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A Novel and Very Active "Vanadium-based" Metathesis Catalyst. The Metathesis of Alkenes over $SnMe_4$-V_2O_5/Al_2O_3

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The first successful vanadium-based catalyst system for olefin metathesis was found as $SnMe_4$-V_2O_5/Al_2O_3, which was prepared by depositing $SnMe_4$ on V_2O_5/Al_2O_3 preheated at high temperatures. The catalytic activity of the new system greatly depended on the loading of $SnMe_4$ and also on the composition and pretreatment temperature of V_2O_5/Al_2O_3.

A variety of heterogeneous or homogeneous catalysts have been reported to be active in the metathesis of olefins.[1)] However, highly active metathesis catalysts have been limited to those based on W, Mo or Re. In addition, although some alkylidene complexes of other transition metals, Ti, Ta, Nb, etc., are known to be metathetically active to some extent, there has been no report on a vanadium-based metathesis catalyst.

Besides, Tanaka et al. and Mol et al. have reported that the addition of alkyltins to some supported MoO_3 or Re_2O_7 catalysts greatly increases their catalytic activity in the metathesis of propene.[1-3)] We have shown that even a "transition metal-free" system, $SnMe_4/Al_2O_3$, exhibits a significant metathesis activity, but in this case preheating the alumina at high temperatures(873-1223 K) is necessary.[4)] These studies have stimulated our interest in developing new effective metathesis catalysts other than W-, Mo-, and Re-based ones by using $SnMe_4$ as an activator.

Thus, we added $SnMe_4$ to a variety of metathetically inactive, supported transition metal oxides(M_xO_y/Al_2O_3 or SiO_2;M_xO_y=TiO_2, ZrO_2, V_2O_5, Nb_2O_5, Ta_2O_5, Cr_2O_3, MnO, Fe_3O_4, etc.; preheated at 523-1223 K), and examined the metathesis of alkenes(C_3H_6, etc.) over the resulting systems. In these experiments, we found that a vanadium-based system, $SnMe_4$-V_2O_5/Al_2O_3, is very effective for the metathesis, although the other $SnMe_4$-added oxide systems were much less active or almost inactive. In this letter, we report the first example of vanadium-catalyzed olefin metathesis, describing catalytic features of the new system, $SnMe_4$-V_2O_5/Al_2O_3, in the metathesis of propene or some other alkenes.

The metathesis of propene was examined in detail by a flow method by using a gas-flow-typed reaction apparatus having a quartz tubular reactor and gas chromatographs. Besides, the metathesis of 1-hexene or 2-pentene in benzene was briefly studied by using a batchwise reaction technique.

The alumina used in the preparation of V_2O_5/Al_2O_3(catalyst precursor) was JRC-ALO-4(extra pure γ-Al_2O_3, 195 m^2/g).4) The catalyst precursors with different V_2O_5-loadings were prepared by impregnating the alumina(80-100 mesh) with an aqueous solution of NH_4VO_3(extra pure, Kanto Chem.), drying at 393 K for 24 h, and then calcining in air at 823 K for 2 h. $SnMe_4$-V_2O_5/Al_2O_3 catalysts were prepared, each time in the reactor just before the reaction, by depositing $SnMe_4$ in a He flow(50 cm^3/min) at 298 K onto the respective V_2O_5/Al_2O_3 supports which were previously preheated there in a He flow at different temperatures(T_p: see Fig. 1) for 1 h, where $SnMe_4$ was introduced as a pentane solution(0.02 mol/dm^3) and the solvent was evaporated. The reaction was started 30 min after the introduction of the $SnMe_4$ solution, by flowing pure propene(0.1 MPa, 15 cm^3/min) or by introducing a benzene solution of 1-hexene or 2-pentene over the catalysts at 298 K. The reaction products were analyzed by gas chromatography. The reagents and gases employed in these experiments were purified in the same manners as described in our previous letter.4)

In the light of our previous study on $SnMe_4/Al_2O_3$,4) we examined the effect of the pretreatment temperature(T_p) of V_2O_5/Al_2O_3 and that of the amount of $SnMe_4$ added on the catalytic activity of $SnMe_4$-V_2O_5/Al_2O_3 in the metathesis of propene at 298 K. In these experiments the effect of the V_2O_5-loading was also examined. Typical results of these experiments appear in Figs. 1, 2, and 3, where the loadings of $SnMe_4$ and V_2O_5 being shown as atomic ratios Sn/V and V/Al, respectively.

