Shape selective cracking of *n*-octane and 2,2,4-trimethylpentane over an alumina-pillared clay

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A mixture of *n*-octane (nC_8) and 2,2,4-trimethylpentane (224-TMP) was cracked over an alumina-pillared montmorillonite (Al-PILC) acid catalyst as a means of characterising its pore structure and shape selectivity. The shape selectivity of the catalyst was quantified by a time dependent parameter analogous to the constraint index, called the selectivity ratio (SR), and defined as log(fraction of nC_8 remaining)/log(fraction of 224-TMP remaining). The SR was measured over Al-PILC, a 0.16 wt% Pt loaded Al-PILC, a Y zeolite, and an amorphous silica–alumina. The SR was greater over Al-PILC compared with Y-zeolite even though the pore openings of the Al-PILC were of similar or larger size than those in the Y-zeolite. Doping Al-PILC with Pt caused a large increase in the SR. As found with constraint index measurements, internal pore dimensions and reaction mechanisms appear to be the determinants of SR. However, SR is better capable of discriminating larger pore microporous materials.

Keywords: Pillared clay; Al_{13}; shape selectivity; cracking; acid catalyst

1. Introduction

Pillared clays are a class of porous, high surface area materials with applications as catalysts and adsorbents. The application of alumina pillared montmorillonite (Al-PILC) as a cracking catalyst for gas oil has been demonstrated [1,2]. One commonly cited advantage of pillared clays is that they can be prepared with larger pore openings than the most common commercially used Y-zeolite cracking catalysts. Stable large pore acid catalysts would have a huge potential for cracking the larger hydrocarbon molecules in heavier fractions of refinery feedstocks.

Average pore sizes in pillared clays are a function of the pillar height, which is determined by the diameter of the dehydroxylated pillaring species, and the pillar density. Calcined Al-PILC has a pillar height of about 0.7 nm. The pillar density is a function of the surface charge of the clay and the charge on the intercalated spe-

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cies, which must balance to maintain electro-neutrality. Some variation in pillar density has been achieved by varying the Al/clay ratio of the pillaring solution in a narrow range (1.6–2 mmol Al/g clay) [3]. The pillar density can also be varied by changing the cation exchange capacity of the clay by a partial ion-exchange with Ni^{2+} prior to pillaring [4].

Various techniques to calculate pore sizes in pillared clays include purely geometric ones, based on pillar height (from XRD) and pillar density (from chemical analysis, assuming all extra Al is as Al_{13} polymers), or methods involving the adsorption of various probe molecules [3,5].

Although these techniques do serve to indicate pore dimensions, the critical test is how the catalyst behaves during reaction. Different methods have been devised to measure pore size under reaction conditions. Thus Frilette et al. [6] were able to discriminate between various medium pore zeolites by cracking a 50/50 mixture of *n*-hexane (nC_6) and 3-methylpentane (3MP) over them. They defined a constraint index as CI = log(fraction of nC_6 remaining)/log(fraction 3MP remaining), after 20 min reaction time. The higher the CI the higher the degree of shape selectivity of the catalyst. The CI suffers some limitations in that it is temperature dependent and is affected by coking [6] but it provides a rapid, straight-forward method for measuring shape selectivity. The CI has been applied to pillared clays and found to be an inappropriate parameter for differentiating pore sizes because both nC_6 and 3MP can diffuse into without any steric hinderance [7,8]. Bruce et al. [8] found the CI for Al-PILC = 0.7, close to the CI for large pore zeolites and amorphous silica–alumina (0.4–0.6), where only intrinsic reaction rate differences are observed.

To extend the usefulness of CI, especially for large pore catalysts, a more general reaction constraint parameter is proposed. The selectivity ratio, SR is based on cracking a 50/50 mixture of two alkanes with the same number of carbon atoms and defined as

$$\mathrm{SR} = \frac{\log(\text{fraction of less branched isomer remaining})}{\log(\text{fraction of more highly branched isomer remaining})}\,.$$

With the above definition, the "constraint index" becomes a subset of the "selectivity ratio". As with the CI, when the reactions are first order, the SR is approximately the ratio of the first order rate constants. The SR can be calculated at a range of reaction times which allows the effect of secondary reactions such as coking to be monitored. The SR is a more flexible parameter since probe molecules can be chosen from a manifold of alkanes to more closely match the catalyst pore size in any particular cracking situation. However, when referring to the SR the two particular test isomers need to be specified. In this paper *n*-octane (nC_8) and 2,2,4-trimethylpentane (224-TMP) were chosen as probe molecules. Their vapour pressures are sufficiently low to enable them to be fed to the reactor by means of a saturated He gas stream. Also they have kinetic diameters a little smaller than the

Al-PILC pores, the kinetic diameters of nC_8 and 224-TMP being 0.44, and 0.55 nm respectively [7].

