

CATALYTIC ACTIVITY AND SELECTIVITY OF $\text{Re}_2\text{O}_7\text{-Al}_2\text{O}_3$ FOR THE METATHESIS OF CYCLOOCTADIENE

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The metathesis of cyclooctadiene was studied over fourteen kinds of oxides or binary oxides at 40°C in a liquid phase. Only $\text{Re}_2\text{O}_7\text{-Al}_2\text{O}_3$ was found to be active. The conversion was 100 % when the concentration of cyclooctadiene was low and the selectivity for the formation of C_{12} , C_{16} , and C_{20} cyclopolyenes was 64 %. The distribution of $\text{C}_{12}\text{--C}_{32}$ cyclopolyenes was entirely different from that in homogeneous catalyst system.

The metathesis reaction of acyclic olefins is known to be catalyzed by both homogeneous and heterogeneous catalysts to yield different olefins. Both the catalyst systems containing the compounds or complexes of transition metals such as rhenium, molybdenum and tungsten showed high activities.¹⁻³⁾ It is also known that cycloolefins yield polymers in the presence of homogeneous catalysts mentioned above.^{4,5)} In the reaction of cyclooctene or cyclooctadiene (COD) with $\text{WCl}_6\text{-C}_2\text{H}_5\text{AlCl}_2\text{-C}_2\text{H}_5\text{OH}$ in a homogeneous phase, low and high molecular weight macrocycles (oligomers and sesqui-oligomers) as well as polymers were found as the products.⁶⁾ However, no study has been made on the reaction of cycloolefins over heterogeneous catalysts. In the present communication, we report a highly active heterogeneous catalyst for the metathesis of COD.

Catalysts containing Re_2O_7 were prepared by immersing various metal oxides in an aqueous solution of ammonium perrhenate (Engelhard), by drying over a water bath and then by calcining in air at 600°C for more than 3 hr. A $\text{MoO}_3\text{-Al}_2\text{O}_3$ was prepared by immersing Al_2O_3 in an aqueous solution of ammonium molybdate (Wako Pure Chemical Ind. Ltd., GR) similarly as above. Alumina, $\text{SiO}_2\text{-Al}_2\text{O}_3$, and MgO used were an activated Al_2O_3 of Nishio Ind. Ltd., N631(L) (Al_2O_3 :15 wt %) supplied by Nikki Chemical Co., and a guaranteed reagent of Kanto Chemical Co., respectively. Titanium oxide, ZnO, ZrO_2 , SnO_2 and La_2O_3 were prepared by the hydrolysis of titanium tetrachloride (Wako, GR), zinc nitrate (Nakarai Chemicals, Ltd., GR), zirconium oxychloride (Wako, GR), stannic chloride (Wako, GR), and lanthanum nitrate (Nakarai, extra pure) with 28 % ammonia water, respectively, followed by washing, drying and calcining at 500°C for 3 hr. Thorium oxide and WO_3 were prepared by thermal decomposition of thorium nitrate (Wako, GR) at 500°C for 1 hr

and para ammonium tungstate (Wako, GR) at 550°C for 10 hr, respectively. A MgO-ZnO (molar ratio = 1:9) was prepared by calcining the coprecipitate at 500°C for 3 hr, which was obtained by the hydrolysis of $\text{Zn}(\text{NO}_3)_2$ and MgCl_2 with 28 % ammonia water. COD and n-heptane used as a solvent were purified by passing through a column packed with molecular sieves 3A. The reaction was carried out by stirring a COD solution in n-heptane (0.5-50 wt %) together with a catalyst in a reaction vessel with a magnetic stirrer at $40 \pm 1^\circ\text{C}$. The reaction products were analyzed by a temperature-programmed gas chromatograph with a 1 m column of SE-30 for C_8 - C_{28} cyclopolyenes and C_{11} hydrocarbon as an internal standard or with a 1 m column of Dexsil 300 GC 3 % on Chromosorb W for C_{32} - C_{56} cyclopolyenes. The amount of polymers was obtained by subtracting the amount of cyclopolyenes from the amount of the converted COD.

All of Re_2O_7 -MgO, Re_2O_7 - TiO_2 , Re_2O_7 -ZnO, Re_2O_7 - ZrO_2 , Re_2O_7 - SnO_2 , Re_2O_7 - La_2O_3 , Re_2O_7 - ThO_2 , Re_2O_7 -MgO-ZnO, and Re_2O_7 - SiO_2 - Al_2O_3 which contain 7 wt % of Re_2O_7 , and MoO_3 - Al_2O_3 (MoO_3 : 7 wt %) and WO_3 did not show any catalytic activity at all for the formation of cyclopolyenes and polymers. Only Re_2O_7 - Al_2O_3 was active for the reaction. A rhenium heptoxide or Al_2O_3 itself was inactive. These results seem to indicate that a particular combination of Re_2O_7 and Al_2O_3 is important as an active catalyst for the reaction of COD.

