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Cumene Disproportionation on a Commercial Hydrocracking Catalyst: Effects of Zeolite Unit Cell Size on Reaction Rate and Catalyst Deactivation

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We have previously reported on our efforts to characterize the behavior of a typical commercial hydrocracking catalyst by means of appropriate probe reactions. The Co–Mo function of fresh, deactivated, and regenerated catalysts was tested earlier using the hydrogenation of cyclohexene (*1*, *2*); more recently the acidic function has been studied via the disproportionation of cumene. Our earlier work on the latter (*3*, *4*) with a differential microreactor has shown that since catalyst samples deactivate slowly during experiments, the data may be reproducibly extrapolated to zero time to yield estimates of the initial rate of reaction. These rates are consistent with a Langmuir–Hinshelwood reaction model involving two adjacently adsorbed cumene molecules. We have also demonstrated that the effects of hydrogen pressure on both the reaction rate and the rate of catalyst deactivation are consistent with the proposed reaction model (*5*, *6*).

In the present paper we focus on the apparent importance of the unit cell size of the zeolite component of the hydrocracking catalyst on the rates of the probe reaction and catalyst deactivation.

EXPERIMENTAL

The reactor system used in this work was a conventional once-through microflow reactor, operated at cumene conversions typically less than 10%. Reaction temperatures ranged from 428 to 498 K; cumene partial pressure was less than 0.3 atm in the presence of hydrogen at a pressure of 8.1 atm or helium at a pressure of 8.5 atm. Product analysis was by gas chromatography. Further details of the apparatus and experimental procedures are given elsewhere (*5*).

The catalysts investigated were commercial hydrocracking catalysts supplied by Amoco Oil Company. These typically contain cobalt and molybdenum oxides deposited on a support consisting of crystalline aluminosilicates (i.e., zeolites) dispersed in a porous matrix of SiO_2/Al_2O_3. Three different catalyst samples were used in the present study and these have been designated NU-D, NU-C, and AM-F for present purposes. It may be noted that NU-D is a sample of fresh catalyst while the other two are samples of NU-D which have been deactivated under commercial reaction conditions and later regenerated. Some pertinent physical properties of these catalysts are listed in Table 1. It should be noted that these catalysts have very similar surface areas and carbon contents but unit cell sizes which differ significantly, given the accuracy of such measurements (±0.01 Å).

All catalyst samples were crushed and screened to a 0.2-mm average particle size and pretreated with flowing nitrogen for 1 h at each of the following temperatures: 25, 365, and 25°C.

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TABLE 1

Physical Properties of Catalyst Samples

Catalyst	Unit cell size (Å)	Wt% carbon	Surface area (m^2/g)
NU-D	24.46	0.11	318
AM-F	24.40	0.24	309
NU-C	24.35	0.21	277

RESULTS

Reaction kinetics. The object of the kinetic experiments was to determine the rate of benzene formation via cumene disproportionation under various conditions. Since the catalyst deactivated during these experiments, it was necessary to extrapolate the conversion-versus-time data back to zero time to obtain an initial rate of reaction. These extrapolations were accomplished by two different techniques as detailed previously (*4*). Since the results were quite comparable, values based on one extrapolation technique, the Voorhies-type extrapolation indicated by Eq. (1), are presented here. Initial rates of reaction were calculated by Eq. (2) and fit to the kinetic model, Eq. (3), using nonlinear regression techniques. Additional details of these operations are presented elsewhere (*4, 5, 7*).

$$x_2'(t) = x_2'(0)\exp[-at^{0.5}] \qquad (1)$$

$$r_b'(0) = Fx_2'(0)/W \qquad (2)$$

$$r_b'(0) = \frac{k_1K_2^2P_c^2}{[1 + K_2P_c]^2}. \qquad (3)$$

Initial probing experiments were carried out with the three catalysts at 428 K and a cumene partial pressure of 0.14 atm. The resultant initial reaction rates in the presence of hydrogen (8.1 atm) or helium (8.5 atm) are listed in Table 2 and show that catalyst AM-F is more active than either of the others tested and that reaction rates are somewhat lower in hydrogen than in helium. The effect of hydrogen on the rate of cumene disproportionation has been discussed elsewhere (*5, 6*).

TABLE 2

Initial Reaction Rates in Hydrogen and Helium at 185°C

Catalyst	$r_b'(0)$ (g mole/g cat/min)	
	In hydrogen	In helium
NU-D	5.18×10^{-5}	5.48×10^{-5}
AM-F	8.22×10^{-5}	9.73×10^{-5}
NU-C	5.76×10^{-5}	5.91×10^{-5}

Experiments were then carried out in hydrogen at various cumene partial pressures to estimate the values of the parameters in Eq. (3). The results are listed in Table 3. On the basis of some studies of parametric sensitivity (*7*) and reproducibility (*5*), it was determined that the values of K_2 were essentially the same for each catalyst. The parameter fitting process was then repeated with the constraint that K_2 was constant. The three sets of initial rate data were analyzed to determine the k_1 value for each catalyst and the single value of K_2 which minimized the total sum of the squares of the residuals. The results of this regression analysis are presented in Table 4. Good agreement was obtained between the model and the experimental data, as indicated by the values of $\langle d \rangle$, the average deviations, listed in the table.

