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SYNTHESIS OF ISOAMYLENE FROM METATHESIS OF ISOBUTENE WITH CIS-2-BUTENE

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Metathesis of isobutene with cis-2-butene was studied over MoO_3-Al_2O_3 and Re_2O_7-Al_2O_3 catalysts using a flow reactor. Effects of alkali addition to MoO_3-Al_2O_3 and of reaction temperature on the reaction results were investigated. With Re_2O_7-Al_2O_3 , a satisfactory yield of isoamylene was obtained with a high degree of selectivity.

Since its report in 1964 by Banks and Bailey1), the disproportionation of olefines has been investigated by many other workers2)-8), including Bradshaw who proposed a quasi-cyclobutane intermediate theory. As a result of these studies, a number of catalysts that were effective for promoting this reaction were discovered. For example, WO_3-$SiO_2$1)9)10) for the triolefin process; MoO_3-$Al_2O_3$11)12), CoO-MoO_3-$Al_2O_3$2)6)13), Re_2O_7-$Al_2O_3$14) for a heterogeneous reaction system; and $(C_5H_5N)_2Mo(NO)_2Cl_2$/$C_2H_5AlCl_2$for a homogeneous system8)15)16). In an attempt to obtain a high yield of isoamylene from the metathesis of isobutene with cis-2-butene using a flow type reactor, our studies have involved the use of MoO_3-Al_2O_3 and Re_2O_7-Al_2O_3 catalysts. Effects of alkali addition to MoO_3-Al_2O_3 and of reaction temperatures on the reaction were also studied.

The catalysts were prepared by the wet mixing method, which entailed the respective slurring of powdered ammonium molybdate and rhenium heptoxide with alumina sol for 3 hr, followed by drying on a water bath. The resulting solid masses were calcined at 550°C for 5 hr. The reaction products were analyzed by gas chromatography.

Table 1 shows the effects of alkali addition to MoO_3-Al_2O_3 catalyst and of reaction temperature on isoamylene yield and isoamylene content in the pentene fraction produced. The reactions were performed with isobutene (partial pressure 0.1 atm.) and cis-butene (partial pressure 0.9 atm.). The results indicated increases in the yield of isoamylene with increasing electronegativities of the alkali atoms. As the amount of KOH was changed, the yield reached a maximum at K/Mo=1/7.7 (atomic ratio) (see Table 1).

These results may be attributed to the preferential poisoning of acidic sites by the alkali hydroxide for the dimerization of isobutene. It can be seen from Table 1 that the yield of isoamylene was highest at 150°C, while with even higher temperatures the yield gradually decreased. This decrease in yield of isoamylene can be attributed to the isomerization of cis-2-butene to 1-butene. The amylene fraction obtained consisted mostly of isoamylene, while the amount of n-amylene produced from metathesis of 1-butene with 2-butene was rather small. From the above results, it was concluded that alkali addition to the catalyst and low reaction temperature were desirable in order to obtain isoamylene selectively over MoO_3-Al_2O_3.

Table 1. Effects of alkali addition to MoO_3-Al_2O_3 catalyst and of reaction temperatures on the isoamylene yield.

Catalyst	*atomic ratio	reaction temperature	iso-C_5' yield(%)		iso-C_5'/C_5'(%)		reactants mole ratio iso-C_4'/C-2-C_4'
			after 10 min	after 90 min	after 10 min	after 90 min	
Mo-Al	—	150°C	9.1	6.5	44.7	42.7	1:9
Li-Mo-Al	1:7.77	"	11.3	4.1	67.2	64.4	"
Na-Mo-Al	"	"	22.3	6.5	67.3	69.4	"
K-Mo-Al	"	"	30.0	10.7	83.9	82.4	"
Rb-Mo-Al	"	"	27.5	12.5	73.5	71.0	"
K-Mo-Al	0	"	9.1	6.5	44.7	42.7	"
K-Mo-Al	1:19	"	24.6	8.5	71.0	71.1	"
"	1:7.77	"	30.0	10.7	83.9	92.4	"
"	1:4	"	21.4	17.2	75.8	79.6	"
"	3:7	"	6.9	4.1	85.7	87.0	"
"	2:3	"	1.7	1.1	94.1	93.5	"
K-Mo-Al	1:7.77	110°C	19.1	6.5	96.2	98.0	"
"	"	150°C	30.0	10.7	83.9	82.4	"
"	"	200°C	10.8	5.0	48.6	40.9	"
K-Mo-Al	1:4	150°C	10.7	6.1	99.2	99.3	1:1
Rb-Mo-Al	1:7.77	"	18.1	9.0	98.6	99.3	"

