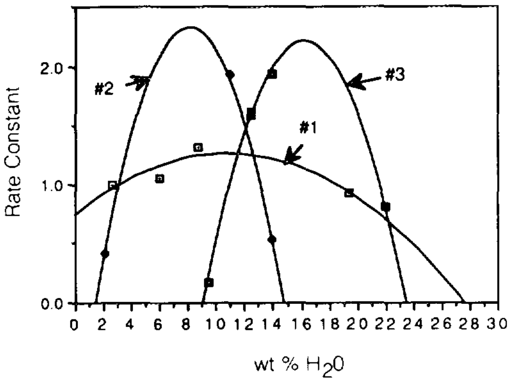

FIG. 1. Amount of $H_2O$ vs rate constant. Catalyst #1. Ca CuY-54 zeolite. Before ammonia reduction this solid had an elemental composition of 2.21 wt% sodium, 7.74 wt% aluminum, 23.2 wt% silicon, 2.35 wt% calcium, and 3.61 wt% copper (4.7% on a dry basis) as determined by X-ray fluorescence, 15 wt% silica binder (100°C). Catalyst #2. Cu, liquid ammonia-Y-54 zeolite, 7.2 wt% copper determined after ammonia was stripped, 15% silica binder (100°C). Catalyst #3. Cu(II) ion exchanged, 8.24 wt% copper determined before reduction with hydrazine hydrate Y-52 powder (115°C). A second degree polynomial appears to be a reasonable expression for fitting the catalytic data, although catalyst #1 could be as adequately defined by a straight line.

could be prepared by a direct nonaqueous (liquid ammonia) ion exchange of Cu(I) into the host zeolite (catalysts #2). The anhydrous pseudo unit cell for a Na zeolite Y is $Na_{54}[Si_{138}Al_{54}O_{384}]$ which contains 16 site I positions located at the center of the hexagonal prisms. Cations located at S(I) are inaccessible to the majority of adsorbates since they are buried at a sixfold coordination site. After introduction of Cu(I) from liquid ammonia/CuI, the resultant solid contains 7.2 wt% Cu on a dry basis which translates to 17 Cu(I) and 37 $Na^+$ ions per unit cell (see Table 1). Upon heating to 350°C, a material was prepared that had a high cyclodimerization activity at optimal hydration levels, catalyst #2 in Fig. 1. Catalyst #2 was hydrated by placing an open vial of water in close proximity to the 350°C dried material in a glove box. The catalyst was removed from the glove box in a sealed container for occasional weighing until a known amount of water had been adsorbed. The 350°C heating appears necessary for removal of the excess ammonia and concurrent copper ion migration from the supercages into the inaccessible S(I) hexagonal prism and S(I') sodalite cage sites. Stripping at lower temperatures produces low activity catalysts presumably due to incomplete destruction of Cu(I) ammonia complexes which are resistant to complexation and reaction with butadiene.

The most common method to prepare intrazeolite Cu(I) is by initially introducing Cu(II) into the zeolite by ion exchange followed by reduction to Cu(I) by either gas or aqueous phase reductants. Reduction via gaseous ammonia generates an ammonium site to maintain charge balance on the zeolite for each Cu(II) ion reduced. During high temperature stripping of residual ammonia, the ammonium site becomes a Brønsted acid site. Maxwell *et al.* (9) have indicated the protonic acid sites causes deposition of butadiene polymer.

Catalyst preparations were made via normal ion exchange procedures. The calcium-containing material (catalyst #1) was first calcium exchanged, followed by a 350°C calcination before the exchange with copper occurred. Reduction of this catalyst was done by gas phase ammonia followed by a 250°C strip of excess ammonia. Catalyst #3, the other Cu(II) ion exchanged catalyst, was reduced in a basic aqueous slurry with complete consumption of slightly less than a stoichiometric amount of hydrazine and required no stripping. Catalyst #3, also exhibits activity sensitive to the hydration level, similar to the Cu(I)-exchanged material, except that the maximum activity is found at a higher degree of hydration. The nearly identical peak activities are misleading for these two catalysts as the dimerization reaction was run at different temperatures. The difference in absolute activity of the catalysts is probably closely related to the copper loading and to the effectiveness of generating the active metal species by different reduction techniques. More important is the relationship between the water content of the catalyst and the associated rate constant. The cocation can have a profound influence upon the catalytic behavior. The insensitivity of the activity versus hydration level for CuCaNaY, catalyst #1 in Fig. 1, is in stark contrast to the behavior in the absence of calcium.

