JOURNAL OF CATALYSIS 16, 232–238 (1970)

Quinoline Titration of Cumene-Cracking Activity on Type-Y Molecular Sieve Catalysts

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Received June 3, 1969; revised July 14, 1969

Quinoline poisoned the activity of cerium-, calcium-, and ammonium-exchanged type-Y molecular sieves for cumene cracking. The concept of "minimum titers" and corresponding "minimum temperatures" was introduced. The minimum titers for all of the sieves occurred around 400°C and were equal to 1 quinoline molecule/supercage. Experiments with partially exchanged (Na,H)-Y sieves showed that the quinoline titers were also nearly the same for all degrees of ion exchange provided there was at least 1 active site/supercage.

INTRODUCTION

Molecular sieves, in various cation exchanged forms, are acid catalysts. Over the past few years the types-X and -Y seives have become important as promoters for cracking catalysts (*1*). Not all of these sieves are equally good as cracking catalyst promoters and several hypotheses have been advanced to explain why some are better than others (*2–5*).

One of the factors responsible for the high catalytic activity of molecular sieves as compared to amorphous silica–alumina is the relative density of active sites in the two materials. The experiments reported here were initiated with the intention of measuring acid-site densities on a variety of sieves.

Quinoline was titrated onto the sieves to poison their activity for the acid-catalyzed cracking of cumene to benzene and propylene. The experimental procedure was similar to procedures used by other workers (*3*, *6*) with the exceptions that we used a continuous rather than a pulsed system and that we also studied the temperature-dependence of the quinoline titers. Since the titers were temperature dependent, we defined a quantity called the *minimum titer* and compared the sieves in terms of it. The void volume in the structure of types-X and -Y sieves is composed of interconnecting supercages (*7*). Surprisingly, the minimum titers for all of the sieves were simply equal to the densities of their supercages. This led us to conclude that quinoline titers on molecular sieves did not measure acid site densities in the usual sense.

EXPERIMENTAL METHODS

Catalysts and Reagents

Cumene, Phillips' pure grade (99 mole % minimum purity) was chromatographed in an atmosphere of nitrogen over a column of alumina. The purified cumene was collected and stored under nitrogen until it was used. Quinoline, Fisher Scientific's reagent grade, or Eastman's white label, was used without further purification.

The catalysts were all ion-exchanged type-Y molecular sieves. Their analyses, expressed as molar ratios of the oxides and corrected to a dry basis, are in Table 1. The ammonium-exchanged sieve, H_2Y in Table 1, was also exchanged to other ratios of Na_2O: $(NH_4)_2O$ and these compositions appear as data in Fig. 6.

Reactor System

The reactor system is shown schematically in Fig. 1. The reactor itself was a

TABLE 1
MOLECULAR SIEVES

	Na_2O	$(NH_4)_2O$	CaO	$Ce_{2/3}O$	Al_2O_3	SiO_2
$Ce_{2/3}Y$	0.10			1.08	1	5.20
CaY	0.20		0.67		1	4.93
H_2Y	0.26	0.71			1	4.89
Na_2Y	0.93				1	4.98

1.75-in. length of 0.18-in. i.d. stainless steel tubing. It was housed in a heated air bath. A coil of stainless steel tubing at the inlet of the reactor served as a vaporizer and preheater. The flow of liquid reactants was metered with a Sage syringe pump from a Hamilton gas tight syringe. The liquids were introduced into a stream of helium in the vaporization section through a long flexible hypodermic needle. The effluent from the reactor passed through a heated gas sampling manifold from which it could be introduced into a gas chromatograph with a thermal conductivity detector. A 6 ft $\times$ 0.25-in. column packed with SE-30 was used in the chromatograph at 150°C. The carrier gas was helium at about 30 ml/min. The usual reaction conditions were: P_{He}, 0.95 atm; P_{cumene}, 0.047 atm; $P_{quinoline}$, 0.0019 atm; P_{total}, 1.0 atm; F_{He}, 40 ml/min; and WHSV (cumene), 2.1 hr^{-1}.

