Hydroisomerization of *n*-Pentane with Pt-Catalysts Over Various Supports

SARA MIKHAIL†, A.A. AL-AHMADI and G. EL-KADY*

Umm Al-Qura University
Faculty of Applied Sciences
Makkah Al-Mukarramah, Saudia Arabia

Various prepared Pt-catalysts impregnated on different supports such as charcoal, clay, silica gel, alumina and Na-Y-zeolite were studied for the isomerization of *n*-pentane. The isomerization reaction was carried out in a bench scale unit, designed to operate under atmospheric pressure in the temperature range of 250°–350°C, space velocity of 4 hr^{-1} and hydrogen flow rate of 40 ml/hr. Results indicate that, the extent of the isomerization varied on using the different catalysts, and the Pt-Y-zeolite catalyst is the most selective one for isomerization of *n*-pentane. The type of cations on zeolite plays an important role in the extent of isomerization. The isomerization activity increases in the order,

Na < Mg < Ca < H-Y-zeolite
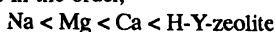
INTRODUCTION

Isomerization or hydroisomerization, is a catalytic process for converting low-octane straight chain paraffins into higher octane branched paraffins. The isomeric forms are of great interest in the petrochemical industries in particular the production of high components for aviation gasoline as well as for lowering the pour and freezing points in fuels.

Isomerization of *n*-paraffins generally takes place by dual functional catalysts[1-4]. It has been claimed, that the catalytic isomerization of paraffinic hydrocarbons proceeds through a carbonium ion intermediate in the case of acidic and dual function catalysts[5]. For introducing a noble active component into the cavities of zeolite, impregnation[6,7] and ion exchange techniques[8] are the most suitable and widely used. Waxy hydrocarbons have been converted to oily non waxy by contacting it with an acidic aluminosilicate zeolite preferably combined with a hydrogenation component (*e.g.*,palladium) at elevated temperature and pressure[9].

Pt/La-Y-zeolite catalyst prepared by cation exchange with competition technique was previously employed by Mikhail *et al.*[10] for the isomerization of high molecular weight paraffin wax.

Rabo, Minachev and their coworkers[11,12] have demonstrated that sulphur tolerance of Pt-containing zeolite catalysts depended on the atomic dispersion of the metal in the zeolite lattice. In their study, the catalyst prepared via ion exchange contained a higher metal (Pt) dispersion and exhibited higher sulphur tolerance than the catalyst prepared via the pore filling technique, which had a lower metal dispersion.

Many refineries have been adding pentane and hexane isomerization capacity to meet the octane shortfall caused by the phase-out of tetraethyl lead in gasoline. Refinery expansions for this process alone accounted for 20% of all refinery capital expenditures in 1986. Presently, both noble metal containing amorphous and zeolite catalysts are used in this process that operates under moderate pressures in the presence of hydrogen. The zeolite catalysts, typically Pt on mordenite in an alumina binder, are preferred for their resistance to poisoning by impurities such as sulphur or water[13].

The aim of the present paper is to measure the activity and selectivity of the different prepared catalysts towards isomerization of n-pentane under atmospheric pressure. The catalysts composed mainly of 0.5 wt. % Pt impregnated on different supports such as charcoal, clay, silica gel, alumina and Na-Y-zeolite. The effect of replacing Na^+ by H^+, Ca^{2+} or Mg^{2+} on the catalytic activity was also investigated.

EXPERIMENTAL

Charcoal, clay, silica gel, alumina and Na-Y-zeolite were used as different supports in this work. Some catalysts were prepared by impregnating each previous support with chloroplatinic acid solution of 0.5 wt.% Pt as follows: The desired amount of chloroplatinic acid is dissolved in a certain volume of distilled water, correspond to the moisture capacity of the support, added, dried at about 120°C, cooled and pressed into tablets. Two other samples of silica gel were used for preparing acidic and alkaline silica catalysts. The silica gel is treated with 1N HCl solution in the first case and 1N NaOH solution in the second case, then impregnated with 0.5 wt.% Pt as previously stated.

Ca, Mg and H-Y-zeolite catalysts were prepared from the Na-Y-zeolite by the conventional cation exchange procedure. The three exchanged forms were impregnated with 0.5 wt.% Pt as described above.

