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The Conversion of Propene and Ethene over $AlPO_4$-11

Bhatia and Phillips (*1*) have recently reported the conversion of 1-butene to C_6–C_8 aromatics over the aluminophosphate molecular sieve $AlPO_4$-11 in the temperature range 673–873 K. A mechanism was proposed in which dehydrogenation of 1-butene was followed by dimerization of the resulting 1,3-butadiene; the dimer could either cyclize to an aromatic or crack to lighter products. The conversion to aromatics was much less than that observed over H–ZSM-5 and was attributed to the known weak acidity of $AlPO_4$-11 (*2*). The absence of C_9^+ aromatics in the product supported the proposed mechanism; steric hindrance in the elliptical pores (0.67 × 0.44 nm (*3*)) prevented butene trimers from forming. To further the understanding of olefin reactions over $AlPO_4$-11, the conversion of ethene and propene has been studied.

METHODS

$AlPO_4$-11 was synthesized in a Teflon-lined autoclave following example 32 of Wilson *et al.* (*4*) utilizing the modification of Bhatia and Phillips (*1*). The X-ray diffraction pattern obtained using a Phillips 1120/60 X-ray diffractometer with a Ni-filtered Cu$K\alpha$ source was in good agreement with published patterns (*4, 5*) and with that obtained by Bhatia (*6*), although evidence of a small amount of noncrystalline product was apparent. The Al : P atom ratio determined using inductively coupled argon plasma spectroscopy was 1.01.

The catalyst (0.5 g) was supported between glass wool plugs and calcined *in situ* in flowing air (CANOX) at 773 K for 4 h; after cooling to 673 K in N_2 (CANOX), H_2 (CANOX) was passed over the catalyst overnight. This procedure was followed after each run to decoke the catalyst. Gas flow rates were controlled by a Matheson gas rotameter (No. 7352 with 610A tubes). After metering, ethene (Matheson) or propene (Canadian Liquid Air) passed through a preheater and then entered the downflow microreactor (both $\frac{1}{2}$-in.-o.d. SS 316). Liquid product was condensed in a 273 K trap; after each 2-hr run, the liquid product mass was measured and its composition determined using a Hewlett–Packard HP 5790A gas chromatograph equipped with a 30-m capillary column (5 μm DB1$^+$; J & W Scientific) with an FID. The exit gas flow rate was measured using a bubble flow meter; its composition was determined using a 1.8-m Porapak S column with a TCD. Activities were compared with those of two amorphous aluminophosphate samples obtained from Professor J. B. Moffat (Nos. 2 and 3 in Table 1B of (*7*)).

RESULTS AND DISCUSSION

The effect of temperature (630–790 K) at WHSV = 2 and 8 hr^{-1} on the total conversion and percentage conversion (mass basis) of propene to both C_6 aliphatic and cracked (C_1–C_4) products is plotted in Fig. 1. Figure 2 presents these data as a function of propene WHSV at 673 and 730 K. Only ~1% conversion both to C_9 aliphatic and total C_6–C_9 aromatics was observed; conversion to C_7, C_8, and C_{10}^+ aliphatic products was even lower. 1,3-Butadiene was the major component of the cracked gases; above 760 K, methane replaced 1,3-butadiene as the major gaseous product. The major products below 700 K were the hexene isomers; all methylpentene-1 and methylpentene-2 isomers were present as were small amounts of 1-hexene and 2-hexene. Either increased temperature or increased contact time increased the rate of cracking,

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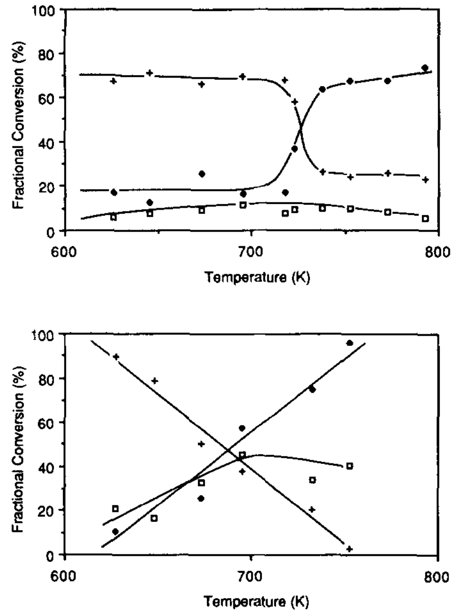

