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Effect of Exchange Cations and Silica to Alumina Ratio of Faujasite on Coke Selectivity during Fluid Catalytic Cracking

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Hydrothermally treated fluid-cracking catalysts containing zeolites of varying chemical composition were used in cracking experiments with commercial gas oils and a model hydrocarbon compound. An observed linear relationship between coke yields for a given catalyst and a second-order kinetic conversion parameter was used to assess coke selectivity as a function of zeolite composition as measured by the unit cell constant. Coke selectivity was sensitive to the unit cell constant in the 24.57- to 24.33-Å range. Both parallel and consecutive coking reactions were suppressed in the presence of the smaller unit cell zeolite catalyst. Below 24.33 Å, coke selectivity was less sensitive to the unit cell constant. Exchange cations like sodium and mixed rare earths did not independently influence coke selectivity at a given unit cell constant. Reduction in coke selectivity for the zeolites with smaller unit cell constants can be attributed to the lower density of acid sites in those zeolites.

INTRODUCTION

Coke formation during catalytic cracking of gas oils proceeds through olefinic and aromatic precursors (*1*, *2*). A dual-site mechanism of coke formation involving hydrogen transfer from aromatic coke precursor species has been proposed (*1*). Cracking tests with mixtures of naphthenes and olefins indicated that two-point contact between coke precursor species and catalyst is essential for hydrogen transfer and coke production (*3*). Hence, the density of acid sites in a catalyst could determine its propensity to yield coke (*4*). Studies using olefins as test reactants (*5*, *6*) indicate that both Brønsted and Lewis sites are responsible for coking reactions.

The measurements of Breck and Flanigen (*7*) describe the relationship between unit cell constant a_0 and the number of Al atoms per unit cell, N_{Al}, as $N_{Al} = 115.2 (a_0 - 24.19)$. Al atoms in the framework of the zeolite can be associated with Brønsted acid sites (*1*). Thus, the unit cell constant is a measure of acid site density and hence can influence coke selectivity. Cracking activity, selectivity for production of light hydrocarbons, gasoline, and olefins among steam-deactivated zeolite catalysts have been shown to correlate with the unit cell constant (*8*). However, data on coke selectivity were not presented in the above work. Exchange cations like rare earth have been postulated to influence zeolite coke selectivity (*9*, *10*). There is, thus, a need to determine the independent effects of exchange cation and unit cell constant on coke selectivity of steam-deactivated zeolite catalysts. This was done by preparing zeolites with varying chemical composition and testing them for coke selectivity using commercial feedstocks. Hydrothermal treatment of zeolite catalysts was used to duplicate the catalyst deactivation in a commercial FCC unit.

METHODS

A. Zeolite Preparation

Faujasite zeolites that were prepared can be classified into three categories: (a) zeolites with variable rare earth (1 to 5 in Table 1), (b) zeolites with variable sodium (6 to 10

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TABLE 1

Properties of Faujasite Zeolites

No.	Starting zeolite	Average dehydrated unit cell composition of finished zeolites $Na_a\ RE_b\ (NH_4,H)_c\ [(AlO_2)_x\ (SiO_2)_y]$					Unit cell constant for finished zeolite Å
		a	*b*	*c*	*x*	*y*	
1.	NaREY	3.8	13.0	12.2	55	137	↑
2.	↑	4.8	8.6	24.4	55	137	
3.		3.0	4.2	39.4	55	137	
4.		1.6	2.1	47.1	55	137	
5.	$NaNH_4Y$	3.1	0	51.9	55	137	24.67
6.		2.1	4.1	40.6	55	137	
7.		4.2	3.9	39.1	55	137	
8.		6.2	4.1	36.5	55	137	
9.		7.7	4.1	35.0	55	137	
10.	↓	13.4	4.1	29.3	55	137	↓
11.	Z-14 USY	0.5	0	18.5	19	173	24.36
12.	Z-14 USY	0.5	2.8	10.1	19	173	24.36
	Average dehydrated unit cell composition of starting zeolites						
	NaREY	14.8	13.4	0	55	137	
	$NaNH_4Y$	13.9	0	42.1	55	137	
	Z-14 USY	13.1	0	22.9	36	156	

in Table 1), and (c) dealuminated zeolites. All the zeolites were prepared by carrying out ion exchange and calcination processes on one of three commercially available (Davison Chemical Division, W. R. Grace & Co.) faujasite zeolites (NaREY, Na NH_4Y, and Z-14US). Properties of the zeolites prepared in the laboratory as well as those of commercial zeolites used as starting materials are summarized in Table 1. Ion exchanges with rare earth elements were carried out with mixed rare earth chloride solution having the following rare earth distribution: 34% La_2O_3, 39% CeO_2, 19% Nd_2O_3, 5% Pr_6O_{11}, and 3% Sm_2O_3. Ammonium sulfate solution was also used for ion exchange. After each ion exchange step, the zeolite was washed free of soluble salts using hot (95°C) deionized water.