2. Experimental

2.1. MATERIALS

The Al-PILC was made from a solution of commercially available aluminum chlorohydrate and a Na^+-exchanged montmorillonite gel as previously described [9]. The Al/clay ratio in the pillaring solution was 12 mmol Al/g clay. The washed and dried Al-PILC was crushed and sized to 60–80 mesh before calcination for 1 h at 500°C. The final Al-PILC had the following properties: basal spacing, $d_{001} = 1.73$ nm; apparent BET surface area, $S_{BET} = 257$ m^2/g; total pore volume, $V_{tot} = 0.145$ ml/g; micropore volume, $V_\mu = 0.078$ ml/g. The Pt/Al-PILC was the same catalyst used and described by Doblin et al. [9]. Its physical properties were: $d_{001} = 1.64$ nm, apparent $S_{BET} = 164$ m^2/g, $V_{tot} = 0.132$ ml/g, $V_\mu = 0.036$ ml/g. Calcined rare-earth exchanged Y zeolite (CREY – W.R. Grace) powder was pelletised, ground and sized to 60–80 mesh, as was amorphous silica–alumina (Davison, Grade 979, low-alumina).

The main impurities in nC_8 (99.0%, Ajax Chemicals) were 3- and 2-methylheptane (0.5 and 0.2% respectively), and in 224-TMP (99.2%, Ajax Chemicals) the main impurities were 2,3-dimethylpentane, *n*-heptane and 2,2-dimethylhexane (0.3, 0.1 and 0.1% respectively) as determined by GC.

2.2. CRACKING REACTIONS

Reactions were carried out in a U-shaped vertical upflow quartz fixed bed microreactor (3.9 mm i.d.) loaded with about 0.3 g (accurately weighed) catalyst and operated at atmospheric pressure. Helium carrier gas (>99.99%) was saturated with liquid hydrocarbon feed by passage through a bubbler, the temperature of which was set at 40°C to maintain a total hydrocarbon vapour pressure of 6.7 kPa. In the nC_8/224-TMP mixtures, the fraction of either reactant in the vapour was adjusted to be within the limits 0.5 ± 0.05. Cracking was performed at WHSV = 0.54 h^{-1} and 325°C over the pillared clays and Y-zeolite, and at 500°C over amorphous silica–alumina. Reactions were performed for at least 60 min. Analysis was by on-line capillary GC. FID sensitivities of the starting materials and products were sufficiently similar to obviate the need for corrections [10]. Experiments were performed in duplicate and results averaged. Reported conversions are total conversions including coke. Theoretical mass and heat transfer calculations indicated that under the given reaction conditions external temperature gradients and interphase concentration gradients should not exist [11].

3. Results

From a comparison of the conversions and selectivity ratios over the different catalysts after 10, 30 and 60 min reaction (table 1), it was found that CREY was the most active cracking catalyst followed by the two pillared clays. However, the pillared clays deactivated faster than the other catalysts. The Pt/Al-PILC had a slightly higher initial activity than the Al-PILC (on a mass basis) but was also deactivated more rapidly. The SR decreased in the following order: Pt/Al-PILC > Al-PILC > CREY > amorphous silica–alumina. The SR decreased with reaction time except with amorphous silica–alumina where it remained constant (0.27 ± 0.1). The total hydrocarbon conversion of the 50/50 C_8 mixture, as well as the individual isomers, was lower over the pillared clays compared with the CREY catalyst. During 60 min reaction time, coke production over Pt/Al-PILC, Al-PILC and CREY was estimated to be about 15, 6 and 3 wt% of total feed, respectively.

Detailed product distributions were obtained for cracking over Al-PILC and Pt/Al-PILC and the major products are shown in table 2. After 30 min on stream, the product distribution was virtually constant except for 2-methylpropane and 2-methylpropene, with increasingly more 2-methylpropene produced at the expense of 2-methylpropane. No methane and only very small quantities of C_2, C_6 and C_7 were observed with Al-PILC. In contrast, C_6's and C_7's accounted for about 15 wt% of products over Pt/Al-PILC. The ratio of trans/cis-but-2-ene remained constant at 1.52 ± 0.01 and 1.38 ± 0.07 over Al-PILC and Pt/Al-PILC, respectively. The product distributions in terms of number of moles of product per 100 moles of cracked feed over Al-PILC, Pt/Al-PILC and CREY remained steady for each carbon number (table 3). Product distributions with respect to carbon number are all similar, however CREY produced more C_3 and C_5 at the expense of C_4 compared with the pillared clays. Only 1.93 to 1.99 moles of product were produced per mole of cracked feed indicating that only primary cracking was taking place (table 3).

