

## 전이금속-Zeolite Y 촉매에서의 *n*-Butane 및 1-Butene 의 반응

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## Reactions of *n*-Butane and 1-Butene on Transition-Metal-Zeolite Y Catalysts

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**요약.** Zeolite Y를 합성하여 Co, Ni 및 Pd 이온으로 이온교환하고 수소기류중에서 환원함으로써 전이금속-zeolite Y 촉매를 얻었다. 이들 Co-, Ni-, Pd-Y와 La-이온교환한 Y (LaY) 촉매에서의 1-butene 및 *n*-butane의 분해반응을 micro-catalytic pulse 방법으로 연구하였다.

1-Butene 분해반응에 있어서는 Ni-, Co-, Pd-Y 및 LaY 모두 높은 활성을 보여주었고 1-butene 분해반응에 대한 활성은 촉매상의 금속성분과는 큰 관계없이 산성 성분만이 주로 관련되고 있는것 같다. LaY에서는 400°C에서 *n*-butane 분해반응에 대한 활성을 나타내지 않았으나 소량의 1-butene을 가함으로써 분해반응이 촉진되었다.

Ni- 및 Pd-zeolite Y에서는 *n*-butane의 분해반응이 현저하게 일어났다. 분해반응에 대해서는 수소에 의한 환원온도가 높고 또 금속성분 함량이 많은 것이 활성이 높았다. *n*-Butane 분해반응에 있어서는 금속성분에서의 butene으로의 탈수소반응이 첫 단계인 것으로 본다.

Ni-Y에서는 1-butene과 수소 혼합반응물 및 *n*-butane의 분해생성물이 모두다 C<sub>1</sub>뿐이었다. *n*-butane은 Ni-Y에서는 butene으로 탈수소되고 이어서 C<sub>1</sub>으로 hydrocracking 되는 반응과정을 밝고 있다고 본다.

**ABSTRACT.** Transition-metal-loaded zeolite Y catalysts were prepared from Na Y by exchanging with cobalt, nickel and palladium ions, followed by reduction in a hydrogen stream. The reactions of 1-butene and *n*-butane were studied on Co-, Ni- and Pd-loaded Y as well as La-exchanged Y using micro-catalytic pulse technique.

For 1-butene reaction Ni-, Co-, Pd-loaded Y and La-exchanged Y all showed high activity suggesting that the acidic component, not the metallic component, was primarily responsible for the activity. For *n*-butane reaction on La-exchanged Y, the addition of 1-butene enhanced the activity.

Significant cracking conversion of *n*-butane was observed for Ni- and Pd-loaded Y. Activity was higher on samples reduced at higher temperature and of higher metal content. It seems that the

dehydrogenation to butenes at metallic sites is the primary step in the *n*-butane cracking reaction.

On Ni-Y the cracking product was C<sub>1</sub> both from the mixture of 1-butane and hydrogen and from *n*-butane. It may be that on Ni-Y, *n*-butane is dehydrogenated to butenes and subsequently hydro-cracked to C<sub>1</sub>.

## INTRODUCTION

In general, olefins undergo cracking much more readily than paraffins. Catalytic cracking of olefins occurs at considerably lower temperature than that of paraffins. Among paraffins, higher molecular weight paraffins undergo cracking more readily. The addition of a small amount of olefins enhances the cracking activity of paraffins<sup>1</sup>. It was suggested that for the cracking of paraffins, a small amount of olefins which may be present in the initial feed or formed in the gas phase serves as the proton acceptor to form the chain initiating carbonium ion.

When paraffin feed was passed through the two reactors, the first one containing platinum metal on an alumina support, and the second reactor containing acid mordenite, the activity of the catalyst for isomerization and cracking became greater with increased dehydrogenation activity of platinum to produce olefins<sup>2</sup>.

We have previously reported a study of 1-butene reaction over cation-exchanged faujasite type zeolite<sup>3</sup>. The results showed the activities for 1-butene cracking and isomerization reactions were strongly dependent on the acidic nature of the catalyst.

In this study transition metal loaded zeolite catalysts are prepared by reducing the cation-exchanged form of zeolite Y and the reactions of *n*-butane, which is relatively stable for cracking, is studied to see the effect of

metallic component on the catalytic activity for the cracking conversion of *n*-butane.

## EXPERIMENTAL

Zeolite Y used in this study was synthesized from a mixture of colloidal silica (Nissan Kagaku Snow-Tex), sodium aluminate and sodium hydroxide. The reaction mixture seeded with Linde Zeolite Y Lot #968050009 and having an overall composition of 4Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-10SiO<sub>2</sub>-180H<sub>2</sub>O was aged for 1 day and crystallized for three days at 100°C.

The X-ray powder diffraction measurements were made on a DIANO XRD-800 X-ray diffractometer using CuKα, 35 kv, 30 mA, scan speed 1°/min. For the purpose of determining Si/Al ratio from the lattice parameter, X-ray measurements were made using Ni as internal standard and scan speed of 0.4°/min.

