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THE CODIMERIZATION OF PROPYLENE WITH ETHYLENE OVER NiO-WO_3-Al_2O_3

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The codimerization of propylene with ethylene on various solid catalysts was investigated and the results compared with the dimerization reaction of ethylene and propylene. NiO-WO_3-Al_2O_3 catalyst was found to be most active for codimerization. Besides dimerization reactions, isomerization was also observed on these catalysts.

Although the dimerization of olefines over solid catalysts has been extensively studied, there are very few reports on the codimerization of propylene with ethylene [1-2]. In paticular, these does not appear to be any record in the literature of a gas phase codimerization of propylene with ethylene. As isopentenes are important raw materials for the production of isoprene, a convenient synthesis for these materials is therefor desirable. With this aim in mind, we proceeded to examine the codimerization of propylene with ethylene over various solid catalysts in a gas phase using the usual flow type reactor.

The catalysts used were prepared by impregnating active alumina made from alumina sol with solutions containing varying concentration of nickel nitrate and para tungsten ammonium. After drying, the catalysts were activated for 5hr with air at 500°C. Fig. 1 shows the results of the codimerization of propylene with ethylene on NiO-WO_3-Al_2O_3 catalysts having different compositions. With the exception of WO_3-Al_2O_3 catalyst, there were no significant changes in the mole ratio of pentenes for the different catalysts.

The effect of reaction temperature on the isomer distribution is shown in Fig. 2. With increasing temperatures, there was observed a marked increase isobutene and isopentenes contents respectively. For example, when the reaction temperature was raised from 200°C to 390°C, the isopentene contents increased from 18% to 60%.

Fig. 3 shows the effect of reaction temperature on the isomerization of 1-pentene. The composition of isopentenes was very similar to that shown in Fig. 2. However, the distribution of isopentenes in the total pentenes obtained in the isomerization of isopentenes was quite different from that observed in the codimerization of propylene with ethylene. From these results, it was suggested that the main initial products formed by codimerization were n-pentenes (1- and 2-pentene), while isopentenes were secondary products, a consequence of skeletal isomerization of n-pentenes.