The major difference in the product distribution over Al-PILC and Pt/Al-PILC was the alkenes/alkanes ratio (fig. 1). Over Al-PILC the ratio was around 1

Table 1
Conversions and selectivity ratios (SR) for cracking 50/50 mixtures of n-octane and 2,2,4-trimethylpentane

Time on stream (min)	Al-PILC[a]			Pt/Al-PILC[a]			CREY[a]			Amorphous silica–alumina[b]		
	nC_8	iC_8[c]	SR	nC_8	iC_8	SR	nC_8	iC_8	SR	nC_8	iC_8	SR
10	41	25	1.9	69	10	11.5	55	84	0.43	6.5	23	0.26
30	17	13	1.3	19	1.8	11.2	41	70	0.41	6.0	20	0.28
60	9.4	7.8	1.2	8	1	8.3	28	61	0.34	5.6	19	0.27

[a] Reaction conditions: $T = 325°\text{C}, p = 101\,\text{kPa}, \text{WHSV} = 0.54\,\text{h}^{-1}, \text{He/HC} = 15\,\text{mol/mol}$.
[b] Reaction conditions: $T = 500°\text{C}, p = 101\,\text{kPa}, \text{WHSV} = 0.54\,\text{h}^{-1}, \text{He/HC} = 15\,\text{mol/mol}$.
[c] 2,2,4-trimethylpentane.

Table 2
Major products for cracking nC_8/224-TMP over Al-PILC and Pt/Al-PILC [a]

Cracked product (wt%)	Al-PILC reaction time (min)		Pt/Al-PILC reaction time (min)	
	30	150	30	150
C_3	13	12	11	8
2-methylpropene	11	21	42	52
2-methylpropane	43	32	10	3
cis- and trans-but-2-ene	8	12	12	12
n-butane	5	4	0	0
2-methylbut-2-ene	2	4	7	6
2-methylbutane	11	8	2	1
n-pentane	2	2	1	0

[a] Reaction conditions: $T = 325°C, p = 101\,kPa$, WHSV $= 0.54\,h^{-1}$.

and remained constant, whereas over Pt/Al-PILC the ratio started at about 2 and increased steadily with time. At the same overall conversion, more C_4 and less C_3 and C_5 were produced over CREY than Al-PILC. The product distribution of the cracked mixture was very similar to the sum of individually cracked isomer product distributions, suggesting nC_8 and 224-TMP were cracked independently of each other.

4. Discussion

The results of conversions and coking rates presented here are in general agreement with previously made comparisons for cracking hydrocarbons over pillared clays and zeolites. Pilot plant and microactivity data [1,2] for cracking heavy gas oil over samples which had undergone mild thermal pretreatment, indicated pillared clays had only slightly lower overall conversions and gasoline selectivity, but

Table 3
Product distributions (mol/100 mol cracked feed) for cracking a 50/50 mixture of nC_8 and 224-TMP [a]

	Al-PILC	Pt/Al-PILC	CREY
C_1	0	0	0
C_2	0.3	4	1.5
C_3	31	25	45
C_4	134	130	115
C_5	27	20	34
C_6	2	8	2.5
C_7	1	4	0.5
sum	195.3	193	198.5

[a] Reaction conditions: $T = 325°C, p = 101\,kPa$, WHSV $= 0.54\,h^{-1}$.

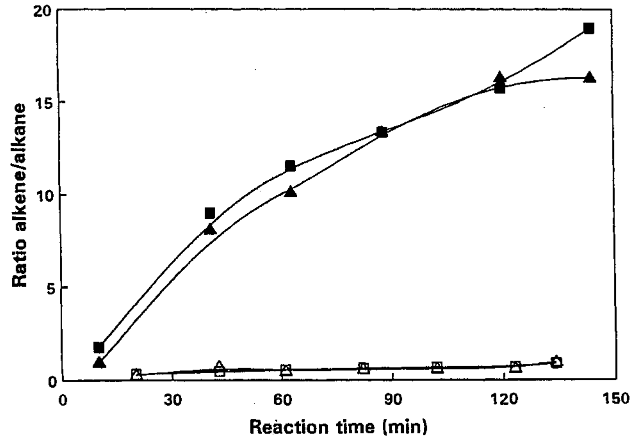

Fig. 1. Ratio of alkenes/alkanes in cracked product for cracking 50/50 mix of nC_8 and 224-TMP over Al-PILC (open symbols) and Pt/Al-PILC (closed symbols). C_4's (△, ▲); C_5's (□, ■).

higher light cycle oil selectivity and produced more coke than commercial zeolite-containing catalysts.

