

Direct amination of olefins: A comparative study over erionite and Y zeolites

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The catalytic activity of erionite and Y zeolites in the H form for amination of ethylene and their pattern of deactivation as the result of coke formation was evaluated at 365°C. H-Y undergoes linear deactivation (0.17% conversion loss per day) with extensive coking. Thermal regeneration is accomplished only at 600°C with partial loss of activity. In contrast, after an initial deactivation period (ca. 37% relative loss with 20 d), conversion and selectivity with H-erionite are almost stable. Catalyst activity is recovered without loss of crystallinity by thermal regeneration at 400°C.

Keywords: H-Y zeolite; H-erionite; ethylene amination; deactivation

INTRODUCTION

The catalytic activity of zeolites derives from specific acid sites located within their intracrystalline cavities. The number and strength of these sites determine catalytic properties of the zeolite, given that reactants, intermediates, and products are capable of diffusion throughout the zeolite structure. One characteristic of small- and medium-pore zeolites is their unique catalytic property of shape-selective catalysis.¹⁻³ Of several possible parameters, pore size and structure have been identified as key factors that determine selectivity, ease of coke formation, and deactivation rates for zeolite catalysts. Rollman and Walsh⁴ have demonstrated that intracrystalline deposition of carbonaceous residues is a shape-selective reaction; this conclusion was recently confirmed by Hammon *et al.*⁵ In addition, Rollman and Walsh investigated the mechanisms of coke formation.⁶⁻⁸ In the presence of olefins, coking can occur via a network of acid-catalyzed reactions that form polycyclic aromatics, immediate precursors of coke. Pore plugging and eventual catalyst deactivation result from coke formation. However, coke formation may be minimized or prevented by steric constraints imposed by the dimensions of the zeolite channels. Such constraints impede, and may prevent, production of cycloparaffins or naphthenes that are coke precursors.⁸

Recently, we described a new route to lower alkylamines via the direct amination of olefins with ammonia in the presence of zeolites.⁹⁻¹² Alumino-, ferro-,

and boro-substituted pentasil zeolites have also been used for olefin amination.¹³⁻¹⁵ Activity for amination with several zeolitic catalysts was related to the number of strong acid sites.^{10,11} Here, we report the effect of zeolite pore size and structure on catalyst deactivation in the olefin amination reaction. Specifically, performance of H-Y, which has a large pore diameter (7.4 Å), and H-erionite, a small pore (3.6 × 5.1 Å) catalyst, are compared.

EXPERIMENTAL

Materials

The hydrogen form of Y-zeolite (LZY-72) and sodium erionite were obtained from Linde Division, Union Carbide. The hydrogen form of erionite was prepared by double ion exchange with 2 M NH₄NO₃ at reflux. Drying at 100°C and calcination at 450°C provided H-Y and H-erionite (sodium content of each < 0.5 atom% after exchange, by XRF). Ammonia and ethylene were obtained from Air Products (Specialty Gas Division) in high purity (> 99.9%).

Equipment

Catalytic aging for ethylene amination was evaluated in an isothermal tubular fixed-bed reactor that contained 10 g of catalyst. The reactor consisted of a 316 stainless-steel tube (40 × 1 cm i.d.) that was mounted inside an ACE[®] oven. To monitor catalyst temperature, the reactor was equipped with a movable, axially mounted thermocouple. Ethylene was introduced as a gas, and its flow was controlled with a Brooks Model 5841 Flow Controller. Ammonia was metered to the reactor as a liquid using an ISCO

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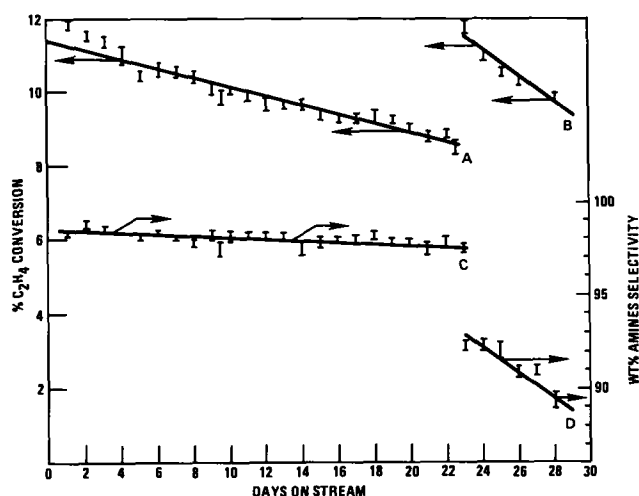


Figure 1 Dependence of conversion of ethylene amination with H-Y catalyst (4/1 ammonia/ethylene, 760 psia, and 1000/h GHSV at STP): (A) at 365°C; (B) at 375°C. Dependence of selectivity of ethylene amination with H-Y catalyst: (C) at 365°C; (D) at 375°C

Model 314 high-pressure syringe pump. Prior to introduction to the reactor, the feeds were vaporized and mixed in a countercurrent mixer maintained at 150°C. Flow rates of ammonia and ethylene were adjusted to obtain a total GHSV of 1000/h (STP) with an ammonia/ethylene molar feed rate of 4/1.