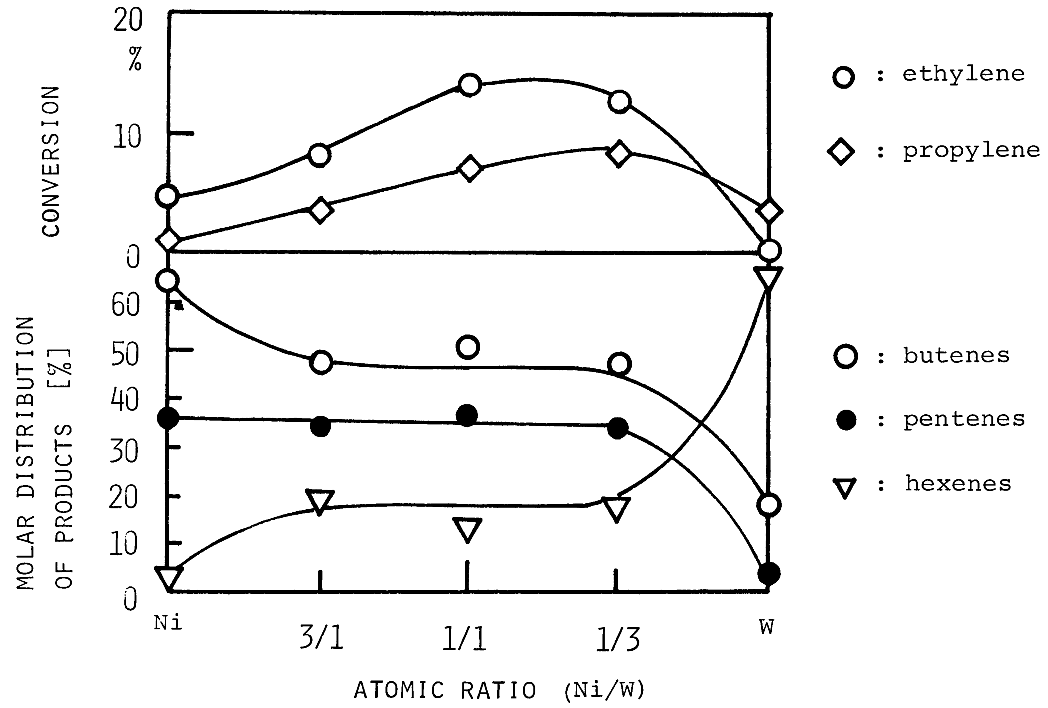

Fig. 1 Effect of catalyst composition on conversion.
catalyst: (Ni+W):Al=5:95, catalyst volume: 10cc,
reaction temperature: 200°C, feed rate: 30 cc/min,
mole ratio of reactants: $C_2H_4/C_3H_6=1$

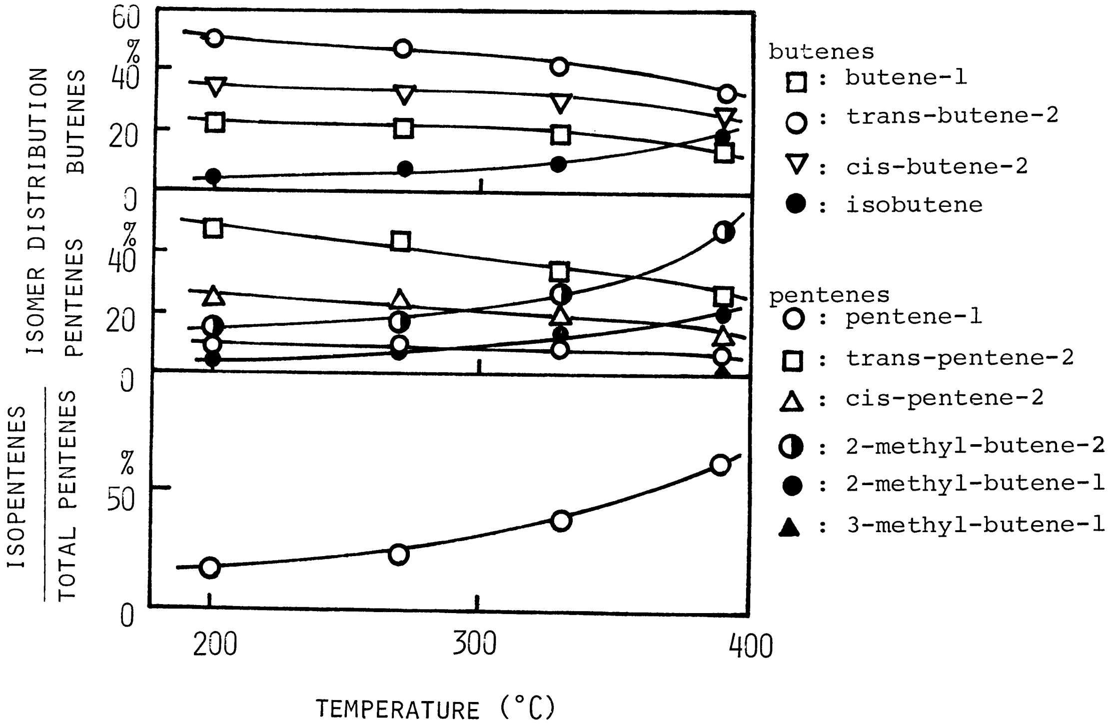

Fig. 2 Effect of the reaction temperature on butenes and pentenes produced.
catalyst: Ni:W:Al=2.5:2.5:95, catalyst volume: 10cc,
feed rate: 30 cc/min,
mole ratio of reactants: $C_2H_4/C_3H_6=1$