Quinoline Titration

The catalyst was heated in air for 1 hr at 1100°F. Then about 0.2 g of it was loaded into the reactor. Helium flowed over the catalyst until the system heated up to

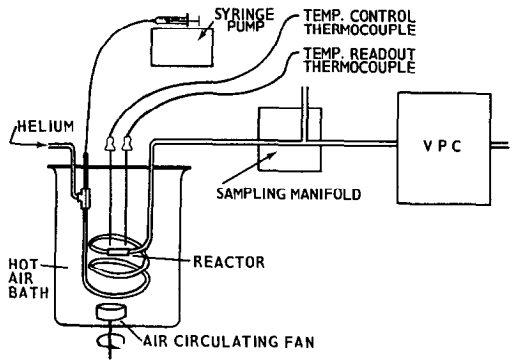

FIG. 1. Reactor system for the cumene cracking and quinoline poisoning experiments.

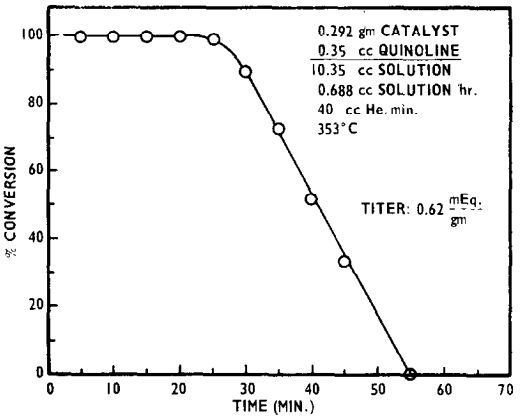

FIG. 2. A titration curve for $Ce_{2/3}Y$ below the "minimum temperature."

the reaction temperature, then the cumene and quinoline were introduced. Samples of the product were analyzed at 5-min intervals. Only propylene, benzene, and cumene were found in the product. The initial conversions were usually 100% and with time they fell to zero. A typical titration curve is shown in Fig. 2. In this case it took 55 min to completely poison the catalyst and the titer was 0.62 meq/g.

Quinoline Adsorption

Quinoline adsorption was measured gravimetrically in a dynamic system with a Cahn electrobalance, Fig. 4. About 100 mg of sieve were pretreated by heating at 550°C in a vacuum until the weight became constant. Then the temperature dropped to

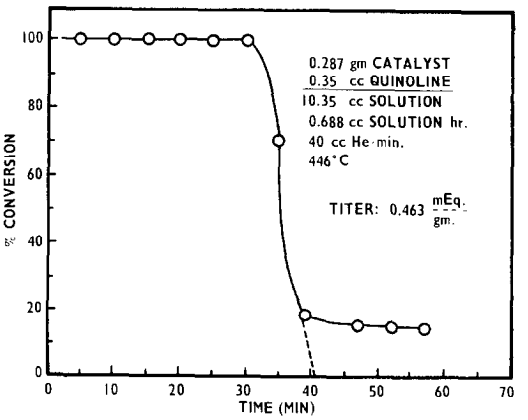

FIG. 3. A titration curve for $Ce_{2/8}Y$ above the "minimum temperature."

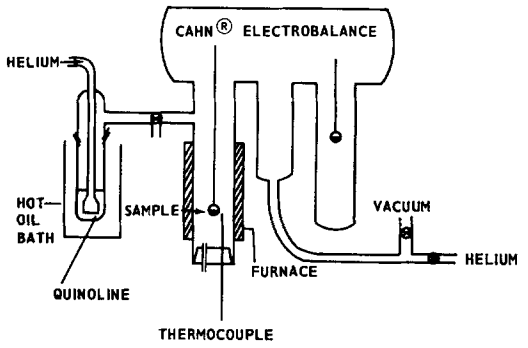

FIG. 4. System for the equilibrium adsorption of quinoline.

350°C. The system was filled with helium and a flow of helium was established over the sieve. Quinoline was introduced through a saturator into a second helium stream, shown on the left in Fig. 4. The manifold lines between the quinoline saturator and the sample section were heated to avoid condensation. The two helium flows, with and without quinoline, were set at 0.09 and 0.03 ft^3/hr. In this way we avoided the possible problem of condensation in the upper section of the system where the electro-mechanical parts of the balance were housed. The partial pressure of quinoline flowing over the sample was ¼ the partial pressure at which it left the saturator.

