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NOTES

Aromatization of *n*-Hexane by Platinum-Containing Molecular Sieves

III. Reactivity of Platinum Aluminophosphates

In our accompanying reports we describe a vapor phase impregnation procedure for loading highly dispersed platinum into the intracrystalline voids of molecular sieves (*1*) and the catalytic behavior of platinum-containing aluminosilicate and silicate materials for the aromatization of *n*-hexane (*2*). Here we report on the reactivity of platinum-containing aluminophosphate molecular sieves and compare the results to those obtained from platinum-impregnated zeolites. All details of material synthesis and reaction conditions are described in our accompanying papers (*1*, *2*).

Table 1 lists the conversions and product distributions from the reaction of *n*-hexane over Pt/$AlPO_4$-5, Pt/VPI-5, and Pt/SSZ-24 at various levels of conversion and temperature. Since the weight loading of platinum and H/Pt are nearly the same for these samples (*1*), the catalytic behavior should illustrate the effects of the physicochemical properties of the molecular sieves alone. To that end, the comparison of Pt/$AlPO_4$-5 to Pt/SSZ-24 will reveal differences that relate entirely to the composition of the framework, since both $AlPO_4$-5 and SSZ-24 have the AFI topology and no charge balancing cations (both frameworks are neutral). As previously described (*2*), the strong correlation between benzene selectivity and *n*-hexane conversion mandates that all comparisons be made at the same level of conversion. The data listed in Table 1 clearly show that at nearly the same level of conversion the platinum-containing aluminophosphates react *n*-hexane in a completely different manner than Pt/SSZ-24. Specifically, the formation of benzene is suppressed and *n*-hexenes (primarily 2-hexene with a *trans*/*cis* ratio of approximately 2) are formed in great quantities over Pt/$AlPO_4$-5 and Pt/VPI-5 when compared to Pt/SSZ-24. These trends exist at least over the temperature range of $460°C \leq T \leq 510°C$ and at conversion levels of less than 50% (we did not study higher conversion levels).

Table 1 lists the catalytic results from Pt/SSZ-24 and Pt/silica at 460°C and conversion levels near 15%. Since the weight loading of platinum and H/Pt are nearly the same for these two samples, the selectivity to benzene is not affected by the absence or presence of microporosity for a given H/Pt (*2*). However, note that Pt/SSZ-24 produces significant amounts of MP and MCP while Pt/silica yields *n*-hexenes (mainly 2-hexene with a *trans*/*cis* ratio of approximately 2). From these data it may be speculated that the reason Pt/$AlPO_4$-5 and Pt/VPI-5 show high *n*-hexene selectivity is that the platinum has migrated from the micropores to the surface of the crystals. Several lines of reasoning are given below to rule out this possibility. First, in Part I of this series (*1*) we show by TEM that platinum does not migrate from the intracrystalline voids to the surface of the crystals of Pt/$AlPO_4$-5 and Pt/VPI-5 during *n*-hexane reaction conditions. Second, we reacted Pt/$AlPO_4$-5, Pt/VPI-5, and Pt/SSZ-24 with 2-hexene (H_2/2-hexene = 6, $460°C \leq T \leq 510°C$) and found that the conversions primarily to *n*-hexane are nearly the same for all three materials. Thus, if the platinum is sintering during reaction it must sinter in the same fashion on Pt/$AlPO_4$-5, Pt/VPI-5, and Pt/SSZ-24. Third, we prepared an Al/P = 1 aluminophosphate

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solid that has no microporosity. This sample has a surface area of approximately 30 m^2g^{-1}. Upon loading platinum onto the surface of the aluminophosphate (denoted Pt/$AlPO_4$), the weight percent platinum was found to be only 0.05 wt%. Because of the low platinum loading we were unable to measure H/Pt. We suspect that the H/Pt ratio from the Pt/$AlPO_4$ is lower than those from Pt/$AlPO_4$-5 and Pt/VPI-5. The catalytic data obtained from Pt/$AlPO_4$ reveal that significant quantities of *n*-hexenes are produced. However, note that the selectivity to benzene is much higher for Pt/$AlPO_4$ than for Pt/$AlPO_4$-5. Since we have observed that the benzene selectivity is a function of H/Pt (*2*), it is expected that if a Pt/$AlPO_4$ could by synthesized with a H/Pt similar to Pt/$AlPO_4$-5, the benzene selectivity would approach that of Pt/SSZ-24 and Pt/silica. Fourth, the selectivity to MP and MCP are different for Pt/$AlPO_4$, Pt/$AlPO_4$-5 and Pt/VPI-5. Since Pt/$AlPO_4$-5 and Pt/SSZ-24 produce significant amounts of MP and MCP while Pt/VPI-5 does not, the formation of these products may be influenced by the size of the micropore. These arguments taken in total lead us to believe that the data shown in Table 1 for Pt/$AlPO_4$-5 and Pt/VPI-5 are indicative of platinum contained in the micropores of aluminophosphate molecular sieves.