Product analyses were carried out by on-line gas liquid chromatography with a Varian Model 6000 Gas Chromatograph equipped with a 6 foot \times 1/4 inch 20% Ucon on Chromosorb 103 column and a VISTA 402 Chromatography Data System. Product analyses were performed every hour. Identities of major products were confirmed by g.c./MS.

Catalyst aging and regeneration

Typically, the catalyst (12- to 18-mesh particles) was heated in the reactor under a slow flow (30–50 cm³/min) of nitrogen at 100°C and ambient pressure for several hours. The reactor was then heated to 365°C over 2–3 h and maintained at that temperature throughout the testing period. Nitrogen was shut off. Ammonia was introduced, and system pressure set to 760 psia with the back pressure regulator. Ethylene was then introduced to obtain the required ammonia/olefin feed ratio of 4/1. In the evaluation of Y zeolite, reaction temperature was increased to 375°C after the initial 23 d on stream at 365°C.

Catalyst regeneration was accomplished by standard combustion techniques.¹⁶ Used catalyst was heated under a slow flow (30–50 cm³/min) of dry air from ambient temperature to the desired temperature at 5°C/min and maintained at the regeneration temperature for 1 h prior to cooling.

Activity measurements

After activation as described above at 400°C under nitrogen in a DuPont Model 951 Thermogravimetric Analyzer, ammonia was adsorbed onto the catalyst at

20°C. T.p.d. indicated the number of strong acid sites, given as millimoles of ammonia chemisorbed at 200°C per gram of catalyst.

RESULTS AND DISCUSSION

General comments on zeolite performance

Olefin amination is typically carried out at elevated pressure (> 500 psia) with stoichiometric excesses of ammonia (mole ratio ammonia/olefin \geq 2).^{9–15} Anhydrous ammonia is a strong base, which poisons the very strong acid sites of both H-Y and H-erionite and moderates the reactivity of the remaining acid sites under reaction conditions (> 325°C). This effect occurs on introduction of ammonia during reaction start up. It is maintained during the catalyst evaluation period by excess ammonia in the feed. Consequently, the changes in activity observed with both catalysts result from olefin oligomerization/polymerization induced by the (ammonia-moderated) acidic zeolites.

Aging characteristics of H-Y zeolite

Conversion of ethylene over H-Y zeolite was monitored for 23 d. Initial ethylene conversion was 12% at 365°C and 760 psia, as shown in *Figure 1*. Selectivity to ethylamines was > 98 wt%; mono- and diethylamine were obtained in a 7/1 weight ratio. Only traces (< 1.0 wt%) of triethylamine were found owing to steric control of amination by the Y zeolite.¹⁶ Conversion of ethylene decreased linearly with time on stream (see *Figure 1*). After 23 d of continuous operation, conversion was 8%. Selectivity to ethylamines remained high (> 97 wt%); small amounts of ethylene oligomers were obtained as byproducts.

Examination of the used catalyst showed black discoloration as the result of coking. No loss in crystallinity was found by XRD. The linear deactivation of H-Y during ethylene amination resulted from continuous formation of coke in the catalyst pores. Further, the linear loss of activity as a function of operating time indicated that the Y zeolite supercages were fully accessible to the reactants and that coke formation was selectively poisoning the acidic sites. Despite coke deposition, the zeolite retained greater than 60% of its original activity.

The linear loss in catalyst activity was also observed when the aging test was continued at 375°C. Conversion of ethylene initially increased to 12% at 375°C (see *Figure 1*); selectivity to total ethylamines was 92.5 wt%. After 6 d, ethylene conversion decreased to 9%, and selectivity to total ethylamines was less than 90 wt%. Moreover, the rate of deactivation was markedly higher at 375°C (0.5% loss per day) than at 265°C (0.17% loss per day; see *Figure 1*). Owing to use of the same feed composition (mole ratio ammonia/ethylene of 4) at both temperatures, the higher rate of deactivation reflects an increase in coke formation, rather than further acid-site neutralization by ammonia. In all instances, the balance of the reaction products consisted of ethylene oligomers.

Analysis of the used catalyst (XRD) again indicated no loss of crystallinity. Consequently, the increased rate of deactivation is related solely to increased coke formation. Moreover, production of hydrocarbon byproducts at the expense of ethylamines selectivity is a clear indication of catalyst deactivation via coking.

Attempted regeneration of the used H-Y by t.p.d. under nitrogen atmosphere produced no change in activity. This observation further supports the interpretation that catalyst deactivation did not result from neutralization of the acid sites by ammonia.