It has been suggested that the presence of iron in pillared clays is the reason for their strong coking tendencies [1], however work by Occelli et al. [13,14] showed that iron catalysed reactions are not the main cause of coking in pillared montmorillonite clays. The level of coking does influence the shape selectivity of the catalysts but other factors are obviously more significant (table 1). Since coke is only a minor reaction product other reaction mechanisms appear to be the key to understanding the shape selective processes.

Amorphous silica–alumina was used as a benchmark since it contains negligible microporosity and exhibits no shape selectivity. Over this catalyst, both octane isomers reacted according to their intrinsic reaction rates with minimal diffusional limitations. Therefore, a SR of 0.27 over amorphous silica–alumina represents a lower limit and higher values of SR (up to 11 in table 1) are an indication that the catalysts exert some shape selectivity.

The SR over the amorphous silica–alumina remained constant, an indication that catalyst deactivation of the active sites was non-preferential with regard to the reactants present. The change in SR with reaction time over the microporous catalysts is therefore probably related to their pore structure. The decrease in SR with reaction time over the microporous catalysts can be accounted for by progressive blockage of the micropores by coking. Pore blockage is such that neither reactant can gain access to the pore and the active sites within it. This would result in an overall decrease in activity and proportionally more reaction taking place on the external surface of the catalyst.

Since the SR was greatest in the pillared clays one might expect that the pore openings in the pillared clays are smaller than those in CREY. However, the average pore opening in the pillared clays is as least as large, if not larger than Y zeolite. Thus, from XRD patterns the average pore heights of Al-PILC and Pt/Al-PILC are 0.77 and 0.68 nm, respectively. By analysis of the extra Al content of the clay resulting from the pillars (2.1 Al atoms per Si_8O_{20} unit cell of clay) and geometric considerations the average pore dimensions of the pillared clays would be 0.79 × 0.77 nm in Al-PILC and 0.68 × 0.79 nm in Pt/Al-PILC. Although the uniformity of pillar distributions in pillared clays is not well established, a fractal analysis of adsorption data by Van Damme and Fripiat [14] concluded that the pillars of Al-PILCs have a close to homogeneous distribution. Similarly, Tsvetkov and White [15] calculated variations in interpillar distances of up to 0.23 nm, in montmorillonite pillared with organo-metallic species. If 0.23 nm represents the typical variation in pore width for the pillared clays then the vast majority of pores in Al-PILC will be <1.0 nm, smaller than the 1.2 nm supercage of CREY. This analysis is supported by the hydrocarbon adsorption data of Vaughan and Lussier [5]. They found an Al-PILC prepared under similar conditions as the Al-PILC in this study, was able to adsorb substantial quantities of 1,3,5-trimethylbenzene (kinetic diameter = 0.76 nm) but not 1,2,3,5-tetramethylbenzene (k.d. = 0.8 nm) and concluded their Al-PILC had a reasonably regular pore structure with pore openings between 0.8 and 0.9 nm.

We suggest the higher SR in Al-PILC compared with CREY is due to smaller internal dimensions of the pores in the former. Internal pore dimensions become a factor in determining the shape selectivity of a catalyst if some of the transition-state complexes which occur during reaction are sterically constrained by the size of the pores [16]. The size of pore openings only plays a role in reactant and product shape selectivity. Transition-state selectivity has also been observed in ZSM-5 with nC_6 and 3MP [17], even though both nC_6 and 3MP, (k.d. = 0.44 and 0.50 nm respectively), are both smaller than the 0.52 × 0.54 nm elliptical pores of ZSM-5 [18]. Similarly, with pillared clays and Y zeolite transition-state shape selectivity will be the most influential since both reactants and all products have kinetic diameters less than the pore dimensions of the catalysts.

