The effect of intermetallic hydrogen acceptor on catalytic aromatization of propane

O.V. Chetina [1], T.V. Vasina [1] and V.V. Lunin [2]

[1] *N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Science, 117913 Moscow, Russia*
[2] *Chemistry Department, Moscow State University, 119899 Moscow, Russia*

Received 4 March 1992; accepted 15 March 1992

The effect of the hydride-forming intermetallic compound Zr_2Fe on the aromatization of propane over high-silica zeolites of CVM type (Russian equivalent of ZSM-5) modified by Zn, Ga or Pt cations has been investigated. Aromatics yield and selectivity of aromatization are shown to increase essentially as a result of releasing hydrogen elimination by the intermetallic acceptor. The effect of hydrogen acceptor on propane conversion and product distribution appeared to be different depending on the composition of the catalyst used. Possible changes in the reaction mechanism in hydrogen removal conditions are discussed.

Keywords: Catalysis; aromatization; propane; ZSM-5; hydrogen acceptor; intermetallic compound; hydride

1. Introduction

The catalytic aromatization of C_2–C_4 alkanes is of great industrial interest as it widens the raw material base of aromatics production [1]. It is known that aromatization of propane proceeds readily at temperatures higher than 500°C over high-silica zeolites of ZSM-5 type incorporating gallium [2–4], zinc [4–6] or platinum [7,8]. But this reaction is accompanied by hydrocracking, dealkylation and hydrogen transfer, concurrent processes which are more marked at higher partial pressure of hydrogen in the reaction mixture [2]. It might therefore be expected that the elimination of hydrogen released during aromatization will significantly improve the yield of desired products.

Using a hydrogen-permeable membrane reactor with a thin palladium film supported on the outer space of a porous alumina cylinder as a membrane Kikuchi and co-workers [9] managed to obtain over a gallium-loaded H-ZSM-5 catalyst a 1.7 fold higher aromatics yield from propane than the yield observed in a conventional packed bed reactor. The higher yield of aromatics in the membrane reactor was credited to the suppression of the formation of the byproducts, methane and ethane, due to selective removal of hydrogen from the reaction system.

Application of a hydride-forming intermetallic compound for elimination of hydrogen during aromatization of ethane over Zn, Ga or Pt modified pentasils appeared to be more effective as it allowed us to get 4 to 6-fold higher aromatics yields compared to those obtained without hydrogen acceptor in the same reaction conditions [10,11].

In this contribution we report the results obtained during studies of the hydride-forming intermetallic compound Zr_2Fe on the aromatization of propane. The reaction was carried out over several catalysts of CVM type (Russian equivalent of ZSM-5) modified by Zn, Ga or Pt cations.

2. Experimental

The catalysts were prepared on the base of protonic CVM pentasil with $SiO_2:Al_2O_3$ ratio 42 and Na_2O content lower than 0.1%. Modifying elements were introduced by impregnation [12]. 10 g of zeolite were stirred in 150 ml of metal nitrate or H_2PtCl_6 solution at 0°C for 20 min and then at 25°C for 24 h. After evaporation of water in a vacuum rotary evaporator the catalysts were dried at 130°C and calcined in air stream at 520°C for 5 h. The intermetallic compound was prepared by alloying of pure metals according to the ordinary method [13].

The reaction was carried out in a continuous-flow reaction system at atmospheric pressure. The reactor was a quartz tube with inner diameter 10 mm. Thoroughly mixed 1 cm^3 (0.7 g) of catalyst and 1 cm^3 (3 g) of intermetallic compound were packed in the reactor and heated in Ar stream up to the reaction temperature of 450°C. After that propane flow passed through the reactor with space velocity 600 h^{-1} and the reaction was studied. The reactor was connected with a heated gas sampling valve of the gas chromatograph. The products were analyzed with three columns: a molecular sieve 5A column for hydrogen analysis, a Separon N column for C_1–C_5 analysis and 15 wt% Carbowax on Chromaton for aromatics analysis.

