Selective deep catalytic cracking process (SDCC) of petroleum feedstocks for the production of light olefins.
I. The Catlever effect obtained with a two reaction-zones system on the conversion of *n*-hexane

R. Le Van Mao *, S. Melancon, C. Gauthier-Campbell and P. Kletnieks

Laboratories for Inorganic Materials and Catalysis Research Laboratory, Department of Chemistry and Biochemistry, Concordia University,
1455 De maisonneuve W., Montreal, Quebec H3G 1M8, Canada

Received 30 November 2000; accepted 27 February 2001

The “*n*-hexane and steam” gaseous mixture was first sent through a precatalytic zone containing quartz beads (temperature T_1), and then through a catalyst bed (T_2). The latter contained a ZSM5 zeolite or a zeolite-containing hybrid catalyst. By moderately increasing T_1 (T_2 being kept constant), significant increases in the total *n*-hexane conversion and in the total yield of light olefins were obtained. The ethylene/propylene product ratio could be varied widely, for instance, from 1.0 to 2.0 by varying T_1 from 660 to 720 °C. Such temperature effect of zone I on the overall process performance was explained by the formation of selectivity modifiers such as diolefins. With the hybrid catalyst, the enhanced production of light olefins was also assigned to the formation of large olefins on the Cr–Al-containing cocatalyst.

KEY WORDS: selective deep catalytic cracking of *n*-hexane; light olefins; production flexibility; Catlever effect; two reaction-zones system

1. Introduction

Steam cracking of light paraffins (ethane, propane and butane, obtained mainly by extraction from various natural gas sources) or naphthas or other heavier petroleum cuts, produces [1]

(i) primarily ethylene and propylene;

(ii) secondarily, depending on the feedstock employed, a C_4 cut rich in butadienes and a C_{5+} cut with a high content of aromatics, particularly benzene;

(iii) and finally, hydrogen.

The feedstocks of choice are ethane and LPG for the USA, and naphthas and gas oils for Europe. However, in recent years, the situation has changed dramatically with most of the refiners moving towards the utilization of heavier hydrocarbon feedstocks. It is worth noting that steam cracking is one of the core processes in the petroleum chemical industry with a world production of ca. 100 million metric tons/year of ethylene and propylene [1].

Steam cracking is a thermal cracking process performed in the presence of steam, a diluant which is cofed with the hydrocarbon mixture. The reaction temperature ranges from 700 to 900 °C according to the type of feedstock treated (the longer the hydrocarbon molecular structure, the lower the temperature of cracking) while the residence time ranges from a few seconds to a fraction of a second.

Today, market demands are focussed on propylene and on some longer isolefins such as isobutene and isopentenes. The latter enter in the synthesis of alkyl ethers used as octane boosters for transportation fuels. However, the steam cracking with today’s technology is not sufficiently flexible to respond to these market trends.

More than ten years ago, a process aiming at upgrading the products of propane steam cracking was developed in our laboratory [2]. This consists of adding a small catalytic reactor to the conventional steam cracker of propane. The catalysts used were based on the ZSM5 zeolite modified with Al and Cr [3]. Significant increases in the yield of ethylene and aromatics were obtained.

A few years later, a process analogous to ours [2], now called deep catalytic cracking (DCC), was developed in China [4]. This technology makes use of zeolites to produce light olefins, in one of two operating modes: maximum propylene and maximum isolefins. DCC maximum propylene operation employs both riser and bed cracking at severe reactor conditions. Maximum isoolefin operation utilizes riser cracking, at slightly milder conditions.

However, the prior art has so far partially failed to develop a process which, by varying only one operating parameter, can provide simultaneously an enhanced production of the most commercially valuable products, i.e., light olefins including ethylene and propylene, and a higher production flexibility for these two important olefins, i.e., a wider range of variation for the ethylene/propylene ratio. It is therefore an object of this work to provide a novel process based on the catalytic lever or Catlever concept, which can achieve

---

* To whom correspondence should be addressed.

1011-372X/01/0500-0181$19.50/0

these two goals. In fact, with our new technology, the cracking activity of the ZSM5-zeolite-based catalysts using various petroleum feeds is dramatically improved and a considerable flexibility of production of ethylene and propylene is obtained, so that the new process can now be called selective deep catalytic cracking.