Comparison of these data with those of Table 1 indicates that the reaction rate parameter of the present working model goes through a maximum at an intermediate unit cell size of the catalyst zeolite component. We return to this point for further discussion below.

TABLE 3

Kinetic Model Parameters at 185°C

Catalyst	k_1[a]	K_2 (atm^{-1})	$\langle d \rangle$
NU-D	3.03×10^{-4}	5.03	9.52
AM-F	6.59×10^{-4}	4.03	7.15
NU-C	3.46×10^{-4}	5.03	7.68

[a] g mole/g catal/min.

TABLE 4

Kinetic Model Parameters at 185°C, K_2 = 4.84 atm^{-1}

Catalyst	$k_1{}^a$	$k_1/(k_1)_{\text{NU-D}}$	$\langle d \rangle$
NU-D	3.10×10^{-4}	1.00	9.15
AM-F	5.11×10^{-4}	1.65	7.03
NU-C	3.55×10^{-4}	1.15	8.82

[a] g mole/g cat/min.

Catalyst deactivation. The deactivation parameter of the decay correlation, "*a*" in Eq. (1), was also found to vary somewhat for these catalysts. To be sure, it is difficult to determine this parameter precisely, as shown in Table 5. The values reported are for three different experiments with catalyst NU-D and show considerable variation despite the apparent close agreement of the corresponding initial rates of reaction. Nevertheless, trends in the average values of "*a*" are of interest. In Fig. 1, average values of "*a*" have been plotted against cumene partial pressure for each of the three catalysts. Clearly, the magnitude of "*a*" is significantly different for NU-D and NU-C. The limited data for AM-F are less definitive, but we believe the deactivation parameter for that catalyst is intermediate between those of the other two catalysts over most of the range of these experiments. It thus appears that catalyst deactivation rate varies inversely with zeolite unit cell size. However, with data for AM-F only available at two cumene pressures this conclusion must remain somewhat speculative.

It should also be noted that the initial carbon contents of catalysts AM-F and NU-C are essentially the same and are higher than that of NU-D (see Table 1). An alternative interpretation might be that deactivation rate varies directly with initial carbon content. However, this appears unlikely in view of more extensive data obtained for a wider range of carbon contents (*5*).

TABLE 5

Reproducibility of Deactivation Parameter "*a*," Catalyst NU-D, Temperature = 185°C

Experiment	$r_0'(0)$ (g mole/g cat/min)	a (min$^{-0.5}$)
(1)	5.15×10^{-5}	0.0509
(2)	5.24×10^{-5}	0.0490
(7)	5.14×10^{-5}	0.0591

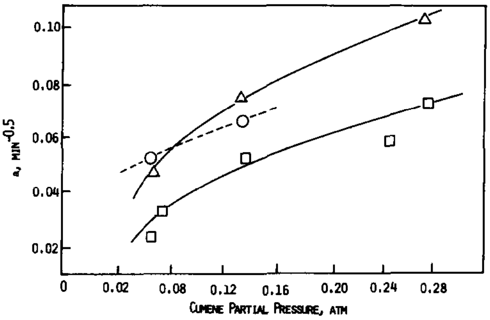

FIG. 1. Dependence of catalyst deactivation on cumene partial pressure and unit cell size. Temperature = 185°C, hydrogen pressure = 8.1 atm. Catalyst and unit cell size (nm): □—NU-D, 2.446; ○—AM-F, 2.440; △—NU-C, 2.435.

DISCUSSION

Unit cell size and the Si/Al ratio. The results presented above suggest that the zeolite unit cell size can be correlated, although not in the same way, with both the activity of the catalysts for cumene disproportionation and the deactivation parameter "*a*." Catalyst deactivation is no doubt initiated by formation of a coke precursor on appropriate sites not necessarily the same as those active for cumene disproportionation and the deactivation parameter may be considered to be a measure of the extent of that precursor formation reaction. These two reactions occur simultaneously, and consequently, unit cell size may be regarded as a determinant of both the activity and the selectivity of a given catalyst. This was originally proposed by Pine *et al.* (*8*) who studied the behavior of ultrastable Y (USY)-based catalysts in the cracking of a light vacuum gas oil. They found that the gas oil cracking activities increased while production of light gases (C_3's) decreased with increasing unit cell size in the range from 24.23 to 24.32 Å. They concluded that unit cell size is a suitable correlating parameter because it is a measure of the Si : Al ratio of the zeolite framework which in turn determines the number and type of acid sites present in the zeolite crystal structure.

