

RACKING OF HYDROCARBONS ON ZEOLITE CATALYSTS

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ABSTRACT

Intensive research in connection with the development of industrial zeolite cracking catalysts, contributed towards a better understanding of hydrocarbon cracking reactions and of the factors governing catalyst efficiency. Investigations on FCC catalysts are in progress with the aim of improving selectivity control (gasoline yield, octane number, metal and coke resistance), better pollution control, and the processing of higher boiling feedstocks. Such work includes the simultaneous optimization of both matrix and zeolite properties.

The potential value of partially dealuminated zeolites Y as a highly active and selective catalyst component is demonstrated together with that of ZSM-5 addition, by which the yield of light synthesis olefins can be improved.

INTRODUCTION

Of all the cracking processes in the world petro-chemical industry, catalytic cracking is the most common. 75 percent of cracking is achieved by the catalytic process, whereas the hydrocracking, visbreaking and coking processes occupy only 25 percent.

At present, a total of about 12 percent petroleum in the world and 30 percent in the USA (250 million t/a) are transformed by the FCC process /1, 2/.

In 1979, overall consumption of cracking catalysts was about 205 kt and is continuously increasing. The overall capacity of the firms Akzo, Crosfield, Davison Chemical/W. R. Grace, and Katalistiks International will, it is estimated, reach 85 kt in 1985 /3/. Today, the specific catalyst consumption in the cracking of gas oil amounts to about 0,5 kg/t of feedstock.

Although the first industrial plant for catalytic cracking was in operation as early as 1937, (fixed-bed plant), the revolutionary development of catalytic cracking did not start until 1962, when zeolite catalysts were introduced. The high activity of zeolites led to the introduction of a new process: the riser cracking process. As a result of short contact times between catalyst and feedstock, this form of process permitted optimal utilization of the activity and selectivity of microspherical zeolite catalysts. The first plant for this process was introduced in industry in 1971, and since then riser cracking has been used exclusively in all new FCC units. The chemistry and engineering of catalytic cracking have been reviewed in a large number of publications, e. g. /4-6/.

In the present paper, some problems connected with the development and mode of action of modern catalysts are discussed and analyzed. Special attention is given to partially dealuminated zeolites Y.

MECHANISM AND KINETICS OF HYDROCARBON CRACKING

Hydrocarbon cracking of gas oil involves quite a series of reactions:

Paraffins are cracked to give olefins and highly branched smaller paraffins, the iso/n paraffin ratio often exceeding thermodynamic equilibrium.

Olefins undergo isomerization, cracking into smaller olefins, hydrogen uptake (by transfer from naphthenes or coke), and disproportionation in the case of low molecular weight olefins.

Alkyl aromatics undergo dealkylation, side-chain scission and alkyl group transfer: unsubstituted aromatics are scarcely attacked.

Naphthenes give olefins; cyclohexane is preferentially converted into benzene.

Condensation reactions of aromatics and olefins finally result in coke formation.

Since the work of WHITMORE /7/, THOMAS /8/ and GREENFELDER et al. /9/, the catalytic cracking of the C-C bond has been generally accepted to proceed as an acid catalyzed elimination reaction involving a carbenium ion chain mechanism which consists of a hydride transfer step followed by beta scission. Three possibilities can be considered for the formation of the first carbenium ions, which are responsible for the starting of the carbenium ion chain: 1. Abstraction of a hydride ion from the paraffin molecule by a Lewis site at the catalyst surface.

2. Protonation of the paraffin by a super-acidic Brønsted site, accompanied by the formation of hydrogen and the carbenium ion.
3. Protonation of an olefin at a Brønsted site. The olefin may be contained in traces in the substrate, or may be formed by thermal cracking of the paraffin used. Formation of carbenium ions from olefins is suggested by the strongly protonating action of olefins in the cracking reaction and the direct dependence of the rate of cracking on the olefin content of the substrate /10/.

The role of Lewis sites as catalytic or cocatalytic sites is still a subject of discussion /11, 12/, their role in oligomerization reaction has been demonstrated /13/.

Besides the carbenium ion chain discussed above, some modified mechanisms have been proposed to explain peculiarities observed in product distribution:

i) The catalyst acts as a super acid, and the reaction proceeds via pentacoordinated carbonium ions /14/. However, although some acidic zeolites, e.g. H-mordenites, exhibit a protonating action comparable to that of super acids, it is hard to believe that under reaction conditions and in the presence of a high excess of basic molecules such as olefins, aromatics and coke, they are capable of acting as super acids.

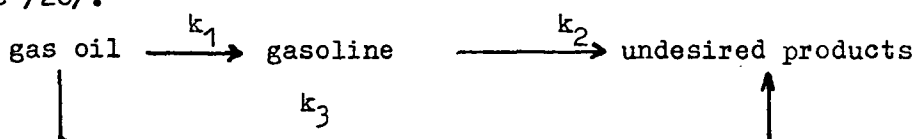
ii) Once the possibility of the formation of cation radicals /15/ and allyl carbenium ions /11/ has been proved, there is still the question of whether or not these entities are relevant to the cracking reaction /16/. The low energetic allylic cation preferentially would take part in oligomerization reactions.

It should be pointed out that any deviation from the product distribution expected to occur in the free-carbonium ion mechanism does not necessarily arise from a different mechanism, but may only be due to the fact that no free ions but ion pairs are available, which are formed by carbocations and nucleophilic sites on the catalyst surface. In this case, variations in selectivity can be described by reactivity-selectivity relationships /17/ as common in organic chemistry. Strong adsorption and diffusion limitations exert a pronounced influence on product distribution. This has to be taken into consideration, e.g. for ZSM-5 as a catalyst.

The simultaneous occurrence of the cracking reactions mentioned above makes mechanistic investigations difficult. In the extreme case, even random isotopic C scrambling is found /18/. Hence individual hydrocarbons have often been used for mechanistic inves-

tigations and for better characterization of the mode of action of the catalyst. To characterize FCC catalysts in the conversion of gas oil feedstocks under conditions close to industrial operation been ditions on a laboratory scale, conventional procedures have been elaborated and widely accepted in recent years /19/.