Samples of cation-exchanged forms of zeolite Y were prepared from the sodium form of zeolite Y by ion-exchange with Ni(NO<sub>3</sub>)<sub>2</sub>, Co(NO<sub>3</sub>)<sub>2</sub>, LaCl<sub>3</sub> and Pd(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub> solutions. The degree of ion-exchange of the samples as determined by chemical analysis is given in the following Table.

Cation-exchanged samples were subsequently treated with hydrogen for 3 hrs at 300 or 400°C to obtain metal-loaded zeolite samples.

Reactions were studied using pulse micro-catalytic technique. The apparatus consists of sampling device with 6-, and 4-port valves,

Table.

Sample	NiY(A)	NiY(B)	CoY(A)	CoY(B)	LaY(A)	LaY(B)	PdY
% Ion exchange	70	85	75	90	57	51	64

micro-catalytic reactor and a gas-chromatograph as shown in Fig. 1. 0.3g of samples were pelleted into a cylinder form of 1/8" in diameter and 1/8" in length. The reactor was a stainless steel tubing of 1/4" O.D. Reaction products were analyzed using a 10ft. column of 20wt% dinonyl phthalate on 80/100 chromosorb W. (column temp.: 20°C, He flow rate: 60 ml/min). *n*-butane, 1-butene and hydrogen gases were Matheson C. P. Grade and He AirCo Product (99.995%).

## RESULTS

Zeolite Y synthesized for use in this study was of high quality as judged by the X-ray diffraction method and by cyclohexane adsorption. The lattice parameter determined from the X-ray diffraction measurement was 24.64Å. From the relationship between the lattice parameter and the Si/Al ratio for sodium synthetic faujasites<sup>4,5</sup>, the Si/Al ratio was then found to be 2.7.

Fig. 2 shows the conversion of *n*-butane between the reaction temperature of 350 and 500°C on Ni-, Pd- and Co-loaded Y catalysts which were prepared from Ni-, Pd- and Co-exchanged Y by reducing with hydrogen at 300 and 400°C. Samples reduced at 400°C exhibited much higher activity than those reduced at 300°C. Co-Y showed quite low activity. Ni-Y(B)

which had higher nickel content than Ni-Y(A) showed higher activity than Ni-Y(A). Pd-Y had a lower effective cracking temperature than Ni-Y but Ni-Y showed a steep increase in activity with increase in the reaction temperature. Fig. 3 compares the percentage conversion of 1-butene with that of *n*-butane on Ni-Y, Co-Y and Pd-Y catalysts. High conversion of 1-butene was observed on all the samples studied between 300 and 500°C whereas the conversion of *n*-butane was quite low compared with the conversion of 1-butene.

On Samples of La Y which were not subjected to the reduction treatment by hydrogen, no conversion of *n*-butane was observed at 400°C while the mixture of *n*-butane with 10% of 1-butene showed overall conversion of 28%.

Table 1 shows the product distribution of *n*-butane and 1-butene reactions on Pd-Y and Ni-Y at 400°C. Products obtained for 1-butene reaction were C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>, 2-butenes, *iso*-butene and C<sub>5</sub> similar to the pattern obtained on

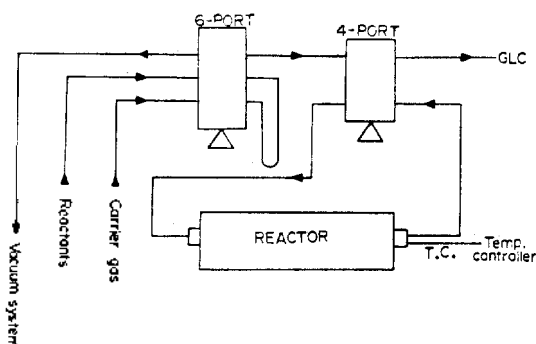


Fig. 1. Schematic diagram of the reactor system.

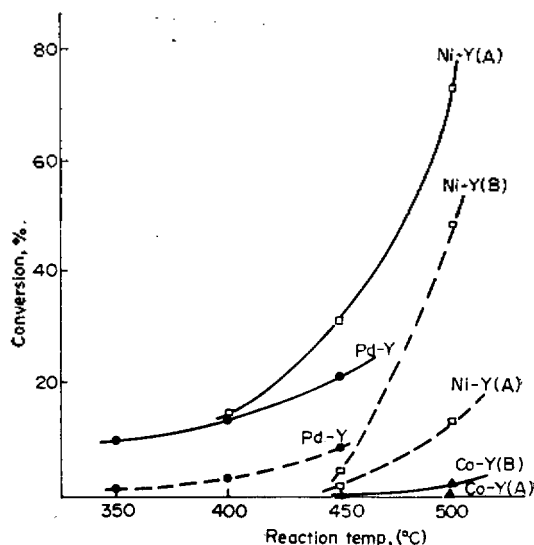


Fig. 2. Conversion of *n*-butane on Ni-Y, Pd-Y and Co-Y. — samples reduced at 400°C, .....at 300°C.

cations—exchanged faujasite type zeolites previously reported<sup>3</sup>. On Ni-Y, C<sub>1</sub> was the major reaction product and for the mixture of hydrogen and 1-butene C<sub>1</sub> was the only cracking product. For the *n*-butane reaction on Pd-Y, C<sub>1</sub> and C<sub>3</sub> were major products giving no C<sub>5</sub>. The percentage of production of C<sub>1</sub> increased with increasing reaction temperature between 400 and 500°C studied. On Ni-Y, C<sub>1</sub> was the only cracking product of *n*-butane.

