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Cracking of *n*-Hexane Over LaX Catalysts

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Catalytic cracking of *n*-hexane over LaX catalysts was studied at 611 K, after a variety of outgassing and water pretreatment procedures. Infrared, TGA, adsorption and X-ray results were used to characterize the zeolites. The catalytic results appear to indicate that two kinds of cracking mechanism can occur concurrently, which involve radicals and carbonium ions, respectively. The pretreatment determines the relative importance of these. Infrared absorption intensity at about 3600 cm^{-1} was correlated with carbonium ion activity, and the assignment of this band, and the reasons for its absence in the spectrum of LaY are discussed. TGA and X-ray results showed that more than one cation distribution can persist at a given water content, so that the detailed history of the zeolite must be expected to influence its catalytic activity. Loss of activity after outgassing at 770 K cannot be explained as being simply due to the removal of water which is required as a co-catalyst for reaction.

Exchange of sodium ions by rare earth cations in faujasite type zeolites results in profound changes in catalytic activity, both in respect of reaction rates and product distributions. Details of the results obtained depend greatly on the degree of ion exchange and the outgassing history of the sample used. This can be readily understood in general terms as a result of the varying accessibility of different cation sites to guest molecules, and the known tendency for the distribution of cations among sites to depend on the water content of the zeolite.

This work was undertaken in the hope that recently published structural information (*1*, *2*) would allow a more thorough appraisal of catalytic results. Complementary adsorption, infrared and TGA measurements were made to characterize the catalysts further. Hydrocarbon cracking was chosen as a test reaction because of the industrial importance of zeolites in this field, the variety of product distributions which can be achieved, and the possibility of involvement of zeolitic water in the reaction mechanism. *n*-Hexane was used because this molecule is large enough to yield an informative range of products without making the necessary chemical analysis too difficult. Approximate calculations (*3*) showed that transport of materials to and from the catalytic centers should not significantly influence the observed kinetics.

METHODS

The materials, apparatus, and experimental procedures used were in most cases the same as those of McLaughlin and Pope (*4*). This section will thus be mainly confined to the points of difference.

A. *Materials*

$La_{60}X$ and $La_{78}X$ were prepared from binder free molecular sieve 13X, manufactured by Linde, and marketed by B.D.H. Ltd. (Batch No. 0003940). Reagent grade lanthanum nitrate (B.D.H.) was used to prepare the exchange solutions, and these were analyzed using standard EDTA solution according to the procedures of Wilson and Wilson (*5*). Lanthanum uptake estimated in this way was consistent with the sodium ion concentration in the exchange solution as measured by flame photometry.

$La_{100}X$ was prepared by the method of Sherry (*6*). Exchange was performed at 373 K, and used 13 successive 24 hr treatments with fresh batches of 1 *M* lanthanum nitrate solution. Analysis was carried out on a sample of the washed zeolite dissolved in concentrated HCl. Precipitated silica was centrifuged off, and then the total $Al^{3+} + La^{3+}$ was determined by a back titration method using EDTA and $CuSO_4$ solutions (*5*). The aluminum content was finally estimated separately by atomic absorption (*7*). These procedures were tested by analyzing a standard solution containing La^{3+} and Al^{3+}, and by re-analyzing $La_{78}X$ by this method. Sodium analysis confirmed that exchange was essentially complete, as only about 0.5% of the initial sodium ions were retained.

B. Catalyst Pretreatment

Outgassing procedures have been described previously (*4*). In some experiments, catalysts which had been outgassed at 770 K were cooled to room temperature and then treated with a measured dose of water vapor which was completely adsorbed very rapidly. A standard contact time of 36 hr was then allowed before subsequent re-outgassing to 611 K prior to reaction. Variations in contact time between 12 hr and several days did not affect the results obtained.

C. Infrared Experiments

Self supporting discs, about 20 mg cm^{-2} thick, were prepared from zeolite samples from which the coarser particles (diameter > about 1 μm) had been removed by sedimentation. A pressure of 1.5×10^7 kg m^{-2} was used. The infrared cell was similar to that described by Angell and Schaffer (*8*). Spectra were measured on a Perkin-Elmer 421 spectrophotometer. Absorption wavelengths and intensities were estimated by comparison with a standard polystyrene film sample.