Besides mechanistic considerations, the kinetics of hydrocarbon cracking is studied to determine the overall conversion rates, and to predict the effect of catalyst variation and modification as well as of refinery operation conditions on the product distribution. Hence, it has become general practice today to provide a process model together with the process license. The most general behaviour of catalytic cracking reactions can be described by a three-lump scheme /20/.



Gasoline cracking (k_2) which produces undesired products, including coke and "overcracked" light compounds, is lower under piston flow conditions. This is one of the advantages of modern riser tube reactors, in which the reaction regime is more closely approximated to the piston flow.

The constants k_1 - k_3 being functions of feedstock composition, the three-lump model is inadequate for the case of feedstock changes. JACOB et al. /21/ developed a ten-lump model dividing aromatic rings and alkyl chains into separate species. WEEKMAN /22/ showed this model to be useful for optimizing unit operation.

MODERN FCC CATALYSTS

Conventional zeolite cracking catalysts consist of about 5 to 20 wt.% of zeolite and an X-ray amorphous matrix. Depending on preparation conditions, composition and activation conditions, both components interact in different ways and with different intensities. Both components are subject to definite requirements concerning the access of the hydrocarbon to the zeolite (transport pores $> 4,0$ nm) and to the active sites in the zeolite (pore openings $\sim 0,8$ nm), the nature and concentration of active sites in the zeolites and the matrix, the thermal and hydrothermal structural stability of the zeolite, the mechanical stability of the microspherical catalyst particles, and the compatibility of the catalyst with metals.

New trends have appeared in the development and optimization

of the matrix properties for commercial catalysts /22, 23/. Thus, the DA-200 to DA-400 of the Davison Chemical/W. R. Grace are modified as compared with the Super-D Extra as follows: increased Al_2O_3 content up to nearly 50 wt.%, reduced specific surface area and pore volume, nearly doubled mean pore diameter. These changes in composition and texture result in decreased diffusion, "selective" cracking of long-chain hydrocarbons at the matrix, and higher thermal and hydrothermal stability as well as compatibility of the matrix with metals. Similar results were achieved by Katalistiks International with their catalyst series EKKZ, SIGMA, RMZ, and CENTURY /24/.

PRODUCTION OF FCC CATALYSTS

Cracking catalysts containing 5 to 20 wt.% of zeolites are mainly produced in two ways: Either the zeolite component is synthesized and modified in a separate step with subsequent dispersion in a synthetic or natural aluminosilicate matrix, or the partial zeolite crystallization is carried out in situ in the natural aluminosilicate matrix. Whereas most firms use the former procedure, others, e.g. Engelhard, synthesize their catalysts from clay or metakaolin by the last-mentioned method.

In most cracking catalysts, the matrix component consists of synthetic, semi-synthetic, or natural clay based aluminosilicate. Sometimes special oxides (e.g. TiO_2) are also added. The matrix must meet the following requirements:

- large pores (>4.0 nm) in order to facilitate mass transfer to the active sites of the zeolite and, if possible, to prevent diffusion limitation. This property is of special importance for the cracking of heavy and residue oils.
- small specific surface area ($30 - 50$ m²/g) which is a precondition for high compatibility with metals and hence selectivity.
- small, but selective cracking activity for long-chain hydrocarbons, such that the cracking reaction at the finished catalyst proceeds in the following way:

feedstock	matrix →	medium cracked products	zeolite →	gasoline and light cycle oil
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- great thermal, hydrothermal and mechanical stability which is resistant to reaction and regeneration conditions.

The necessary properties of the active zeolite component are the following:

- unidisperse pore structure (pore openings $\sim 0,8$ nm).
- high activity (10^2 to 10^4 times that of the matrix), and, above all, high selectivity for hydrocarbons within the boiling range of gasoline.
- low tendency for coke formation.
- high thermal and hydrothermal stability and high compatibility with metals.

When the zeolite synthesis is not carried out in situ in the matrix during the preparation of the catalyst, a special binding agent, of which no detailed information is given by the firms, is used to promote homogeneous distribution of the zeolite in the matrix and to increase the mechanical stability of the microspheres. Under the reaction and regeneration conditions of the FCC process, intensive interaction between matrix and zeolite component may be expected to occur which, apart from cation redistribution, leads to structural stabilization of the zeolite in the matrix.

As regards the active zeolite component, X and Y type zeolites in the H^+ and/or RE^{3+} form are used with their alkali content being decreased to 0,3 wt.% Na_2O by the ion exchange. Alkali and alkaline earth metals decrease the activity of the active zeolite component in the order $Na^+ > K^+ > Mg^{2+}, Ca^{2+}$. To prevent overcracking (which is favoured by too many strongly acidic sites) on the fresh catalyst, only a small portion is added to the circulating equilibrium catalyst. Under activation, reaction and regeneration conditions, the fresh catalyst is transformed into the equilibrium catalyst, i.e. the hydrothermal conditions of this treatment affect partial dealumination of the zeolite, along with a change in the acidity spectrum. The properties of the Y zeolite contained in the equilibrium catalyst are comparable to those of a non-extracted, ultra-stable zeolite Y, named US(w). The lattice constant of the starting Y zeolite being 2.46 - 2.47 nm, that of the zeolite in the equilibrium catalyst will range between 2.43 and 2.44 nm, i.e. the SiO_2/Al_2O_3 molar ratio is increased from about 5 to about 20-30. For a priori adjustment of such an acidity spectrum and hence of catalytic activity and selectivity, it appeared reasonable to start from ultrastable Y zeolites.

