

Cumene Cracking over Prepared Alumina Catalysts

Salwa A. El-Khatib and Latifa Kh. Mohamed

Egyptian Petroleum Research Institute, Nasr City, Cairo, Egypt.

ABSTRACT

The cracking properties of three prepared catalysts of γ -alumina having various acidities were investigated using cumene cracking as a model reaction. The experiments were performed in a microcatalytic reactor attached with a gas chromatograph. The reactions were carried out under atmospheric pressure in a temperature range of 370°-460°C. The influence of reaction temperature and the intrinsic acidity of the catalysts on their cracking efficiency and the distribution of the final products have been evaluated. It has been found that the amount of acid sites of certain strength has the responsibility for a certain reaction to proceed, but not the total acidity of the catalyst.

INTRODUCTION

The cracking of hydrocarbons is one of the most important industrial processes, which permits the transmuting of heavy natural oils into more useful lighter products. The produced lower molecular weight components can be utilized for numerous purposes such as a fuel for combustion engines, as starting materials for a wide variety of plastics, pharmaceuticals, and also as industrial solvents.

Cracking can occur thermally or by employing catalysts. Each of these two types of cracking is accomplished through a different reaction mechanism and consequently yields entirely different product distribution. In catalytic cracking, carbonium ions are implied as intermediates, whereas thermal cracking proceeds via free radical reactions (1). The catalytic cracking of

hydrocarbons is much more selective than thermal cracking and gives rise to relatively smaller amounts of C_1 and C_2 fragments (2).

Most cracking catalysts are known to envice acidic properties (3-7). The accepted suggestion for the mechanism of acid catalyzed cracking reaction comprise the arising of a carbonium ion on the catalyst surface through the addition of a proton to an olefin or aromatic, or by the abstraction of a hydride ion from a saturated hydrocarbon. Thereafter, the various ionic reactions can proceed.

Interpretation of results obtained from an industrial catalytic cracking process is very intricate, due to the prevalence of various reactions and the complexity of the gas oil feed. Hence, for characterizing a cracking catalyst, it is convenient to choose a pure reactant that could undergo a typical cracking reaction and gives a few products. Cumene has received considerable attention for such purpose (8-12). The product distribution of cracked cumene is comparatively simple where benzene and propylene are the major products.

The present work is devoted to evaluate the cracking activity of some prepared alumina catalysts, using cumene as a probe molecule. The effect of reaction temperature on the reactant conversion and the product distribution have been elucidated. Moreover, it is known that the acidic character of solid surfaces play the central role in defining their catalytic efficiencies (5, 13-15). Therefore, this study also demonstrates the importance of the intrinsic acidity of the catalysts in directing the course of reactions and the responsibility of the strength of acid sites for the constituents of the final products obtained.

EXPERIMENTAL

a) Materials Used:

- Cumene, C_9H_{12} : BDH
- Sodium aluminate $NaAlO_2$: Supplied by Morgan Chemical Industries
- Sulphuric acid, H_2SO_4 : Laboratory Chemicals Prolabo, ADWIC

b) Catalyst Preparation:

Alumina catalysts were prepared via $Al(OH)_3$ which was precipitated from a 10% solution of sodium aluminate by dilute sulphuric acid. The precipitate was washed, dried and finally calcined at $400^\circ C$ for 4 hrs.

On the basis of the above procedure, three samples of alumina were obtained by varying the preparation factors which involve H_2SO_4 concentration, acid: sodium aluminate ratio and the drying time. The prepared alumina samples and their respective preparation conditions are compiled in Table 1.

c) Acidity Measurement:

The amount of acid as a function of acid strength were determined by amine titration method using color indicators (16). A set of Hammett indicators was selected to cover the range from $pK_a + 5$ (methyl red) to $pK_a - 8.2$ (anthraquinon). The method of measurement has been described in detail elsewhere (17,18).

d) catalytic Activity Tests:

The catalytic experiments for cumene cracking were carried out under atmospheric pressure using the pulse technique. A stainless steel microcatalytic reactor of 12 cm length and 3.5 mm internal diameter was employed. It is placed in a tube furnace and directly attached to a gas chromatographic apparatus; [PERKIN-ELMER SIGMA -3b] fitted with a flame ionization detector (FID), and connected to an electronic recorder. The reaction products were separated at $80^\circ C$ in a 2m column packed with penton

34 with 5 wt% diisodecylphthalate on chromosorb W 80-100 mesh. Nitrogen was used as a carrier gas.

RESULTS AND DISCUSSION

The reaction of cumene cracking was carried out on each alumina catalyst at 370°-460°C, with temperature interval of 30°C. The reaction products composed mainly of benzene and propylene and accompanied by side reaction depending upon several factor including the reaction temperature and the acidity of catalyst.

[A] Effect of Reaction Temperature:

Cumene cracking results of Al_{10%} sample is illustrated in Table 2, and Figs. (1-3). A significant conversion has obtained at 370°C and gradually increased from \approx 85 wt% to reach the maximum (100%) at 460°C. The produced yield composed mainly of benzene with quantities depending markedly upon the reaction temperature. It represents \approx 56 wt% of the product at the lowest temperature and progressively increased to 73.2 wt% at elevated temperature.

Propylene is also a principal product in this reaction. It is involved in the yield with an amount equal to \approx 20.5 wt% at 370°C and come to be \approx 23.4 wt% at 400°C. The concentration of propylene gas remains approximately constant at higher temperature.

In the catalytic cracking of alkyl aromatics, benzene rings are not cracked and the side chains are split off as the corresponding olefins. However, it has been noticed that the mole ratio of propylene to benzene in the product are always less than unity. The deficiency in propylene when compared to benzene may be attributed to its transformation to coke particularly at higher temperature (19,20).

In addition, toluene and ethylbenzene have been identified in small amounts. Their formation may be ascribed to the cracking of cumene molecule. Also, the cracked fragments (i.e., methyl and ethyl groups) can undergo alkylation reaction with benzene, to a limited extent, under the applied reaction temperatures.

The existence of some n-propylbenzene at 370°C seems to be a result of either the direct isomerization of cumene, or to the alkylation of benzene with propylene (21). Both reactions are inhibited at higher temperatures and led to the disappearance of this component from the reaction products.

The effect of reaction temperature on cumene cracking over Al₂O₃ catalyst is shown in Table 3 and Figs. (1-3). It can be observed that pronounced conversion of cumene amounts to 89 wt% at 370°C. A slight increase of temperature is accompanied by an improvement in the total conversion to attain 97.4 wt% at 400°C, beyond which the activity remained almost constant up to 460°C.

It is evident from the data that, more than 55 wt% of the reactant was transformed to benzene at 370°C. A noticeable improvement in this amount has occurred upon raising the reaction temperature to 400°C to become 62 wt%. Higher temperatures have insignificant effect on the concentration of benzene.

The amount of propylene formed from cumene cracking varied from ≈ 20.2 wt% to ≈ 27 wt% throughout the range of temperature applied. A slight increase in the concentration is achieved with increasing the temperature from 370° to 400°C. At more elevated temperature some of this propylene was missed due to coke formation (19,20).

n-propylbenzene is also detected as a result of side reactions due to either isomerization of cumene or alkylation of benzene with propylene as mentioned previously.

In addition, a quantity of 6.7 wt% of diisopropylbenzene was found in the reaction yield at 370°C and enhanced with temperature to become 8.9 wt% at 460°C. Since alkylation reactions are usually proceed at relatively lower temperatures, this lead us to encourage the belief that diisopropylbenzene resulted from the disproportionation reaction of cumene rather than from the alkylation of cumene with propylene product (22). This is in agreement with the observations of Murakami et al.;(23), who found that propylene was not involved in the product of the dialkylaromatic.