DISCUSSION

LaY has strong acid site<sup>6</sup> and exhibits generally high activity for hydrocarbon cracking reactions. La exchanged Y showed high activity for 1-butene cracking but no activity for *n*-butane cracking at 400°C, and addition of small amount of 1-butene to *n*-butane enhanced the cracking of *n*-butane. This indicate that *n*-butane is relatively stable in the presence of LaY when no butene is present in the reactant or there is no chance of forming olefin thermally or by dehydrogenation.

When the metallic component is introduced into acid type catalyst to serve as the dehydrogenation component, it is expected that the activity for cracking of *n*-butane is enhanced. The enhancement in activity may be greatly dependent on the state of metallic component. For 1-butene reaction high conversion was observed on all the Ni-, Co- and Pd-loaded catalyst between 350 and 500°C. The presence of metallic component had little effect on the activity. This suggests acidic component is primarily responsible for the cracking conversion of 1-butene.

For *n*-butane reaction 10 and 8.4% conversion was observed on Ni- and Pd-loaded zeolite Y which were prepared from Ni- and Pd-exchanged form by reducing with hydrogen at 400°C at the reaction temperature of 400°C while no conver-

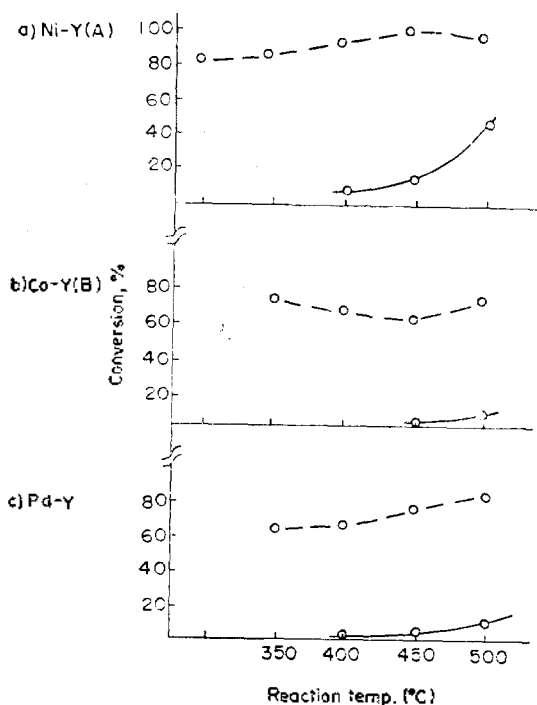


Fig. 3. Conversion 1-butene and *n*-butane. .... 1-butene, — *n*-butane.

Table 1. Product distribution of *n*-butane and 1-butene conversion on Pd-Y and Ni-Y at 400°C.

Catalyst	Reactant	Product Distribution (Product mol. %)					
		C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	Is <sub>o</sub> -C <sub>4</sub>	2-C <sub>4</sub>	C <sub>5</sub>
Pd-Y	<i>n</i> -Butane	41	6	42	1	10	—
	1-Butene	20	3	41	24	5	7
Ni-Y	<i>n</i> -Butane	100	—	—	—	—	—
	1-Butene	70	5	4	18	—	3

sion was observed for La-exchanged and original Na-form of zeolite Y samples. It seems that the dehydrogenation to butenes at the metallic sites is the primary step in *n*-butane cracking reaction.

The fact that Ni-, Pd- and Co-loaded Y catalyst samples obtained by reducing at 400°C showed higher activity than those reduced at 300°C, and that Ni-Y(B) which had higher Ni content than Ni-Y(A) showed higher activity suggest the cracking activity for *n*-butane depends greatly on the dehydrogenative activity of metallic component. The products patterns for 1-butene cracking on Ni-, Pd and Co-loaded Y are similar to those obtained on La exchanged Y.

Appearance of C<sub>5</sub> products in 1-butene cracking may be due to reaction process involving condensation-scission mechanism<sup>7</sup> or the results of the combination of C<sub>4</sub> with the methyl radical or methyl carbonium ions formed. Ni-Y differs from Pd-Y and other cation-exchanged X and Y catalyst studied in that it formed higher percentage of C<sub>1</sub> product in 1-butene cracking reactions. From the reaction of equimolar mix-

ture of hydrogen and 1-butene on Ni-Y at 400°C complete conversion to C<sub>1</sub> was observed. Also for *n*-butane cracking on Ni-Y between 400 and 500°C C<sub>1</sub> was the only cracking product. The fact that the cracking product was C<sub>1</sub> both from the mixture of 1-butene and hydrogen and from *n*-butane indicate that on Ni-Y *n*-butane was dehydrogenated to butenes and subsequently hydrocracked to C<sub>1</sub>.

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