HYDROTHERMAL TREATMENT OF FCC CATALYSTS

Hydrothermal treatment at temperatures ≥ 800 K causes dissolution of aluminium from lattice positions, with simultaneous restoration of the remaining lattice defects. The resulting zeolite lattice,

which is richer in SiO_2 , exhibits increased thermal and chemical stability ("ultrastabilization"). The effect of such hydrothermal pretreatment on the catalytic properties of an FCC catalyst containing REY zeolite is demonstrated in Fig. 1.:

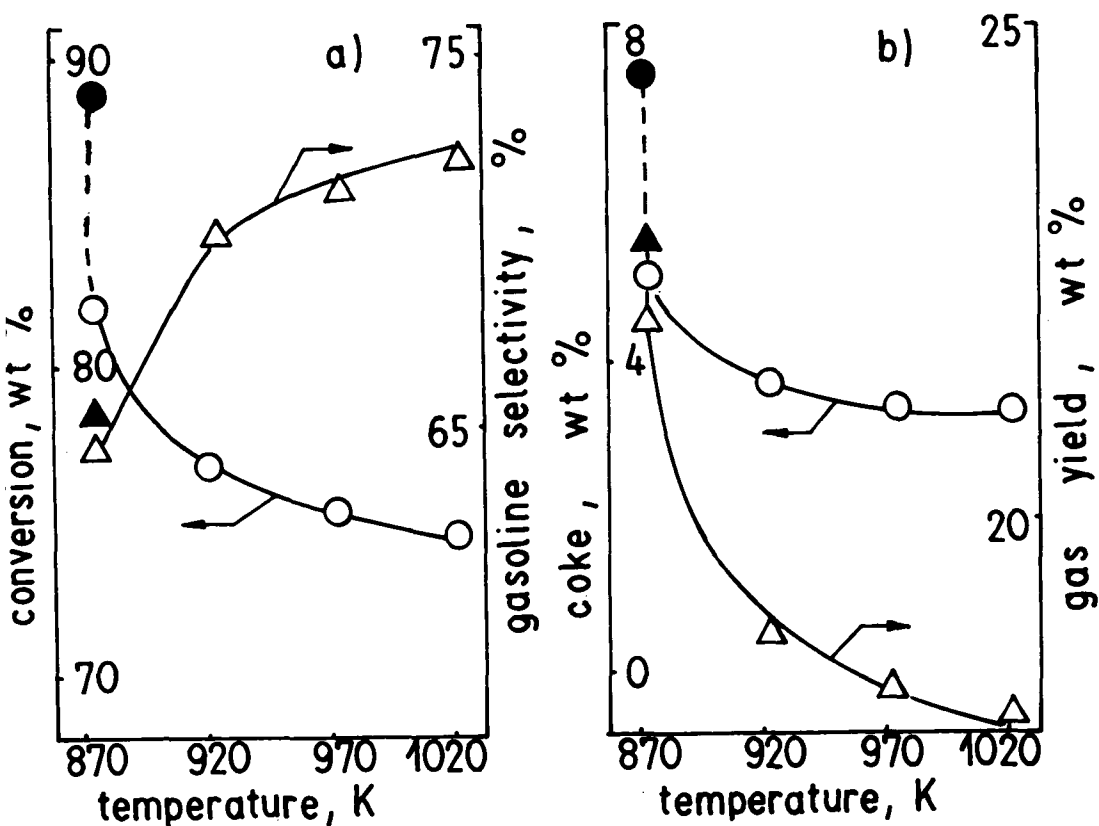


Fig. 1. Effect of hydrothermal pretreatment on the conversion, gasoline selectivity, coke and gas yield in the cracking of gas oil over a FCC catalyst (20 wt.% zeolite HRE-Y in silica-alumina matrix). Davison MAT: 760 K, 5 g catalyst, WHSV 20 h^{-1} . \blacktriangle , \bullet - not hydrothermally but only thermally pretreated samples.

Gasoline selectivity is drastically increased, and the formation of coke and gaseous products is suppressed.

As has already been pointed out by Moscou and Moné /25/, gasoline selectivity increases with increasing pretreatment temperatures up to 1020 K. These drastic changes in the catalytical activity of the FCC catalyst suggests that the influence of lattice dealumination should be investigated separately.

HIGH-SILICA ZEOLITES Y

Recently, highly dealuminated ultrastable zeolites Y of good crystallinity with silica to alumina mole ratios up to 350 have been prepared from $\text{NH}_4\text{-Y}$ zeolites at high temperatures under hydrothermal conditions /26-27/. From the USY samples obtained in this way, the non-framework aluminium can be extracted using diluted mineral acid, which results in USY-ex samples. Structure and adsorption properties have been described in some recent publications /28-30/. The decrease in the concentration of acidic sites, which accompanies the dealumination, leads to a decrease of the cracking activity of the USY-ex zeolites with progressing dealumination /31/. However, the coking velocity is more strongly reduced by dealumination than the cracking activity is: The reduction of site concentration by partial dealumination of the zeolite results in an improvement of the activity-time dependence by decreasing the rate of the coking reaction more rapidly than the cracking reaction rate. This effect can be understood assuming a 2-center mechanism for the coking reaction, whereas cracking follows a 1-center mechanism (equation 1 is derived on this basis).

Table 1

Acidity and catalytic properties of modified Y zeolites in the cracking of gas oil (M = mole ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$)

	RENa-Y	USY-ex ($M=17$)	USY-ex ($M=350$)
Acid strength	$\text{H}_0 \approx -8$	$\text{H}_0 \approx -12$	$\text{H}_0 \approx -8$
Acid site concentration	$5.5 \cdot 10^{-1}$	10^{-1}	about 10^{-2}
Conversion, wt%	82.5	85	82
coke, wt% on catalyst	5.5	3.3	1.7

In Table 1 the acidic and catalytic properties in gas oil cracking over three modified Y zeolites are compared: A Rare Earth NaY zeolite (mole ratio $M = \text{SiO}_2/\text{Al}_2\text{O}_3 = 5.2$; cation exchange degree = 65 %) and two USY-ex zeolites with $M = 17$ and 350, respectively. At a comparable conversion degree the most striking feature is the varying amounts of coke formed by the three samples. The sequence of coke formation clearly follows the acid site concentration. At the same acid strength on the RENA-Y and on the USY-ex ($M = 350$), coke formation is strongly reduced in the case of the USY-ex ($M = 350$). This effect of acid site concentration even overcompensates an increase in acid strength going from RENA-Y to USY-ex

(M = 17).