The data obtained from the catalytic cracking of cumene over Al_{30} hr catalyst are presented in Table (4) and Figs. (1-3). It can be perceived that this sample possesses comparatively the lowest activity for cumene cracking. Less than 7 wt% of cumene was converted at 370°C. However, the reaction temperature has a considerable influence for augmenting the conversion to become ≈ 53 wt% at 460°C.

Benzene and propylene are not detected at lower operating temperature, but started to appear at 400°C with an amount equal to 21.6 wt%. Further increase in temperature enhances the formation of benzene to attain ≈ 32 wt% at 460°C. Nevertheless, the propylene concentration is reduced because of transformation of this olefinic gas to coke.

The product distribution of Al_{30h} specimen reflects a significant difference in its catalytic behavior in comparison with the other forementioned catalysis. A pronounced selectivity to dimerization reaction is indicated through the formation of heavy alkylaromatic with a considerable amounts,

ranging from ≈ 6.2 wt% at 370°C to 10.6 wt% at 460°C . Disproportionation reaction also occurs, as some molecules of cumene dimer were subsequently cracked to give ethylbenzene and cymene in quantities equal to 3.35 wt% and ≈ 5.9 wt at 460°C , respectively.

[B] Effect of the Catalyst Acidity:-

The acidities of the examined alumina catalysts are illustrated in Table (5). The data reveal that the three samples incorporate approximately the same amount of total acidity. An average acid center concentration of $\approx 0.55 \pm 0.05$ mmol/gm was obtained for those specimens. However, the strength distribution of the acid sites varies widely for each sample.

$\text{Al}_{10\%}$ catalyst exhibits the strongest acid sites. More than 55% of the acidic centers possess a high acid strength corresponding to H_0 value of ≤ -8.2 . The remainder sites have a moderate strength. With respect to $\text{Al}_{1:1}$ it is obvious that, the acid centers of this sample has strength level lower than that of $\text{Al}_{10\%}$ which spread along a wide range of H_0 (i.e. + 5 to -8.2). Al_{300} involves the lowest acid sites strength which fall in H_0 range of + 5 to + 0.8.

The strong relationship between the catalytic activity and the acidity of the investigated aluminas can be elucidated by comparing the results in Tables (2-4) with Table (5). The reported data reflect the highest efficiency of $\text{Al}_{10\%}$ catalyst towards cumene conversion particularly to cracking reaction. Majority of the product constituents are cracked components at all reaction temperatures applied. This leads us to propose that, strong acid sites are required for the accomplishment of the cracking reaction (24). Some alkylation has also been achieved and proceeded more favorable at relatively lower reaction temperature with the formation of small fractions of toluene, ethyl benzene and n-propyl benzene. Presumably, this reaction pertains to the acid centers with moderate strength that also exist in this sample.

Although $Al_{1:1}$ has almost the same total number of acid centers as that of the pervious sample, there is a marked difference in their acidity spectra. As mentioned before, the acid sites of this catalyst are distributed over a wider range of acid strength. Hence, not less than three types of reactions are recognized. Cracking, which is the main reaction has occurred on the strongest acid sites. Alkylation is also proceeded over the acid centers with milder strength, and disproportionation reaction takes place on the weakest acid sites.

With Al_{30h} the dealkylation of cumene molecule restricted on such weak acid sites, particularly at lower temperature. Instead, polymerization and disproportionation are the most predominant reactions, since they need the lowest acid strength to be achieved. Cracking of some cumene dimer, which is relatively easier than cumene itself, has occurred to some extent.

Thereby, the reaction can be arranged descendingly according to their relative strength of acid sites as follows:

Cracking > Alkylation > Disproportionation and Polymerization

From this comparison, a strong parallelism between the occurrence of a given catalyst reaction and the presence of acid sites of a certain strength has been established. That explains the wide variance in the distribution of cumene cracking products by alumina catalysts, even, if the same reaction conditions prevail. This finding implies that acidity control both conversion and the selectivity of catalysts.