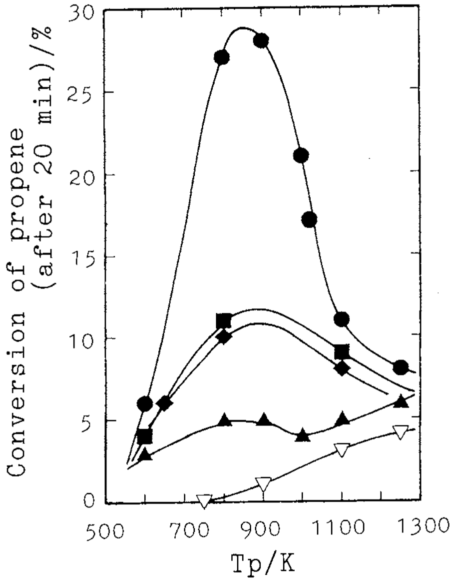

Fig. 1. Effect of pretreatment temperature(T_p) of V_2O_5/Al_2O_3 on catalytic activity of $SnMe_4$-V_2O_5/Al_2O_3 in propene metathesis at 298 K. Sn/V=0.05; V_2O_5/Al_2O_3:0.5 g, V/Al: ▲1.3/98.7, ■2/98, ●3/97, ♦4/96, C_3H_6:15 cm^3/min, ▼: 7.5 μmol-$SnMe_4/Al_2O_3$(0.5 g)

Figure 1 shows that the metathesis of propene is effectively catalyzed by $SnMe_4$-V_2O_5/Al_2O_3, although the catalytic activity markedly depends on T_p and the composition(V/Al) of V_2O_5/Al_2O_3 employed as the support for $SnMe_4$. In every run, the reaction products were only ethene and 2-butene($C_2H_4/C_4H_8 \simeq 1$), indicating that the new catalyst system is extremely selective for this metathesis. As shown in Fig. 1, the catalytic activity of this system appears in the T_p region above ca. 550 K, and reveals a characteristic maximum around T_p=850 K, although in the case of low V_2O_5-loading it still increases with T_p in a higher T_p region(note:that of the vanadium-free system, $SnMe_4/Al_2O_3$, appears in such a higher T_p region and simply increases with T_p of Al_2O_3). Figure 1 also indicates that the catalytic activity is maximized around V/Al=3/97(5.23wt% as V_2O_5).

In similar experiments, we found that the catalytic activity of the new system also markedly depends on the loading of $SnMe_4$ or atomic ratio Sn/V, and confirmed that each V_2O_5/Al_2O_3 itself was inactive for this reaction even when preheated at the high temperatures(Fig. 2). It is noteworthy that the activity becomes maximal in a narrow Sn/V range(i.e. Sn/V=0.05-0.08) regardless of the difference in V_2O_5 loading or V/Al, as the activity curves in Fig. 2 show.

Very active and extremely selective metathesis catalysts were thus obtained from metathetically inactive V_2O_5/Al_2O_3. In addition, Fig. 3 shows that these catalysts are substantially stable during the reaction, although their catalytic activities decrease to some extent in the early stage of the reaction. Figure 3 also indicates that some $SnMe_4$-V_2O_5/Al_2O_3 catalysts are even more effective than $SnMe_4$-MoO_3/Al_2O_3 and Re_2O_7/Al_2O_3, which have been known as most active metathesis catalysts.[1-3] Table 1 shows that the vanadium-based catalyst system is also very effective in the liquid-phase metathesis of 1-hexene or 2-pentene.

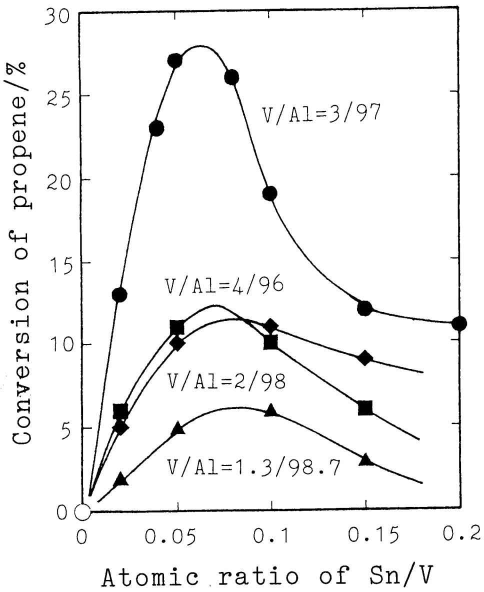

Fig. 2. Effect of $SnMe_4$-loading on catalytic activity of $SnMe_4$-V_2O_5/Al_2O_3 in propene metathesis at 298 K. V_2O_5/Al_2O_3:0.5 g, T_p=783 K, C_3H_6:15 cm^3/min