Assuming that unit cell size is, indeed, a measure of the Si : Al ratio, one may calculate these ratios for the catalysts used in the present study by means of the relationship developed by Breck and Flannigen (*9*). This yields Si : Al ratios of 5.2, 7.0, and 9.5, for the catalysts NU-D, AM-F, and NU-C, respectively. Our experiments suggest, therefore, that cumene disproportionation activity is maximum at a Si : Al ratio between 5.2 and 9.5, which corresponds to a $SiO_2 : Al_2O_3$ ratio between 10.4 and 19.0.

Several previous experimental studies in the literature have reported maxima in catalytic activity with increasing Si : Al ratios. For example, Topchieva and Huo (*10*) reported a maximum in cumene disproportionation activity over NaHY at a $SiO_2 : Al_2O_3$ ratio of 8. Koradia *et al.* (*11*) studied the *n*-pentane isomerization activity of Pd/HM catalysts at 260°C and found a maximum in activity and i-C_5 selectivity at a $SiO_2 : Al_2O_3$ ratio of 17. Similarly, Bremer *et al.* (*12*) examined the hydrocracking of *n*- and i-octane over Ni/HM catalysts and reported a maximum in hydrocracking activity at a $SiO_2 : Al_2O_3$ ratio of 23. The existence of such maxima is also supported by fundamental studies of Pine *et al.* (*8*) and Mikovsky and Marshall (*13*).

The variation of unit cell size upon dealumination of the zeolite framework and the fate of the aluminum thus liberated have been studied by several investigators and the following picture has emerged. At high temperatures, water vapor attacks aluminum atoms in the zeolite and removes them in the form of aluminum oxide/hydroxide clusters $[AlO]_p^+$ (*14*) which then migrate into the sodalite cages of the zeolite (*15*). Removal of aluminum atoms leaves tetrahedral vacancies that are apparently filled by migrating silicon atoms which then form Si–O bonds that are smaller than the original Al–O bonds—resulting in shrinkage of the unit cell size (*16–20*). However, it has been pointed out (*15*) that determination of the Si : Al ratio by X-ray diffraction alone is difficult in steam-stabilized zeolites because the unit cell size is affected in opposite directions by silicon enrichment of the framework and the incorporation of aluminum oxide/hydroxide clusters in the sodalite cages. The electronic interactions and resultant changes in catalytic properties have been discussed elsewhere (*14, 21–23*).

Interpretation of the adsorption parameter K_2. The constancy of the kinetic model parameter K_2 merits some further discussion. According to the classical approach used in deriving this model, K_2 is an adsorption equilibrium constant which characterizes the adsorption properties of the catalyst. Constancy of K_2 at fixed temperature implies, therefore, that the adsorptive properties and thus the nature of the reaction sites for cumene disproportionation are the same for the three catalysts investigated. Pansing and Malloy (*24*) used such reasoning to conclude that steaming and commercial use did not affect the adsorptive properties of amorphous silica–alumina catalysts for the cumene cracking reaction. Accordingly, they ascribed changes in observed rates to changes in the number rather than the nature of the catalytically active sites.

Adopting this argument, it may be assumed in the present case that the nature of the catalytic sites of catalysts NU-D, AM-F, and NU-C is the same over the range of unit cell sizes and $SiO_2 : Al_2O_3$ ratios involved, and thus activation energies and sorption enthalpies should be equal for all three catalysts at the same temperature. Apparently, removal of some aluminum atoms does not affect the catalytic and adsorptive properties of those which remain. Some additional support for such an interpretation is provided by the previous work of Abbas *et al.* (*25*) who studied cyclopropane isomerization over H-faujasites which

TABLE 6

Initial Reaction Rates in Helium at 225°C

Catalyst	$r'_0(0)$ (g mole/g cat/min)
NU-D	10.3×10^{-5}
AM-F	9.17×10^{-5}
NU-C	9.13×10^{-5}

they prepared by dealuminating USY zeolites to various degrees by steaming and acid extraction of the extra-lattice aluminum. They observed a large range of Si : Al ratios, from 5 to 15, over which activation energies and sorption enthalpy were essentially constant, although the former increased at lower and higher ratios.

The effect of temperature on deactivation. A further test of the similarity of the active sites for cumene disproportionation on the three catalysts investigated was attempted by carrying out additional kinetic experiments. At a higher temperature reaction rates on each catalyst should be higher but in the same ratio as at 185°C if the activation energies are equal. Table 6 presents results of some experiments done in helium at 225°C which show that catalyst NU-D is somewhat more active at that temperature than the others, contrary to the results obtained in helium at 185°C (Table 2). Furthermore, the activity of AM-F apparently decreased slightly despite the 40°C temperature change, while both NU-D and NU-C showed increased activity. These surprising results are probably due to rapid catalyst deactivation which masks the true effect of temperature on the disproportionation reaction and invalidates the planned test of constancy of activation energy.