REFERENCES

1. Corma, A.; Wojciechowski, B.W., *J. Catal. Rev., Sci. Eng.*, 24, 1 (1982).
2. Corma, A.; Wojciechowski, B.W., *Catal. Rev. Sci. Eng.*, 24, (1), 1-56 (1982) in "Marcel Dekker, J. of Adv. Cata. ", N.Y. Edt. H. Heinmann.
3. Aberuagba Folorunsho; Kumar Manoj; Gupta Jai Krishna; Muralidhar Gudimella; Sharma Lakshmi Datt, *Reaction Kinetics and Catalysis Letters*. Vol. 25. No.2. pp. 245-250 (2002).
4. Macedo Jose Carlos D; Mota Claudio J-A; de-Menezes Sonia M C; Camorim Vera; *Applied Clay Science*. Vol. 8, No. 5 Jan, pp. 321-330. (1994).
5. El-Khatib, S.A.; Mohamed, L.Kh; Hassan, H.A., *J. Egpt. Sco. Eng.*, 31 (4), pp.89-93 (1992).
6. Bautista FM; Campelo JM; Garcia A; Luna D; Marinas JM; Romero-AA, *Applied Catalysis A: General* Vol. 104, No.2, Oct. 20, pp. 109-135. (1993).
7. Mostafa MR, *Adsorption Science and Technology*. Vol. 16, No. 1, pp.11-19. (1998).
8. Ahmed H.S; El-Kady F.Y. and Selim M.M., *Bulletin of Faculty of Science. Mansoura University*, Vol. 27 (2), Dec., (2000).
9. Rana Mohan .S; Dhar G Murali; Rao TSR Prasad; Maity SK; Ancheyu J., *Applied Catalysis A: General*. Vol. 258, No. 2, Feb. 20, pp. 215-225. (2004).
10. Al Madfai Suham; Abbas Abdullah A; Ali Ahmed J., *Can J Chem Eng.* Vol. 64. No. 6, Dec., pp. 977-981. (1986).
11. Sato Satoshi, Sodesawa Toshiaki; Nozaki Fumio; Shoji Hiroshi, *J. Mol. Catal.* Vol. 66, No. 3, Jun 15, pp. 343-355. (1991).
12. Acharya D-r; Hughes R; Li K, *Appl Catal.*, Vol. 52, No.1-2, Jul. 17, pp. 115-129. (1989).
13. El-Khatib, S.A.; Mohamed. L.Kh; Hassan, H.A. *Ain Shams Science Bulletin*. 29 (Part A) pp.473-486 (1992).
14. B. Grzybowska Swierkosz, *Polish J. Chem.*, 77, pp. 627-636 (2003).
15. Gayubo Ana G; Benito Pedro L; Aguayo Andres T; Olazar Martin; Bilbao Javier, *Journal of Chemical Technology and Biotechnology*. Vol. 65, No.2, Feb. pp. 186-192. (1996).
16. Laine, J; Yunes, S., Brito, J. and Andreu, P., *J. Catal.*, Vol.62, No.157, (1980).
17. El-Khatib, S.A.; Mohamed. L.Kh; Hassan, H.A., *J. Egyp. Soc. Eng.*, 31, (3), pp.38-42 (1992).