All of the adsorptions were measured at 0.8 Torr of quinoline. The sequence of adsorption temperatures were 350, 400 and 450°C. Therefore, after the first adsorption, quinoline was actually desorbed to equilibrate at the higher temperatures. Several hours were required to equilibrate at each temperature.

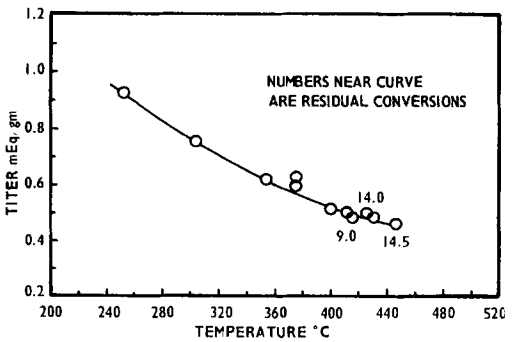

FIG. 5. Quinoline titers for $Ce_{2/3}Y$ at several different temperatures. The numbers near the points at the higher temperature are the residual percentage conversions.

DETERMINATION OF MINIMUM TITERS

The minimum titer was defined as the titer at the highest temperature where the fully poisoned catalyst could no longer convert any cumene. To illustrate this, Figs. 2 and 3 are shown as typical titration curves at temperatures below and above the minimum temperature, respectively. Below the minimum temperature, Fig. 2, there was no residual conversion, whereas above the minimum temperature, Fig. 3, there was about 12% residual conversion and the titer was smaller. Titers at several different temperatures were plotted in Fig. 5. The numbers associated with the lower points were residual conversion, such as the 12% in Fig. 3. The titers decreased with increasing temperature and the highest temperature where there was still zero residual conversion was 400°C. The titer at this temperature, 0.51 meq/g, was the minimum titer.

With respect to the quinoline titers, we have implicitly assumed that the catalyst adsorbed all of the quinoline that passed over it during the titration. However, some of the quinoline must surely have desorbed from the catalyst before the titration was complete. Nevertheless that amount of quinoline was small and we have not corrected for it. We concluded that it was small from results reported by Tkhoang *et al.* (*8*) who analyzed a dynamic system very similar to our own and also from the rather close correspondence between the quinoline titers and the quinoline adsorptions for H_2Y in Tables 4 and 6.

CALCULATION OF SUPERCAGE DENSITY

The supercage density is simply the reciprocal of the formula weight for a sodalite unit.

$$\text{Supercage density, mole/g} = \frac{1}{\text{Formula wt of sodalite unit}}. \quad (1)$$

The simple relationship exists because there is effectively 1 sodalite/supercage. Actually there are 10 sodalites/supercage, but each sodalite is also shared by 10 supercages. The formula weight for a sodalite unit is the weight of the chemical formula proportioned to 24 metal atoms (i.e., 24 silicons and aluminums). The calculated supercage densities in Table 5 take into account the imperfect stoichiometry of the actual chemical analyses. For example the formula of a sodalite for the first sieve in Table 1 was taken as:

$$Ce_{7.20/3}Na_{0.67}(AlO_2)_{6.67}(SiO_2)_{17.33}$$

This formula has 1.20 too many cation equivalents. Evidently this is not a perfectly pure cation-exchanged molecular sieve.

Results

The quinoline titers for $Ce_{2/3}Y$, CaY, and H_2Y are in Tables 2, 3, and 4. Minimum titers taken from these data are in Table 5. The supercage densities for these same sieves, also expressed in meq/g, are included in Table 5 to show how closely they correspond to the experimental minimum titers.

TABLE 2
Quinoline Titers for $Ce_{2/3}Y$

Temp. (°C)	Titer (meq/g)	Residual conversion (%)
252	0.923	
304	0.756	
353	0.620	
375	0.623	
375	0.593	
400	0.512	
412	0.499	9
415	0.488	9
425	0.486	16
426	0.496	14
446	0.463	14

The Na_2Y sieve did not crack cumene at all under the conditions used with the other catalysts reported here, so effectively it always had a zero titer.