2. Experimental

2.1. Preparation of the porous precatalyst and catalysts

2.1.1. Porous precatalyst packed in the precatalytic zone (zone I)

Quartz (fused silicon oxide granules from Aldrich) was used as a porous precatalyst for the conversion in zone I without any further treatment. It has the following physical properties: mesh size = 4–16 mesh (particle size ca. 350 μm), surface area = 0.3 m^2/g, porosity = all mesopores and macropores.

2.1.2. Parent ZSM5 zeolite catalyst (for zone II)

This catalyst (Zeocat PZ-2/50, H-form, 1/16″ extrudates) was purchased from Chemie Uetikon AG (Switzerland). It contains ca. 20 wt% of an unknown binder. Prior to the catalytic testing, it was activated in air at 700 °C overnight. Its main physical properties are: surface area = 389 m^2/g, microporosity = 177 m^2/g and Si/Al = 44.5. This reference catalyst is referred to as HZSM5.

2.1.3. Hybrid catalyst containing the ZSM5 zeolite and the Cr–Al cocatalyst (for zone II)

(i) The ZSM5 zeolite used was the Zeocat PZ-2/50, H-form, powder, purchased from Chemie Uetikon AG (Switzerland). It was activated in air at 700 °C overnight. Its main physical properties are: surface area = 483 m^2/g, microporosity = 277 m^2/g, and Si/Al = ca. 50. This material is referred to as HZ.

The cocatalyst was prepared in the following way: the solid material (20 g) obtained by drying the colloidal silica Ludox AS-40 from Dupont and then activated in air at 700 °C overnight, was impregnated with an aqueous solution of Cr and Al obtained by dissolving 10.0 g of $Cr(NO_3)_3$, 9 H_2O and 9.0 g of sodium aluminate, all from Aldrich, in 30 ml of water. After being 10 min at room temperature, the solution was slowly (and under stirring) evaporated to dryness on a hot plate. The resulting solid material was dried at 120 °C overnight, and finally activated in air at 700 °C for 5 h. This cocatalystis referred to as Cocat.

(ii) The final hybrid catalyst, referred to as Hyb. Cat., was obtained by extrusion with bentonite as follows: first, HZ and Cocat (70 and 15 wt%, respectively) were carefully mixed (1 h of stirring in dry conditions); then, bentonite clay used as binder (15 wt%) was added to the previous mixture. The resulting solid mixture was stirred for another hour. Water was then added dropwise until a malleable paste was obtained. The final catalyst extrudates were dried at 120 °C overnight and finally activated in air at 700 °C for 5 h.

2.2. Experimental set up

Experiments were performed using a Lindberg triple zone series tubular furnace coupled to a Lindberg type 818 temperature control unit capable of regulating, individually, the temperature of each zone. The reactor vessel consisted of a quartz tube 95 cm in length and 2 cm in diameter. As mentioned in section 2.1, zone I (reactor inlet, zone heated at T_1 ca. 10 cm in length) was packed with quartz granules. Zone II (reactor outlet, catalyst bed ca. 7 cm in length) was packed with catalyst extrudates. Several thermocouples were used to control the temperatures of these zones. Zone III which was in between zones I and II, was used as cooling zone because the temperature T_1 of zone I was always set slightly higher than the temperature T_2 of the catalytic zone (zone II). Even with such small temperature difference, care was taken in order to avoid the overheating of the catalytic reactor (zone II). For that purpose, the heating surfaces of zones I (10 cm long) and II (7 cm long) were completely isolated with insulating discs from the intermediary zone (zone III) whose length (80 cm) and much lower temperature (by at least 150 °C, when compared to zone I) ensured the proper cooling of the stream coming from zone I before this reached the catalyst bed (zone II).

2.3. Testing procedure and data reporting

n-hexane was used as model molecule for the conversion of petroleum naphthas. Liquids, namely *n*-hexane and water, were injected into a vaporizer using two infusion pumps. In the vaporizer, nitrogen used as carrier gas was mixed with *n*-hexane vapors and steam. The gaseous stream was then sent into the tubular reactor, first in zone I and then in zone II.

The testing conditions are as follows: weight of catalyst = 5.0 g, WHSV (weight hourly space velocity = grams of reactant, i.e., *n*-hexane injected per hour per gram of catalyst) = 1.21 h^{-1}, water/*n*-hexane molar ratio = ca. 1.0 (0.21 g/g), nitrogen flow rate = 10 ml/min duration of a run 3.5 h.

