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# MOMENTARY MATERIAL BALANCE FOR ZEOLITE DEACTIVATION OF *N*-DODECANE CATALYTIC CRACKING

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## ABSTRACT

*The deactivation of zeolite can be explained by the method of momentary material balance. In this case, the catalytic cracking of n-dodecane on Y-zeolite at 723 K and 200 kPa, with neopentane as a reference substance, was used as a model. The amount of coke and the selectivity of cracked products were determined as a function of time-on-stream. For the comparison of catalyst deactivation process, the propane/propene mole ratio was considered together with the rate of coke formation, both of which decreased rapidly. In addition, the number of moles of aromatic compounds have been investigated in order to provide more understanding of the structures of cokes.*

## INTRODUCTION

Momentary material balance is one of the analytical techniques used to study the changes in catalyst activity during the course of a run. This catalyst deactivation has been previously described using the Time-on-Stream[1] and Coke-on-Catalyst[2] theories. In this particular work, the catalytic cracking of *n*-dodecane on Y-zeolite was selected for the development of an analytical determination of the material balance using a reference substance. In the previous trials by Schulz and Geertsema,[3] 2,2-dimethylbutane was used as a reference compound. During this work, the apparatus was improved so that the standard could be mixed in a known ratio with the feed components at the outlet of the reactor. Neopentane is used as a reference compound for these experiments since it has been shown not to be a product of *n*-dodecane cracking.[3] An effective chromatographic separation of the reference substance from the product components has been demonstrated which permits an accurate calculation of the material balance.[4]

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Catalyst activity can be estimated using either the propane/propene mole ratio or production rate of *iso*- and normal paraffins. At the same time, the amount of cokes and aromatics should be determined. When following transients in catalyst activity, all of these parameters need to be determined as a function of time.

# EXPERIMENTAL SECTION

## Apparatus

The flowchart of the apparatus is presented in Fig. 1(a). *n*-Dodecane (purity 99.25%) was fed into the vaporizer (A1), using an electronic metering pump, where it was mixed with the carrier gas, nitrogen. In order to achieve a constant *n*-dodecane evaporation rate, the temperature in the vaporizer was controlled at 431 K.

The reaction took place in a fixed-bed, stainless steel micro-reactor, 9.6 mm in diameter and 200 mm long (C1). The temperature of the catalyst was controlled using an electronic oven. A thermocouple was set in the middle of the catalyst-bed. The cross-section of the micro-reactor is shown in Fig. 1(b).

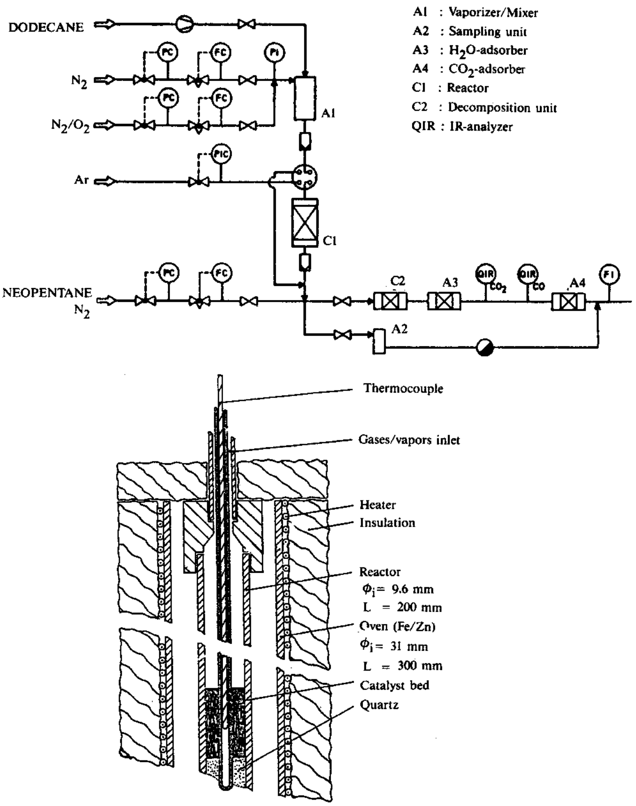


**Fig. 1** (a) Flowchart apparatus for catalytic cracking of *n*-dodecane on Y-zeolite.
(b) Cross-section of micro-reactor.