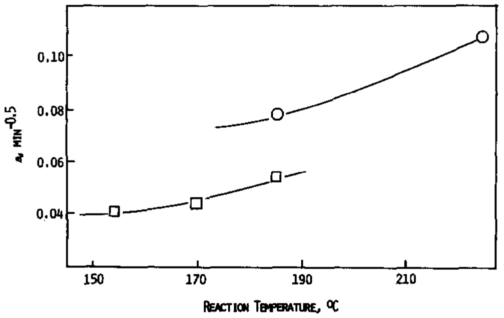

FIG. 2. The effect of reaction temperature on catalyst deactivation; NU-D catalyst, cumene pressure = 0.14 atm. ○—Helium, 8.5 atm; □—hydrogen, 8.1 atm.

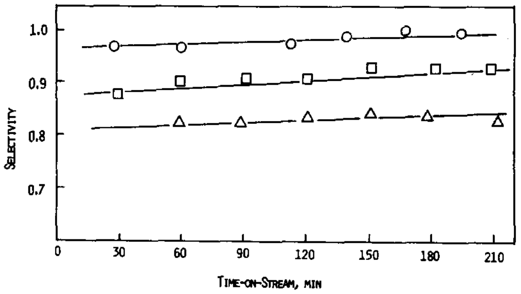

FIG. 3. Cumene reaction selectivity as a function of time-on-stream and reaction temperature; NU-D catalyst. ○—185°C, □—225°C, △—239°C.

Figure 2 shows that the deactivation parameter "*a*" (and hence the rate of the deactivation process for catalyst NU-D) increases with increasing temperature in both hydrogen and helium. (The difference due to carrier gas has been discussed elsewhere (*6*).) This increase in deactivation can be attributed to an increase in the rate of the coke precursor reaction as temperature is raised and to the increased presence of light gases from cumene cracking which further promote deactivation. As shown in Fig. 3, while cumene disproportionation is dominant at 185°C, cracking becomes more significant as the temperature is increased. Indeed, at the lower temperature (185°C) thermodynamic calculations suggest that cumene dealkylation reaction should proceed to a maximum of only about 3%, while at 225°C equilibrium conversion would involve as much as 10% cracking of the cumene. In addition to producing benzene, the cracking reaction yields C_3's. It is well known that such light gases can promote deactivation and formation of carbonaceous deposits as shown by Karge *et al.* (*26*) and by Eisenbach and Gallei (*27*).

Therefore, it is likely at the higher temperature that catalyst deactivation was increased significantly by the presence of C_3's formed during the cracking of the cumene. During the first 30 min of these experiments (prior to the first check of catalyst activity), enough deactivation and modification of the catalyst surface must have occurred to interfere seriously with the determination of correct cumene disproportionation rates. Undoubtedly, a much shorter sampling time is necessary to monitor activity properly at temperatures as high as 225°C if the masking effects of very rapid deactivation are to be avoided. Unfortunately, the present apparatus did not permit representative sampling at times less than 30 min.

CONCLUSIONS

The data obtained in this study strongly suggest that changes in the unit cell size of the zeolite component of a commercial hydrocracking catalyst can have a dramatic effect on the rate of cumene disproportionation. The rates of catalyst deactivation reactions also appear to vary with unit cell size. Thus, unit cell size can be used as a parameter for correlating catalyst activity and selectivity.

It has also been shown that the initial rate method for studying kinetics in the presence of deactivation reactions may not be useful under conditions of fast deactivation unless the first checks of catalyst activity can be made shortly after reaction is initiated.

APPENDIX: NOMENCLATURE

a	Deactivation parameter in decay correlation, Eq. (1), $\text{min}^{-0.5}$
$\langle d \rangle$	Average deviation, defined as $$\langle d \rangle = 100 \times \frac{r_b'(0)_{\text{obs}} - r_b'(0)_{\text{pred}}}{r_b'(0)_{\text{obs}}}$$
F	Cumene molar flow rate, g mole/min
k_1	Forward rate constant of kinetic model, Eq. (3), g mole/g cat/min
K_2	Adsorption equilibrium constant of kinetic model, Eq. (3), atm^{-1}
P_c	Cumene partial pressure, atm
$r_b'(0)$	Initial rate of benzene formation as determined by Voorhies-type correlation, Eqs. (1) and (2)
S	Cumene reaction selectivity, rate of cumene disproportionation divided by cumene disappearance by disproportionation and cracking
t	Time-on-stream, min
$x_b'(t)$	Fraction of cumene converted to benzene via disproportionation as determined by Voorhies-type correlation, Eq. (1)
W	Mass of catalyst in reactor, g cat

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