3. Results and discussion

Fig. 1 shows the ability of Zr_2Fe to eliminate hydrogen from its mixture with inert gas at 500°C. If the space velocity of the feed gas is 20 ml/min and the hydrogen content in it is 8 mol% then 1 g of intermetallic compound absorbs almost all hydrogen from the stream during about 30 min. From this data it is possible to calculate the volume of absorbed hydrogen. It is about 100 ml/g. The absorption ability of intermetallic compounds is known to increase with

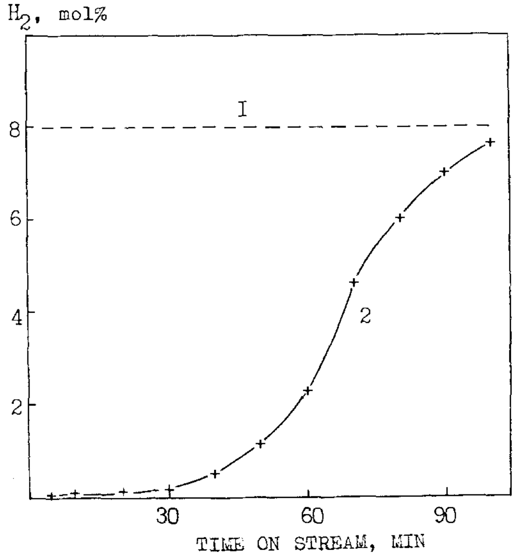

Fig. 1. Absorption of hydrogen by intermetallic compound Zn_2Fe from the mixture H_2+Ar at 500°C; hydrogen content at the inlet (1) and outlet (2) of the reactor.

hydrogen partial pressure in the gas phase and with decreasing temperature [14]. Therefore in the reaction conditions chosen for aromatization of propane the duration of acceptor action seemed to be enough to study its effect on the reaction. It is necessary to note that in these conditions Zr_2Fe itself is inactive in the conversion of propane.

The aromatics yield and hydrogen content versus time on stream during propane conversion over the Zn/HCVM catalyst itself and over a mixture of the catalyst with Zr_2Fe are compared in fig. 2. When the hydrogen acceptor was present the aromatics yield was 2-fold higher than in the absence of intermetallic compound. At the same time the hydrogen concentration in the reaction stream was only 0.2 mol%, i.e. almost all hydrogen released during aromatization was absorbed by the acceptor. Gradual saturation of the intermetallic compound was followed by the increase of hydrogen content in the reaction mixture and aromatics yield decrease.

Similar correlations between aromatics yield and hydrogen concentration in the reaction stream were observed during aromatization of propane over protonic CVM and over pentasils modified by gallium or platinum in the presence of hydrogen acceptor. The data obtained in these experiments relating to the initial period (10 min) of the reaction when the intermetallic compound is more active in hydrogen absorption are summarized in table 1. It is seen that in all cases elimination of hydrogen from the reaction stream by the acceptor is almost complete but at the same time the effect of this on aromatics yield is quite different depending on the catalyst used. Thus, over HCVM and Zn/HCVM

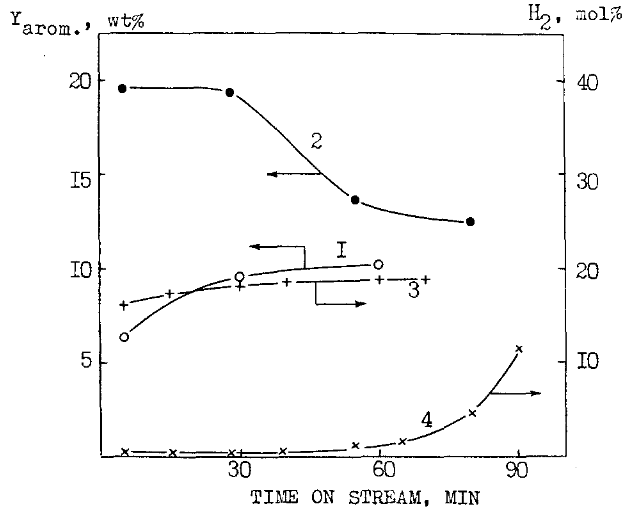

Fig. 2. Aromatics yield (1, 2) and H_2 content in the reaction stream (3, 4) during aromatization of propane over Zn/HCVM in the absence (1, 3) and presence (2, 4) of Zr_2Fe.