18. El-Khatib, S.A.; Mohamed. L.Kh; Hassan, H.A., Bulletin of Faculty of Science, Mansura Univ., 19 (1), pp. 19-30 (1992).
19. Wang Fu Min; Xin Feng; Liao Hui; Li Shao Fen. Shiyou Xuebao, Shiyou Jiagong Acta Petrolei Sinica (Petroleum Processing Section) Vol.18, No.5, pp.28-33. October (2002).
20. Brito A; Gonzalez AR; Borges ME; Garcia MT, Applied Catalysis A: General. Vol. 205, No. 1-2, pp.173-182. Jan. (2001).
21. Douglas, J.E.; and Roberts, R.M., Chem. Ind., pp.926 (1959).
22. Pansing, W.F.; Malloy, J.B., and Thomas, C.L., Ind. Eng. Chem., 41 (11), 2564 (1949).
23. Murakami, Y.; Hattori, T., and Hatton, T., J. Am. Chem. Soc., 10, 123 (1968).
24. Brei Vladimir V; Khomenko Konstantin N; Shystka Dmitriy V, Reaction Kinetics and Catalysis Letters, Vol. 81, No. 1, pp. 197-202. (2004)

Table 1: Alumina Catalysts and Their Preparation Conditions

Catalyst	H ₂ SO ₄ concentration	Ratio of H ₂ SO ₄ : Na AlO ₂	Drying time, h
Al 10%	10%	1/2 : 1	12
Al 1:1	5%	1:1	12
Al 30	5%	1:1	30

Tables (2) Effect of Reaction Temperature on The Product Distribution of Cumene Cracking Using alumina 10% Catalyst.

Product distribution	Reaction temperature, °C			
	370	400	430	460
Propylene	20.46	23.42	24.42	24.85
Benzene	55.86	69.37	70.23	73.2
Toluene	2.02	1.94	1.67	0.9
Ethylbenzene	3.24	2.77	1.63	1.05
Cumene	15.05	2.5	2.05	---
n-propylbenzene	3.37	---	---	---
Total conversion	84.95	97.5	97.95	100
Cracking Selectivity %	96.03	100	100	100

Tables (3) Effect of Reaction Temperature on The Product Distribution of Cumene Cracking Using alumina 1:1 Catalyst.

Product distribution	Reaction temperature, °C			
	370	400	430	460
Propylene	25.89	27.155	24.16	20.2
Benzene	55.21	62.39	64.97	68.28
Cumene	10.33	2.56	2.79	2.01
n-propyle-benzene	1.84	0.795	0.58	0.58
Diisopropyl benzene	6.73	7.1	7.5	8.93
Total conversion	89.67	97.44	97.21	97.99
Cracking selectivity %	90.44	91.89	91.68	90.29

Tables (4) Effect of Reaction Temperature on The Product Distribution of Cumene Cracking Using alumina 30 hr Catalyst.

Product Distribution	Reaction temperature, °C			
	370	400	430	460
Propylene	---	7.2	4.84	1.06
Benzene	---	21.57	28.57	31.97
Ethylbenzene	---	1.03	1.4	3.35
Cumene	93.13	62.39	54.51	47.16
Cymene.	0.70	1.01	2.72	5.86
Heavy alkyl aromatic	6.17	6.8	7.96	10.6
Total conversion	6.87	37.61	45.49	52.84
Cracking selectivity %*	6.78	79.23	76.52	68.84

* The cracking selectivity is due to dealkylation of cumene and also for cracking of the dimmers

Table (5) Acid Strength Distribution of Various Samples Ref.(13)

H ₀	Acidity m mol / g		
	Al 10%	Al 1:1	Al 30 hr
+ 5.0 to 3.3	0	0.1	0.2
+ 3.3 to 2.8	0.05	0.1	0.1
+ 2.8 to 0.8	0.15	0.1	0.3
0.8 to - 3	0.05	0.05	0
- 3 to - 5.6	0	0.05	0
- 5.6 to - 8.2	0	0.1	0
- 8.2 to < - 8.2	0.3	0	0
Total acidity	0.55	0.5	0.6