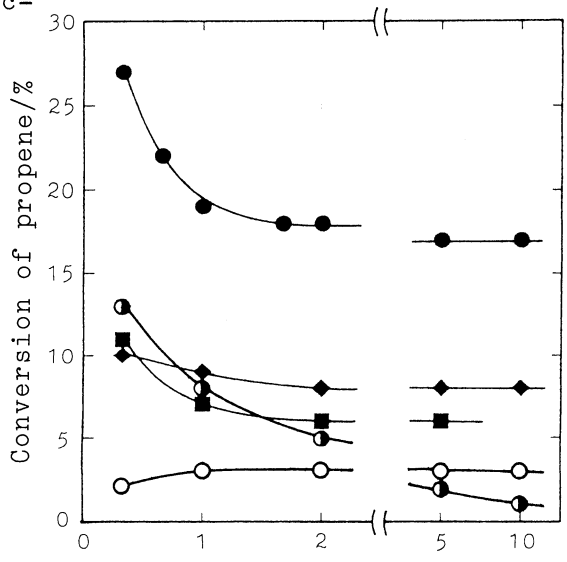

Fig. 3. Time course of catalytic activity in propene metathesis. $SnMe_4$-V_2O_5/Al_2O_3(Sn/V=0.05; V_2O_5/Al_2O_3:0.5 g, T_p=783 K, V/Al:■2/98, ●3/97, ◆4/96), $SnMe_4$-MoO_3/Al_2O_3 (Sn/Mo=0.05; MoO_3/Al_2O_3:0.5 g, Tp=783 K, Mo/Al:◑3/97), Re_2O_7/Al_2O_3 (0.5 g, Tp=783 K, Re/Al :○3/97), Reaction conditions:see Fig. 1.

The results shown above indicate that the initial active sites for the metathesis on $SnMe_4$-V_2O_5/Al_2O_3 are formed by the reaction between $SnMe_4$ and some vanadium oxide species which are considered to be formed on the alumina during the pretreatment of V_2O_5/Al_2O_3. Although the structure of the effective precursor of the active sites is yet unknown, we can currently suggest the following scheme(Eq. 1) as a probable key reaction for the formation of the active sites(initial carbene species) on $SnMe_4$-V_2O_5/Al_2O_3 by analogy with the schemes proposed for $SnMe_4$-MoO_3/Al_2O_3, WCl_4/$SnMe_4$, etc.[1-3] In fact, CH_4 was evolved during the deposition of $SnMe_4$ onto V_2O_5/Al_2O_3, and a fairly good correlation was recognized between the catalytic activity and the amounts of CH_4 evolved as Table 2 shows.[5] We can also suggest that Al_2O_3 plays an important role in the active site formation, since similarly prepared $SnMe_4$-V_2O_5/SiO_2 catalysts were much less active(conversion of C_3H_6: 0.5% at most); however, the role of the alumina is yet unknown. The reasons why the catalytic activity is maximized around 850 K are also unknown, although we can imply that the dehydration or dehydroxylation of V_2O_5/Al_2O_3 is insufficient at lower T_p,[5] while at higher T_p the sintering and decomposition of the vanadium oxides on the alumina become significant.[6]

$$VO_x/Al_2O_3 \xrightarrow{2SnMe_4} CH_2{=}VO_y/Al_2O_3 + CH_4 \qquad (1)$$

Table 1. Metathesis[a] of 1-hexene or 2-pentene over $SnMe_4$-V_2O_5/Al_2O_3[b]

Reaction time/min	%Conversion of $1\text{-}C_6H_{12}$	$2\text{-}C_5H_{10}$
10	12	15
30	28	37

a) At 298 K in benzene(4 cm^3), alkene:1 cm^3; b) Sn/V =0.05, V_2O_5/Al_2O_3 : 0.5 g, V/Al=3/97, Tp=783 K

Table 2. Amounts of CH_4 evolved during the deposition of $SnMe_4$ to V_2O_5/Al_2O_3[a] preheated at different temperatures(T_p) and catalytic activity of the corresponding $SnMe_4$-V_2O_5/Al_2O_3 catalysts[b]

T_p/K	CH_4 /μmol	Conv. of C_3H_6/%[c]
573	3.3[d]	7.2
783	8.7	27.5
923	3.9	17.0
1073	2.7	11.5

a,b) V_2O_5/Al_2O_3: 0.5 g, V/Al= 3/97, $SnMe_4$: 14 μmol(Sn/V = 0.05. c) Reaction conditions: see Fig.1. d) See Ref. 5.

References

1) Y. Imamoglu, B. Zumreoglu-Karan, and A.J. Amass, "Olefin Metathesis and Polymerization Catalysts," Kluwer Academic Publishers (1989).
2) K. Tanaka and K. Tanaka, J. Chem. Soc., Chem. Commun., 1984, 748.
3) A. Andreini, Xu Xiaoding, and J.C. Mol, Appl. Catal., 27, 31(1986).
4) H.-G.Ahn, K.Yamamoto, R.Nakamura, and H.Niiyama, Chem. Lett., 1992, 503.
5) At lower T_p, the reaction of $SnMe_4$ with OH groups on V_2O_5/Al_2O_3 should be predominant, giving an additional evolution of CH_4.[4]
6) The color of V_2O_5/Al_2O_3 heated up to ca. 900 K was lemon yellow, while it turned gray at higher T_p implying that V_2O_5 on the alumina decomposes to lower oxidation states; the mp of V_2O_5 powder is ca. 963 K.

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