Catalytic cracking by the classical mechanism has two major steps, a hydride transfer step to convert the feed reactant to a carbenium ion, followed by β-scission [19]. Hydride transfer is bimolecular and although 224-TMP can be accommodated readily by the catalyst pores, the larger dimensions of the bimolecular transition-state complex may be such that whereas it can fit in the 1.2 nm diameter internal cage of a Y zeolite it cannot fit in many of the pores of the Al-PILC. The cross-sectional dimensions of the transition-state complexes that are presumed to exist, were measured from molecular models and are shown in fig. 2. The sizes of the cross-sections suggest that the nC_8 transition-state complex with a 0.49 × 0.6 nm cross-section is readily accommodated by an Al-PILC pore, whereas the 0.6 × 0.7 nm 224-TMP transition-state complex may have more difficulty fitting. These calculations support the assertion that Al-PILC exhibits restricted transition-state shape selectivity with C_8 isomers. If this explanation is correct, then a

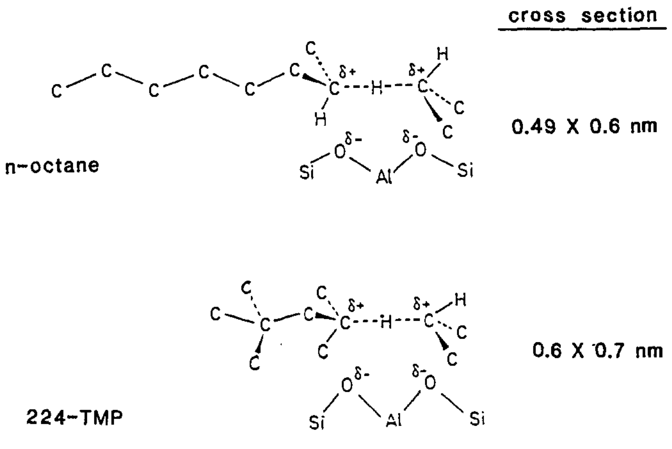

Fig. 2. Transition-state complexes formed during cracking of $n\mathrm{C}_8$ and 224-TMP.

large proportion of the voids between the Al-PILC layers have dimensions less than 1.2 nm, i.e. the cage size of Y zeolite.

The very large increase in SR over the Pt/Al-PILC catalyst compared with that for the Al-PILC catalyst suggests that different reaction mechanisms are in operation. An analogous effect was observed with the CI in H-ZSM-5. Guisnet et al. [20] found that when H-ZSM-5 was loaded with 0.43 wt% Pt there was a four-fold increase in the CI as well as an increase in cracking activity. The increase in activity was attributed to the formation of alkenes which when present in small quantities, are known to increase cracking rates of alkanes [21]. In the present situation, there are abundant quantities of alkenes (see fig. 1). More recently Santilli [21] has shown that over H-ZSM-5, the cracking rate of $n\mathrm{C}_6$ is increased much more by the presence of alkenes, than that of 3MP. The reason cited by Guisnet et al. [20] for the observed increase in CI was that the presence of alkenes causes more feed to be cracked via the classical carbenium ion reaction mechanism in favour of the less sterically constrained carbonium ion mechanism, which occurs via a monomolecular transition complex [22]. It is likely that when $n\mathrm{C}_8$/224-TMP mixtures are cracked over Pt/Al-PILC some of the feed forms alkenes by dehydrogenation on the active Pt sites and that $n\mathrm{C}_8$ forms alkenes preferentially to 224-TMP.

5. Conclusions

The CI is not a useful measure of shape selectivity over pillared clays. Al-PILC and Y zeolites induce shape selective cracking of C_8 alkanes. The extent of shape selectivity has been examined by a modified CI parameter (selectivity ratio). The SR, which increases with an increase in shape selectivity, was greater for cracking a 50/50 $n\mathrm{C}_8$ and 224-TMP mixture over Al-PILC than for the same reaction over CREY zeolite even though the pores were on average larger in the pillared clay. It is suggested that the 1.2 nm diameter cages of Y zeolite are large enough to contain the transition-state complexes formed during cracking, whereas fewer pores of similar size are present in Al-PILC. The shape selective behaviour of pillared clays depends not only on their pore size but also on the type of reactions that are occurring. The addition of 0.16 wt% Pt to the Al-PILC increased the SR by a factor of 5. The large increase in SR is attributed to a change in the dominant reaction mechanism which involves a smaller transition-state intermediate. As with CI, care needs to be taken when using the SR of one catalyst/reaction system for the prediction of shape selective behaviour of another catalytic system, especially if the reaction mechanisms are complex or not well understood.

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