In this series of runs, the temperature T_2 of zone II was kept constant at 650 °C while the temperature T_1 of zone I was varied from 660 to 720 °C

Liquid and gaseous fractions were collected separately using a system of condensers. The gas phase components were analysed using a Shimadzu Mini-3 FID gas chromatograph equipped with a 3 m long Haysep micropacked column while the liquid phase analysis was carried out using a Hewlett–Packard 8790 FID gas chromatograph equipped with a 50 m PONA capillary column.

The total *n*-hexane conversion (mol% or wt%) is expressed as follows:

$$C_t = \frac{\text{moles of converted } n\text{-hexane}}{\text{moles of } n\text{-hexane fed}} \times 100.$$

The selectivity (to product i) is expressed in C at% (or approximately in wt%) as follows:

$$S_i = \frac{\text{number of carbon atoms of product } i}{\text{number of carbon atoms of converted products}} \times 100.$$

The yield in product i is expressed (in wt%) as follows:

$$Y_i = \frac{C_t S_i}{100}.$$

3. Results and discussion

3.1. The Catlever concept

This work describes a new method to carry out selectively the deep catalytic cracking of petroleum naphthas and other hydrocarbon feedstocks. The concept on which the process of the present work is based on, also called Catlever, is schematically shown in figure 1. This says that if in the precatalytic zone (zone I), the feed undergoes partial thermal cracking and eventually some other reactions over the solid surface of the precatalyst, some molecules which can modify the selectivity of the catalytic reaction in zone II, are produced. The latter species when passing through the catalyst bed together with the unconverted feed can change the final product spectrum of the catalytic reaction. Therefore, the entire process can be more selective than that using only the catalyst bed as reaction zone. In addition, in almost all experimental conditions, the final conversion is increased owing to the combined effect of the two reaction zones.

Thus, the Catlever concept consists of using a precatalytic zone to modify the final product selectivities and possibly to increase the total conversion. To provide more flexibility to the process, the variation of the product selectivity has to be continuous in addition of being significant. Moreover, the activity change has to be induced by an operating parameter which can be easily varied at the level of a bench reactor or a commercial plant. Thus, the precatalytic zone and the catalytic zone act as the two ends of a lever whose moves result solely from the variations of the chosen operating parameter. In our work, the operating parameter of choice is the temperature and its effect on the activity and product selectivity of the overall process is important, as shown in the following section.

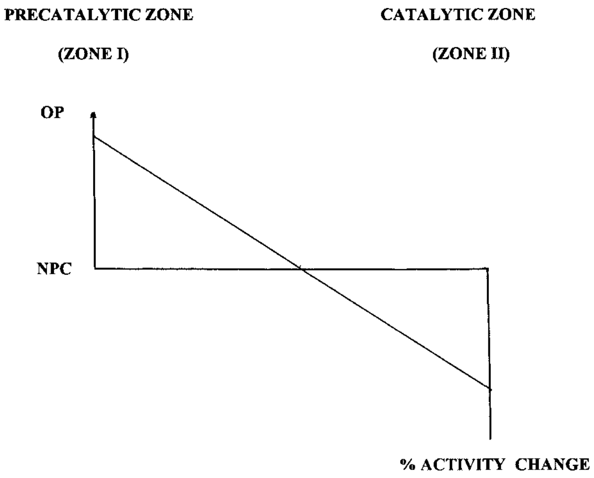

Figure 1. The concept of catalytic lever (Catlever). OP = (in arbitrary units) operating parameter used to obtain the Catlever effect; NPC = no precatalytic zone, % change in activity when compared to the parent HZSM5 zeolite used as catalyst, alone in zone II.

3.2. Steam-cracking conversion of *n*-hexane in the precatalytic zone, i.e., zone I

Table 1 reports the data obtained with the runs performed with the zone I set at various temperatures T_1 (660–720 °C). These temperature values were slightly higher than the temperature T_2 of the catalytic bed (650 °C). In this series of runs, the catalyst bed was empty and zone II was not heated.

The conversion was low at 660 °C but it increased quite rapidly with the increasing temperature. The yields in light olefins increased significantly while the yield in aromatic hydrocarbons remained quite low. Within the C_4 unsaturates, the yield in butadienes was quite high and increased with the temperature T_1. The ethylene/propylene ratio (R) increased steadily with the temperature.