Bench scale unit designed to operate under atmospheric pressure was used in this investigation. 10 Ml catalyst was placed in the hot zone of the reactor between two layers of inert silica. The temperature was gradually raised to 500°C in a stream of pure air for 4 hrs to calcinate the catalyst, then with pure nitrogen to sweep off the air. The temperature was then lowered to 400°C in purified hydrogen flow gas for at least 4 hrs to reduce and activate the catalyst. The charge feed stock (n–pentane) was then introduced itno the reactor by a dosing pump.

The isomerization reaction of n-pentane was carried out in the temperature

range of 250–350°C, space velocity 4 hr^{-1} and at a hydrogen flow rate of 40 ml/hr.

At the end of the reaction, the liquid material which includes both products and unreacted *n*-pentane was collected by an ice water condenser. The gases leave the system were measured by displacement of saline water which felled a calibrated gas collector. Both gaseous and liquid products were analyzed by gas liquid chromatography.

The chromatographic analysis identify the presence of methane, ethane, propane and butane in the gaseous products while isopentane and *n*-pentane in the liquid products.

The percentages of conversion, cracking and selectivity were calculated from the equations (Appendix A).

RESULTS AND DISCUSSION

The role of supports on the catalytic activity

The effect of reaction temperatures on the products distribution resulted form the isomerization reaction of *n*-pentane over the catalysts, Pt/silica, Pt/Na-silica, Pt/H-silica, Pt/charcoal; Pt/alumina, Pt/clay and Pt/Na-Y-zeolite are illustrated in Fig. 1.

From Fig. 1-a, it is quite obvious that the total conversion increases with the increase in the reaction temperature from 250° to 350°C. The relation is identical for most catalysts except for the Pt/Na-silica catalyst which shows a maximum at 300°C and then decreases to zero conversion at 350°C.

Data in Fig. 1-b shows that, the yield of *iso*pentane with most of the prepared catalysts attained a maximum at 300°C, except for both Pt/alumina and Pt/clay catalysts. The yield of *iso*pentane produced on using these two catalysts decreases with the increase in temperature. On using Pt/alumina catalyst, the yield is twice that on Pt/clay catalyst at each reaction temperature. The results can clearly indicate that, isomerization activity is very high on using Pt/Na-Y-zeolite as compared with the other catalysts.

Fig. 1-c shows that the amount of the hydrocarbon gaseous products (C_1—C_4) increases with the increase in the reaction temperatures for most catalysts investigated and there is a parallelism between the three catalysts, Pt/H-silica, Pt/silica and Pt/charcoal. However, for Pt/Na-silica, there is a maximum at 300°C followed by a sharp decrease up to zero with further increase in temperature up to 350°C.

The formation of C_1–C_4 hydrocarbon gases indicates that the reaction of *n*-pentane isomerization is accompanied by a cracking side reaction.

The isomerization selectivity as represented in Fig. 1-d, relating the weight per cent of the *iso*pentane to the conversion weight per cent in a definite reaction temperature and at constant space velocity of 4 hr^{-1}. The selectivity for the