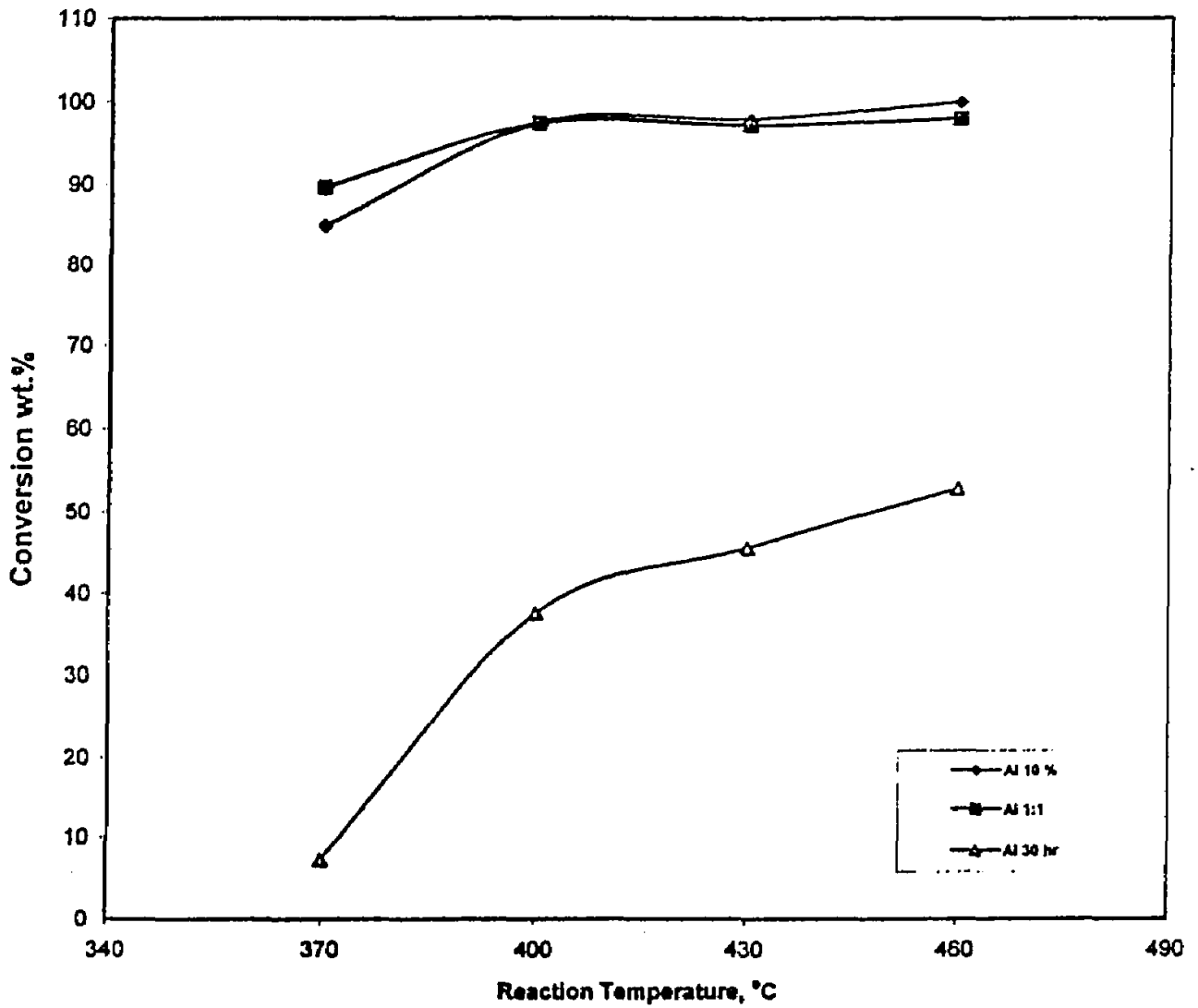


Fig. (1) Effect of Reaction Temperature, on Cumene Conversion Using Alumina Catalysts