3.3. Performance of the catalysts tested in Catlever conditions (table 2)

(i) All the catalysts tested under the Catlever conditions (both reaction zones used) showed an *n*-hexane conversion:

  - almost equal to (for $T_1 < 700$ °C) or higher than (for $T_1 \geqslant 700$ °C) that obtained with the HZSM5 zeolite tested under conventional conditions (i.e., with the catalyst bed only, which was heated at 650 °C).
  - much higher than that of the steam cracking occurring in zone I alone (table 1).

(ii) Heating zone I at a temperature even slightly higher than that of the catalyst bed resulted in large increases of the yields in light olefins and aromatics. In particular, increasing the temperature T_1 increased dramatically the yield in ethylene while the yield in propylene did not significantly change although the latter was much higher than the yield obtained with the steam cracking alone. As a consequence, the ethylene/propylene product ratio increased steadily. This ratio varied in a way which was quite comparable to the ratio reported for the conversion at zone I alone (table 1).

(iii) The yield in butadienes of the zeolite-based catalysts tested in the Catlever conditions was significantly lower when compared with that obtained with the precatalytic zone heated alone (tables 1 and 2). This shows that the diolefins (butadienes) were used by the zeolite catalysts to increase significantly the yields in butenes and aromatics, in accordance with equations (V) and (VI) of figure 2.

Table 1
Steam-cracking conversion of n-hexane in the precatalytic zone at different temperatures investigated.[a]

Zone I T_1 (°C)	Zone II	C_t	Y_{eth}	Y_{pro}	Y_{but}	Y_{buta}	Y_{me}	Y_{p2-4}	Y_{aro}	Y_{ole}	$Y_{ole+aro}$	R
660	–	31.0	10.8	9.2	0.7	4.8	2.0	2.9	0.3	25.5	25.8	1.17
680	–	55.0	20.9	16.3	1.0	7.0	3.7	5.4	0.7	45.2	45.9	1.28
700	–	67.1	27.1	19.5	1.3	7.6	4.9	6.4	0.7	55.5	56.2	1.39
720	–	84.1	36.3	19.7	1.1	7.2	7.1	11.5	1.1	64.3	65.4	1.84

[a] Y = yield (wt%); C_t = total n-hexane conversion (wt%); eth = ethylene, pro = propylene, but = butenes, buta = butadienes, me = methane, p2–4 = C_2–C_4 paraffins, liq = liquid hydrocarbons, ole = olefins, aro = aromatics; R = ethylene/propylene product ratio (wt/wt); the yield of hydrogen is not available.

Table 2
Activity and selectivity of the catalysts tested in Catlever conditions.[a]

Zone I T_1 (°C)	Zone II (catalyst)	C_t	Y_{eth}	Y_{pro}	Y_{but}	Y_{buta}	Y_{me}	Y_{p2-4}	Y_{aro}	Y_{ole}	$Y_{ole+aro}$	R
No	HZSM5	84.0	23.9	23.7	3.7	2.5	3.0	25.0	2.2	53.8	56.0	1.01
660	HZSM5	82.0	26.3	22.4	6.1	4.1	5.8	12.5	4.8	58.9	63.7	1.17
700	HZSM5	88.0	33.3	21.6	3.8	2.5	9.5	12.8	4.5	61.2	65.7	1.54
660	Hyb. Cat.	80.1	26.4	24.4	6.2	4.2	5.6	9.2	4.1	61.2	65.3	1.08
680	Hyb. Cat.	86.2	32.9	24.0	5.1	3.4	7.1	9.2	4.5	65.4	69.9	1.37
700	Hyb. Cat.	89.1	37.7	23.3	2.9	1.9	9.0	9.8	4.5	65.8	70.3	1.62
720	Hyb. Cat.	99.5	44.3	22.5	3.5	2.3	10.4	9.9	6.6	72.6	79.2	1.97

[a] For symbols see table 1.

(iv) The use of the hybrid catalyst which contained a Cr–Al cocatalyst, increased further the yields in light olefins and in light olefins + aromatics.

