

Pt/MoO₃/SiO₂ 촉매하에 골격 이성질화반응에 의한 n-Butene 으로부터 MTBE의
원료인 i-Butylene 합성

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Skeletal isomerization of 1-butene into i-butene over Pt/MoO₃/SiO₂ for
MTBE

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Abstract

Thermodynamically possible maximum yield is attained at 100°C with Pt/MoO₃/SiO₂ while by-products except 2-butene does not form. Skeletal isomerization mechanism is proposed as two elementary step such as, 1st, carbonium ion formation over Pt crystallites by hydrogen spillover, 2nd, carbenium ion formation over MoO₃ followed by formation of iso-butene.

Introduction

According to current trend of unleaded gasoline after Clean Air Act in USA on 1990, the demand of i-butylene has increased suprisingly in recent 5-6 years and it is anticipated that shortage of supply come in near future (1, 2, 6). A worldwide attention has been paid to the research to synthesize iso-butylene from 1-butene because of low cost of initial investment and operation (2).

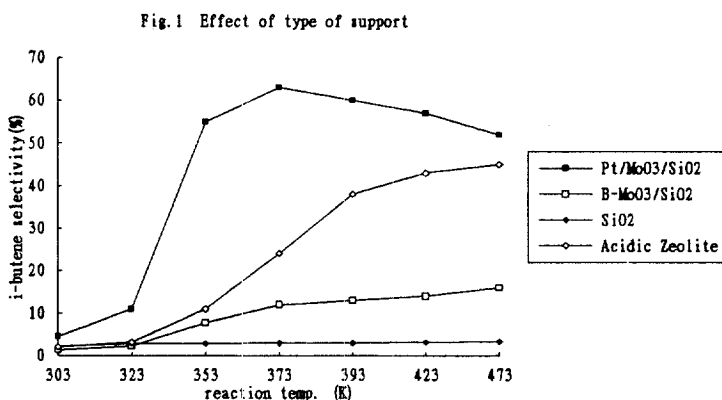
Catalyst Pt/MoO₃ demonstrates the surprisingly high capacity of storing H₂ into MoO₃ as H_xMoO₃. To investigate the morphological effect on the skeletal isomerization, temperature programmed reduction into H_xMoO₃ was used as a characterization tool in conjunction with CO chemisorption and transmission electron microscopy. Intrinsic isomerization kinetics was clearly explained from the view of hydrogen spillover (4, 5).

Experimental Method

$\text{MoO}_3/\text{SiO}_2$ structure as catalyst support were determined using back-filling method in x-ray powder diffraction. Temperature programmed reduction was employed as a tool to monitor the H_2 uptake into H_xMoO_3 done under 1% 1-butene balanced with N_2 . Intrinsic kinetics for skeletal isomerization of 1-butene into i-butene for different morphologies were evaluated using Gas chromatograph (Young-In Model 680D).

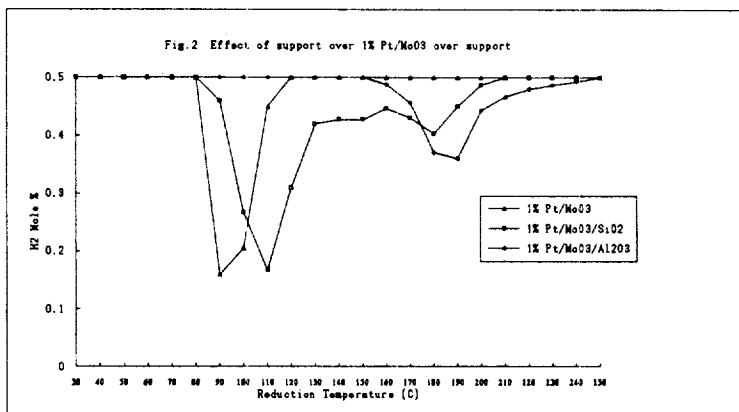
Results

All the MoO_3 based support are found to be orthorhombic MoO_3 substructure by x-ray diffraction. It has been understood that skeletal isomerization of 1-butene into i-butene is controlled by acidic sites. As a strategy for the qualitative assessment of intrinsic kinetics, every single points should be experimentally evaluated before the conclusion can be drawn out. These are such as type of support, acidity of support, Pt amount, MoO_3 content, overlayer formation, H_2 spillover rates over surface and bulk between Pt and MoO_3 and etc. Effect of support were explained as in Figure 1.



Evaluated skeletal kinetics were compared with support itself and Pt over support. $\text{Pt}/\text{MoO}_3/\text{SiO}_2$ demonstrates much better yield toward i-butene than acidic zeolite that has been known as one of the best catalyst in the literature and market (1, 7, 8).

Pt/MoO₃/SiO₂ shows higher yield at lower temperature than acidic zeolite at higher temperature limited by thermodynamic equilibrium. Initial H₂ spillover rates are demonstrated under TPR as in Figure 2.



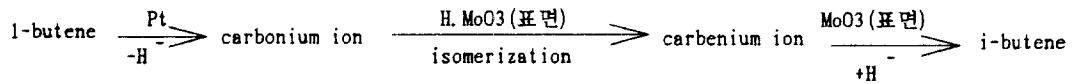
Discussion

As shown in Figure 1, skeletal isomerization of n-butene into iso-butene shows maximum yield at low temperature (100°C - 150°C) which is more favourable condition based on the view of thermodynamics. Compared to acidic zeolite and alumina, Pt/MoO₃/SiO₂ catalyst can accelerate the formation of carbonium ion using spillover step of proton according to result of TPR and highest yield of i-butene is attained at 100°C while by-products except 2-butene do not form.

As in figure 2, it is assumed that yield of i-butene is controlled by formation of carbonium ion through proton spillover, because, first, Pt/MoO₃/SiO₂ and Pt/MoO₃/Al₂O₃ show approximately equal yield of i-butene at 100°C after MoO₃ surface is saturated with proton as shown TPR experiment, second, they show higher yield of i-butene than zeolite and Pt/SiO₂ do.

Conclusion

- Thermodynamically possible equilibrium yield reach as maximum at 100°C.
- Skeletal isomeration is dominated by H₂ spillover rates causing carbonium ion over Pt crystallites and modelled in the following scheme.



References

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