Instead of mixing the reference substance with the reactant at the vaporizer as in previous studies,[3] neopentane (0.49 % in nitrogen, purity 99.999 %) was mixed with the effluent at the outlet of the reactor. The advantage of using this injection point was that the reference compound was not passed through the catalyst and therefore was not cracked. However, the vaporizing rate of *n*-dodecane and the flow rate of neopentane had to be controlled in order for a constant mole ratio of *n*-dodecane/neopentane to be achieved.[4] The flow rate of the gas mixture was controlled with a needle valve at the outlet of the test equipment. In addition, argon was also added at the outlet of the reactor to account for the gas volume shrinkage during reaction.

A glass ampule technique [5] was used to collect the samples every minute. In Fig. 2 the principle of the sampling unit (A2) is presented. The preheated evacuated glass ampule with capillary was inserted into the high temperature compartment. The reactor effluent flowed into the ampule after its capillary was broken with the capillary breaker. The gas flow rate and temperature had to be set such that there was no condensation occurring in the ampule. Subsequently, the ampule capillary was sealed with a burner and kept for analysis.

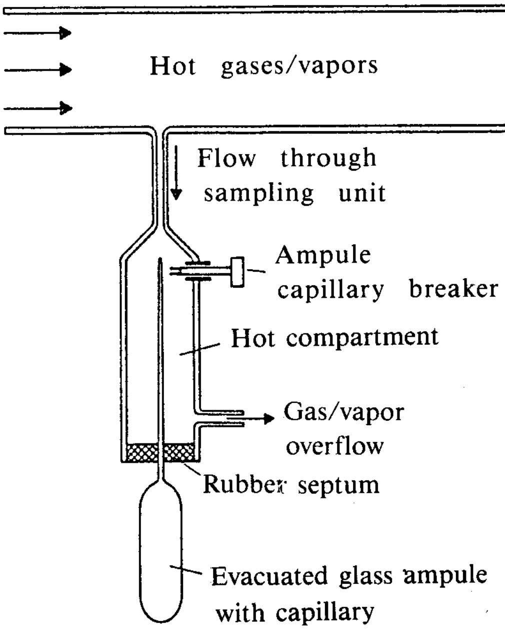


**Fig. 2** Sampling unit with evacuated glass ampule.

## Procedure

The reaction conditions are shown in Table 1. The catalyst used is supplied by LEV-AIRE no. S-1282. Before the reaction was started, the mole ratio of *n*-dodecane/neopentane had to be determined. The stream of *n*-dodecane/nitrogen was switched to bypass the reactor where it was subsequently mixed with neopentane/nitrogen downstream of the reactor outlet.

**TABLE 1** Reaction conditions for the catalytic cracking of *n*-dodecane on Y-zeolite

| | |
|---|---|
| Temperature, K | 723 |
| Pressure, kPa | 200 |
| Volume of catalyst, $mm^3$ | 500 |
| Contact time, s | 0.39 |
| WHSV, $h^{-1}$ | 1.93 |

At the sampling unit, the reactant stream flowed into the evacuated glass ampules which were subsequently analyzed. When a consistent mole ratio of *n*-dodecane/neopentane was reached, the reactant stream was passed over the Y-zeolite catalyst in the reactor. The product stream and neopentane were sampled in the same way as the reactant stream.

When the reaction was complete, $O_2$ (in air) was allowed to pass through the vaporizer and the reactor, the temperature of which was initially set at 673 K and increased to 823 K with a 50 K increment every 30 minutes. The decomposition unit was set in order to achieve a complete decomposition reaction, which could be observed by a CO IR-analyzer (QIR-CO). The accumulated amount of coke (C-%) could be calculated by the amount of $CO_2$, which could be observed by a $CO_2$ IR-analyzer (QIR-$CO_2$) and confirmed by a $CO_2$ adsorber (A4). In addition, C/H ratio could be calculated by the amount of $CO_2$ and $H_2O$ from a $H_2O$ adsorber (A3).