Outgassing and pretreatment of the discs followed the procedures used with the catalyst samples as closely as possible. Experiments involving pyridine addition to the discs used the techniques of Ward (*9*). Excess pyridine was pumped off at 523 K.

RESULTS

A standard reaction temperature of 611 ± 3 K was used in each cracking experiment. Reaction rates obtained with catalysts from the same bulk sample, outgassed under similar conditions were generally reproducible to better than ±30%. Product distributions showed almost no variation in the same circumstances.

Experiments in which the catalyst was outgassed at 770 K, cooled, contacted with a measured dose of water vapor at room temperature, and then re-outgassed at 611 K also gave highly reproducible product distributions, but the reaction rates were more scattered.

Despite the fact that the reaction rates observed were often strongly dependent on the catalyst composition and pretreatment, the following common features emerged:

1. No product of molecular weight greater than *n*-hexane was ever observed. In two experiments, traces of 2-methylpentane and 3-methylpentane were found. *n*-Pentane was the only C_5 molecule obtained, and this was a relatively minor product (<7 mole %).
2. The disappearance of *n*-hexane, and the formation of all products apart from ethane and methane showed an induction period, and then followed straight-line kinetic curves. Generally reaction was followed until about 40–50% of the hexane had reacted. Methane and ethane also showed zero order kinetics, but had no induction period.
3. The rate of removal of *n*-hexane from the gas phase depended far less on the catalyst type and pretreatment than did the rate of product formation, and the product distribution.

Examination of the rates of formation of all gas phase products indicated that two patterns of catalytic activity might be present. The formation of methane and ethane appeared to be correlated, as did the production of ethene, isobutane, *n*-butane and *n*-pentane. Propane and propene could not be resolved by our analytical

TABLE 1

REACTION TEMPERATURE 611 K, EXCEPT FOR NaX WHICH WAS USED AT 790 K[a]

Zeolite	Outgassing temp (K)	R	Rates of formation of							Rate of removal of n-hexane	Fraction of carbon appearing as gas phase products
			Methane	Ethane	Ethene	C_3 hydrocarbon	n-Butane	Isobutane	n-Pentane		
NaX	778	3.2	0.12	0.035	0.090	0.083	0.024	0.000	0.000	0.012[b]	—[b]
$La_{60}X$	606	0.67	0.00038	0.00082	0.00040	0.0020	0.0000	0.0000	0.0000	0.42	0.01
$La_{78}X$	612	0.33	0.0020	0.0025	0.0021	0.030	0.0000	0.0020	0.0000	0.19	0.10
	764	0.87	0.00097	0.0015	0.00058	0.0030	0.0000	0.0000	0.0000	—[b]	—[b]
$La_{100}X$	551	0.08	0.0030	0.026	0.030	0.74	0.70	0.24	0.036	0.56	1.0_4
	561	0.07	0.0044	0.012	0.043	0.88	0.029	0.29	0.029	0.89	0.7_4
	614	0.08	0.0041	0.0096	0.046	1.00	0.010	0.41	0.011	0.90	0.9_7
	723	0.13	0.0037	0.0065	0.019	0.31	0.004	0.042	0.019	0.17	1.0_7
	763	0.13	0.0009	0.0025	0.0080	0.21	0.0020	0.072	0.019	0.18	0.9_2
	791	0.15	0.0032	0.0048	0.0065	0.11	0.0000	0.023	0.0000	0.36	0.2_1
	833	0.36	0.00073	0.0015	0.0033	0.020	0.0000	0.004	0.0000	0.19	0.0_8

[a] Data are included for each observed gas phase product. Reaction rates expressed as μmol min^{-1} (g hydrated catalyst)$^{-1}$. R = ratio of (methane + ethane + ethene) to C_3 hydrocarbon in products.

[b] Estimates not available, or rather unreliable.

techniques, but the peak shapes on the chromatograms strongly suggested that propene belonged to the methane–ethane group, and propane with the other products. Catalyst activity for production of the former group of compounds was always rather small, and was much less dependent on the pretreatment used.

When the chromatographic technique was changed to allow the detection of hydrogen (*4*), only trace amounts were found, and this product was generally assumed absent. Mass balance calculation supported this view.