Partially exchanged sodium–ammonium Y sieves did crack cumene, and titers are plotted in Fig. 6 for a series of them with different degrees of ion exchange. These titers were measured at 375° and, since the minimum temperature is probably around 400°C, they are not minimum titers. The degree of exchange, on the abscissa, has been labeled "active sites per supercage." Actually those numbers are the difference

TABLE 3
Quinoline Titers for CaY

Temp. (°C)	Titer (meq/g)	Residual conversion (%)
377	1.123	
410	0.846	
421	0.723	3
434	0.696	8
447	0.608	8

TABLE 4
Quinoline Titers for H_2Y

Temp. (°C)	Titer (meq/g)	Residual conversion (%)
350	1.165	
375	1.160	
377	1.114	
385	1.108	
400	0.962	
403	0.731	
412	0.997	3
413	1.052	2
413	0.971	5
424	0.651	9
435	0.965	5
448	0.455	18
453	0.828	22
453	0.561	23

TABLE 5
Minimum Titers

Catalyst	Min temp. (°C)	Min titer (meq/g)	Supercage density (meq/g)
$Ce_{2/3}Y$	400	0.51	0.56
CaY	410	0.86	0.64
H_2Y	408	0.98	0.71

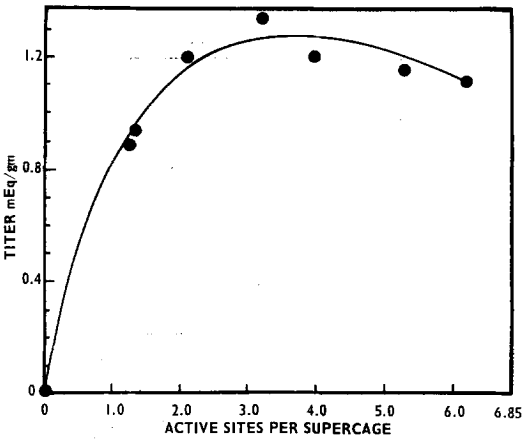

FIG. 6. Quinoline titers for partially exchanged (Na,H)-Y sieves at 375°C.

between the concentration of sodium ions per supercage and 6.85, the stoichiometric concentration of univalent ions per supercage for a Y sieve with an SiO_2/Al_2O_3 ratio of 5. There may be a maximum in the curve around 3 sites/supercage (45% exchange) but the outstanding feature of the curve is that it falls off so sharply when the density of active sites drops below 1/supercage. The decline of cumene conversion with time in a blank run has been plotted in Fig. 7. The small loss of conversion over the period of a titration, an hour or less, was insignificant compared to the total loss of conversion in that period when quinoline was present. However, if the cumene was not prepurified before use, or if it stood in the room for more than about 1 week, even in a closed bottle, the self-poisoning was much greater. All the present experiments were done with prepurified cumene and no correction was made for self-poisoning.

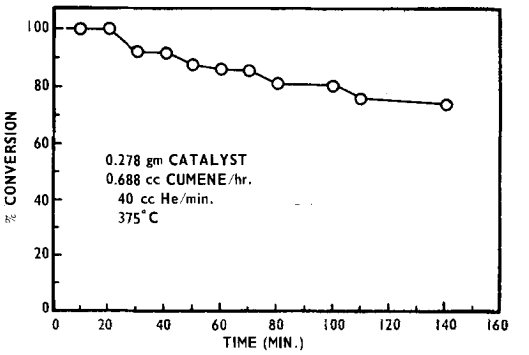

FIG. 7. Blank run for the decline of cumene cracking over $Ce_{2/3}Y$ at 375° with no quinoline added.

Equilibrium adsorptions of quinoline on H_2Y and Na_2Y are in Table 6 together with the experimental minimum titers and the calculated supercage densities. The adsorption conditions, 0.8 Torr (0.00105 atm) quinoline and adsorption from a stream of helium were selected because they were similar to the conditions in the reactor during the titration experiments.

TABLE 6
QUINOLINE ADSORPTION AT 0.8 TORR

Catalyst	Temp. (°C)	Ads (meq/g)	Min titer (meq/g)	Supercage density (meq/g)
H_2Y	350	0.74		
	400	0.67	0.98[a]	0.71
	450	0.62		
Na_2Y	350	1.49		
	400	0.91	0	0.63

[a] Temperature corresponding to the minimum titer was actually 408°C.