## Analysis

The glass ampules were analyzed using a gas-chromatograph with flame ionization detector (Hewlett-Packard 5880 A). The pneumatic ampule breaker (Fig.3) was the extension unit of the gas-chromatograph. This unit was kept controlled at high temperature in order to evaporate all of the component in the glass ampule. When the ampule was broken, the component therein would pass through the capillary column with the wash up gas which was nitrogen at the starting time. As soon as the component had passed through the injection port of the chromatograph, hydrogen would be used as the carrier gas to obtain a good separation.

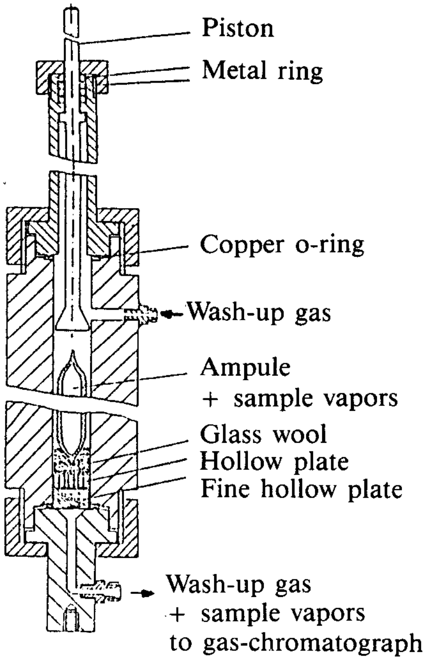


**Fig. 3** Glass ampule breaker.

Component separation was achieved on a quartz cappillary column, 0.25 mm in diameter and 50 m long, coated with 5% phenyl-methyl silicone using the temperature program shown in Table 2.

**TABLE 2** Temperature program for analysis of cracked products

| | |
|---|---|
| Start | -80°C 1.8 min |
| Step 1 | 30°C/min to -40°C 6.0 min |
| Step 2 | 20°C/min to 30°C |
| Step 3 | 7°C/min to 110°C |
| Step 4 | 8°C/min to 202°C |
| Step 5 | 12°C/min to 262°C 5.0 min |

When this stationary phase was used with the appropriate temperature program, the reference substance, neopentane, could be separated from the cracked products, especially *trans*-2-butene,[4] as shown in Fig. 4