Dealuminated zeolites (11 and 12 in Table 1) were prepared by ammonium ion exchange, treatment with pH 2 sulfuric acid for 1 h at 95°C, and steam dealumination (3 h at 650°C) of a Davison Z-14US faujasite sample. A portion of the dealuminated zeolite was ion exchanged with mixed rare earth chloride solution.

The chemical compositions of the unit cells of zeolites 1 through 10 were calculated from chemical analysis lumping all the rare earth elements together with an average atomic weight. Unit cell compositions of dealuminated zeolites 11 and 12 were calculated assuming no defect sites. The average number of rare earth and sodium atoms per unit cell in these preparations vary from 0 to 13 and 2.1 to 13.4, respectively.

B. Catalyst Preparations

Each of the zeolites 1 through 10 was mixed intimately with alumina binder and kaolin clay diluent and spray-dried to produce fluid-cracking catalyst microspheres (diameter range: 20–140 μm). The zeolite content of these catalysts was varied from 15 to 40 wt% to achieve catalysts of comparable gas oil cracking activity after hydrothermal treatment. Properties of these catalysts are given in Tables 2 and 3.

Each of the dealuminated zeolites 11 and 12 was mulled with kaolin clay (10% zeolite, 90% kaolin by weight), and the mixture was extruded and crushed to a particle size range similar to those found in fluid-cracking catalysts.

C. Hydrothermal Treatment of Cracking Catalysts

The catalysts prepared with alumina binder (Tables 2 and 3) were hydrothermally deactivated prior to testing. Hydrothermal deactivation methods were designed to duplicate the deactivation of the cracking catalyst in a commercial FCC unit. Since a single deactivation method may not be suitable for catalysts of varying compositions (*11*), two methods were employed and some catalysts were deactivated by each of the two methods. The first method [S1] was an 8-h treatment at 732°C with 100% steam at 2 atm. The second method [S2] was a 12-h treatment at 827°C with 20% steam at 1 atm. Catalysts prepared from steam-dealuminated zeolites 11 and 12 were not hydrothermally deactivated.

TABLE 2

Properties of Fluid-Cracking Catalysts Prepared from Zeolites with Variable Rare Earth Content

Zeolite properties						
Na/unit cell	3.1	1.6	3.0	3.0	4.8	3.8
RE/unit cell	0	2.1	4.2	4.2	8.6	13.0
wt% zeolite in catalyst	40	28	20	25	25	15
Catalyst properties						
wt% Na_2O	0.43	0.15	0.25	0.26	0.43	0.23
wt% RE_2O_3	0.10	0.71	1.27	1.52	2.96	2.76
wt% Al_2O_3	45.9	45.4	46.1	46.0	45.8	50.2
BET surface area ($m^2\ g^{-1}$)	222	207	192	211	232	127
Water pore volume ($cm^3\ g^{-1}$)	0.38	0.38	0.35	0.36	0.32	0.28
Bulk density ($g\ cm^{-3}$)	0.66	0.71	0.78	0.75	0.81	0.85
Conversion of paraffinic gas oil (wt%)[a]	73[b]	76[b]	75[c]	78[c]	83[c]	76[c]
Unit cell constant after hydrothermal treatment (Å)						
S1	—	—	24.32	24.33	24.42	24.55
S2	24.25	24.28	—	24.32	—	24.57

[a] Reactor conditions: temperature = 500°C, WHSV = 16, catalyst contact time = 75 s.
[b] After hydrothermal treatment S2.
[c] After hydrothermal treatment S1.