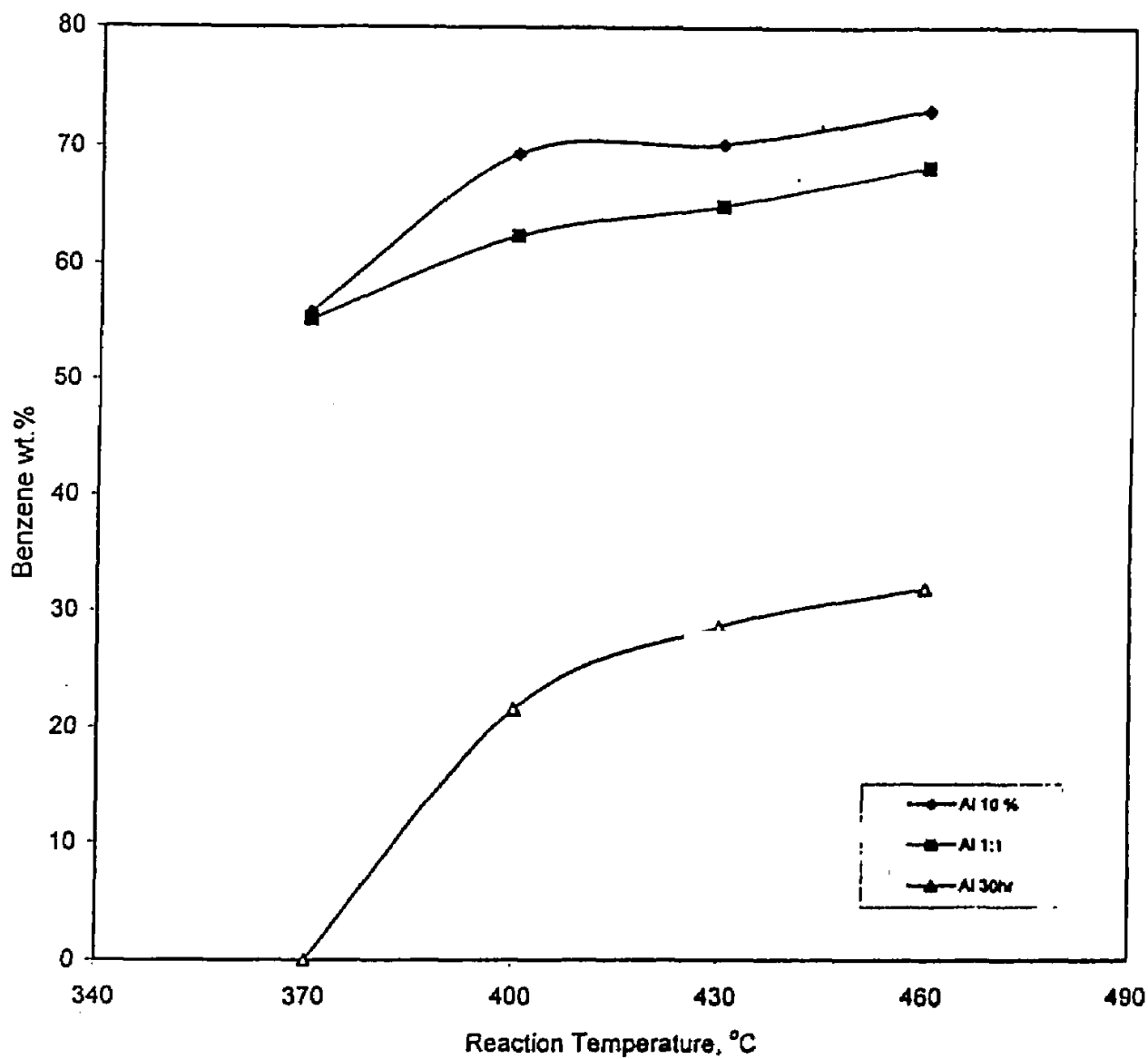


Fig. (2) Effect of Reaction Temperature on Benzene Formation