Some of the more important features of the reaction in the absence of water pretreatment are detailed in Table 1. The effect of varied outgassing temperatures is shown in the results obtained with $La_{100}X$ (Figs. 1,2). From 561 to 763 K there is little change in the product distribution, although the activity goes through a maximum at about 623 K. As the outgassing temperature is raised further, the rate of removal of *n*-hexane is not much affected, but the product distribution changes sharply to yield more light hydrocarbons. At and below 763 K, the mass balance between reactant lost and gas phase product formed is exact, within experimental error, but at higher temperatures this is no longer the case. At 833 K only about 8% of the reactant carbon appears as gas phase products.

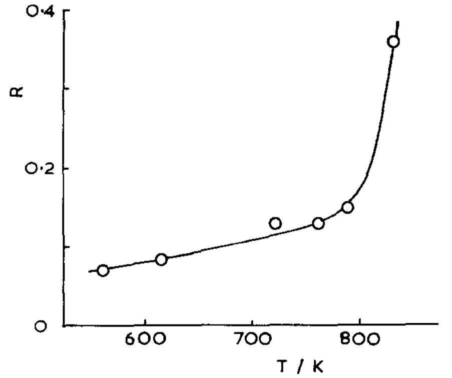

FIG. 1. The effect of outgassing temperature on the products of hexane cracking over $La_{100}X$ at 611 K. *R* is the mole ratio of $(C_1 + C_2)$ to C_3 hydrocarbons. Ordinate: R; abscissa: outgassing temp (K).

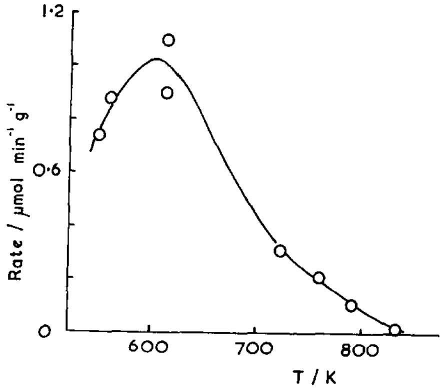

FIG. 2. The effect of outgassing temperature on the rate of production of (propane + propene) from hexane over $La_{100}X$ at 611 K. Ordinate: rate/μmoles min^{-1} g^{-1}; abscissa: outgassing temp (K).

The effect of adding water to the zeolite which had been deactivated by outgassing to 773 K, and then re-outgassing to 611 K are shown in Fig. 3. Results after simple outgassing at 611 K are included for comparison. The product distribution reverts to the form shown at lower outgassing temperatures after about 0.02 H_2O molecules per La^{3+} have been added. Larger doses all give similar results. Reaction rates were more difficult to reproduce, but appear to require up to 1 H_2O/La^{3+} for complete restoration. A dose of 0.02 H_2O/La^{3+} was approximately sufficient to quadruple the activity of the outgassed catalyst. Induction periods appeared to decrease with increasing catalyst activity in a similar way for water-dosed and undosed samples.

$La_{60}X$ and $La_{78}X$ both showed low cracking activity, even when outgassed at 611 K. These materials both behaved like $La_{100}X$ outgassed at $T > 773$ K in respect to the rate of the cracking reaction, and product distribution. It was again noted that little of the removed *n*-hexane was converted to gas phase products.

The krypton adsorption capacity at 77 K of $La_{100}X$ increased about 3% on raising the outgassing temperature from 553 to 611 K, and then remained constant within experimental error up to the maximum temperature studied of 791 K. No evidence was found for changed adsorption capacity after a cracking experiment had been per-