3.4. More comments on the application of the Catlever concept to the conversion of n-hexane

Let us examine the mechanism of the Catlever conversion when applied to the deep catalytic cracking of n-hexane.

n-hexane, when sent together with some steam through zone I, undergoes steam cracking (thermal cracking). The products of this conversion include shorter paraffins, olefins and diolefins from primary cracking [1]. Secondary cracking and dehydrogenation produce ethylene and then acetylene. Cycloadditions and dehydrogenations result in aromatics (benzene mostly) and then coke [1]. It is worth noting than zone I is different from the feed-preheating zone normally used in commercial chemical or catalytic processes because: (i) the role of zone I is well-defined: to produce some selectivity modifiers (of the main catalytic reaction) and to help increase the final total conversion obtained at the outlet of the catalytic reactor (zone II), and (ii) the temperature of zone I is higher than the temperature of the catalyst bed.

Zone II contains a ZSM5-zeolite-based catalyst or, preferably, a hybrid zeolite catalyst. The latter has been prepared by combining the ZSM5 zeolite with a Cr–Al-containing cocatalyst in accordance with the method of formation of a pore continuum [3]. The reaction mechanism of hydrocarbon conversion over cracking zeolite catalysts is well-known [5,6] and can be depicted by the pathways shown in figure 2.

Cracking:
Paraffin → smaller paraffin + smaller olefin + hydrogen (I)

Dehydrogenation:
Paraffin → olefin + hydrogen (II)

Olefin dissociation:
Olefin → ← 2 smaller olefins + hydrogen (III)

Hydrogen transfer:
Naphthene + olefin → aromatic + paraffin (IV)
Diolefin + paraffin → olefin + olefin (V)

Aromatization:
Olefins, diolefins, naphthene → aromatics + hydrogen (VI)

Figure 2. Main reaction pathways with zeolite catalysts.

3.4.1. Parent ZSM5 zeolite in zone II

The beneficial effects of the method based on two zones of conversion (with the parent ZSM5 zeolite packed in zone II) when compared to the conventional one-zone catalytic reaction (parent ZSM5 zeolite) are as follows:

(i) Generally higher total conversion and always higher selectivity to light olefins (and aromatics) as evidenced by the yield increases in light olefins and “light olefins + aromatics” of 24 and 29%, respectively.

(ii) A wide variation of the ethylene/propylene product ratio, depending on the temperature T_1 of zone I. This is certainly not entirely due to the partial thermal cracking in zone I because, although the trend for R was the same, the total conversion obtained with the Catlever runs with the HZSM5 catalyst (table 2) was, however, much higher than the total conversion reported for the corresponding steam cracking (table 1). Thus, to maintain the same ethylene/propylene ratio while the total conversion increased, the following reaction pathways applied at the level of zeolite acid sites:

- butadienes promoted the hydrogen transfer reaction with unconverted hexane in accordance with equation (V) of figure 2:

$$\text{butadiene} + \text{hexane} \rightarrow \text{butene} + \text{hexene}$$

- the resulting olefins undergo dissociation in accordance with equation (III) of figure 2:

$$\text{butene} \rightarrow \text{ethylene} + \text{ethylene}$$

$$\text{hexene} \rightarrow \text{propylene} + \text{propylene}$$

So that, 1 mole of butadiene might help convert 1 mole of unreacted *n*-hexane to yield 2 moles of ethylene and 2 moles of propylene. However, butadienes might also yield aromatics following the reaction path (VI) of figure 2, as also reported in table 2 (HZSM5 alone and HZSM5 tested in Catlever conditions).

3.4.2. Hybrid catalysts in zone II

In particular, with the more active (Cr–Al) hybrid catalyst (tested with the two-zone conversion setup) when compared to the parent ZSM5 zeolite (tested in the conventional tubular reactor), the yield increases in light olefins and “light olefins + aromatics” reached the values of 35 and 41%, respectively (table 2). In addition, the ethylene/propylene product ratio varied from 1.0 (equal to the value for the parent ZSM5 zeolite, obtained using the conventional reactor) to 2.0 (figure 3).

The higher reactivity of the hybrid catalyst when compared to the parent HZSM5 zeolite, both tested in the Catlever conditions, was probably due to the dehydrogenation effect of the Cr–Al cocatalyst [7] which produced more hexenes and butenes. These large olefins underwent dissociation to smaller olefins, so that the total yield of light olefins obtained with the hybrid catalyst was much higher than that of the parent HZSM5 zeolite, both catalysts being tested in the same Catlever conditions (table 2).