FIG. 1. Propene conversion (mass%) vs temperature (K): upper, WHSV = 8 hr^{-1}; lower, WHSV = 2 hr^{-1}; +, conversion to hexenes; ◆, conversion to cracked products; □, total conversion.

lowering the temperature of transition from hexene to cracked gases.

The presence of hexene isomers indicates that both methyl group and double-bond shifts have occurred, consistent with the xylene isomerization activity of $AlPO_4$-5 reported by Choudhary and Akolekar (*8*) (both $AlPO_4$-5 (*8*) and $AlPO_4$-11 (*2*) having weak acidity). Under similar conditions, propene conversion over H–ZSM-5 results in an equilibrium olefin distribution (*9*). Vedrine *et al.* (*10*) have proposed a conjunct polymerization mechanism for propene oligomerization over H–ZSM-5; 4-methylpentene-1 is the dimer product which then dehydrocyclizes to benzene, isomerizes, or undergoes additional oligomerization. Apparently, the second oligomerization step which gives the continuous olefin distribution does not occur on $AlPO_4$-11.

Propene conversion over the amorphous aluminophosphate samples was low (~3% to ethene and the butenes at WHSV = 1, 673 K) and decreased with decreasing contact time; Fig. 2 demonstrates the tenfold greater conversion achieved over $AlPO_4$-11 under similar conditions. Increased temperature increased the conversion, but methane, ethane, and ethene were the major products. That the dimerization activity of $AlPO_4$-11 appears to be a consequence of its porous structure supports the observation of Bhatia and Phillips that lower activity results from poorly crystalline material (*1*, Table 1).

Figure 3 presents the percentage conversion of ethene to its three principal products: 1,3-butadiene, ethane, and methane, as well as total conversion as a function of WHSV at 673 K. No butanes or C_5^+ products were detected; the ratio of 1,3-butadiene to total butenes was >10 : 1. Increasing ethene contact time increased the yield of the major cracked product, methane. The low reactivity of ethene over $AlPO_4$-11 is in agreement with its poor reactivity over H–ZSM-5 (*10*).

A further consequence of the weak acidity of $AlPO_4$-11 is the low yield of aromatics. The rate-determining step in aromatization is cyclization which occurs on strong acid sites (*11*). Over H–ZSM-5, the

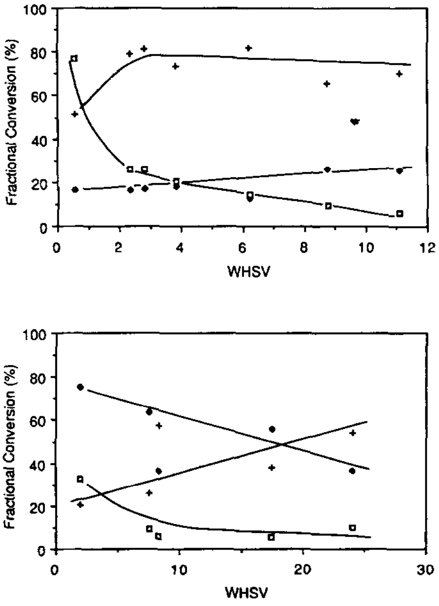

FIG. 2. Propene conversion (mass%) vs WHSV (hr^{-1}): upper, T = 673 K; lower, T = 730 K; +, conversion to hexenes; ◆, conversion to cracked products; □, total conversion.