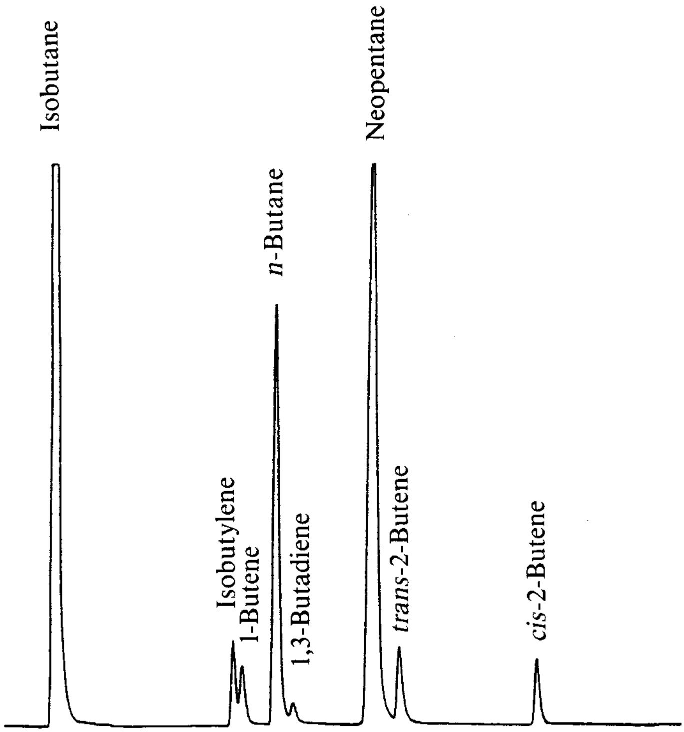


**Fig. 4** Part of chromatogram of cracked products, showing separation of neopentane from *trans*-2-butene.

## RESULTS AND DISCUSSIONS

The material balance for the catalytic cracking process was determined using neopentane as the reference substance. The following equations were used to calculate *n*-dodecane conversion (Eqn 1), the yield of coke formation (Eqn 3), and the selectivity of each product (Eqn 4).

$$\text{Conversion}_c = \frac{\dfrac{\dot{n}^{\,in}_{c\,(Doc)}}{\dot{n}^{\,in}_{c\,(NP)}} - \dfrac{\dot{n}^{\,out}_{c\,(Doc)}}{\dot{n}^{\,out}_{c\,(NP)}}}{\dfrac{\dot{n}^{\,in}_{c\,(Doc)}}{\dot{n}^{\,in}_{c\,(NP)}}} \cdot 100\% \ldots\ldots\ldots\ldots(1)$$

$$\text{Yield}_c = \frac{\dot{n}^{\,out}_{c\,(products)}}{\dot{n}^{\,out}_{c\,(NP)}} \cdot \frac{\dot{n}^{\,in}_{c\,(NP)}}{\dot{n}^{\,in}_{c\,(Doc)}} \cdot 100\% \qquad \ldots\ldots\ldots\ldots(2)$$

$$\text{Yield}_{c\,(coke)} = \text{Conversion}_c(\%) - \text{Yield}_{c\,(products)}(\%) \ldots\ldots\ldots\ldots(3)$$

$$\text{Selectivity}_c = \text{Yield}_c / \text{Conversion}_c \cdot 100\% \ldots\ldots\ldots\ldots(4)$$

Where $\dot{n}_{c\,(Doc)}$ : moles of *n*-dodecane per minute (based on carbon)
$\dot{n}_{c\,(products)}$ : moles of product(s) per minute (based on carbon)
$\dot{n}_{c\,(NP)}$ : moles of neopentane per minute (based on carbon)

The typical trends of conversion and yield of coke formation versus time-on-stream are shown in Fig. 5. It can be seen that a high coke yield occurred simultaneously with a high rate of conversion of the *n*-dodecane. This observation indicates that the initial high activity of catalyst causes rapid coke formation which deteriorates the catalyst selectivity.