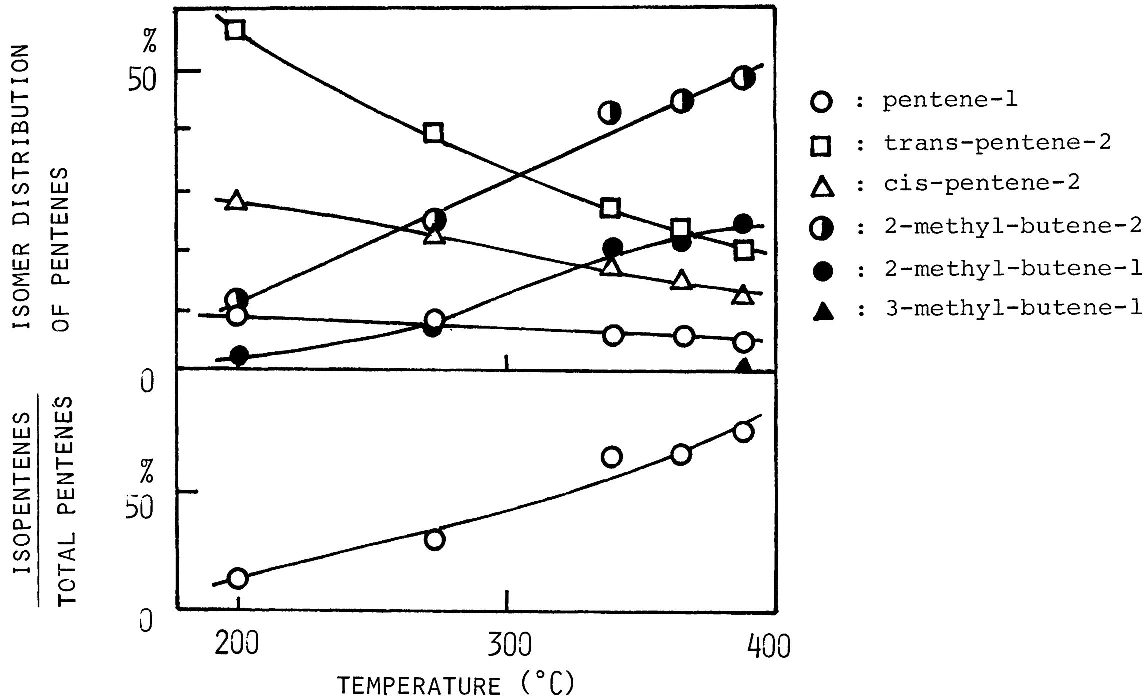

Fig. 3 Effect of the reaction temperature on the isomerization of 1-pentene.
catalyst: Ni:W:Al=2.5:2.5:95, catalyst volume: 10 cc,
feed rate: 30 cc/min, partial pressure of 1-pentene: 0.03 atm in N_2.

In the case of the dimerization reactions, most products were dimer and their reactivities on these catalysts were as follows;

for ethylene; $NiO\text{-}WO_3\text{-}Al_2O_3 > NiO\text{-}Al_2O_3 > WO_3\text{-}Al_2O_3 \approx 0$

for propylene; $NiO\text{-}WO_3\text{-}Al_2O_3 > WO_3\text{-}Al_2O_3 > NiO\text{-}Al_2O_3$

These results showed the same sequence of catalytic activity for the codimerization of propylene with ethylene (see Fig. 1).

Both $NiO\text{-}Al_2O_3$ and $NiO\text{-}WO_3\text{-}Al_2O_3$ were effective catalysts for the codimerization of propylene with ethylene, while $WO_3\text{-}Al_2O_3$ failed to effect codimerization. The reason for this is that ethylene does not react on $WO_3\text{-}Al_2O_3$. From the above results, it was concluded that the $NiO\text{-}WO_3\text{-}Al_2O_3$ catalyst was effective for promoting the codimerization of propylene with ethylene, and the significant feature of this reaction is that a desirable distribution of pentenes can be obtained by controlling the reaction temperature. It appears that higher temperatures are desirable for the production of high yield of isopentenes.

REFERENCES

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