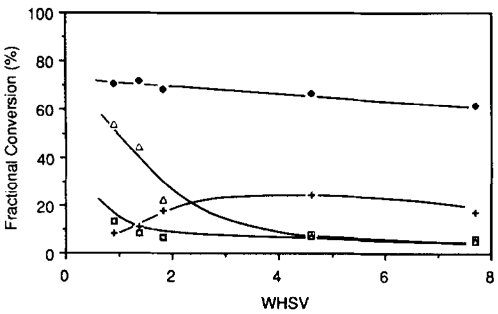

FIG. 3. Ethene conversion (mass%) at 673 K vs WHSV (hr^{-1}): +, conversion to 1,3-butadiene; ◆, conversion to ethane; □, conversion to methane; △, total conversion.

aromatics yield greatly exceeds that of methylcyclopentane for temperatures above 673 K; however, over $AlPO_4$-11, the yield of methylcyclopentane always exceeded that of the aromatics. Dehydrogenation of naphthenes over H–ZSM-5 occurs via hydrogen transfer to olefins (*10*), a reaction unlikely to occur in the unidirectional $AlPO_4$-11 pores due to steric hindrance. Aromatic formation must then occur via naphthene dehydrogenation as proposed by Bhatia and Phillips (*1*). The low conversion to aromatics from propene is due to the cracking of the hexene product at temperatures below which dehydrogenation is possible. Conversion of 1-butene to both 1,3-butadiene and C_8 aromatics has also been observed over Zn–borosilicate (also a weak acid) (*12*); the aromatic yield maximum occurred at 850 K compared with 793 K over $AlPO_4$-11 (*1*).

The production of ethane from ethene exceeded that predicted from stoichiometry. To verify whether the H_2 pretreatment supplied the additional hydrogen required, the catalyst was purged for 3 days with N_2 at room temperature; no difference between results after a 1- and a 72-hr purge was observed. Lack of any H_2 pretreatment resulted in catalyst activity decreasing with each successive run. The excess H-to-$AlPO_4$ (mol) ratio was ~2.5 : 1 suggesting that the H_2 pretreatment supplied the protons necessary for the catalysis and which are lacking in the $AlPO_4$-11 structure.

These results demonstrate that $AlPO_4$-11 is a shape-selective oligomerization catalyst, albeit one with low activity due to its weak acidity. It is highly selective for dimerization, and under properly selected conditions high dimerization yields will result.

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REFERENCES

1. Bhatia, T. K., and Phillips, M. J., *J. Catal.* **110,** 150 (1988).
2. Ji, M., and Xu, Q. H., *Cuihua Xuebao* **8,** 41 (1987).
3. Bennett, J. M., Richardson, J. W., Pluth, J. J., and Smith, J. V., *Zeolites* **7,** 160 (1987).
4. Wilson, S. T., Lok, B. M., and Flanigen, E. M., U.S. Patent 4,310,440 (1982).
5. Wilson, S. T., Lok, B. M., Messina, C. A., Cannan, T. R., and Flanigen, E. M., *Amer. Chem. Soc. Symp. Ser.* **218,** 79 (1983).
6. Bhatia, T. K., M.A.Sc. thesis, University of Toronto, 1986.
7. Schmidtmeyer, A., and Moffat, J. B., *Mater. Chem. Phys.* **13,** 409 (1985).
8. Choudhary, V. R., and Akolekar, D. B., *J. Catal.* **103,** 115 (1987).
9. Garwood, W. E., *Amer. Chem. Soc. Symp. Ser.* **218,** 383 (1983).
10. Vedrine, J. C., Dejaifve, P., Garbowski, E. D., and Derouane, E. G., *in* "Catalysis by Zeolites" (B. Imelik, *et al.*, Eds.), p. 29. Elsevier, Amsterdam, 1980.
11. Derouane, E. G., and Vedrine, J. C., *J. Mol. Catal.* **8,** 479 (1980).
12. Ono, Y., Kitigawa, H., and Sendoda, Y., *J. Chem. Soc. Faraday Trans. 1* **83,** 2913 (1987).

G. W. NORVAL
C. CRIMI[1]
M. J. PHILLIPS[2]

Department of Chemical Engineering
and Applied Chemistry
University of Toronto
Toronto, Ontario, Canada M5S 1A4

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[1] Present address: Ontario Ministry of the Environment, Waste Management Branch, Toronto, Ontario, Canada M4V 1P5.

[2] To whom correspondence should be addressed.