■   Pt. / Na - zeolite   υ   Pt. / Acids - silica
●   Pt. / Alumina   Δ   Pt. / Silica
▲   Pt. / Clay   x   Pt. / Alkaline - silica
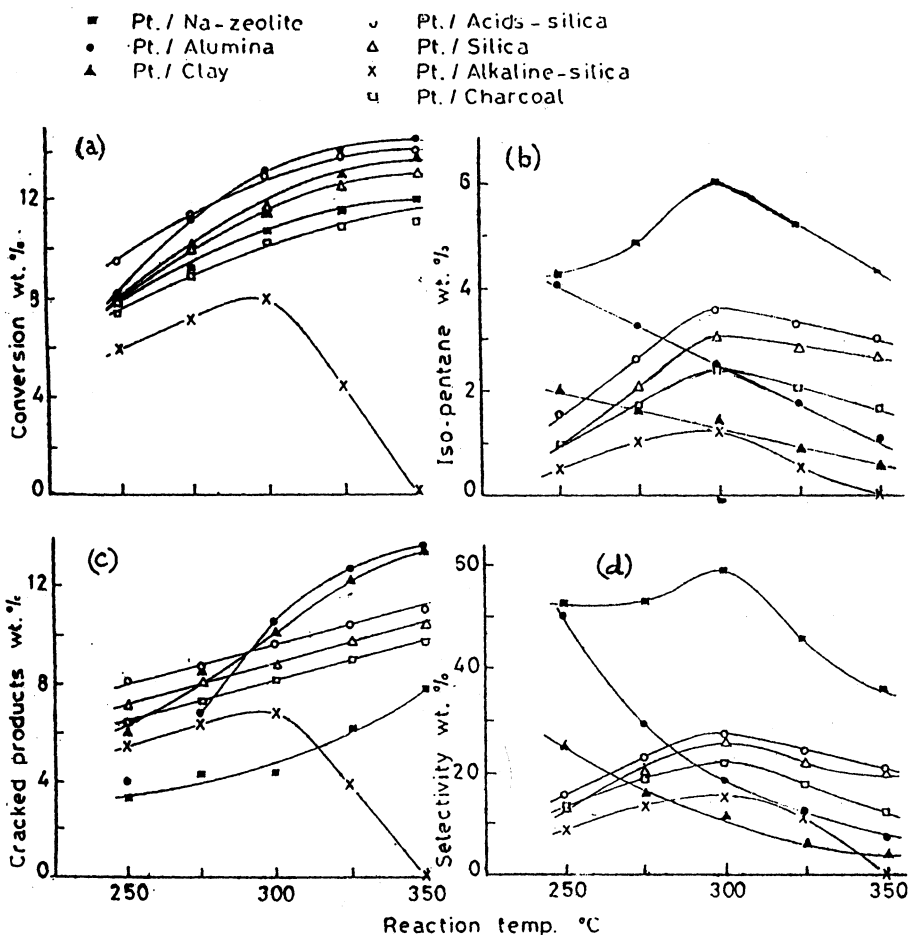   ч   Pt. / Charcoal

Fig. 1.   Effect of reaction temperatures on: (a) conversion, (b) *iso*pentane yield, (c) cracked products and (d) selectivity.

catalysts, Pt/Na-silica, Pt/charcol, Pt/silica, Pt/H-silica and Pt/Na-Y-zeolite, shows a maximum at 300°C. On the other hand, the selectivity decreases with the increase in the reaction temperature for Pt/alumina and Pt/clay catalysts. The variation in the extent of isomerization by using different catalysts was attributed to the variation in the frame structure of the supports.

The results represented in Fig. 1 (a-d) indicate that, skeletal isomerization to *iso*pentane was the predominant reaction on the Pt/Na-Y-zeolite catalyst. This means that the rate for carbonium rearrangement is greater than the rate of carbonium ion cleavage. Nevertheless, the reaction over the Pt/zeolite had a higher selectivity for the formation of isomerization product versus hydrogenolysis products that did the reaction over the Pt/catalysts. On the other hand, hydrogenolysis to hydrocarbons of lower molecular weights, Fig. 1-c, was the

preferred reaction all over the other catalysts (Pt/charcoal, Pt/silica, Pt/clay and Pt/alumina).

It is well known that the hydroisomerization catalysts have hydrogenation, dehydrogenation sites and acidic sites[14-16]. The acidic sites isomerize and cracked olefins formed at the dehydrogenation sites. Accordingly, the first step in the isomerization of the normal paraffins is the dehydrogenation to an olefin. The following steps are the formation of a carbonium ion on the acid site and subsequent rearrangement of the carbonium ion[17]. Reaction of the carbonium ion and a hydride ion results in the formation of the *iso*paraffin. Therefore, Pt/acidic silica gel has a pronounced effect on the isomerization of *n*-pentane than both Pt/Na-silica and Pt/silica catalysts. This effect may be due to the formation of active sites covered by protons which are supplied by the hydrochloric acid solution during the preparation of the Pt/acidic-silica catalyst.

Thus, it may be suggested that, the nature of the catalytically active sites in most supported catalysts (charcoal, silica, alumina and clay) is not completely active to isomerization. Usually, a small fraction of the over all structure constitutes the active sites. As a results, the bulk of catalytically non active structure masks the specific properties of the active sites which influence the yield of *iso*pentane, (Fig. 1-b). The Pt/Y-zeolite showed enhanced selectivity for isomerization of *n*-pentane as compared with the other supported catalysts although the particle size of the metal was almost the same in all supports.

