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n-PENTANE ISOMERIZATION OVER SUPPORTED BINARY IODIDE CATALYSTS PREPARED FROM INTERMETALLIC-I_2 SYSTEMS

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γ-Al_2O_3 or SiO_2 supported binary iodide catalysts, which were prepared by impregnation of the mixtures formed from reacting $ErAl_3$ with I_2, exhibited the high ability to catalyze the n-pentane conversion at room temperature. The conversion easily progressed to form iso-pentane along with production of C_4 and C_6 hydrocarbons. Properties of the catalysts prepared closely related to supports used.

Skeletal isomerization of straight-chain hydrocarbons is of important significance for improving the octane number. It has been known for many years that Lewis acids associated with co-catalysts are active as conversion catalysts[1]. In previous studies[2,3] it was shown that the reaction of various intermetallic compounds with halogen elements readily occurred and that the resulting mixed materials effectively catalyzed the isomerization of n-pentane to iso-pentane at 0 °C under liquid phase conditions. Among the intermetallics studied to date some alloy systems were found to produce soluble materials in a CH_2Cl_2 solvent and to be exceptionally active for the conversion reaction, indicating possibility of preparing supported binary halide catalysts by means of the impregnation method. In the present investigation attention was directed toward catalytic ability of iodinated alloys supported on inorganic substances for the n-pentane conversion in the gas phase.

The intermetallic compound employed in this study was $ErAl_3$. Further details about the preparation procedures of the alloy are described in another paper[3]. n-Pentane was distilled in the presence of sodium wire. Methylene chloride was reagent grade and its purification was done by distillation over phosphorous pentoxide. Iodine, which was an extra pure reagent, was used after sublimation treatments. SiO_2, γ-Al_2O_3, MgO, TiO_2, ZrO_2, ThO_2 and activated carbon were used as a support. These compounds were subjected to evacuation at 300 - 450 °C before use. The reaction of intermetallic with I_2 was conducted at room temperature under an atmosphere of purified nitrogen. I_2 was added to finely ground alloy (1 mmol) suspended in CH_2Cl_2 (12 ml). The halogenation occurred to form a homogeneous solution with yellowish brown color. Preparation of supported binary iodide catalysts was accomplished by the impregnation techniques, adding various supports to this solution, and then evacuation to $\sim 10^{-4}$ torr at room temperature. The isomerization was carried out at room temperature by admitting 210 mmHg of n-pentane in a gas recirculation system having a volume of about 300 cm^3. To measure the extent of the conversion an aliquot of the reacting gas taken periodically from the system was analyzed by gas chromatography with a VZ-7 column.

The data on the conversion are summarized in Table 1 together with the results obtained from the liquid-phase reaction$^{3)}$. The addition of I_2 (6 mmol) to $ErAl_3$ (1 mmol) corresponds to formation of binary mixtures ErI_3-$3AlI_3$, based on a stoichiometric reaction. However, it is informative to notice that a mere mixture of these iodides had no indication of solubility in CH_2Cl_2. This appears to imply producing some special complexes from $ErAl_3$ and I_2. Activities were represented by the extent of the n-pentane conversion per gram-binary iodide without any supports. It was found that catalytic behaviors were significantly dependent upon differences in supports used, probably suggesting intimate interactions between binary substrates and supports. γ-Al_2O_3 or SiO_2 supported $ErAl_3$ systems showed approximately equal activities to the support-free system if one assumes that the present reaction also follows first order kinetics, as well as the liquid-phase reaction$^{3)}$. Accordingly, it seems that the supported catalysts with high dispersion were prepared. The activities of the present catalysts, for example, were at least several times larger than those of the combined mixtures of metal salts which Ono et al.$^{4)}$ recently reported. The reaction took place to form iso-pentane along with substantial production of C_4 and C_6 hydrocarbons and hence the selectivity for iso-pentane wasn't so high in all cases, compared to the results in the liquid phase. The questions as to how the supports are operative in the catalyst system, also containing the reasons for a decrease in the selectivity, remain unanswered at the present stage.

Table 1. Data obtained for various catalysts.

Run	Catalyst	Conversion (%/g)	Selectivity(%) iso-C_4	n-C_4	iso-C_5	C_6
1	$ErAl_3$(1 mmol)-I_2(6 mmol)/γ-Al_2O_3	$50^{a)}$	52	0	45	3
2	" /SiO_2	$57^{a)}$	51	0	46	4
3	" /MgO	$7.2^{a)}$	17	0	83	trace
4	" /ThO_2	$21^{a)}$	25	0	70	5
5	" /TiO_2	$31^{a)}$	24	0	70	6
6	" /ZrO_2	$38^{a)}$	23	0	72	5
7	" /Activated Carbon	$1.7^{b)}$	15	0	85	trace
$8^{d)}$	$ErAl_3$(1 mmol)-I_2(6 mmol)	$35^{c)}$	10	trace	88	2

a) Conversion after 1 hr. b) Conversion after 12 hrs. c) Conversion after 30 min.

d) Run 8 expresses the results obtained from the liquid-phase reaction, which was undertaken at 0°C over the $ErAl_3$-I_2 system dissolved in a CH_2Cl_2 solvent(8 ml) introducing n-pentane(2 ml).

References

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