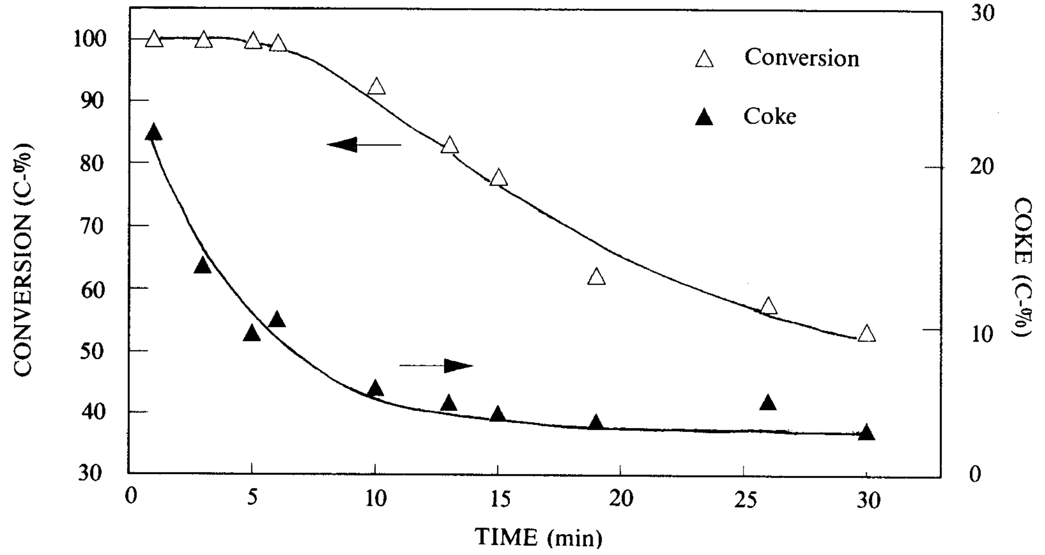


**Fig. 5** Conversion of *n*-dodecane on Y-zeolite and yield of coke formation as a funciton of time-on-stream at 723 K.

## Product Selectivity

The material balance and product selectivity for *n*-dodecane conversion reaction on Y-zeolite at 723 K as a function of time-on-stream is shown in Fig. 6. Large amounts of paraffins were formed at the beginning while olefin production increased throughout the experiment. The high initial selective paraffin production can be explained by a high catalyst activity for hydride ion transfer to form saturated hydrocarbons at starting time. To elucidate this trend more precisely, the propane/propene mole ratio can be used as a probe.[6,7] In Fig. 7, the variation in the mole ratio of propane/propene with time is shown. The shape of the deactivation curve is typical of exponential decay and indicates a fast deactivation of the catalyst.

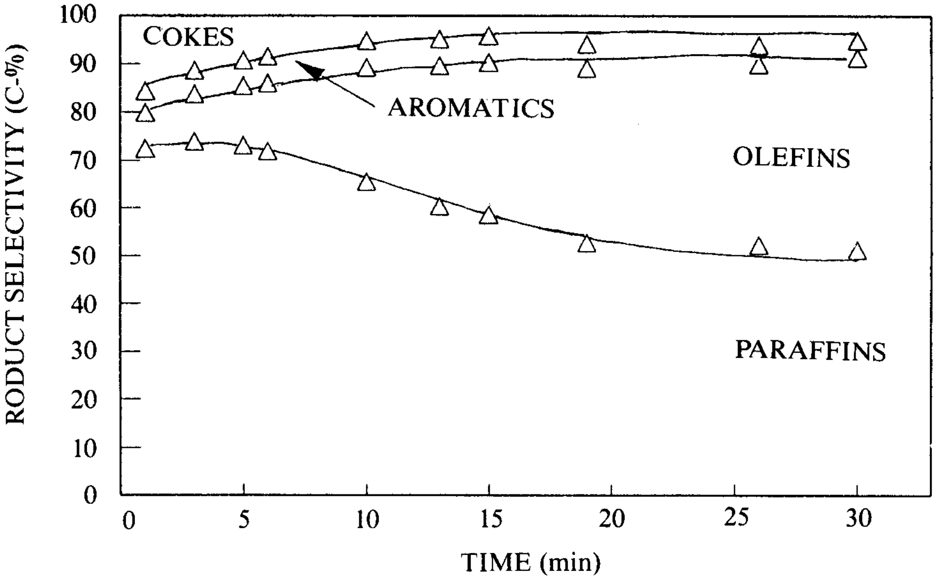


Fig. 6 Cumulative diagram of product selectivity of $n$-dodecane conversion as a function of time.

