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Effects of phosphorous promoters on catalytic performance for oligomerization of butene over Ni-based catalysts

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Abstract

In order to evaluate the potential of C_4 raffinate II as a feedstock for oligomerization reactions, the effects of 1,3-butadiene in C_4 raffinate II on catalyst life were tested over Ni/Al_2O_3 catalysts in a fixed bed reactor. Catalytic deactivation by butadiene in the oligomerization of industrially produced C_4 raffinate II could be mitigated by a reduction of 1,3-butadiene content, from 0.15 to 0.004 wt.%, through selective hydrogenation. To improve catalytic performance, phosphorous compounds were adapted as a promoter for the Ni/Al_2O_3 catalyst and octene selectivity was enhanced. The branching index of the product over the Ni–P–triphenyl phosphine oxide/Al_2O_3 catalyst is higher than that over other catalysts, which is desirable for the production of octenes as a raw material for gasoline blending.

Keywords: Ni/Al_2O_3 catalyst; Phosphorous compounds; Oligomerization; C_4 raffinate II

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1. Introduction

C_4 raffinates are produced largely as raffinate II from MTBE processes or as raffinate III after 1-butene extraction from raffinate II. Most raffinates are used as cheap fuels after hydrogenation, but olefins, such as *n*-butenes in C_4 raffinate II or III, can achieve higher chemical value via oligomerization. Mixed octenes, which are the main products of oligomerization, are used as gasoline components or as feedstock for the oxo process.

One industrial process already used in the dimerization of *n*-butenes is the homogeneous catalytic IFP Dimersol process [1]. A number of studies using a variety of homogeneous catalyst systems have been carried out in order to improve catalytic performance and to meet the needs of commercial use [2,3]. An interesting approach to olefin dimerization is the effort to develop an Ni-based catalyst containing phosphine ligand [4–6]. Homogeneous catalyzed processes, however, have some disadvantages, such as the need for catalyst destruction and fraction separation steps. For heterogeneous catalytic dimerization processes, the UOP Octol process was developed for the production of high-octane gasoline [7]. Works on various Ni/zeolites have been focused on optimizing catalyst preparation to achieve optimum gasoline yield [8–11].

When dimerizing *n*-butenes to mixed octenes, mixed dodecenes (C_{12} olefins) are produced simultaneously as a result of trimerization, a side reaction. The industrial needs for mixed dodecenes are very small compared to those of mixed octenes. For the production of raw materials such as plasticizers or high-octane gasoline, it is necessary to find a method that enhances the selectivity of dimerization.

In addition to high dimers' selectivity, it is highly desirable to maximize branched octenes. Branched octanes are particularly suitable for use as high-octane additives. It is therefore of interest to convert olefinic butene dimers into octanes by hydrogenation. Table 1 gives the research octane number (RON) and the motor octane number (MON) of the three alkanes resulting from the hydrogenation of olefinic butene dimers [12]. Therefore, high-octane number alkanes can be produced from olefinic butene dimers by minimizing the *n*-octane content and maximizing the branched octane content.

Industrially produced C_4 raffinate II contains a low level of 1,3-butadiene, but even in small quantities, 1,3-butadiene can influence oligomerization rates [7]. If C_4 raffinate II is to be considered a feedstock for oligomerization, it is necessary

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Table 1
Octane numbers of octane isomers [12]

Isomer	RON	MON
Dimethylhexanes	55.5–76.3	55.7–83.4
Methylheptanes	21.7–26.7	23.8–39.0
n-Octane	19.0	19.0

to assess the impact of 1,3-butadiene on the behavior of the catalyst.

This study is focused on evaluating the potential of C_4 raffinate II as a feedstock for oligomerization reactions. The effects of 1,3-butadiene in C_4 raffinate II on catalyst life for oligomerization were tested over the Ni/Al_2O_3 catalysts in a fixed bed reactor. In order to investigate the effects of promoters over Ni-based catalyst on conversion and selectivity, the C_4 mixture obtained through selective hydrogenation of C_4 raffinate II was used as a feed for the oligomerization reaction. To enhance butene conversion or octene selectivity, phosphorous compounds were adapted as promoters.