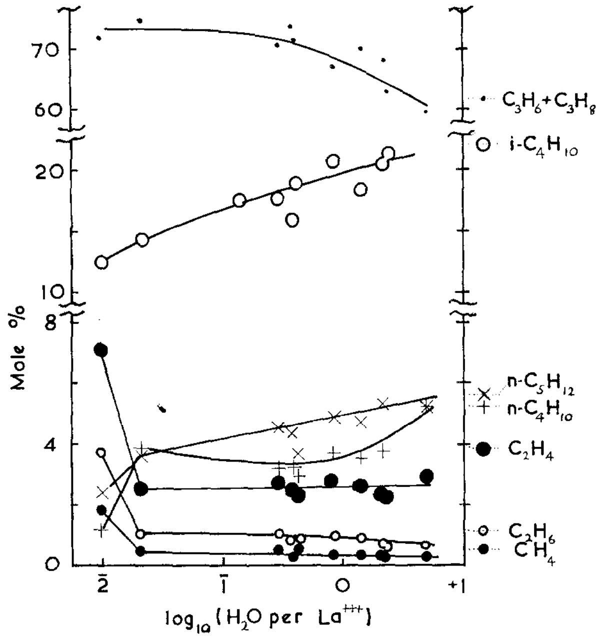

FIG. 3. Complete product distributions from water pretreated $La_{100}X$ samples (see text for details). Data at right side refer to simple outgassing to 611 K. Ordinate: mole % of product; abscissa: $\log_{10}$ (H_2O added per La^{3+} present).

formed. $La_{60}X$, $La_{78}X$ and $La_{100}X$ outgassed at 611 K had the same adsorption capacity per unit cell.

Water uptake was less reproducible. A sample of $La_{100}X$ which had been equilibrated over NH_4Cl solution in the usual way, outgassed at 773 K, and then re-equilibrated over NH_4Cl solution was found to have only re-sorbed about 85% of the water initially present, after several months. The re-equilibrated sample was then subjected to thermogravimetric analysis, and gave results different from the original material (Fig. 4). This new behavior was reproduced when the sample was subjected to a second rehydration/dehydration experiment.

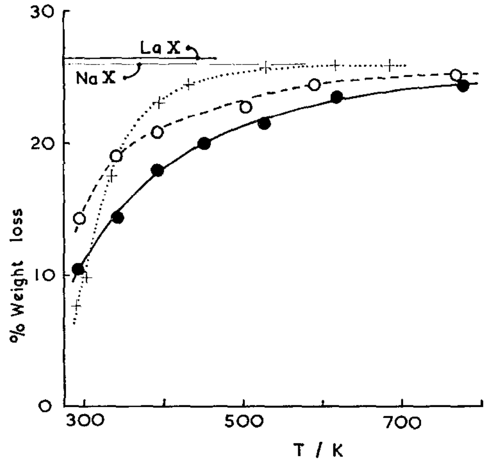

FIG. 4. Outgassing weight loss shown by NaX and $La_{100}X$. Horizontal lines refer to calcination at 1270 K. (+) NaX; (●) $La_{100}X$; (O) $La_{100}X$ after dehydration rehydration. Ordinate: % weight loss; abscissa: outgassing temp (K).

The X-ray diffraction pattern produced by the re-equilibrated sample was also distinctly changed, though there was no evidence of loss of crystallinity. Unfortunately, although we were able to estimate the cation occupancy factors for the original hydrated material (*10*) (occupancy factors at sites of; 0.00 at I, 0.19 at I′, 0.02 at II′, 0.44 at II, 0.00 at V; $R = 0.17$) no satisfactory structure analysis could be obtained for the re-equilibrated sample (best $R = 0.37$).

Infrared spectra from self-supporting zeolite discs, outgassed in a similar way to the zeolite catalysts, were also measured.

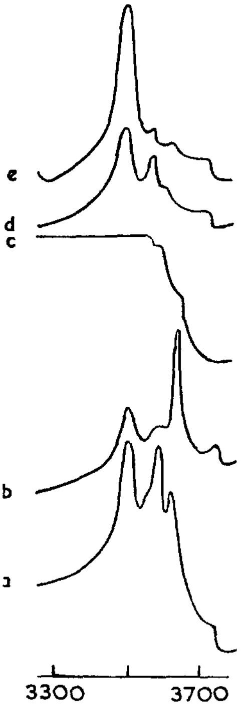

FIG. 5. Infrared spectra from $La_{100}X$. (a) Outgassing temp, 623 K; (b) outgassing temp, 773 K; (c) b after treatment with 2.8 H_2O per La^{3+}; (d) c after re-outgassing at 623 K; (e) d after pyridine treatment. Ordinate: intensity; abscissa: wavelength (cm^{-1}).

The effect of water dosing as in the catalytic experiments, and of pyridine treatment were also examined. A typical series of spectra is shown in Fig. 5. The most interesting feature of those results was the observation of a band near 3600 cm^{-1} which was removed after pyridine treatment, and appeared to correlate to some extent with the catalytic activity (Table 2).