On the basis of the previous results, Pt is more suitable to be supported on Na-Y-zeolite for isomerization against hydrogenolysis. The intention to use Na-Y-zeolite as support was mainly attributed to the assumption that Pt finely dispersed on AlO_4 tetrahydron of zeolitic frame work was cationic (electron deficient) due to the differences in the electronegativity between Pt and oxygen anion, therefore, exhibit high ability to form carbonium ion like species.

Influence of cationic forms of Y-zeolite on activity

The type of cation on zeolite plays an important role in the extent to which a catalytic reaction may proceed. To illustrate this role, the Na-Y-zeolite was exchanged with Mg^{2+}, Ca^{2+} and H^+ forms. Ca and Mg forms were prepared by contacting the Na-Y-zeolite with the corresponding Ca or Mg chloride solution respectively. The H-form was prepared by exchanging the original Na ions with ammonium ions and subsequent decomposition of the ammonium ions at higher tempereature. All exchanged supports were impregnated with 0.5 wt.% Pt and tested for the isomerization of *n*-pentane in the temperature range 250°–350°C and space velocity of 4 hr^{-1}.

Results represented in Fig. 2, indicate that all the exchanged catalysts are active than the Pt/Na-form, and the trend of the curves is similar for all the catalysts investigated. The conversion wt.%, Fig. 2-a, increases with the increase in the reaction temperature. On the other hand, *iso*pentane yield and selectivity, Fig. 2-b,c show a maximum at 300°C, then decreased with the increase in reaction
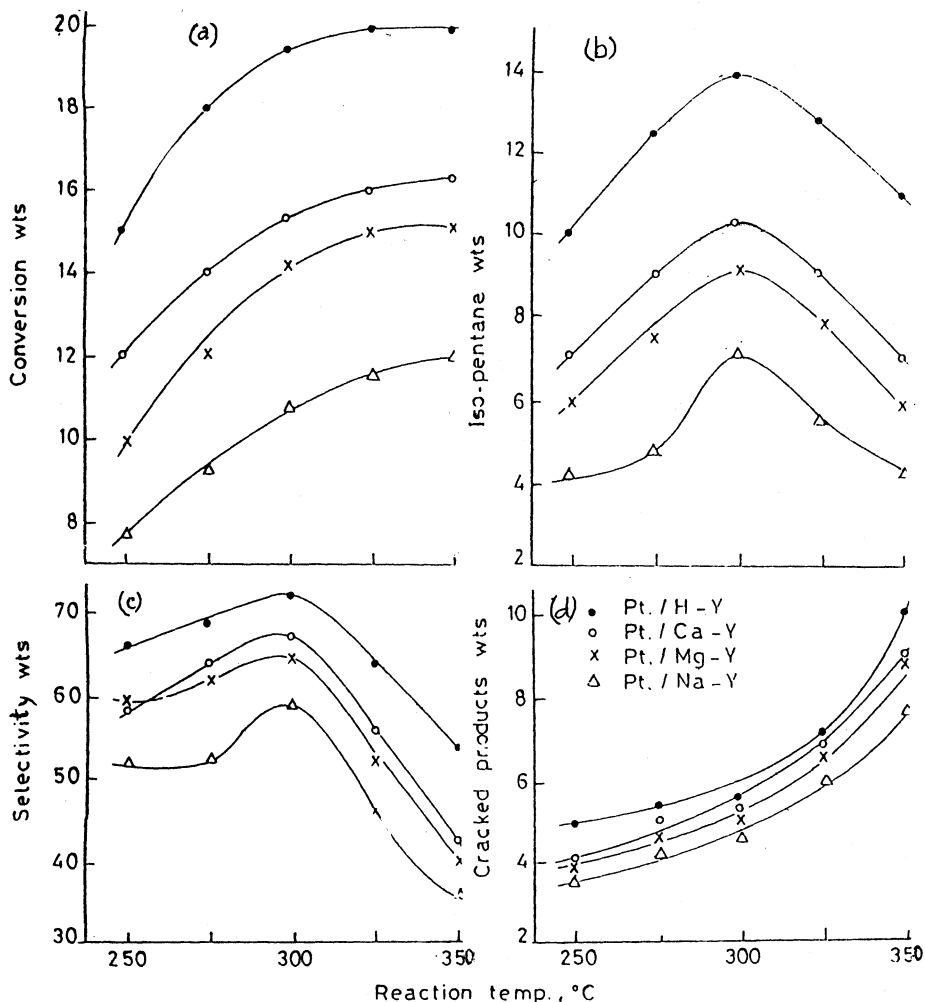
Fig. 2. Effect of reaction temperature on: (a) conversion, (b) isopentane yield, (c) selectivity and (d) cracked products.