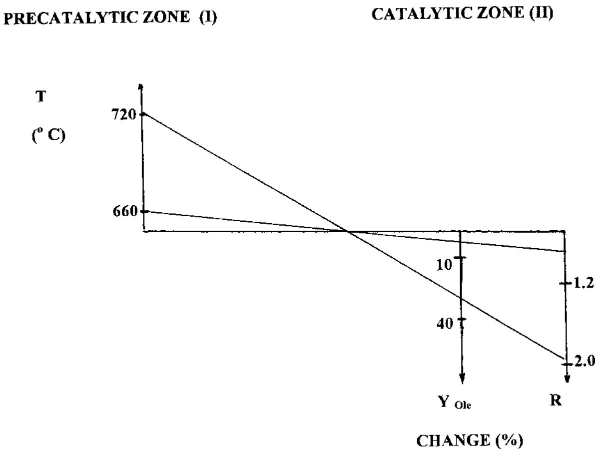

Figure 3. Application of the Catlever concept to the deep catalytic cracking of *n*-hexane. T = temperature of the precatalytic zone; change in Y_{Ole} = yield in light olefins and R = ethylene/propylene ratio.

Finally, the catalyst stability was also taken into consideration in our work. In fact, dealumination of zeolites, mostly when these materials are in protonic forms, may occur under the combined effect of high reaction temperatures and steam present in the feed since the tetrahedral aluminum seems to be subject to hydrolytic attack [8]. However, the quite high Si/Al ratio of our ZSM5 zeolite helps withstand this adverse effect which, when it is severe, usually results in structural collapse and loss of catalytic activity. Several cycles, with each including a 3.5 h reaction and 3 h generation (in air at 550–580 °C), showed no significant deactivation for the hybrid catalyst and the parent zeolite. Nevertheless, a detailed study of such phenomena using X-ray diffraction (degree of crystallinity), BET surface area measurement and ^{27}Al MAS NMR is currently carried out.

4. Conclusion

The presence of the precatalytic zone where only thermal cracking occurs, results in:

- a significant increase of the total conversion of *n*-hexane,
- a dramatic increase in the yield of light olefins,
- some increase in the yield of aromatics (benzene),
- a dramatic change in the ethylene/propylene ratio.

The variation of the ethylene/propylene ratio depends on the temperature of the precatalytic zone, in accord with the Catlever concept.

The use of the zeolite-based hybrid catalyst which contains a Cr–Al dehydrogenating cocatalyst results in much larger production of light olefins and some increase in the yield of aromatics. This is probably due to the combined effect of diolefins (butadienes coming from the precatalytic zone) and hexenes and butenes (produced by the cocatalyst).

Finally, it is also worth mentioning that the Catlever concept can be applied in research for investigating the mechanisms of complex catalytic reactions. In fact, if in zone I a precatalyst can produce inhibitors or accelerators of the main reaction of zone II, it will help elucidate the stepwise or competitive mechanisms of the reaction over the main catalyst.

Acknowledgement

The authors thank the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial support and Mr. David Ohayon for technical assistance.

References

[1] A. Chauvel and G. Lefebvre, in: *Petrochemical Processes*, Vol. 1 (Technip, Paris, 1989) pp. 117–165.
[2] R. Le Van Mao, US Patent 4 732 881 (22 March 1988).
[3] R. Le Van Mao, Micropor. Mesopor. Mater. 28 (1999) 9.
[4] D.A. Hunt, in: *Handbook of Petroleum Refining Processes*, 2nd Ed., ed. R.A. Meyers (McGraw Hill, Boston, 1997) pp. 3.101–3.112.
[5] J. Scherzer, in: *Octane-Enhancing Zeolitic FCC Catalysts*, Chem. Ind. Vol. 42 (Dekker, New York, 1990) pp. 89–98.
[6] D. Decrooq, in: *Catalytic Cracking of Heavy Petroleum Fractions* (Technip, Paris, 1984) pp. 27–31.
[7] B.M. Weckhuysen and R.A. Schoonheydt, Catal. Today 51 (1999) 223.
[8] D.W. Breck, in: *Zeolite Molecular Sieves* (Wiley, New York, 1974) pp. 493.