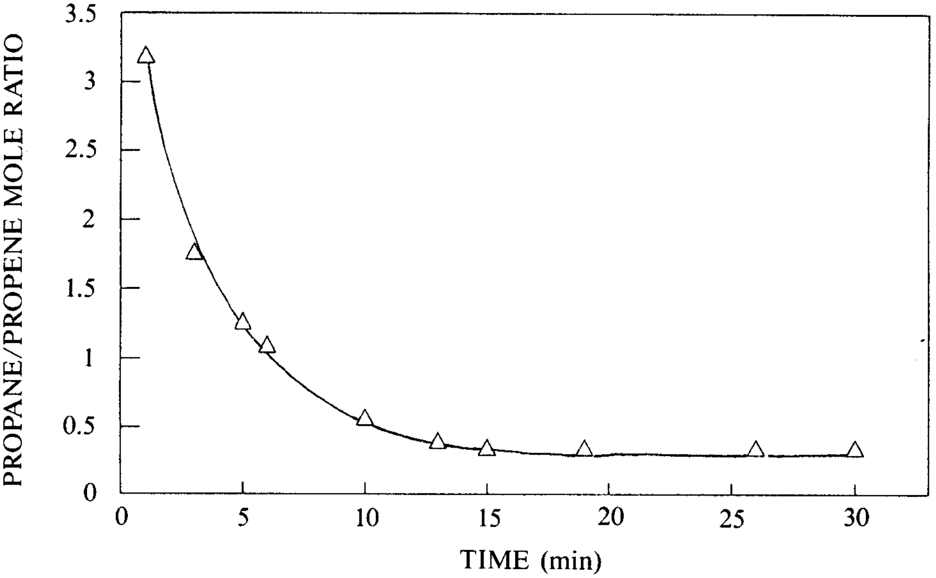
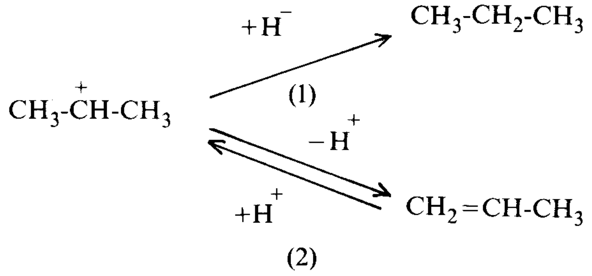


Fig. 7 Propane/propene mole ratio as a function of time.

The reaction scheme that forms the basis for the use of the propane/propene mole ratio as a measure of catalyst activity can be described as follows:



A propyl cation (the precursor of propene and propane) can pick up a hydride ion to form propane. This reaction path (1) occurs quite easily with an active catalyst. On the other hand, a propyl cation can lose a proton to form propene in a reversible reaction with the deactivated catalyst (path 2).

In addition, *iso*- and normal paraffins are also useful indicators of catalyst activity.[8] In this study, isobutane and *n*-butane were chosen. The fresh catalyst with a high concentration of acid sites displayed primary cracking activity which immediately yielded highly stable *tert*-butyl cations. Following the hydride transfer process, isobutane was readily formed. In contrast, a lower selectivity toward isobutane formation was observed with a deactivated catalyst (Fig. 8).

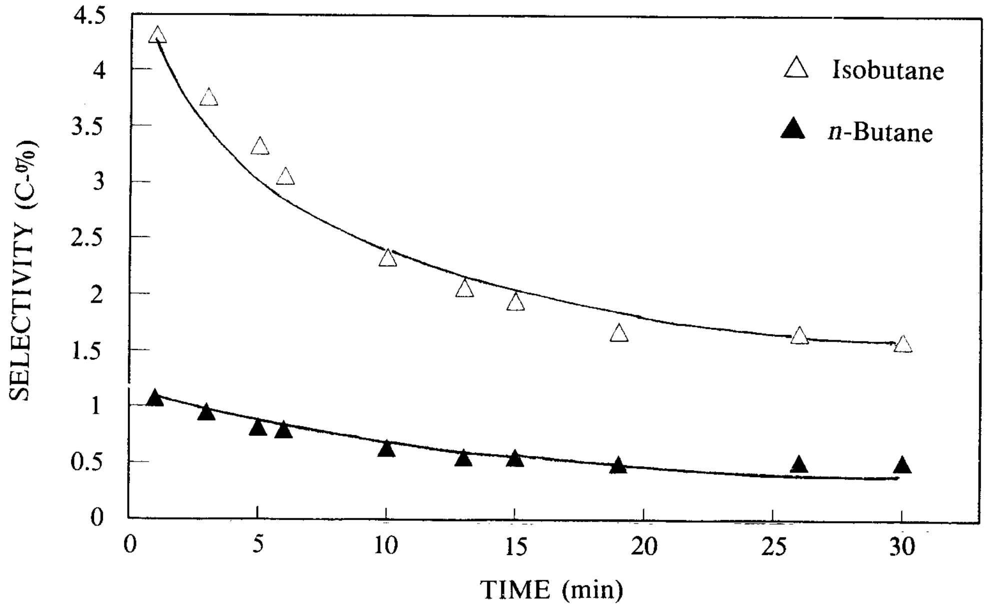
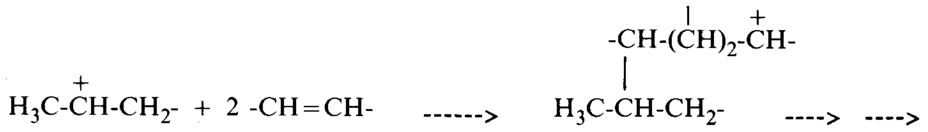