temperature up to 350°C. The cracked products, Fig. 2-d, increases linearly with the increase in temperature.
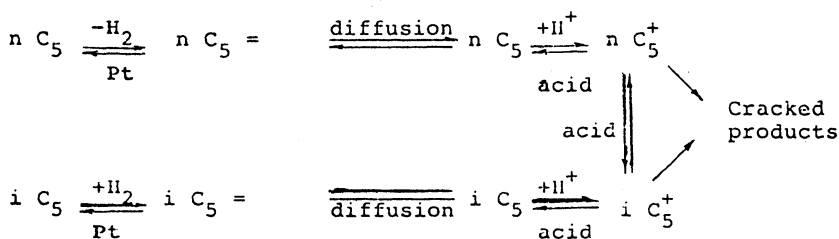
From the previous results, it is clear that isomerization activity increases in the order: Na < Mg < Ca < H. The reason for the high activity of Ca and Mg cover the other catalysts may be attributed to the structure of these metals on the support. Ca and Mg (divalent) are bonded to more than one AlO_4 tetrahydron and they are located nearer to one site than the other. This structural formula creates positive and negative sites, therefore, facilitate the isomerization reaction. The isomerization activity increases from Mg to Ca may be due to the greater ionic radius of Ca than Mg.

Finally, it may be assumed that, both valency and ionic radius of the cations are important factors on determining the extent of *iso*pentane formation.

The overall reaction is rate limited by the formation of carbonium ions which are produced through the mechanism of hydride ion removal shown in the following equation:

$$nC_5 \xrightarrow{-H^-} nC_5^+$$
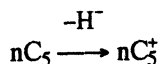
This mechanism is not highly selective for isomerization over cracking[18]. In order to greatly improve the selectiveity of the catalyst toward isomerization and to stabilize the catalyst's performance, a small amount of platinum is dispersed throughout the support base. For the most part, the addition of Pt alters the primary catalytic mechanism to that of a classical dual functioned catalyst. This behaviour was proposed by Zarchy and Shashoum[19] schematically as follows:

$$n\,C_5 \xrightleftharpoons[\text{Pt}]{-H_2} n\,C_5 = \xrightleftharpoons{\text{diffusion}} n\,C_5 \xrightleftharpoons[\text{acid}]{+H^+} n\,C_5^+$$

$$i\,C_5 \xrightleftharpoons[\text{Pt}]{+H_2} i\,C_5 = \xrightleftharpoons[\text{diffusion}]{} i\,C_5 \xrightleftharpoons[\text{acid}]{+H^+} i\,C_5^+$$

acid → Cracked products

While in practice the primary catalytic mechanism is that ot the dual functioned catalyst, Friedel Crafts hydride abstraction occurs simultaneously to a lesser extent. The metal function catalyzes the dehydrogenation of paraffins into olefins. In a properly designed catalyst, sufficient metal should be added to maintain the olefin/paraffin equilibrium. At the acid site provided by the support, the olefin can be protonated to the corresponding carbonium ion. Formation of carbonium ions from olefins proceeds at a much faster rate than by the corresponding hydride ion abstraction from paraffins[20]. The carbonium ion can be rearranged to the isomer form or can break up into cracked products. The *iso*olefin which desorbs can then diffuse to a metal site where it can be hydrogenated to the *iso*paraffin. The metal function also serves as a source for hydrogen ions. This spillover hydrogen from the platinum helps to stabilize the acid sites, shifts the activity from cracking to isomerization and limits the amount of coke deposition on the catalyst[2].

Conclusions

There are two rates controlling the converison of *n*-pentane over Pt/catalysts, rate of carbonium ion rearrangement and rate of carbonium ion cleavages.

On using, Pt/zeolite catalysts, the rate of carbonium ion rearrangement is greater than the rate of carbonium ion cleavage and so the isomerization is more pronounced.

On using, all the other Pt/catalysts, the rate of carbonium ion rearrangement is smaller than the rate of carbonium ion cleavage which enhance the cracking reaction.