The activity-time dependence in pulse catalytic cracking can be described by a 1-parameter equation:

$$\frac{1}{k(n)} - \frac{1}{k(1)} = B(n-1) \quad (\text{Equation 1})$$

in which $k(1)$, $k(n)$ are the rate constants calculated from the first (nth) pulse, and n represents the pulse number. The value of the constant B derived from the slope of the curves obtained by the plot of this function (Fig. 2) reflects the deactivation rate. Deactivation is drastically reduced by dealumination, resulting in an almost time-independent activity at very high dealumination degrees.

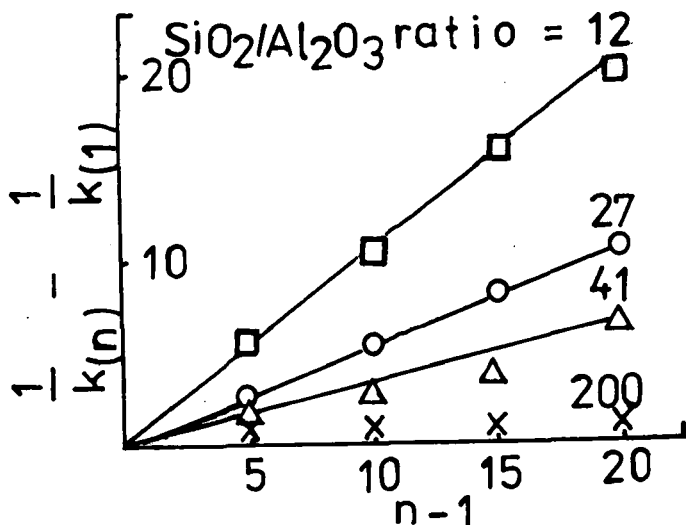


Fig. 2. Deactivation of USY-ex zeolites in hexadecane cracking vs. pulse number n . (k in 10^{-7} mole/ $\text{Pa}\cdot\text{mg}\cdot\text{h}$)

Besides activity and activity-time dependence, other selectivity parameters of USY-ex zeolites in the paraffin cracking reaction are also influenced by partial dealumination. With an increasing degree of dealumination, the long chain paraffins are more selectively cracked from a mixture with paraffins of lower molecular weight: this is demonstrated in Figure 3 with a mixture of hexadecane/octane. As a consequence, overcracking is reduced, and the gasoline yield in the cracking of gas oil increases. This effect can be made even more pronounced by controlled introduction of cations into such partially dealuminated Y zeolites.

The effect of cation introduction into the partially dealuminated zeolite USY-ex(41) on the acidity and catalytic properties is demonstrated by the results given in Table 2. As a measure of acidi-

ty, the extinction $\lg(I_0/I)$ of the 1450 cm^{-1} NH_4^+ band in the ir spectra of ammonia adsorbed on the sample is given. The cracking activity of the fresh, uncoked sample is characterized by the first order reaction rate constant k_1 of n-octane cracking at 473 K (k_1 , in mole/Pa·mg·h). The quotient of the rate constants calculated from the first and tenth pulse, respectively, k_{10}/k_1 , expresses the deactivation rate. U_{C16} represents the conversion of hexadecane measured in a continuous microtest (725 K, 0.5 g catalyst, 1.5 g feed per 3.5 min.), and Δg the gain in gasoline relative to USY-ex(41) at a level of 40 % conversion, measured in the MAT test.

Table 2

Effect of cation introduction into the partially dealuminated zeolite USY-ex(41) on the acidity and cracking properties.

	USY-ex(41)	$\text{Ca}_{0.2}\text{H}_{0.6}\text{USY-ex(41)}$	$\text{SE}_{0.15}\text{H}_{0.55}\text{USY-ex(41)}$	$\text{Sn}_{0.16}\text{H}_{0.36}\text{USY-ex(41)}$
$\lg(I_0/I)$	0.4	0.05	0.15	0.05
$k_1 \cdot 10^9$	22.3	1.6	5.1	2.4
k_{10}/k_1	0.4	0.9	0.7	0.8
U_{C16}	7.5	7.3	41.7	35.1
Δg		8	16	18

As is evident from the data presented in Table 1, the initial activity (k_1) in n-octane cracking as determined by pulse catalysis decreases along with the Brønsted acidity. Simultaneously, the activity-time behaviour improves (k_{10}/k_1 increases). These samples were used for determining the catalytic properties in a flow reactor in hexadecane conversion, according to the Davison microactivity test (cf. Table 2).

As compared with USY-ex(41) recationized samples give higher or equal conversion, which is obviously due to the different activity-time behaviour. The cracking selectivity (gasoline yield) is strongly affected by the exchange of cations. Whereas USY-ex(41) is characterized by rather nonselective cracking of n-paraffins, gasoline yield is increased by Ca^{2+} exchange. SE^{3+} and Sn^{4+} exchanged USY-ex zeolites exhibit high selectivity despite the high conversion.

Thus, the catalytic properties in paraffin cracking can be varied in a wide range by subsequent recationization of the USY-ex zeolites. The initial activity is decreased, the activity-time behaviour is improved (particularly by exchange of RE^{3+} and Sn^{4+}

cations), and the cracking selectivity is increased.