Table 1 shows the activity and selectivity of a Re_2O_7 - Al_2O_3 (Re_2O_7 : 7 wt %) catalyst for the reaction of COD. The reaction products were cyclopolyenes consisting of oligomers, C_{8n} , and sesqui-oligomers, C_{8n-4} , where $n = 2-7$, and polymers. The conversion (the ratio of the amount of reacted COD to that of initial COD) was 100 % in the runs where the concentration of COD was below 5 % and reaction time was long. In general, the lower the concentration of COD, the higher the % conversion. The amount of polymers produced was smaller in cases of lower concentrations of COD than in cases of the higher concentrations. This tendency agrees with the results obtained in a homogeneous catalyst system.⁶⁾

The amounts of the cyclopolyenes decreased as the ring sizes became larger except the first three polyenes, $\text{C}_{12}\text{H}_{18}$, $\text{C}_{16}\text{H}_{24}$, and $\text{C}_{20}\text{H}_{30}$, of which amounts were nearly the same regardless of COD concentration; 24-28, 38-40, and 31-38 %, respectively. The total amount of the first three polyenes was almost the same as the total amount of the other polyenes when the concentration of COD was above ca. 5 wt. % in the reaction system. However, when the conversion was nearly or completely 100 %, C_{12} cyclopolyene was preferentially formed compared with C_{16} and C_{20} cyclopolyenes. On the other hand, the ratio of the amounts of cyclopolyenes formed in a homogeneous catalyst (WCl_6 - $\text{C}_2\text{H}_5\text{AlCl}_2$ - $\text{C}_2\text{H}_5\text{OH}$) system, which was calculated semiquantitatively from a COD extractable chromatogram obtained by Scott et al.,⁶⁾ was as follows.

$$\text{C}_{12}:\text{C}_{16}:\text{C}_{20}:\text{C}_{24}:\text{C}_{28}:\text{C}_{32} = 1:2.6:3.5:1.9:1.2:1$$

A maximum amount was found for C_{20} cyclopolyene. The product distribution in the case of the homogeneous catalyst is evidently different from that in the case of the heterogeneous catalyst, Re_2O_7 - Al_2O_3 (cf. Table 1).

The selectivity for the formation of cyclopolyenes was hardly affected by reaction temperatures over the range of 0-80°C. The catalytic activity of Re_2O_7 -

Table 1. The product distribution of the metathesis of cyclooctadiene catalyzed by $\text{Re}_2\text{O}_7\text{-Al}_2\text{O}_3$

The Reaction Conditions ^{a)}					The Distribution of the Products (%)																	
Run	COD	Solv.	COD concn.	Reactn.	Conv.	Cyclopolyenes (Oligomer and sesqui-oligomer)																Polymers
No.	(g)	(g)	(wt %)	Time	(%)	C ₁₂	C ₁₆	C ₂₀	C ₂₄	C ₂₈	C ₃₂	C ₃₆	C ₄₀	C ₄₄	C ₄₈	C ₅₂	C ₅₆	C _{12-C₂₀}	C _{24-C₅₆}			
1	0.27	51.0	0.5	5 min 9 hr	20 100	12 43	18 10	12 11	6.0 4.3	3.7 2.1	2.2 1.0	0.9 0.5	0.6 0.3	- 0.1	- -	- -	- -	42 64	13 8	45 28		
2	1.03	50.3	2	30 min 9 hr	47 96	10 15	13 12	13 15	8.7 8.6	6.8 6.6	5.3 4.9	4.1 3.9	3.5 3.1	2.8 2.3	2.1 1.8	1.5 0.7	0.8 0.6	36 41	36 32	28 27		
3	2.71	51.5	5	1 hr 27 hr	58 100	8.7 22	8.6 4.5	9.1 7.5	5.9 4.6	4.9 4.1	4.1 3.7	3.2 3.1	2.6 2.4	1.9 1.6	1.4 1.3	0.9 0.9	0.4 0.6	26 34	26 20	48 46		
4	5.01	45.1	10	4 hr 51 hr	20 25	6.1 6.0	9.2 8.9	8.3 7.8	5.9 5.6	4.6 4.5	3.4 3.6	2.9 2.9	2.4 2.5	2.2 2.2	1.8 1.8	1.3 1.5	1.0 1.2	24 23	25 26	51 51		
5	12.1	36.3	25	6 hr	6.9	4.3	5.8	4.3	2.9	2.3	1.7	1.4	1.2	1.0	0.9	0.7	0.6	14	13	73		
6	22.9	22.9	50	1 hr	7.5	2.4	2.3	1.9	1.2	0.9	0.7	0.5	0.5	0.4	0.3	0.3	0.1	6.6	4.8	89		

a) Reaction temperature was $40 \pm 1^\circ\text{C}$. The amount of catalyst was 0.765 g except for run 3 where 2.30 g of catalyst was used. The catalyst was calcined at 600°C for 16 hr in air.

Al_2O_3 increased with the amount of Re_2O_7 mounted on Al_2O_3 up to 3 wt. % of content, but remained constant above the content.

The nature of active sites on the Re_2O_7 - Al_2O_3 catalyst and the reaction mechanism are being studied and will be reported in due course.

References

- 1) G. C. Bailey, Catal. Rev., 3, 37 (1969).
- 2) J. C. Mol and J. A. Moulijn, Adv. Catal., 24, 131 (1975).
- 3) R. J. Haines and G. J. Leigh, Chem. Soc. Rev., 14, 155 (1975).
- 4) N. Calderon, E. A. Ofstead and W. A. Judy, J. Polymer Sci., 5, 2209 (1967).
- 5) G. Dall'Asta, Makromol. Chem., 154, 1 (1972).
- 6) K. W. Scott, N. Calderon, E. A. Ofstead, W. A. Judy and J. P. Ward, Adv. Chem. Ser., No. 91, p.399 (1969).

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