TABLE 3

Properties of Fluid-Cracking Catalysts Prepared from Zeolites with Variable Sodium Content

Zeolite properties					
Na/unit cell	2.1	4.2	6.2	7.7	13.4
RE/unit cell	4.1	3.9	4.1	4.1	4.1
wt% zeolite in catalyst	22	22	22	22	22
Catalyst properties					
wt% Na_2O	0.24	0.32	0.45	0.53	0.85
wt% RE_2O_3	1.26	1.34	1.39	1.28	1.39
wt% Al_2O_3	46.2	48.0	47.8	47.8	47.8
BET surface area ($m^2\ g^{-1}$)	169	165	174	163	165
Water pore volume ($cm^3\ g^{-1}$)	0.32	0.30	0.31	0.28	0.30
Bulk density ($g\ cm^{-3}$)	0.77	0.81	0.78	0.81	0.82
Conversion of paraffinic gas oil (wt%)[a]	74	75	74	73	67
Unit cell constant after hydrothermal treatment SI (Å)	24.34	24.32	24.31	24.31	24.30

[a] Reactor conditions: temperature = 500°C, WHSV = 16, catalyst contact time = 75 s. Catalysts tested after hydrothermal treatment S1.

D. Catalyst Characterization and Coke Selectivity Measurement

Unit cell constants of zeolites 11 and 12, as well as the steam deactivated catalysts, were determined using X-ray diffraction following ASTM procedure D-3942-80. Gas oil-cracking experiments were done using modifications of the fixed bed ASTM D-3907-80 microactivity procedure. The fixed bed reactor was operated at 500°C. For a given catalyst, conversion of gas oil was varied by varying the weight hourly space velocity (WHSV) at a constant catalyst contact time of 75 s. For the purpose of this work coke is defined as the hydrocarbon residue left on the catalyst after the 15-min inert purge recommended by ASTM. Coke on spent catalyst was measured by carbon determinator WR-12 (Leco Corp., St. Joseph, MI). During certain experiments, catalyst in the fixed bed reactor was stratified into six zones with glass microfiber filters. This stratification enabled measurement of the weight fraction of coke on the catalyst as a function of axial position in the fixed bed reactor.

Properties of the paraffinic and aromatic gas oils used for coke selectivity measurements are described in Table 4. Gold label 1-heptene (+99% purity from Aldrich, Milwaukee, WI) was used as the feed in certain experiments.

RESULTS AND DISCUSSION

A. Effect of Hydrothermal Treatment

The previously observed reduction in the unit cell constant due to hydrothermal treatment was observed for all catalysts to varying degrees, and rare earth retarded the unit cell shrinkage associated with hydrothermal treatment (Table 2) (*8*).

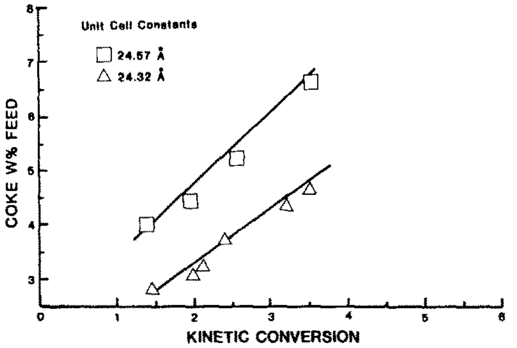

FIG. 1. Coke selectivity of catalysts with differing unit cell constants. Catalysts were subjected to hydrothermal treatment S2. Aromatic gas oil feed.

TABLE 4

Properties of Gas Oils

Feed description	Paraffinic gas oil	Aromatic gas oil
API gravity at 15.6°C	27.4	23.7
Sulfur (wt%)	0.38	3.9
Nitrogen (wt%)	0.07	0.11
Aniline point (°C)	93	94
D-1169 (°C)		
IBP	320	187
5	366	308
10	375	339
20	383	376
40	399	421
60	416	453
80	442	508
90	458	544
FBP	489	Distillation stopped
Mass spectral analysis (*V*%)		
Paraffins	24.6	14.5
Noncondensed cycloparaffins	25.0	14.0
Condensed (2,3 ring) cycloparaffins	26.4	19.1
Aromatics	24.0	52.4

B. Effect of Exchange Cations on Coke Selectivity

Coke yields for a given catalyst with a gas oil feed increased with the conversion of gas oil and exhibited an approximate linear variation with the second-order kinetic conversion parameter (conversion/(100-conversion)), Fig. 1. Thus, measurements of coke yields at different values of kinetic conversion were used to assess coke selectivity of the catalysts.

Zeolite preparations of Table 1 were designed to study the independent effects of exchange cations and acid site density as measured by the unit cell constant on coke selectivity. The number of sodium atoms per unit cell of the zeolite varied from 2.1 to 13.4 for catalysts described in Table 3. Unit cell constants of these zeolites after steam deactivation were within a narrow range (24.30 to 24.34 Å). Gas oil-cracking activity after hydrothermal treatment was lower for zeolites with higher sodium content (Table 3). However, coke selectivities of these zeolites were equivalent (Fig. 2), indicating that, at least in the 2- to 13-atom range, sodium does not affect zeolite coke selectivity. Dempsey (*12*) has suggested that dealuminated faujasites with a unit cell constant of less than 24.49 Å possess only strong acidity. Thus, acid strength distributions of these hydrothermally deactivated zeolites with differing sodium are expected to be equivalent although total acidity may vary. Unit cell constants of these zeolites were comparable. Hence, coke selectivities of these zeolites were equivalent.