**Fig. 8** Selectivity toward isobutane and *n*-butane as a function of time.

From *the* preceding presentation of reaction data, it can be postulated with some certainty that the formation of coke is the major factor that causes catalyst deactivation as well as alters the product selectivity.

While cokes have been widely known to be hydrogen deficient hydrocarbon compounds like the aromatics, it was not until Guisnet *et al.*[9] made their investigation that cokes arising from the catalytic cracking reaction were accepted to have the same structures as aromatics. The formation of these aromatics can be explained via reactions such as oligomerization or polymerization of cracked intermediates. A typical simplified sequence is presented in the reaction pathway below:



$$H_3C\text{-}\overset{+}{C}H\text{-}CH_2\text{-} + 2\ \text{-}CH{=}CH\text{-} \;\text{------>}\; H_3C\text{-}\overset{\overset{\displaystyle \text{-}\overset{|}{C}H\text{-}(CH)_2\text{-}\overset{+}{C}H\text{-}}{|}}{C}H\text{-}CH_2\text{-} \;\text{---->}\;\text{---->}$$

(A)

From reaction intermediate (A), an alicyclic compound can be formed following the attack of another nucleophile at a suitable protonic site. Subsequent dehydrogenation at the acidic sites of the catalyst yields low or high molecular weight aromatics. These may then be desorbed from the catalyst surface into the product stream as aromatics or adsorbed as cokes onto the catalyst. All of these processes occur rapidly on an active catalyst as indicated by the results of this experiment where aromatics could be observed in the product stream in large quantities at the start (Fig. 9).