The quinoline adsorption on H_2Y at 400°C was almost identical to the supercage density, 0.67 and 0.71. It was also only a little less than the minimum titer, 0.98. This difference is in the right direction if the titers are actually approximate equilibrium adsorptions. Since the titers neglect the small amount of desorption that occurs during the period of the titration they should be slightly higher than the true adsorption.

The quinoline adsorption of Na_2Y can not be compared to titers because Na_2Y was a catalytically inactive sieve. Nevertheless the quinoline adsorptions can be compared to the adsorptions on H_2Y and to the supercage density. In both cases the adsorption on Na_2Y was higher.

DISCUSSION

The temperature-dependences of the quinoline titers in Tables 2, 3, and 4 cautioned us against interpreting those data as

measures of acid-site concentrations. Provided that we accepted that the concentration of acid sites should not depend upon the temperature used to measure them, only one of the titers in each table could possibly have been equal to the concentration of acid sites.

It might seem that the minimum titers should measure the concentration of acid sites since they are the lowest titers that still completely poison the catalysts. However, the numerical values for the minimum titers and the fact that they all occurred at about the same temperature, i.e., 400°C, argued against that. The minimum titers for all of the sieves were nearly equal to supercage densities for those sieves. It has also been reported that the quinoline titer for a silver-exchanged Y sieve was nearly equal to its supercage density (*9*). It would seem to be too much of a coincidence for all of these sieves to have the same concentration of active sites, namely 1/supercage.

There are differences of as much as 28% between the minimum titers and the supercage densities in Table 5. However, these differences are understandable and trivial compared to differences between the minimum titers and other estimates for the acid-site densities on catalytically active sieves. For example, estimates can range from as high as about 7 sites/supercage, if every univalent exchange site were an acid site, to as low as 1 acid site/1000 supercages (*9*). The low estimate was derived from absolute rate theory and kinetic parameters for cumene cracking.

Of the three sieves in Table 5, only $Ce_{2/3}Y$ had a stoichiometric excess of cations. The apparent excess was probably due to free cerium oxide. The diluent effect of the free oxide was accounted for in calculating the supercage densities. However, the free oxide probably also competed with quinoline for adsorption of space within the sieve. This can explain why the minimum titer for $Ce_{2/3}Y$ in Table 5 was smaller than the calculated supercage density. For the other two sieves in Table 5, the minimum titers were a bit greater than the supercage densities. The latter behavior was expected because the amount of quinoline adsorbed by the catalysts has to be somewhat less than the amount passed over them, i.e., the titers.

The titration of a series of ammonium-exchanged sieves, Fig. 6, showed that the quinoline titers were nearly the same for all of those sieves so long as there was at least one active site per supercage. Below that concentration of active sites the titers decreased. The small maximum in the curve, Fig. 6, may or may not be significant. However, it happens to correspond to the minimum in the activation energy for cumene cracking over sieves at different degrees of ion exchange (*11*).

The equilibrium adsorption of quinoline on H_2Y at the "minimum temperature" and at the partial pressure used in the poisoning experiments was essentially the same as the "minimum titer" and very nearly 1 quinoline/supercage. The fact that the concentration of adsorbed quinoline is about 10 times larger than the quinoline chemisorption capacity for an amorphous silica–alumina catalyst of the same composition (*10*) contributed to our early thinking that quinoline might measure acid-site densities on sieves as well as on amorphous catalysts. However, these thoughts were dispelled when we learned that more quinoline adsorbed on catalytically inactive Na_2Y than on catalytically active H_2Y.

Conclusion

Quinoline does indeed poison the activity of molecular sieves for the acid-catalyzed cracking of cumene. However, the concentration of quinoline required to completely poison a sieve is not equal to the concentration of active sites in the sieve. Rather it is equal to the density of supercages in those sieves. Apparently, a single molecule of quinoline per supercage is sufficient to block cumene from the active sites, whatever their concentration may be.

Acknowledgments

We acknowledge the assistance of Dr. D. Kemp for the adsorption experiments and Dr. S. F. Adler for helpful discussions.

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