Selective Dimerization of Propene to 4-Methyl-1-pentene by Potassium–Copper based Catalysts

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The dimerization of propene by potassium catalyst was carried out at 180 °C in *n*-heptane to give 4-methyl-1-pentene as a major product. The effects of the addition of metal powders, potassium alkoxides and tertiary amines were investigated. The selective production of 4-methyl-1-pentene on adding metal powders increased in the order of Cu, Ag>Mg, Co>Al, Fe, Ni, Zn. When long-chain alkoxides were added to the potassium-copper catalyst system, potassium catalyst was observed to be dispersed, the relative reaction rates increased, and the isomerization of 4-methyl-1-pentene formed was retarded. Thus, the selectivity increased more than 90% after 40% conversion of propene. The potassium-copper-aliphatic tertiary amine-catalyst system caused the yield of 4-methyl-1-pentene to increase in a similar manner to the potassium-copper-alkoxide-catalyst system and inhibited the formation of the carbonaceous substance covering the surface of the catalyst, and the selectivity was not lowered after a higher conversion of propene.

The dimerization of propene by heavier alkali metal- or alkylalkali-catalysts has been reported to give 4-methyl-1-pentene,[1)] from which a stereoregular polymer with a low density and a higher melting point than polyethylene and polypropylene is obtained, whereas the dimerization catalyzed by an acid[2)] or a transition metal complex[3)] gives a mixture of *n*-hexenes, methylpentenes and 2,3-dimethylbutenes. In the alkali metal- or alkylalkali-catalyzed dimerization, the catalyst system is heterogeneous so that the surface area of the catalyst may have a significant effect upon the reaction. Therefore, the effect of the addition of powdered metals (inert carriers) has been studied. It has been proposed by Wilkes[1c)] that organoalkali intermediates were the active species in this reaction. So we have investigated the effect of the addition of bases such as potassium alkoxides and tertiary amines upon the reaction. These bases may coordinate with the counter cation of carbanions to dissociate the insoluble organoalkali intermediates. These effects of bases have been reported in Grignard reactions in hydrocarbon solvents,[4)] in reactions of organolithium compounds,[5)] and in polymerization of butadiene by alfin catalyst.[6)] A highly selective catalyst system which affords 4-methyl-1-pentene in more than 90% after a higher conversion of propene has been found.[7)]

Results and Discussion

The Effect of Powdered Metals. Potassium was chosen as a catalyst because it is easier to handle: both cesium and potassium have been reported to be effective in the formation of 4-methyl-1-pentene from propene.[1)] The reaction was carried out at 180 °C under pressure with vigorous stirring (*ca.* 1000 rpm) in an autoclave equipped with a magnetic stirrer. *n*-Heptane was used as a solvent. Aromatics such as benzene, used in other reports,[1)] were found to inhibit the reaction.

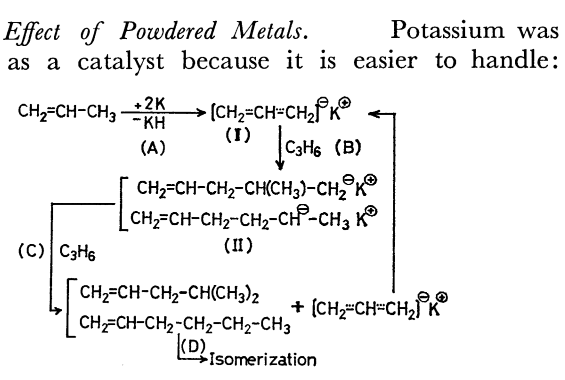

Fig. 1. Reaction scheme for propene-dimerization catalyzed by potassium.

The scheme of the reaction has been considered to be as in Fig. 1,[1)] *i.e.* allylpotassium (I) was formed in step A, followed by the addition step B and the exchange step C to yield the products. The organopotassium intermediates (I) and (II) are insoluble in the reaction medium, and probably aggregate in the course of the reaction. Since the condition of the catalyst surface may influence the reaction, the effect of adding powdered metals was investigated (Table 1). These powdered metals were expected to function as inert carriers and to increase the surface area of the molten potassium.