Coke selectivity data for zeolite catalysts

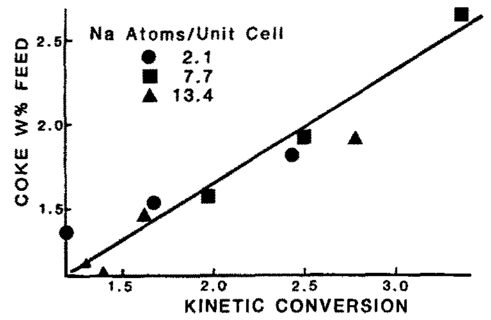

FIG. 2. Coke selectivity of catalysts with varying sodium content. Catalysts were subjected to hydrothermal treatment S1. Paraffinic gas oil feed.

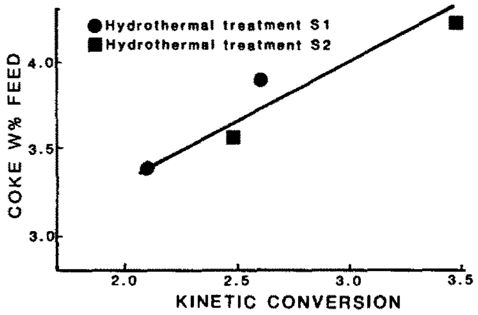

FIG. 3. Coke selectivity of a catalyst after two different hydrothermal treatments. Aromatic gas oil feed.

with the same unit cell constant but differing rare earth content are presented in Table 5. Rare earth atoms, 2.8 per unit cell, in one of the zeolites represent 45% of the exchange capacity of that zeolite and hence are significant. These two zeolites exhibited equivalent activity as well as coke selectivity (Table 5). Thus, for zeolites with the same unit cell constant, exchanged rare earth did not influence coke selectivity. Coke selectivity of a catalyst was also independent of the deactivation method (Fig. 3) at an equivalent unit cell constant.

C. Effect of Acid Site Density on Coke Selectivity

Catalysts described in Table 2 exhibited unit cell constants ranging from 24.57 to 24.25 Å after hydrothermal deactivation corresponding to 44 to 7 tetrahedral Al sites per unit cell. Coke selectivity results for these catalysts on paraffinic and aromatic gas oils are presented in Figs. 1 and 4. Coke yield at 70 wt% conversion of paraffinic gas oil was measured by linear interpolation of coke versus kinetic conversion data. Coke selectivity improved dramatically (lower coke yields at a given conversion) as the unit cell constant was reduced from 24.57 to 24.33 Å. Below 24.33 Å, or about 16 sites per unit cell and 4 sites per supercage, coke selectivity was less sensitive to the unit cell constant. The aromatic gas oil produced higher coke yields than the paraffinic gas oil for a given catalyst. However, the same qualitative trends with respect to the unit cell constant were observed for both paraffinic and aromatic gas oils. Coke yields during cracking of a nearly pure olefinic hydrocarbon (1-heptene) were also measured at WHSV = 16 for catalysts with differing unit cell constants. Conversion of

TABLE 5

Effect of Exchanged Rare Earth on Coke Selectivity

wt% zeolite in catalyst	10		10	
Na/unit cell	0.5		0.5	
RE/unit cell	0		2.8	
Unit cell constant (Å)	24.36		24.36	
WHSV	12	8	12	8
Conversion (wt%)[a]	74.3	84.9	75.2	83.9
Coke (wt% feed)	4.8	6.4	4.5	6.6

[a] Reactor conditions: temperature = 500°C, catalyst contact time = 75 s, paraffinic gas oil feed.

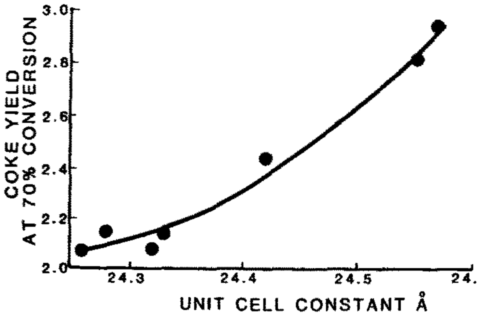

FIG. 4. Coke selectivity as a function of unit cell constant of the zeolite after hydrothermal treatment. Paraffinic gas oil feed.