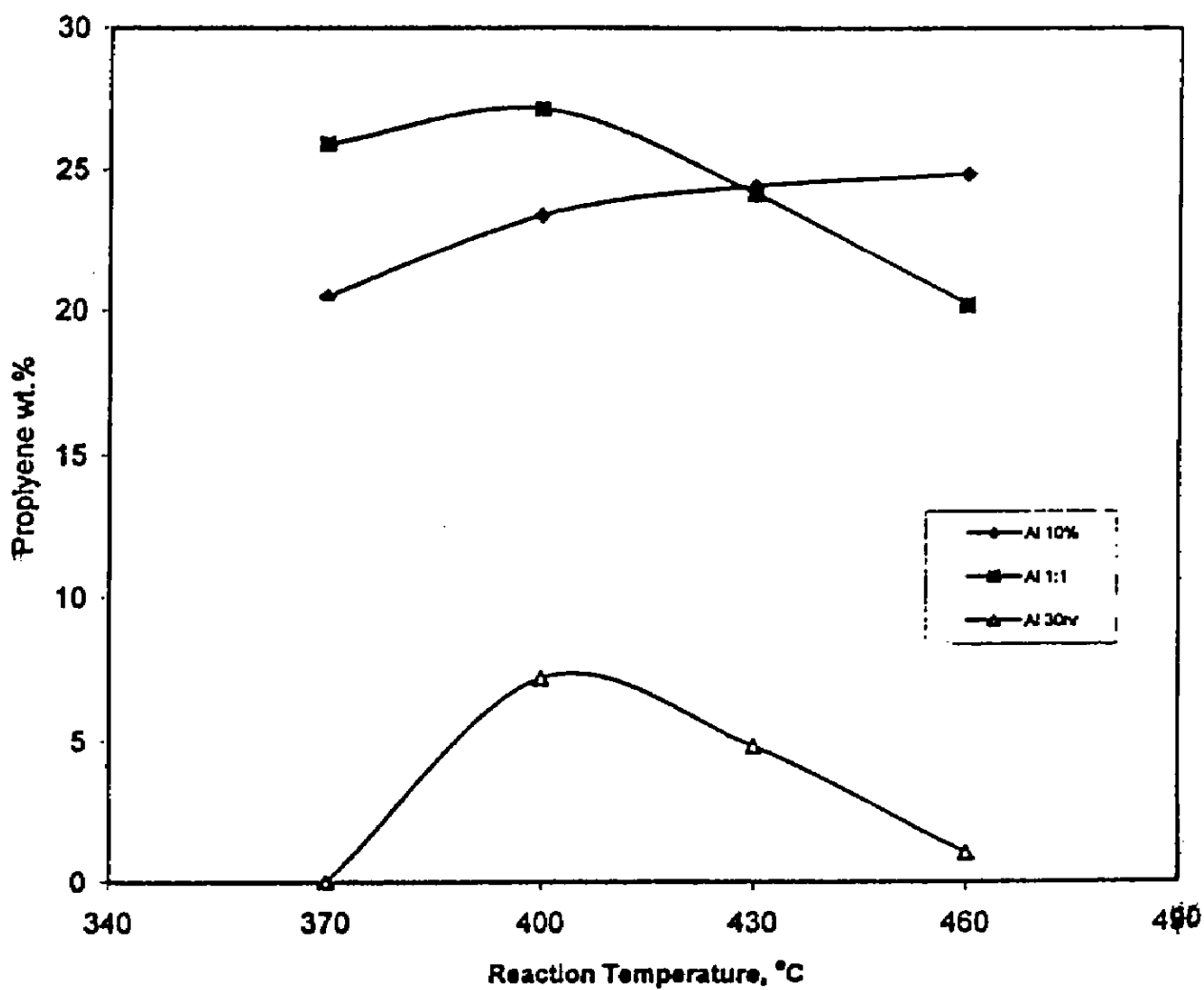


Fig. (3) Effect of Reaction Temperature on Propylene Formation