The selectivity was increased by added metals in the order of Cu, Ag>Mg, Co>Al, Fe, Ni, Zn. The potassium catalyst was observed to be finely dispersed when the powdered metals were added.

Curtin and Koehl reported that coating of lithium with powdered copper was effective in preparing organolithium compounds.[8)] They indicated that it covered the surface of the lithium and inhibited the oxidation of the lithium. They also suggested that the chemical interaction between lithium and copper might be involved. However there has been no report which implies the formation of an alloy or other compounds between potassium and copper. No appropriate explanation for the difference of the effect of the metals can be offered at present.

The Effect of the Addition of Potassium Alkoxides. The reaction step A occurs on the surface of potassium metal. As described above, the reactivity of the catalyst could be increased by an increase in the surface area due to the added powdered metals. In addition, the dissociation of aggregated organopotassium may promote the reaction rate.[5,6)] Thus, the effect of the addition of various potassium alkoxides to the potassium–copper catalyst system was investigated.

Table 1. Effect of added metal powders on the potassium catalyzed dimerization of propene[a)]

Metal[b)] powder	Propene (g)	Reaction time (hr)	Conv. (%)	Yields (%)[c)] (1)	(2)	(3)	(4)	(5)
None	61	5	5	60.8	26.5	4.5	8.2	
Mg	40	5	32	77.7	13.0	4.3	3.9	1.1
Al	38	5.2	7	71.5	17.8	5.9	4.8	
Fe	34	5	8	67.5	22.0	4.9	4.6	1.2
Co	38	5	41	76.5	14.4	4.9	4.4	
Ni	36	5	18	59.4	25.5	4.8	9.0	1.1
Cu	51	3	29	86.7	6.9	4.3	1.8	t
Zn	35	5.2	1	62.6	15.2	6.5	15.7	
Ag	37	5	15	84.2	7.5	4.7	3.6	

a) Reaction conditions: K 2.0 g (0.05 g atom), *n*-heptane 70 ml, 180 °C, 1000 rpm. b) 0.05 g atom of powdered metal (*ca.* 100 mesh). c) Yields on the basis of propene converted. (1) 4-Methyl-1-pentene, (2) *cis*- and *trans*-4-methyl-2-pentene, (3) 1-hexene and 2-methyl-1-pentene, (4) *trans*-2-hexene and 2-methyl-2-pentene, (5) *cis*-2-hexene.

Table 2. Isomerization of the reaction products[a)]

Additive (0.05 mol)	Propene (g)	Reaction time (hr)	Conv. (%)	Yields (%)[c)] (1)	(2)	(1)[b)]	(2)[b)]
None	70	3.0	28.2	88.8	4.5	54.2	28.2
n-BuOK	77	3.0	25.0	95.2	2.0	61.5	27.1
n-Bu_3N	43	3.0	21.0	90.4	2.8	73.0	16.3

a) Reaction conditions: K 2.0 g (0.05 g atom), *n*-heptane 70 ml, powdered copper 3.2 g (0.05 g atom), 180 °C, 1000 rpm. b) Yields obtained upon heating for 6 hr after the removal of unreacted propene. c) See Table 1.