Regeneration with dry air at 500°C did not significantly change catalyst discoloration. Heating at 600°C was required to remove most of the coke from the catalyst. After regeneration at 600°C, the catalyst was gray. Analysis by XRD revealed a 30% loss of crystallinity. In addition, the activity (9% conversion at 365°C, 1000/h GHSV, 760 psia, based on ethylene) of the regenerated catalyst for ethylene amination was 25% lower than that observed with fresh catalyst.

Aging characteristics of H-erionite

At 365°C and 760 psia, initial ethylene conversion over H-erionite was 18%, as shown by Figure 2. During the first 2 weeks of continued operation, catalyst activity dropped severely. However, during the third week, conversion stabilized at 11–12% and then changed little for the balance of the aging test. After 90 d, olefin conversion was 9–10%. Initial selectivity to ethylamines was 95 wt%; mono- and diethylamine were obtained in at least a 13/1 weight ratio as a result of the relatively small pore structure of H-erionite.¹⁷ Linear ethylene oligomers were the principal byproducts. As catalyst activity declined, selectivity to ethylamines increased to 99 wt%; monoethylamine was obtained in 98 wt% selectivity.

In contrast to H-Y, the initial loss of catalyst activity with H-erionite was related to deactivation of the strong acid sites that were responsible for the relatively low amine selectivity. After the initial drop in

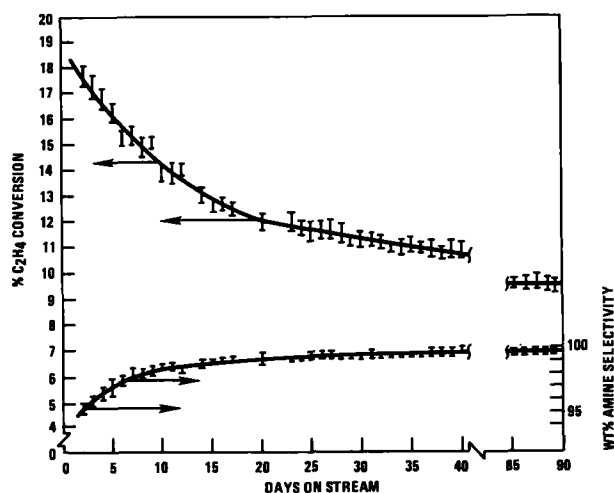


Figure 2 Dependence of conversion and selectivity of ethylene amination with H-erionite catalyst (4/1 ammonia/ethylene, 760 psia, and 1000/h GHSV at STP)

Table 1 Regeneration of H-erionite

	Fresh	Used (90 d)	Heat-treated
Acid sites ^a	1.3	1.0	1.3
Conversion ^b	15.0	9.0	13.5

^a Millimoles of ammonia chemisorbed at 200°C/g of catalyst

^b Based on ethylene

activity, the very high selectivity to monoethylamine (98 wt%) clearly indicates that ethylene amination occurred within the erionite structure. Consequently, we believe that the deactivated acid sites were on the catalyst exterior. Selective erionite deactivation does not result from selective neutralization by ammonia. The pore structure of erionite is sufficiently large to permit diffusion of ammonia throughout the zeolite. Further, such a neutralization would be a rapid process, rather than require more than 2 weeks to reach completion. The loss in catalyst activity and gain in ethylamines selectivity, therefore, reflects catalyst deactivation by coke formation with concomitant loss of strong acid sites that catalyze hydrocarbon conversion and coke formation.

At the end of the life test, no decrease in erionite crystallinity was found by XRD. Activity for ethylene amination was recovered by heating the used catalyst in dry air at 400°C. This treatment removed 3 wt% of carbon from the used catalyst, as judged by t.g.a. After regeneration, catalyst acidity was completely recovered, as determined by ammonia t.p.d.^{10,12} and shown in Table 1. Ethylene conversion increased to 14%, and selectivity to ethylamines was identical to that of fresh H-erionite.

Facile regeneration of H-erionite at 400°C can result only from formation of light hydrocarbons that can be desorbed or burned at this temperature. The stable conversion and selectivity found with H-erionite after initial deactivation is an inherent consequence of its structure. The narrow erionite channels prevent formation of branched and cyclic hydrocarbons that form coke. In contrast to the situation with large pore structures, such as Y zeolites, the absence of heavy coke precursors leads to steady catalyst performance.

CONCLUSION

The influence of pore structure on selectivity, catalyst deactivation, and catalyst regeneration for zeolite-catalyzed olefin amination has been demonstrated. The high concentration of ammonia initially poisons the most acidic sites of each catalyst and moderates the reactivity of the remaining acid sites. In spite of the high concentration of ammonia, coke formation was the principal mode of catalyst deactivation. Owing to the large pore structure of Y-zeolite, high molecular weight coke was formed. Removal of this coke could be accomplished only with partial loss of zeolite crystallinity. In contrast, the small pore structure of H-erionite restricted olefin self-alkylation to

formation of linear low molecular weight hydrocarbons. These low molecular weight residues were readily removed without sacrifice of erionite crystallinity. Conversion of ethylene over both zeolite catalysts, however, depended on the number of strong acid sites.¹⁰

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