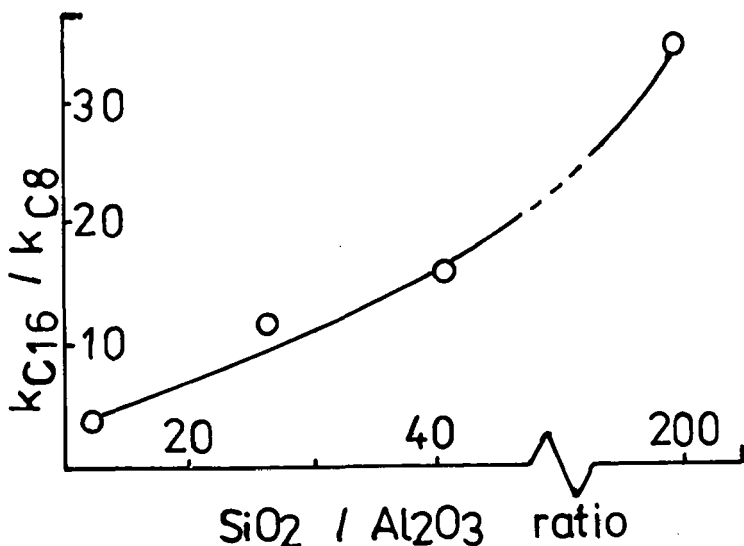


Fig. 3. Selectivity in the simultaneous cracking of hexadecane and octane at 725 K over USY-ex zeolites vs. molar SiO_2 / Al_2O_3 ratio.

Very little information is available on the role of extra lattice aluminium in catalysis. SCHEVE et al. /33/ assume the non-framework aluminium to be an inert diluting material, which only decreases the hydrogen transfer reaction. To illustrate the problem, the impact of the extra lattice aluminium on the catalytic cracking of cumene is shown in Figures 4 and 5.

Comparison of Brønsted acidity and catalytic activity of silica-alumina and ion exchanged zeolites Y permit the conclusion that the Brønsted acid sites are the centers which are catalytically active in the cumene cracking reaction. The unusually high activity of the USY sample deserves special explanation, which can only be based on the role of the extra lattice aluminium. This is clearly evident from the fact that after removal of the extra lattice aluminium by acid extraction, the resulting USY-ex(200) sufficiently matches the activity function common to the other samples. This can be interpreted by assuming the extra lattice aluminium to be adsorption sites for the aromatic molecules, which increase the value of the first order reaction rate constant. The effect of extra lattice aluminium depends on its amount, i.e. on the degree of lattice dealumination during the hydrothermal treatment, as is shown in Figure 5a: Cumene cracking activity increases with increasing lattice dealumination, despite the decreasing Brønsted acidity. On the other hand, both, activity and Brønsted acidity of the USY-ex samples decrease with increasing lattice dealumination. Enhanced adsorption on the extra lattice aluminium should be accompanied by a slower

desorption rate of condensed products, which should result in a more rapid deactivation by coking. This is shown to be true by Fig. 5c.

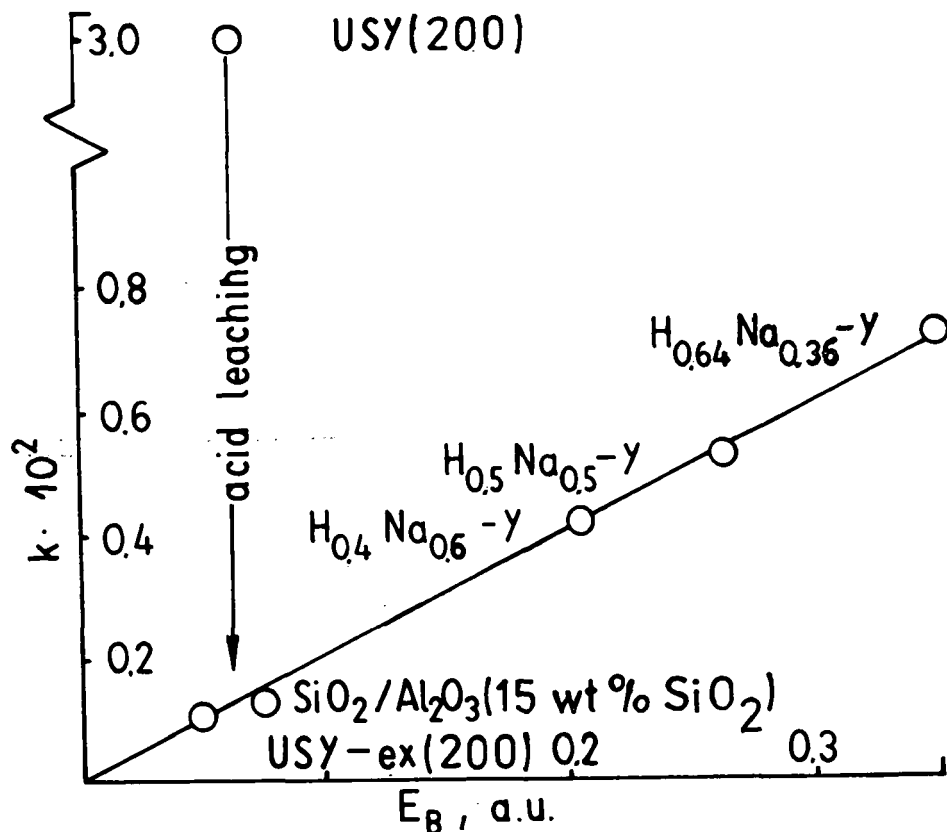


Fig. 4. Brønsted acidity (E_B) and first order reaction rate constant k (mole/MPa · sec · g) of pulse cumene cracking at 575 K / 32/. E_B -extinction of pyridinium ion ir band.

The effect of the new secondary pore system (most frequent pore diameter about 1.8 nm) created in the zeolite by the hydro-thermal treatment can be evaluated by comparing the catalytic behaviour of USY-ex zeolites with that of high silica HY zeolites not having such a new pore system which can be prepared by the method of BEYER with $SiCl_4$ /34/. There are no differences in the cracking of paraffin based gas oil over the high silica zeolites prepared in both ways. However the cracking of fused multi-ring compounds containing oils, including heavy recycle oil is favoured over the USY-ex samples, due to the new pore system.