the yield of aromatics in the presence of intermetallic hydrogen acceptor is 2 to 2.5-fold higher while over Pt/HCVM and Ga/HCVM it is 4 to 5-fold higher compared to that obtained without Zr_2Fe. It is worth to note that there is no correlation between the initial activity of the catalyst in aromatization of propane without the acceptor and its behaviour in hydrogen elimination conditions.

Distribution of the reaction products and some changes in it resulting from hydrogen elimination were also dependent on the composition of the catalyst used (table 2). Besides the cracking products, methane and ethane, the main products of propane conversion over HCVM and Pt/HCVM without hydrogen acceptor were C_4–C_5 alkanes while over Zn/HCVM and Ga/HCVM aromatics. Elimination of hydrogen by the acceptor resulted in a decrease in yield of C_4–C_5 alkanes over all catalysts studied, this being more pronounced over Pt/HCVM and Ga/HCVM than over HCVM. But the decrease in yield of cracking products in the presence of hydrogen acceptor was observed only over

Table 1
The effect of intermetallic hydrogen acceptor Zr_2Fe on aromatics yield Y_{arom} from propane

Catalyst	Without acceptor		With acceptor	
	$[H_2]$ (mol%)	Y_{arom} (wt%)	$[H_2]$ (mol%)	Y_{arom} (wt%)
HCVM	3.2	1.5	0.2	3.8
Pt/HCVM	2.9	1.3	0.6	6.2
Zn/HCVM	18.8	10.3	0.2	19.5
Ga/HCVM	15.5	7.1	1.1	29.4

Table 2
Product distribution and conversion of propane over pentasils with and without hydrogen acceptor

Catalyst	Conversion (%)	Product distribution (wt%)				
		C_1	C_2	$C_{2=}$	C_4+C_5	aromatics
HCVM	12.0	20	22	5	40	13
HCVM+Zr_2Fe	13.0	24	20	4	23	29
Pt/HCVM	13.6	21	24	5	40	10
Pt/HCVM+Zr_2Fe	17.1	22	31	3	8	36
Zn/HCVM	22.0	11	35	1	7	46
Zn/HCVM+Zr_2Fe	31.9	10	26	1	2	61
Ga/HCVM	16.4	10.5	34	2	10.5	43
Ga/HCVM+Zr_2Fe	37.8	7.5	13	0.5	1	78

Zn- and Ga-containing catalysts while over Pt/HCVM it even slightly increased. As regards the conversion of propane it increased markedly over Zn/HCVM and Ga/HCVM with hydrogen acceptor present.

Summarizing the data obtained it is possible to conclude that the use of hydrogen acceptor in aromatization of propane was most effective over Ga/HCVM catalyst as it provided an increase in yield of the desired products, a higher conversion of propane and a reduction of cracking products content. The results coincide with those obtained by Kikuchi and co-workers [9] over Ga/H-ZSM-5 catalyst in a palladium membrane reactor. However, the increase in aromatics yield from propane in the presence of intermetallic compound was higher compared to that observed in the membrane reactor. This is likely to be due to more complete hydrogen elimination from the reaction stream as in the case of intermetallic acceptor only 0.2 mol% of hydrogen remained in the reaction mixture while in the membrane reactor about 5 mol%.