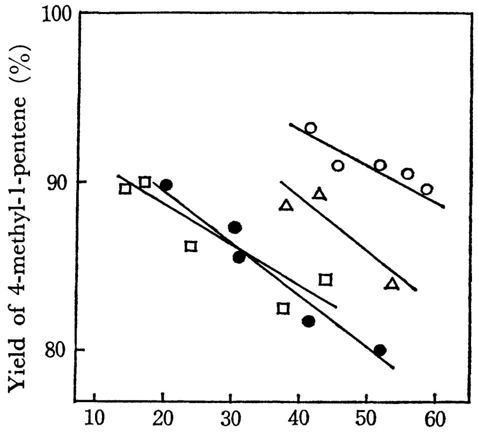

Fig. 2. Variation of the yield of 4-methyl-1-pentene *versus* propene conversion.
●: no additive △: isopropoxide
○: *n*-octyloxide □: *sec*-butoxide
See Table 3 for the other reaction conditions

Figure 2 shows the yields of 4-methyl-1-pentene against the propene conversion for this catalyst system, where the selectivity decreased as the conversion of propene increased. Intermediate organopotassium (I) or (II) in Fig. 1 can also react with primary products resulting in isomerization. So the isomerization of the terminal olefins may become significant as the reaction proceeds. It is compatible with the decreasing selectivity at a higher conversion shown in Fig. 2. Base catalyzed isomerization of methylpentenes and other olefins[9)] are known to occur under milder reaction conditions.

Table 3. Effect of the addition of ROK[a)]

R	Yields (%)[b)] (1)	(1)+(2)	Relative[c)] rate
None	85	94	11
Methyl	88	94	16
n-Propyl	93	95	14
iso-Propyl	88	95	36
n-Butyl	97	97	22
iso-Butyl	91	94	23
sec-Butyl	84	94	22
tert-Butyl	79	89	15
n-Octyl	93	94	40
Benzyl	no reaction		

a) Reaction conditions: K 2.0 g, *n*-heptane 70 ml, powdered copper 3.2 g (0.05 g atom), ROK 0.05 mol, propene 40—60 g, 180 °C, 1000 rpm. b) Yields were calculated at 40% conversion of propene, referred to Fig. 2. See Table 1 for (1) and (2). Isomerization of (1) to the other isomers than (2) is very small. c) (Maximum pressure − minimum pressure) (atm) × 100/maximum pressure/reaction time (hr).

Without propene, isomerization of 4-methyl-1-pentene was also significant in our catalyst systems as shown in Table 2. The yields of 4-methyl-1-pentene at 40% conversion of propene and the relative reaction rates in potassium–copper–potassium alkoxide catalyst systems are shown in Table 3, where added alkoxides in the range 0.5—2.0 mol per mol of potassium produced no significant differences in the results. The long chain alkoxides, such as *n*-butoxide, *n*-octyloxide and *n*-propoxide, were the most effective additives. More branched, short chain, secondary or tertiary alkoxides were less effective. It was noticed that the addition of tertiary butoxide promoted the isomerization of 4-methyl-1-pentene and that the byproducts(carbonaceous substances) covering the catalyst surface served to gradually slow down the reaction rate. This unexpected observation may be due to the instability of the butoxide under the reaction conditions or the pronounced proton transfer from the products on increase of the catalytic activity. Benzyloxide inhibited the reaction as efficiently as aromatic solvents due to the presence of the aromatic nucleus. Since the isomerization of the olefins occurs without any detectable rearrangement of the carbon skeleton in this catalyst system, the ratio of methylpentenes to *n*-hexenes should be determined at step B in Fig. 1. The total yields of methylpentenes shown in the column (1)+(2) in Table 3 were constant. This indicates that the addition of alkoxides does not affect the course of the addition reaction in step B. The added alkoxides suppressed the isomerization of 4-methyl-1-pentene formed as shown in Table 2. When longer chain alkoxides were added, the catalysts were finely dispersed. The observation suggested that the dispersing effect of the alkoxides has a significant role in the nature of the catalyst systems. When the alkoxides were added, the relative rates became considerably larger, but had no direct correlation with the selectivity. More precise studies of the role of the alkoxides are now in progress.

The Effect of the Addition of Tertiary Amines. Tertiary amines are known to coordinate to counter ions in carbanion reactions where the reactivity of carbanions increases.5a) Thus, the effect of the addition of various tertiary amines was investigated with the results shown in Table 4 and Fig. 3. The added aliphatic tertiary amines inhibited the formation of the carbonaceous substance covering the surface of the catalyst and did not lower the selectivity at a higher conversion of propene (Fig. 3). The result has a practical importance in the preparation of 4-methyl-1-pentene. The difference between the effect of the alkoxides and tertiary amines is not yet explained. The other effects of the amines were similar to those of the alkoxides.