TABLE 2

INFRARED ABSORPTION AND REACTIVITY OF CATALYSTS AFTER VARIOUS PRETREATMENTS[a]

Zeolite	I_{1441}	I_{1451}	I_{1545}	I_{3644}	I_{3600}	Relative activity
$La_{100}X$(623)	100	100	100	100	100	100
$La_{100}X$(773)[b]	75	88	78	0	90	110
$La_{100}X$(773)	44	63	33	68	25	20
$La_{78}X$(623)	75	68	50	28	11	5
$La_{78}X$(773)	44	38	29	14	9	0.2
$La_{60}X$(623)	33	35	50	17	2	0.2

[a] Infrared data give relative absorption intensity at frequencies expressed as cm^{-1}. Intensities at 1441, 1451 and 1545 cm^{-1} refer to pyridine treated samples. Catalytic activity is for the formation of C_3 hydrocarbons. Outgassing temp (K) shown in parentheses.

[b] This sample was pretreated with 2.8 H_2O per La^{3+} prior to re-outgassing at 623 K.

DISCUSSION

The relative concentrations of isobutane and C_1 and C_2 hydrocarbons in the reaction products are often used to differentiate between cracking involving carbonium ion intermediates and reaction proceeding via a free radical mechanism. On this basis, it appears clear (Table 1) that $La_{100}X$ outgassed at less than 770 K uses the former mechanism, and NaX and $La_{60}X$ the latter. $La_{78}X$ gives a product distribution between these two extremes, which approaches the radical type as the outgassing temperature is increased. The same trend with outgassing temperature is followed by $La_{100}X$.

Although carbonium ion activity may be expected in lanthanum zeolites, the detailed product distributions obtained when this mechanism appears to be operative are still difficult to explain *(11)*. No gas phase products of greater molecular weight than *n*-hexane, and only traces of other hexane isomers were observed, so that there is little evidence for a mechanism involving addition and disproportionation *(12)*. However, if no addition reactions take place, the only major products should be propane and propene, and C_4 hydrocarbons formed should be accompanied by an equal amount of C_2 hydrocarbon. Table 1 shows that these predictions are inconsistent with the results.

The fact that some of our catalysts, which were still quite active in hexane removal, produced only gas phase products typical of a radical mechanism, and at small yield, also requires explanation.

We believe that our LaX catalysts contained two kinds of active sites. The first was responsible for radical type gas phase products, but produced mainly an involatile polymeric residue. The second led to the formation of carbonium ions from the hexane which could react in several ways. One possibility, namely, reaction with the product from the first kind of site, allows quantitative conversion of hexane to gas phase products. The involvement of two different kinds of site could also explain why the formation of carbonium ion products shows an induction period while that of radical products does not, and why the induction periods observed are approximately inversely proportional to the rate of reaction.

Infrared techniques were used to study the nature of the sites responsible for the carbonium ion activity. The spectra we obtained for $La_{100}X$ outgassed at 770 K were very similar to those reported by Bennett, Smith and Angell (*1*), with sharp peaks at 3506, 3597 and 3645 cm^{-1}. Pyridine addition removed the bands at 3597 and 3645 cm^{-1}, but left the band at 3506 cm^{-1} unchanged. As neither pyridine nor *n*-hexane can be expected to enter the sodalite cages, these results should be directly relevant to the cracking reaction. The assignment of the band near 3500 cm^{-1} to OH groups not accessible from the supercage has been confirmed by benzene adsorption studies (*1*).

After pyridine adsorption, bands which are usually assigned to chemisorbed pyridine (at ~1440 cm^{-1}), pyridine at Lewis acid sites (at ~1450 cm^{-1}) and at Brønsted acid sites (at ~1545 cm^{-1}) appeared (*13*). Table 2 shows that these cannot be correlated with the catalytic activity of the sample, although the hydroxyl band intensity at 3600 cm^{-1} apparently can. It is interesting that LaY, which is also a good cracking catalyst, shows no absorption at about 3600 cm^{-1} (*11*, *14*), and in fact only has two bands in this part of the spectrum, at about 3529 and 3641 cm^{-1}. The band at 3529 cm^{-1} in $La_{91}Y$ does not interact with pyridine, and appears similar to the band at 3506 cm^{-1} in LaX (*15*). We think that both result from the interaction of H_2O with La^{3+} in sodalite cages (*16*).