(*atomic ratio ; alkali/Mo atomic ratio) Mo-Al ; MoO_3-Al_2O_3 , Mo/Al=1/9, W/F=50 [g-cat.hr/mol]

Fig. 1 shows the activity change of Re_2O_7-Al_2O_3 catalyst pretreated with nitrogen at 500°C for 1.5 hr with the reaction time. During the initial 2.5 hr of the reaction,the high catalytic activity remained constant, because presumably equilibrium of this reaction was easily attained. Isoamylene was obtained with 58.6% yield (99% of theoretical value**) and with 99 -100% selectivity under the following conditions: catalyst Re_2O_7-Al_2O_3 ; reaction temperature, 150°C; W/F=27 (g.cat.hr/mol); reactant mole ratio, isobutene/cis-2-butene=1/1.

Compared with the metathesis of isobutene with cis-2-butene, the rate of double bond migration of 2-butene to 1-butene was rather slow. On the contrary, the rate of isomerization from cis-2-butene to trans-2-butene was very fast and it was assumed that the mechanism of this reaction is analogous to that of the disproportionation reaction.

** Thermodynamic equilibrium conversion which was estimated by considering isomers (C_4 and C_5 olefines).

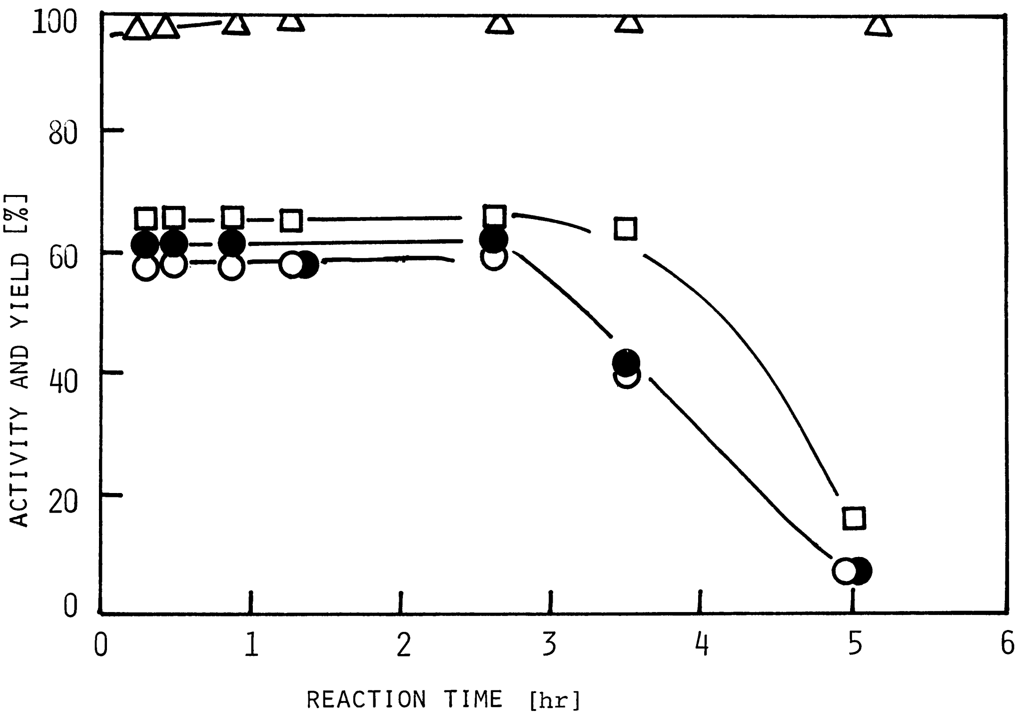

Fig. 1 Activity change of Re$_2$O$_7$-Al$_2$O$_3$ catalyst with reaction time. The catalyst was dried with nitrogen gas at 500°C for 1 hr.
Reaction temperature : 150°C, Composition of feed gas : cis-2-butene 50%, isobutene 50%, W/F=27 [g-cat.hr/mol] 4.3 g of catalyst.
● conversion of isobutene, ○ yield of isoamylene, △ selectivity to isoamylene from isobutene, □ mole fraction of trans-2-butene in 2-butene.

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