The sensitivity of the CuNaY materials, catalysts #2 and 3, to the hydration level appears to be related to the dynamic nature of the siting of the Cu(I) ions. When ion-exchanged Y zeolites are initially prepared with Cu(II) and dehydrated prior to reduction, the majority of the Cu(II) ions locate at the inaccessible sites S(I) and S(I')

TABLE 1

Cation Population of a Unit Cell ($Na_{54}[Si_{138}Al_{54}O_{384}]$ of Zeolite Y (dehydrated) with a Si/Al = 2.6

| Catalyst | #$Cu^{++}$[a] | #$Na^+$ | #$Ca^{++}$ |
|---|---|---|---|
| #1, CuCaNa | 10 | 14 | 10 |
| #2, CuNa, $NH_3$ liq. | 17[b] | 37 | NA |
| #3, CuNa, hydrazine | 15 | 24 | NA |

[a] These populations are per Unit Cell (UC). UC contains 16 SI, 32 SI', and 32 SII'. There exist many supercage sites including SII, SIII, etc. (10).

[b] Copper in this catalyst is as $Cu^+$.

(10). Upon reduction of Cu(II) to Cu(I) in materials with fewer than ca. 16 Cu/UC followed by subsequent drying to low hydration levels, the Cu(I) ions also locate to inaccessible sites (11). Exposure of the "dry" Cu(I) materials to butadiene produces a very low cyclodimerization rate since the active sites are inaccessible to butadiene which is unable to enter the sodalite cages. Strome has previously observed that ethylene is not able to induce a migration of Cu(I) from inaccessible sites into the supercage while adsorbates such as carbon monoxide can induce cation migrations (11). The interaction of butadiene with Cu(I) is similar to that of ethylene and is not strong enough to enable a migration of the cation to accessible supercage sites. Water is not only small enough to gain access into the sodalite cage via the 6-ring windows but its interaction with Cu(I) is much stronger due to its dipole moment. At intermediate hydration levels, water draws the Cu(I) ions into the supercage sites where it is accessible to butadiene. During the course of reaction at these intermediate hydration levels, butadiene coordinates to the Cu(I) ions and dimerizations occurs. As the hydration level is further raised, the Cu(I) ions are still located in the supercages but their coordination shells are now fully occupied by water molecules. Even under reaction conditions, butadiene is not able to gain access to Cu(I) ions and dimerization is either sluggish or, at very high water content, no longer occurs.

The hydration levels at the maximums for catalysts #2 and 3 are significantly different, 8 vs 17 wt%, respectively. This is surprising in light of the fact that both systems contain the same cations at similar exchange levels. The most plausible explanation is that the ratio of Cu(I) to Cu(II) differs between the two samples. Catalyst #2 was prepared by nonaqueous exchange techniques and contains practically all of the copper as Cu(I). Catalyst #3 initially contained all the copper as Cu(II) which was then reduced to Cu(I). This secondary reduction is not fully efficient and some undetermined fraction of copper remains in the divalent oxidation state. The interaction of a Cu(II) ion with water is stronger than the Cu(I) ion water interaction due to the larger permanent charge. At lower hydration levels, adsorbed water will preferentially interact with Cu(II) leaving Cu(I) in the inaccessible sites. Only at higher relative hydration levels will a Cu(I) water interaction cause a migration of the Cu(I) into the supercage. In the absence of Cu(II) ions, catalyst #2, the Cu(I) interacts with initially adsorbed water and migration occurs at lower levels of water.

The addition of calcium to the catalyst system drastically reduces its sensitivity to water, catalyst #1 in Fig. 1. The peak efficiency of this catalyst again appears to be related to the total copper content and degree of reduction. This catalyst contains approximately 10 Cu/UC which is lower than the other two catalyst systems, catalysts #2 and 3. The CuCa system was prepared from a Cu(II) precursor which was subsequently reduced to Cu(I). Although reduction does not occur quantitatively, selective adsorption with carbon monoxide reveals that >90% of the copper exists in the monovalent oxidation state (11). Calcium ions are known to have a high affinity for S(I) sites in dehydrated systems (12). Subsequent ion exchange with Cu(II) does not remove the calcium from the S(I) sites, but causes Cu(II) to be exchanged into the more accessible sites. Upon reduction, these Cu(I) species can readily migrate into the supercage or remain at their present sites. The low sensitivity of the rate of dimerization to water levels is due to the preferential strong interaction of water with the divalent calcium leaving the Cu(I) unhydrated. Only when the water level is high enough that the calcium is fully hydrated does water interact and block Cu(I) from butadiene adsorption.

In conclusion, a strong correlation was observed between the butadiene cyclodimerization rate and the residual water content in the zeolite during reaction. Low cyclodimerization rates were observed in the dehydrated NaCu catalysts, since the active catalyst centers are located at inaccessible sites and butadiene is not a strong enough ligand to enable a migration of the cation to accessible supercage sites. At intermediate hydration levels, water draws the Cu(I) ions into the supercage sites where it is accessible to butadiene and dimerization occurs. At higher hydration levels the Cu(I) coordination shell is fully occupied by water molecules and dimerization no longer occurs. The relative positions of the maximums are most likely related to the amount of Cu(I) present in the catalyst. The addition of calcium to the catalyst system drastically reduces its sensitivity to water. The calcium ions occupy the inaccessible sites and force the copper into butadiene accessible sites, even at very low hydration levels.

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