Pt/H-Y-zeolite is the most active catalyst towards the isomerization of *n*-pentane.

Appendix (A)

$$\text{Conversion wt.\%} = \frac{\text{total amount of converted } n\text{-pentane}^*}{\text{weight of } n\text{-pentane}} \times 100$$

$$\text{Cracking wt.\%} = \frac{\text{total amount of hydrocarbon gases}}{\text{weight of } n\text{-pentane}} \times 100$$

$$\text{Selectivity wt.\%} = \frac{\text{total amount of } iso\text{pentane}}{\text{converted } n\text{-pentane}} \times 100$$

*Converted *n*-pentane includes; hydrocarbon gases, coke deposits and loss.

The amount of coke deposits on the catalyst was determined by heating the catalyst at 500 °C in stream of air for 2 hrs. The carbon dioxide produced was adsorbed by soda lime trap, of known weight, from which the amount of carbon can be calculated.

N.B. Coke deposits is less than % in all the investigated catalysts.

RERERENCES

1. M. Bondart and L.D. Ptak *J. Catalysis*, **16**, 90 (1970).

2. J.R. Anderson R.J. Mardonald and Y. Shimoyama, *J. Catalysis*, **20**, 147 (1971).

3. E. Kikuchi, M. Tsurnui and Y. Morita *J. Catalysis*, **22**, 226 (1971).

4. Kh. M. Minachev and Y.I. Isakova, Zeolite Chemistry and Catalysis, *Am. Chem. Soc.*, Chap. 10 (1976).

5. P.A. Lawrance and A.A. Rawlings, 7th World Petrol Cong., IV, 135 (1967).

6. J.F. Le Page et Coll, Catalyse de Contact, Institute Francais du Petrole, Technip ed Paris, Chap. V (1978).

7. R.L. Moss, Experimental Methods in Catalytic research, Vol. II, R.B. Anderson and P.T. Dawsor. Usademic Academic Press, N.Y., Chap. 2 (1976).

8. F. Rabeiro and Ch. Marcilly, *Rev. de l'institute Francais du Petrol*, **34**, 405 (1979).

9. I.B. Steinmetz and S. David (Furukawa Electric Co., Ltd.), U.S. 3,764,516 (C) 208/27; C 10 g C 07c) 09 Oct. 1973, Appl. 828, 746, 28 May 1969; *Chem. Abstr.*, **80**, 501083j (1974).

10. S. Mikhail A.S. Farag, Y. Barakat and A.A. Hassan, Paper presented in the International Symposium on Zeadilins Portorose, Yugoslavia, Sept. 1984, and published in 2nd Egyptian Cong. of Chem. Eng., 18–20 March, 1984, (Cairo).

11. J.V. Rabo, V. Shomaker and P.E. Picker *Proc. Int. Congress Catal. 1964*, Vol. 2, North-Holland, Amsterdam (1965).

12. Kh. M. Minachev, V.I. Garanin and V.V. Kharlamov, *Heffepererab Neftekhim*, **11**, 36 (1973).

13. N.Y. Chen and T.F. Degnan, *Chemical Eng. Progress*, 32–41, (1988).

14. R.A. Flinn, D.A. Larson and H. Benther *Ind. Eng. Chem.*, **52**, 153 (1960).

15. R.C. Archibald, B.S. Greensfelder, G. Holzman and D.H. Rowe, *Ind. Eng. Chem.*, **52**, 745 (1960).

16. H.L. Coonradt, F.G. Ciapetta, W.E. Garwood, N.K. Leamon and J.N. Miale, *Ind. Eng. Chem.*, **53**, 727 (1961).

17. C.G. Frye, Preprints Div. of Pet. Chem., A.C.S., Meeling, Sept. 9–14, PA–21 (1962).

18. H.W. Kouwenhoven and W.C. Van Zijll, Langhout, *Chemical Eng. Prog.*, **67**, 65 (1971).

19. A.S. Zarchy and E.S. Shamshoum, 10th North American Catal. Society Meeting (May 17–22, 1987).

20. H.C. Pines, The Chemistry of Catalytic Hydrocarbon Conversion, Academic Press, N.Y. (1981).

21. B.C. Gates, The Chemistry of catalytic Processes, McGraw-Hill Chemical Engineering Series, N.Y. (1979).