1-heptene under this condition was between 98 and 99 wt% for all catalysts. Coke yields from 1-heptene also declined with a declining unit cell constant (Fig. 5).

Measurements of weight percent coke on catalyst at different axial positions in the fixed bed reactor for two catalysts with differing unit cell constants are described in Table 6. For either catalyst, the weight fraction of coke on the catalyst downstream in the fixed bed was about 20% higher than the weight fraction in the entrance region. These results suggest that both parallel and consecutive coking reactions (*13*) took place and that the consecutive coking reaction provided marginally larger contributions to the coke yield during cracking of the aromatic gas oil. The results also suggest that both parallel and consecutive coking reactions were suppressed in the presence of the smaller unit cell (24.32 Å) zeolite catalyst.

Polymerization of hydrocarbons leading to coke is expected to be higher than first-order in hydrocarbon concentration while cracking to lighter products is expected to be a first order reaction. Reduced acid site density in the catalyst is expected to reduce the surface concentration of coke precursors and increase the rate ratio of cracking to coke formation. Thus, coke selectivity was improved as the density of acid sites in the catalyst was lowered.

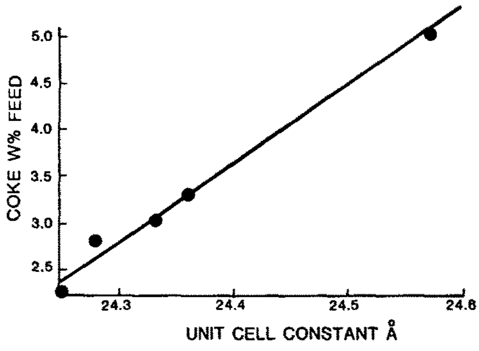

FIG. 5. Coke yield as a function of unit cell constant of the zeolite after hydrothermal treatment. 1-Heptene feed.

TABLE 6

Fixed Bed Reactor Coke Profiles

Axial position	Entrance					Exit
Zone No.	1	2	3	4	5	6
Coke on catalyst (unit cell constant = 24.57 Å)	2.0	2.2	2.3	2.3	2.3	2.2
Coke on catalyst (unit cell constant = 24.32 Å)	1.3	1.5	1.6	1.6	1.6	1.6

Note. Reactor conditions: temperature = 500°C, WHSV = 16, catalyst contact time = 75 s, aromatic gas oil feed.

However, acid site density or unit cell constant need not be the only parameter affecting coke selectivity in faujasites. Moscou and Mone (*14*) have observed that high-temperature calcination of faujasite without added steam, a treatment that is not expected to change unit cell constant significantly, altered its coke selectivity during cracking. Their data can be explained by postulating that alteration of the ratio of Lewis to Brønsted acidity alters coke selectivity. The Lewis-to-Brønsted acidity ratio in faujasites is primarily a function of thermal and hydrothermal treatment (*1*). Thus, high-temperature steam-deactivated catalysts examined in this work are expected to have similar Lewis-to-Brønsted acidity ratios. Hence, site density (or unit cell constant) is the primary structural parameter for determining coke selectivity in these samples.

The parameters affecting coke selectivity appear to be different from the ones affecting the octane number of product gasoline. Pine and co-workers (*8*) found that the octane number was sensitive to the unit cell constant in the range between 24.20 and 24.30 Å. Our observations indicate that coke selectivity is sensitive to the unit cell constant in a different region (24.57–24.33 Å). Also, the level of sodium exchange has no effect on coke selectivity while it has a significant effect on selectivity to produce a higher octane gasoline (*8*). Thus, the catalytic reactions controlling coke and octane selectivity need not be closely related.

CONCLUSIONS

Coke selectivity of hydrothermally treated faujasite zeolites is primarily a function of unit cell constant. For gas oil cracking, coke selectivity varies dramatically in the unit cell constant range between 24.57 and 24.33 Å. Both parallel and consecutive coking reactions are reduced for the zeolite with the lower unit cell constant. Variation below 24.33 Å is less significant. At the same unit cell constant, exchange cations like sodium and rare earth do not affect coke selectivity within the limits examined. Although acid strength distribution and the Lewis-to-Brønsted acidity ratio could affect coke selectivity in faujasites, acid site density as measured by the unit cell constant is the most significant structural parameter affecting coke selectivity among hydrothermally treated faujasite zeolites.

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