Recently, we have shown that VPI-5 can maintain its structural integrity at elevated temperatures if treated properly (*3*). Vogt and Richardson (*4*) claim that VPI-5 can be reversibly transformed to $AlPO_4$-8 at elevated temperatures and suggest that the high temperature properties of VPI-5 may in fact be more like those of $AlPO_4$-8. However, Sorby *et al.* (*5*) and Vinje *et al.* (*6*) show that when VPI-5 is transformed to $AlPO_4$-8 the adsorption capacity (including *n*-hexane) of the sample is dramatically decreased due to stacking disorders (which are irreversible) in the crystals. Thus, if $AlPO_4$-8 were formed, it would decrease the porosity of the sample and greatly affect the catalytic results. Since the catalytic data from Pt/VPI-5 are nearly the same as those from Pt/$AlPO_4$-5, Pt/VPI-5 must be intact at reaction conditions. The results presented here are the first to show that high-temperature catalysis can occur with a VPI-5 molecular sieve.

We have provided evidence to show that variations in the composition of the microporous structure do not affect the aromatization selectivity to benzene on platinum-containing zeolites provided the H/Pt ratio is held constant (*2*). These data

TABLE 1

Conversion and Product Distribution from Reactions of *n*-Hexane on Platinum Catalysts

Catalyst	Reaction temp., °C	Conversion, %	Selectivity, %					
			C_1–C_5	MP[a]	MCP[b]	$nC_6^=$[c]	Benzene	Arom.[d]
Pt/SSZ-24	510	33.3	24.4	15.0	16.8	3.9	39.6	0.3
Pt/$AlPO_4$-5	510	33.1	13.0	16.3	12.1	44.1	12.4	2.1
Pt/VPI-5	510	37.5	17.6	2.1	5.9	56.0	16.5	1.9
Pt/VPI-5	460	20.5	12.5	9.8	21.0	46.3	9.8	0.6
Pt/SSZ-24	460	14.3	16.7	29.4	30.8	0.0	23.1	0.0
Pt/$AlPO_4$-5	460	15.4	11.0	25.3	19.5	37.7	6.5	0.0
Pt/silica	460	15.3	18.9	4.6	7.8	48.4	20.3	0.0
Pt/$AlPO_4$	460	13.8	5.8	9.4	14.5	55.1	15.2	0.0

[a] MP: methylpentanes.

[b] MCP: methylcyclopentane.

[c] $nC_6^=$: mainly 2-hexene.

[d] Arom.: aromatic compounds with $>C_6$.

suggest that the observed differences in the reactivity of Pt/$AlPO_4$-5 and Pt/SSZ-24 are not due to metal–support interactions. Rather, we speculate that there must be differences in the electrostatic fields and/or adsorbate–framework interactions which are sufficiently strong to influence the reaction chemistries occurring on intracrystalline platinum clusters. Thamm *et al.* (*7*) have shown that the difference in the initial heats of adsorption of benzene and *n*-hexane on $AlPO_4$-5 is −8.4 kJ/mol (favors *n*-hexane adsorption). A similar result was also obtained from silicalite (pure SiO_2). In addition, Choudhary *et al.* (*8*) have shown that at elevated temperatures (200–400°C) the difference in the initial heats of adsorption of benzene and *n*-hexane on $AlPO_4$-5 is essentially zero. Finally, Annen *et al.* (*9*) observed the same chemical shift for adsorbed Xe (by ^{129}Xe NMR) in $AlPO_4$-5 and SSZ-24. Thus, at this time there is no evidence to suggest that $AlPO_4$-5 should have substantially different adsorbate–framework interactions from SSZ-24 at elevated temperatures. However, the data in Table 1 clearly show that the catalytic behavior of platinum contained in a microporous aluminophosphate is significantly different than that obtained from either platinum supported on a nonmicroporous aluminophosphate or platinum supported on microporous (SSZ-24) or non-microporous silica. Further study is necessary to determine the underlying mechanisms of these intriguing results.

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REFERENCES

1. Hong, S. B., Mielczarski, E., and Davis, M. E., *J. Catal.* **134,** 349 (1992).
2. Mielczarski, E., Hong, S. B., Davis, R. J., and Davis, M. E., *J. Catal.* **134,** 359 (1992).
3. Annen, M. J., Young, D., Davis, M. E., Cavin, O. B., and Hubbard, C. R., *J. Phys. Chem.* **95,** 1380 (1991).
4. Vogt, E. T. C., and Richardson, J. W., *J. Solid State Chem.* **87,** 469 (1990).
5. Sorby, K., Szostak, R., Ulan, J. G., and Gronsky, R., *Catal. Lett.* **6,** 209 (1990).
6. Vinje, K., Ulan, J. G., Szostak, R., and Gronsky, R., *Appl. Catal.* **72,** 361 (1991).
7. Thamm, H., Stach, H., Jahn, E., and Fahlke, B., *Adsorpt. Sci. Technol.* **3,** 217 (1986).
8. Choudhary, V. R., Akolekar, D. B., Singh, A. P., and Sansare, S. D., *J. Catal.* **111,** 23 (1988).
9. Annen, M. J., Davis, M. E., and Hanson, B. E., *Catal. Lett.* **6,** 331 (1990).

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