The catalytic results suggest strongly that at least after outgassing at 620 K, La_{100} contains La^{3+} ions in the supercage as well. We tentatively assign the infrared band near 3600 cm^{-1} in LaX to water associated with those ions. By analogy with the frequency change from 3506 cm^{-1} in LaX to 3529 cm^{-1} in LaY, we would expect LaY to show absorption at about 3620 cm^{-1}. In practice, both LaX and LaY show a strong absorption at about 3640 cm^{-1}. We think that in LaX this corresponds to a structural OH group in the supercage which is not closely associated with a cation (*1*), but that in LaY it is really the superposition of two unresolved bands, which are analogous to the 3600 and 3640 cm^{-1} bands in LaX. Careful examination of the spectra of the two zeolites suggests that if such super-position did occur, it would be very difficult to resolve experimentally. This proposal could also rationalize some other observations. The decreased intensity of the 3640 cm^{-1} band in LaY as the lanthanum content is increased (*14*), could result from interaction between previously isolated acid OH groups and lanthanum ions. The fact that reconstitution of the 3640 cm^{-1} band in LaY after dehydration rehydration, though not complete (*14*), is more marked than in LaX (Fig. 5) we believe to be due to the rehydration of lanthanum ions being a much more rapid process than rehydroxylation.

The increased activity of $La_{100}X$ catalysts as the outgassing temperature is increased at temperatures below 670 K probably arises from the competition between residual water and hexane for adsorption sites at or near La^{3+} ions. As the outgassing temperature is raised further, La^{3+} ions, in the presence of water, may migrate away from positions accessible to molecules in the supercage (*1*, *2*). At the lower exchange levels in $La_{60}X$ and $La_{78}X$, the small catalytic activity suggests that there are few La^{3+} ions exposed under the conditions used.

Our krypton adsorption results also lead us to believe that there are few lanthanum ions in the supercage in $La_{60}X$, $La_{78}X$ and $La_{100}X$ at outgassing temperatures above 670 K. Although the fully hydrated materials have a significant number of ions in the supercage (*1*, *15*), and migration undoubtedly takes place on dehydration at sufficiently high temperatures (*1*, *2*), the adsorption capacities of each sample were the same within experimental error, and the adsorption capacity of $La_{100}X$ did not change as the outgassing temperature was raised to 790 K.

The dehydration study (Fig. 4) shows an interesting difference between $La_{100}X$ as prepared, and $La_{100}X$ which has been outgassed at 770 K and then rehydrated at room temperature. The rehydrated material contains much less strongly bound water. This is most simply understood as being due to an irreversible transfer of La^{3+} ions to Site 1 where they cannot be rehydrated. This is consistent with our X-ray studies (*15*), and results of Olson, Kokotailo and Charnell (*2*), which show no occupancy of Site 1 by hydrated LaX and CeFj. During ion exchange it is apparently possible for lanthanum ions to pass through the windows into sodalite cages, a process which must involve temporary breaking of cation to water bonds, whereas passage through the same sized windows into Site I, which requires complete de-solvation, is not possible. X-Ray examination of the rehydrated sample after a period of several months confirmed that the structure was still different from that of the original hydrated material, so that it is clear that ion exchange with these samples may not proceed to thermodynamic equilibrium.

In the experiments in which water was dosed at room temperature onto a $La_{100}X$ catalyst which had previously been outgassed to 770 K, it was found that 0.02 H_2O per La^{3+} could produce almost as active a catalyst as much larger doses, and the same product distribution (Fig. 3). This again indicates that few La^{3+} ions are involved with catalytic activity and helps to confirm the previous suggestions about cation distribution. The question remains as to whether the added-back water acts by altering this distribution, or by functioning as a co-catalyst. It seems likely that some cation redistribution is involved on raising the outgassing temperature from 620 to 770 K (*1*, *2*), so that restoration of activity to a catalyst outgassed at 770 K by room temperature dosing and re-outgassing to 611 K appears to require more than co-catalyst involvement alone.

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