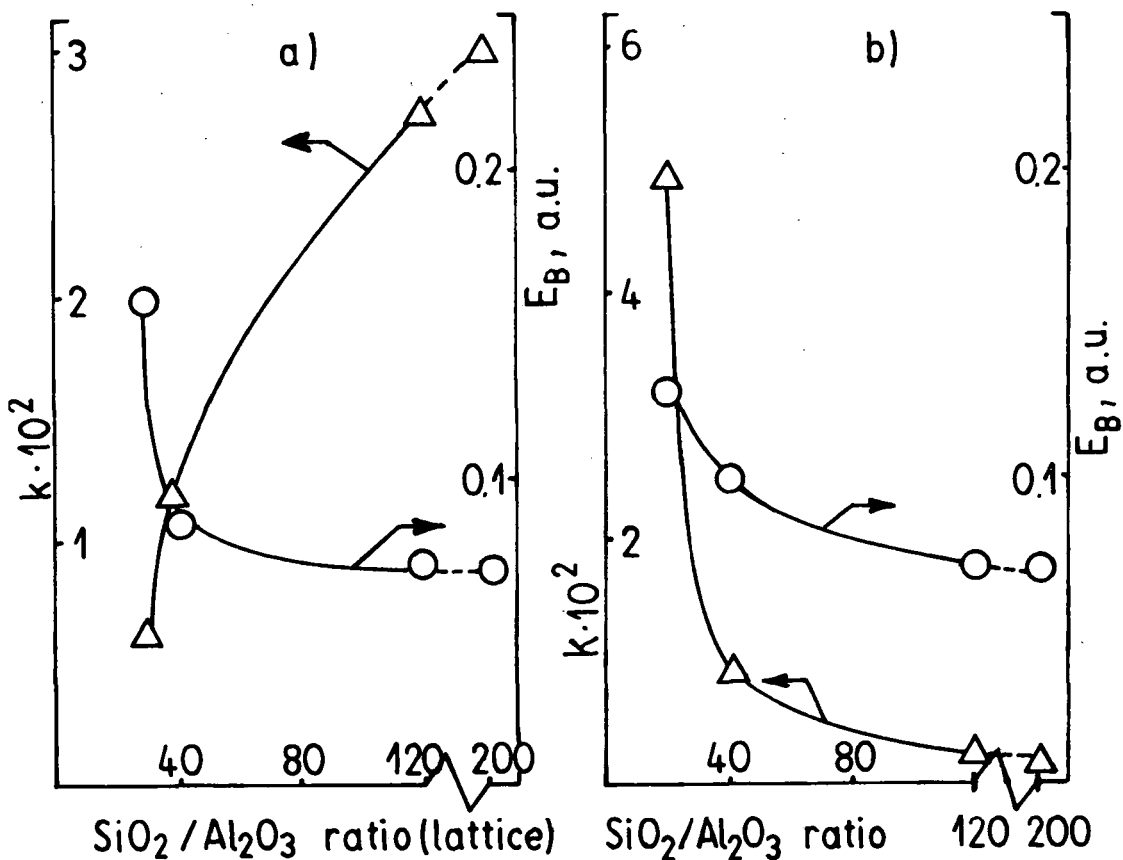
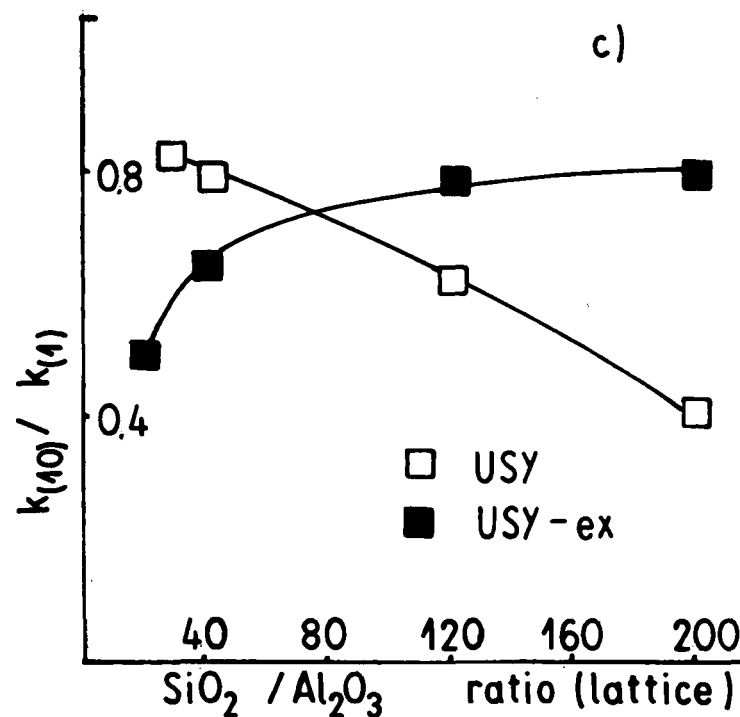


Fig. 5. Catalytic properties (cumene cracking) of hydrothermal pretreated zeolites Y vs. zeolite lattice composition /30/.
 a. Extra lattice containing USY zeolites.
 b. Samples after extraction of extra lattice aluminium.
 c. Activity-time dependency of USY and USY-ex zeolites.
 E_B and k cf. fig. 4.
 k_{10}/k_1 - quotient of the rate constants derived from pulse 1 and 10.



RAISING THE YIELD OF SYNTHESIS OLEFINS

Under certain conditions, the desired selective cracking with partially dealuminated Y zeolites as the active component in FCC catalysts, may result in the portion of low synthesis olefins formed being smaller than is desired. In such cases, the addition of the zeolite ZSM-5 to the FCC catalyst appears to be advisable.