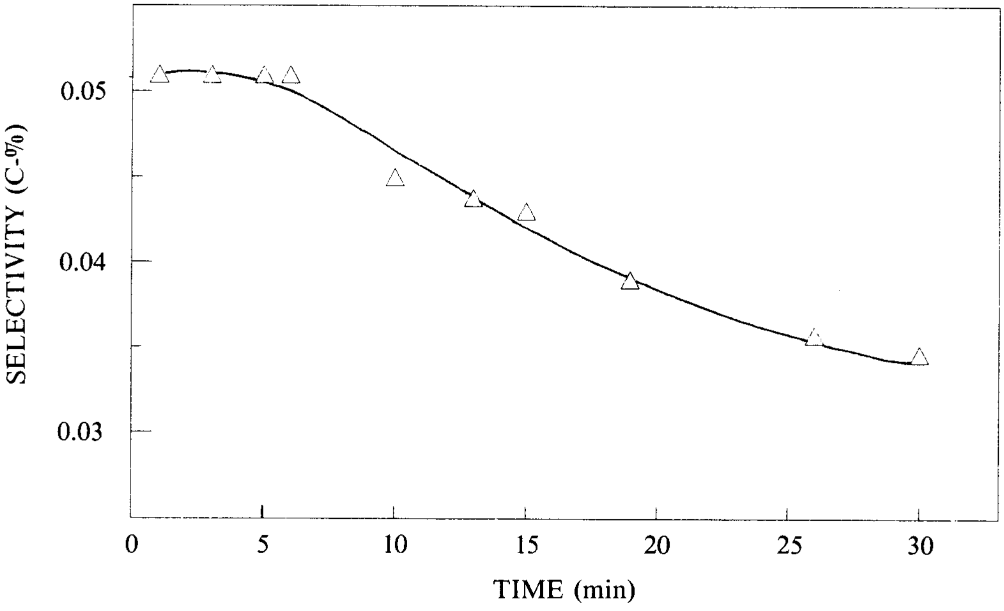


**Fig. 9** Selectivity toward aromatics as a function of time.

Using the technique of momentary material balance, various reaction transients have been monitored that permit the elucidation of the deactivation mechanism for a cracking catalyst. Following from this work, additional research projects should be considered on topics such as the deactivation of catalysts for Fischer-Tropsch synthesis, methanol to gasoline process, and catalytic cracking.

This work was part of the catalytic cracking project performed at the Laboratory of Professor Dr. H. Schulz at Engler-Bunte Institute, University of Karlsruhe, Federal Republic of Germany.

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## REFERENCES

1. Wojciechowski, B.W. (1974). Cat. *Rev-Sci. Eng.* **9 (1)**, 79.
2. Derouane, E.G. (1984). Catalysis by Acids and Bases. In : *Studies in Surface Science and Catalysis*(Imelik, B., *et al.*, eds.), Vol. 20, Villeurbunne, p. 221.
3. Schulz, H. and Geertsema, A. (1977), *Erdöl und Kohe - Erdgas - Petrochemie* **30**, 313.
4. Worayingyong, A., Zhao, S., Niederberger, H. and Schulz, H. (1987). *22th Intern, Sem. für Forschung und Lehre.* Karlsruhe, p. 93.
5. Schulz., H. Böhringer, W., Kohl, C.P., Rahman, N.M. and Will, A. (1984). *DGMK - Forschungsbericht.* Hamburg, p. 320.
6. Hightower, J.W. and Emmett, P.H. (1965). *J. Am. Chem. Soc.* **87**, 939.
7. Schulz, H., Geertsema, A. (1980). *Proc. 5th Intern. Conf. on Zeolites.* Neapel, p. 874.
8. Weitkamp, J. (1978). *Erdöl und-Kohle - Erdgas - Petrochemie* **31**, 13.
9. Guisnet, M., Magnoux, P. and Canaff, C. (1986). *Pro. 7th Intern. Conf. on Zeolites.* Tokyo, p. 701.

## บทคัดย่อ

การสูญเสียกัมมันตภาพเชิงเร่งปฏิกิริยา (catalyst deactivation) ของซีโอไลต์ สามารถอธิบายได้ด้วยวิธีการดุลมวลสาร (material balance) ในที่นี้ปฏิกิริยาตัวแบบที่ใช้คือการแตกตัวของนอร์มอลโดเดคเคนบนตัวเร่งวายซีโอไลต์ (Y-zeolite) ที่อุณหภูมิ 723 เคลวิน ความดัน 200 กิโลพาสคาล โดยใช้นีโอเพนเทนเป็นสารมาตรฐาน ตลอดช่วงเวลาที่เกิดปฏิกิริยาได้วิเคราะห์ร้อยละของการเปลี่ยนแปลงตัวเข้าทำปฏิกิริยา ปริมาณของโค้กและผลิตภัณฑ์อื่น ๆ อันเนื่องจากค่าการเลือกเร่งปฏิกิริยา (catalyst selectivity) ในการพิจารณาการสูญเสียกัมมันตภาพนั้นได้เปรียบเทียบอัตราการลดลงของอัตราส่วนโมลโพรเพนต่อโพรพีน กับอัตราการเกิดโค้กซึ่งอัตราทั้งสองมีค่าลดลงอย่างรวดเร็ว นอกจากนี้ยังมีการวิเคราะห์จำนวนโมลของสารประกอบอะโรแมติกเพื่อเป็นข้อมูลสนับสนุนสมมุติฐานเกี่ยวกับโครงสร้างของโค้ก