As regards the mechanism of hydrogen removal, Kikuchi and co-workers [9] concluded that in such conditions propane was selectively converted to aromatics because dehydrogenation of propane to propene was predominant over cracking to methane and ethane resulting from enhanced desorption of co-produced hydrogen from the surface of the zeolite. This interpretation seems to be incomplete as it cannot explain our results obtained over HCVM and Pt/HCVM catalysts when hydrogen elimination effected only the aromatics yield and hardly influenced the cracking products content.

We propose an alternative interpretation. According to the detailed scheme of propane conversion over pentasils there are two alternative initial routes to alkenes from propane: dehydrogenation to propene and cracking to ethene and methane, the first reaction being thermodynamically limited at lower temperatures. These alkenes readily convert to oligomers over acid sites of the zeolite. Aromatic products are formed from unsaturated oligomers and their fragments with simultaneous hydrogen redistribution and C_2–C_6 alkanes formation.

Over Zn- and Ga-containing catalysts hydrogen elimination is likely to effect the stage of propane dehydrogenation preventing the back hydrogenation of propene. Therefore conversion of propane increases together with aromatics yield. Rapid aromatization of unsaturated oligomers formed from propene over these catalysts suppresses cracking reactions of intermediate and final products.

In the presence of HCVM hydrogen acceptor seems to effect the hydrogen redistribution stage resulting in an increase of both aromatics and saturated hydrocarbons yields. It might be supposed that in the case of Pt/HCVM, hydrogen elimination effects both dehydrogenation and hydrogen redistribution stages. Therefore in the presence of hydrogen acceptor the aromatics yield over Pt/HCVM is 5-fold higher but the C_1–C_2 alkanes content in the reaction products does not decrease.

4. Conclusion

From these results we conclude that the use of an intermetallic compound as hydrogen acceptor in the aromatization of propane over modified pentasils gives opportunity to obtain 2 to 5-fold higher aromatics yield coupled with a 1.8-fold higher selectively of aromatization. This method of hydrogen elimination seems to be more effective than a system composed of palladium membrane. It is ecologically advantageous compared to traditional oxidative dehydrogenation and may be widely used in catalytic aromatization of light alkanes.

References

[1] D. Seddon, Catal. Today 6 (1990) 351.

[2] O.V. Bragin, T.V. Vasina, V.P. Sitnic, N.V. Nekrasov and V.I. Yakerson, Izv. Akad. Nauk SSSR. Ser. Chim. (1990) 1250.

[3] N.S. Gnep, A.M. Doyemet, A.M. Seco, F. Ribeiro and M. Guisnet, Appl. Catal. 43 (1988) 155.

[4] Y. Ono, H. Nakatani, H. Kitagawa and E. Suzuki, Stud. Surf. Sci. Catal. 44 (1989) 279.

[5] T. Mole, J.R. Anderson and G. Greer, Appl. Catal. 17 (1985) 141.

[6] J. Kanai and N. Kawata, J. Catal. 114 (1988) 284.

[7] T. Inui and F. Okazumi, J. Catal. 90 (1984) 366.

[8] O.V. Bragin, T.V. Vasina, E.G. Helkovskya-Sergeeva, M.A. Dobrovolsky and Z. Paal, J. Catal. 109 (1988) 156.

[9] S. Uemiya, J. Koike and E. Kikuchi, Appl. Catal. 76 (1991) 171.

[10] O.V. Chetina, T.V. Vasina, V.V. Lunin and O.V. Bragin, Izv. Akad. Nauk SSSR. Ser. Chim. (1990) 2871.

[11] O.V. Chetina, V.V. Lunin and O.V. Bragin, Kinet. Katal. 32 (1991) 1257.

[12] S. Engels, H. Lausch, B. Matschei, O.V. Bragin, A.V. Preobrazhensky and T.V. Vasina, Catal. Today 3 (1988) 437.

[13] G.G. Libowitz, H.F. Hayes and T.R.P. Gibb, J. Phys. Chem. 62 (1958) 76.

[14] K.H.J. Buschow, P.C.P. Boutin and A.R. Miedema, Rep. Progr. Phys. 45 (1982) 937.