As demonstrated in Figure 6, 5 wt.% of an REZSM-5 are sufficient for achieving a substantial increase in the yield of propene and butenes. In this way the product distribution commonly obtained in cracking /9/ can be changed to a significant degree. In the extreme case, two maxima can be obtained in the product distribution curve, namely in the gasoline range, and for the C_3/C_4 olefins. Both zeolite components - dealuminated Y zeolites and ZSM-5 - also complement each other excellently, in that coke formation in both cases is very slow. One of the consequences of this fact is that ionic H transfer to the product olefins (with coke as a H donator) is strongly suppressed.

INFLUENCE OF METALS ON THE ACTIVITY AND SELECTIVITY OF ZEOLITE-CONTAINING CATALYSTS

All cracking feedstocks contain traces of metals (which are enriched in the residual oils) in concentrations of about 1 - 1000 weight ppm: vanadium, nickel, iron, copper, sodium, which are fully deposited on the catalyst, and may cause some adverse effects /35, 23/. Whereas vanadium destroys the zeolite crystal lattice, the other metals - in particular nickel - cause undesirable dehydrogenation reactions leading to hydrogen and coke formation at the expense of the desired gasoline. A detailed report on the causes of the poisoning of FCC catalysts by vanadium (action of the $V=O$ species) will be given by OCCELLI et al. /36/ at this conference.

Activity and selectivity losses due to metal contamination can be diminished by using cracking catalysts with increased proportions of zeolite (V tolerances of 1000 ppm and Ni tolerances of 500 ppm on equilibrium catalysts in USA FCC units have already been achieved in 1982), or by metal passivation e.g. by additives containing antimony. This type of passivation is particularly beneficial for nickel-containing catalysts, and the firm Davison has successfully developed and utilized a special vanadium passivator "DVT". To maintain the activity and selectivity of an equilibrium catalyst in practice, a definite limit of contamination by metals has to be set,

which must not be exceeded.

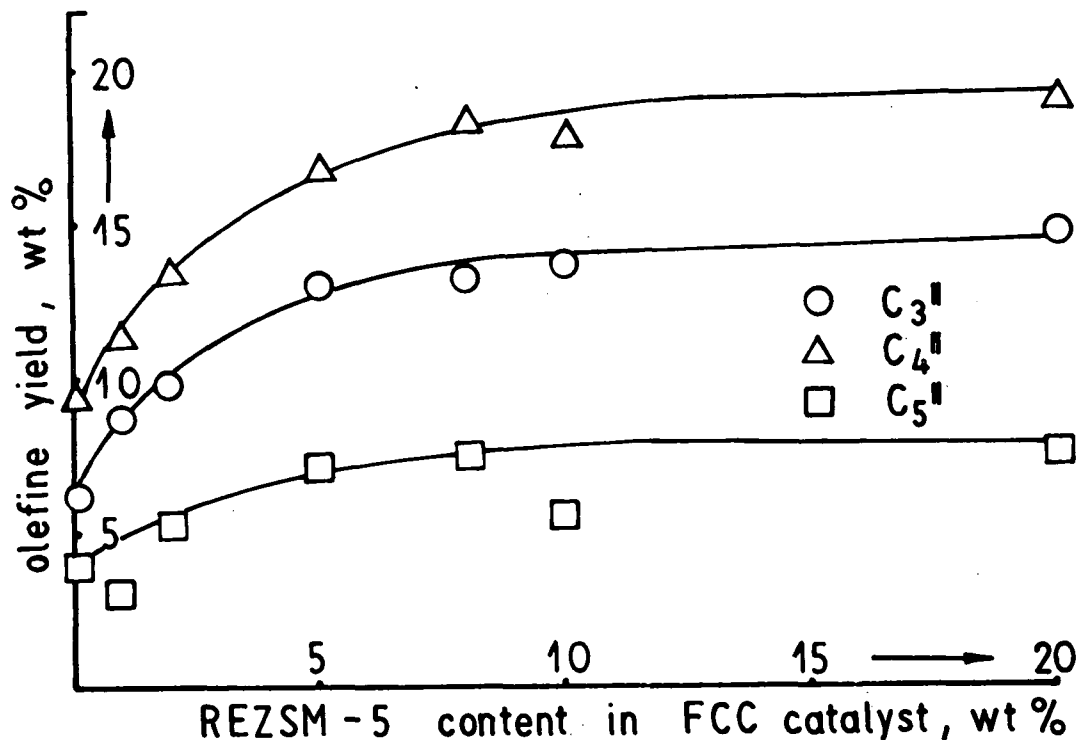


Fig. 6. Influence of the REZSM-5 content on the olefin yield in the cracking of hexadecane under MAT conditions (cf. Fig. 1).

For this reason, the equilibrium catalyst is continuously replaced with fresh catalyst. As is evident from a balance calculation, /2/, the catalyst replacement rate in the cracking of mixtures of vacuum gas oil and residual oil amounts to about 1 kg of catalyst per ton of feed, whereas in the heavy oil cracking process (HOC) 1.9 to 3.7 kg of catalyst per ton of feed are required.

As is evident from experiments on cracking catalysts /37, 38/ which will be presented at this conference by BITTRICH et al. /37/, hydrogen-activating substances (e.g. MoO₃ and WO₃) can increase the activity and selectivity in producing gasoline. Impregnation of a FCC catalyst with these components decreased its activity, whereas a physical mixture results in improved activity. Comparison of the catalytic properties in the cracking of hydrofined vacuum distillates (boiling at 630-820 K) on a commercial catalyst and a catalyst mechanically mixed with SiO₂ (10 wt.%) and WO₃ (0.8 wt.%) is shown

in Table 3 /38/. The effect of the SiO_2/WO_3 additive, which increases the activity and particularly the gasoline yield, is clearly evident. Possible reasons and limits of this effect will be discussed in the announced contribution /37/.