Table 4. Effect of the addition of $\mathrm{R_3N}$a)

R	Yields (%)b) (1)	Yields (%)b) (1)+(2)	Relativec) rate
None	85	94	11
Ethyld)	87	93	21
n-Propyld)	86	92	15
n-Butyld)	90	93	15
n-Hexyle)	90	92	14
n-Octyle)	90	92	11
N-Methylpiperidinef)	91	95	25
Pyridinef)		no reaction	

a) See Table 3 for reaction conditions. b) Yields were the averages of 3 or 5 sets of data in the 25—75% conversion range for propene. See text. c) See Table 3. d) 0.03 mol. e) 0.01 mol. f) 0.06 mol.

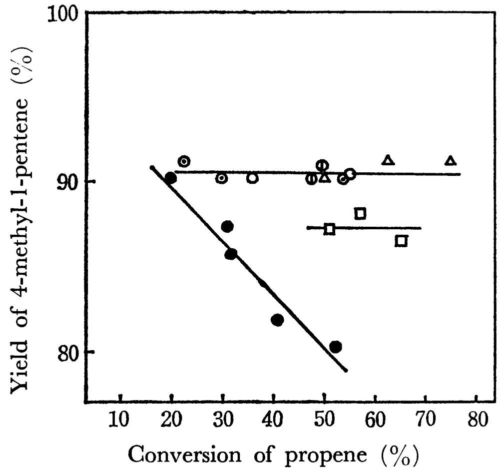

Fig. 3. Variation of the yield of 4-methyl-1-pentene *versus* propene conversion.

●: no additive
△: *N*-methylpiperidine 0.06 mol
□: triethylamine 0.03 mol
○: tri-*n*-octylamine 0.005 mol
⊙: tri-*n*-octylamine 0.01 mol
⦶: tri-*n*-octylamine 0.02 mol

See Table 1 for the other reaction conditions.

Experimental

Materials. Propene of polymerization grade was dried on a column of molecular sieve 3A. *n*-Heptane of guaranteed reagent grade was washed several times with concentrated sulfuric acid and then with water, refluxed over sodium for 20 hr., distilled and stored over sodium. Reagent grade alcohols were dried with magnesium or sodium and distilled. Reagent grade amines were dried with calcium hydride or naphthylisocyanide and distilled. Powdered Mg, Al, Fe, Co, Ni, Cu, Zn and Ag of reagent grade (*ca.* 100 mesh) were dried under vacuum and stored in a desiccator. The oxide coating of reagent grade potassium was removed under *n*-heptane and the potassium was immediately used for the reaction.

Analyses. The reaction products were analyzed at 50 °C on a Hitachi-Perkin-Elmer Model 6DH gas chromatograph using a 2 m column packed with squalane 20 wt% on Diasolid M. Their NMR spectra and relative retention times in glc analyses agreed with those of authentic samples.

Standard Procedure. *n*-Heptane (70 ml), potassium (3.9 g, 0.1 mol), powdered copper (3.2 g, 0.05 mol) and *n*-butanol (3.7 g, 0.05 mol) were placed in a 300 ml autoclave (SUS 32) equipped with a magnetic stirrer and heated at 100 °C under a nitrogen atmosphere for 3 hr to form potassium *n*-butoxide *in situ*. After purging hydrogrn gas formed during the reaction with nitrogn, propene (*ca.* 50 g) was introduced and allowed to react at 180 °C while stirring at 1000 rpm. for several hours. The autoclave was then cooled rapidly. When powdered metals alone or copper plus tertiary amines were used, potassium (2.0 g, 0.05 mol) was used without the above pretreatment.

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