Table 3

Comparison of the catalytic properties of modified cracking catalysts (Davison CAT-A test)

Conditions:

temperature	753 K	C/O ratio	2.8
catalyst weight	5 g	WHSV	20 g/g·h
particle size	$\geq 63 \mu\text{m}$		

Results:

	FCC catalyst	FCC catalyst (+ SiO_2/WO_3)
(amounts in wt.%)		
conversion	65.5	74.3
liquid products	85.2	84.3
gasoline	51.1	58.5
gas	11.6	13.4
coke	2.9	2.4

PROMOTION OF CO-OXIDATION

Since 1975, promoters have been successfully used for reducing the carbon content on the regenerated catalyst and for minimizing the CO content in the flue gas /39, 40/. In most cases, noble metal additives are used for this purpose (up to about 5 ppm Pt per catalyst weight), which are either fed in together with the catalyst, or are fed into the plant as liquid or solid additives.

The effect of Pt, Pd, Fe, Ni and V salts on the CO oxidation activity in regeneration and their effects on the catalytic cracking activity will be presented in detail by our Hungarian colleagues STEINGASZNER et al. /41/ at this conference.

As is evident from the comparison of the results of conventional regeneration with those of a promoted regeneration, using operational data of an industrial plant /40/, the CO content in the flue gas can be drastically reduced, with the gasoline yield remaining the same. Hence, in the presence of a promoter, a greater amount of heat can be generated in the regenerator, or the catalyst supply can be decreased which will reduce the loss of catalyst by mechanical abrasion. Also, with the use of a promoter, the content of residual coke on the regenerated catalyst can be reduced, enhancing catalyst activity and gasoline yield /39/.

MINIMIZATION OF SO_x POLLUTION

Although intensive work in developing catalyst additives for reducing SO_x emissions in flue gas dates back to the 'seventies, successful industrial application was not achieved until 1979 (Davison additives "S" and "R") /23/.

Table 4 shows that the SO₂/SO₃ content in the flue gas can be considerably reduced. The action of such additives (in most cases catalytically inert oxidic materials) is due to the fact that SO₂ in the presence of excess oxygen oxidizes to give SO₃, which is bound on the catalyst as sulfate. In the reducing atmosphere of a riser, sulphides are formed. These sulphides hydrolyze in the stripping part of the reactor, to give H₂S, which is then removed from the cracking gas. Subsequent H₂S conversion to elementary sulphur might render the whole procedure attractive even from an economic point of view.

Table 4

Results obtained with additive "R" from an FCC plant /23/

Catalyst	DA-400 equilibrium catalyst	DA-400 +4 % additive "R"
S in feed, wt. %	0.56	0.56
excess of O ₂ , mole %	2-3	2-3
CO, mole %	0-1.5	0-0.1
temperature of regenerator, K	688-704	688-704
SO ₂ , kg/h	49	20
SO ₃ , kg/h	9	2

FEEDSTOCK PRETREATMENT

Many difficulties can be overcome by proper pretreatment of the feedstock. RITTER et al. /42/ were the first to point out the advantages of the use of hydrotreated FCC feedstocks, including heavy cycle oil. The benefits of cracking hydrogenated feedstocks are: Improved gasoline output, lower sulphur content in the products, lower SO₂ level in the flue gas, strong reduction of metal contamination, less poisoning and less coking of the FCC catalyst due to previous hydrogenation of heterocompounds and highly unsaturated hydrocarbons.

Excellent experience in all these respects has been gained with the DESUS procedure /43, 44/ in the PCK Schwedt in the GDR. This procedure serves to achieve a 85 to 90 percent desulphurization of middle and vacuum distillates at 650 K, 3.5 MPa H₂, and a LHSV

of 2-2.5 v/vh on a hydrotreating catalyst with optimized shape and pores. It has been developed by the Leuna-Werke "Walter Ulbricht".

Comparison of the most important properties, (gasoline yield and quality, catalyst consumption, and SO₂ emission) in the case of unrefined gas oil and gas oil obtained by hydrotreating according to the DESUS procedure, is presented in Table 5.

Table 5

Influence of DESUS pretreatment on FCC parameters /43/

Parameters of gas oil (725-805 K) cracking	feedstock	
	untreated	DESUS pretreated
<u>Yield, wt.%</u>		
gasoline	46	51
light cycle oil	20	17
heavy cycle oil	8	5
i-C ₄	14	16
<u>Quality, ROZ⁺</u> (0.31 g Pb/dm ³)	95	96.5
<u>Catalyst supply,</u>		
kg catalyst/t feed	1.01	0.505
<u>SO₂ pollution,</u> kg/t feed	1.32	0.15

A reduction of the S content from 1.4 to 0.4 wt.% in the oil is associated with increased gasoline yield from 46 to 51 wt.%. This increased gasoline yield is mainly due to selective catalytic conversion of condensed polynuclear aromatics into gasoline derivatives. Simultaneously, the pretreatment of the gas oil results in a decrease of the vanadium content from 2 to 0.2 ppm, and of the nickel content from 0.5 to 0.1 ppm.

TENDENCIES IN FCC CATALYST DEVELOPMENT

Today, intensive work is being carried out to improve the properties of zeolite containing cracking catalysts. The aims of this work are as follows:

- to increase the gasoline yield
- the improvement of gasoline quality (octane number)
- to decrease SO_x and CO emission
- the development of catalysts with high metal compatibility, which also enables heavy feedstocks to be processed.

Increased gasoline yield along (with increased content of aromatics) and reduced coke formation can be achieved when high silica ultrastable zeolites Y are used as active components. However,

due to increased technological expense, production costs of such catalysts are much higher, and their potential use is subject to economical considerations.

When an increased proportion of synthesis olefins is desired in the FCC process, this can be achieved by incorporating an additional proportion of ZSM-5 as a zeolite component into the cracking catalyst.

Other aluminosilicate solids, such as dealuminated mordenites and erionites, as well as smektites may be used as active cracking components, little information is however available concerning their application.

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