2. Experimental

2.1. Catalyst preparation

A 10 wt.% Ni/Al_2O_3 catalysts were prepared by impregnating the support (γ-Al_2O_3, 1/8 in. bead) with an aqueous solution of nickel nitrate. After impregnation, samples were dried at 120 °C, then calcined under air atmosphere at 400 °C for 3 h. The calcined Ni/Al_2O_3 catalysts were activated by diethyl aluminum chloride (DEAC) and $AlCl_3$ mixture in toluene solution under nitrogen atmosphere for 18 h. Excess organic aluminum compounds were washed with toluene and then dried under nitrogen atmosphere.

The catalyst containing phosphorous was prepared by impregnating the support with a mixed aqueous solution of nickel nitrate and phosphoric acid. Other procedures were the same as those for the Ni/Al_2O_3 catalyst. The catalyst containing triphenyl phosphine oxide (TPPO) was prepared by impregnating the $Ni–P/Al_2O_3$ catalyst with a solution of TPPO (1 wt.% as TPPO). The resulting $Ni–P–TPPO/Al_2O_3$ was then dried but not calcined. The activation procedure was same as that for the Ni/Al_2O_3 catalyst.

2.2. Catalytic reactions

A 10 g of activated catalysts were charged into a fixed bed reactor made of VCR fittings, which were 3/4 in. in diameter and 10 cm long. The reaction temperature and pressure were 70 °C and 700 psig, respectively. The butene flow rate was controlled by a high-pressure metering pump and the reaction temperature was controlled by a circulation bath. To maintain reaction pressure, a pressure regulator was connected to the product receiver. A sampling port was connected between the reactor and product receiver.

Analysis of reaction products was performed using a gas chromatography (HP-6890 model, equipped with HP-5 capillary column). Equations for conversion, selectivity, and octene yield are shown below:

$$\text{conversion (\%)} = \frac{\text{weight of used } C_4}{\text{weight of supplied } C_4} \times 100$$

$$\text{octene selectivity} = \frac{\text{weight of produced } C_8}{\text{weight of } C_4 \text{ used}}$$

$$\text{octene yield (\%)} = \text{conversion} \times \text{octene selectivity}$$

Samples of liquid alkene products were hydrogenated under pressure (300 psig) over 5 wt.% Pd/C and a smaller number of species were obtained: the GC peaks corresponding to the C_8 fraction were systematically identified, mostly by comparison with pure samples of octane isomers. This allowed the determination of the average degree of branching of the C_8 fraction through a branching index (BI) defined as $\text{BI} = [\text{Me}_2 \text{ hexanes fraction}] \times 2 + [\text{Me-heptanes fraction}] \times 1 + [n\text{-octane fraction}] \times 0$.

3. Results and discussion

3.1. Effect of 1,3-butadiene

In order to investigate the effects of 1,3-butadiene on catalytic performance in oligomerization reactions, three different C_4 feeds (C_4 raffinate II, C_4 mixture after selective hydrogenation, and pure 1-butene) were used for the oligomerization reactions. C_4 raffinate II contains 73.7 wt.% butenes, 26.2 wt.% butanes, and 0.15 wt.% 1,3-butadiene (Table 2). Selective hydrogenation reaction was adapted to reduce the amount of 1,3-butadiene in C_4 raffinate II. In order to minimize the complete hydrogenation to butane as well as to maximize the hydrogenation of 1,3-butadiene to butene, we select a reaction condition for selective hydrogenation. In a fixed bed reactor containing 250 g of 0.5 wt.% Pd/Al_2O_3 catalyst, C_4 raffinate II was hydrogenated with hydrogen gas at a reaction condition of 50 °C and 120 psig. Flow rates of C_4 raffinate II and hydrogen were 1.2 and 5 ml/min, respectively. After the hydrogenation reaction, a C_4 mix-

Table 2
Composition of C_4 raffinate II and C_4 mixture after selective hydrogenation

Component	Concentration in C_4 raffinate II (wt.%)	Concentration in C_4 mixture after selective hydrogenation (wt.%)
i-Butane	3.52	3.53
n-Butene	22.67	24.71
i-Butene	0.06	0.05
1-Butene	53.48	52.14
trans-2-Butene	12.31	11.94
cis-2-Butene	7.82	7.62
1,3-Butadiene	0.15	0.004

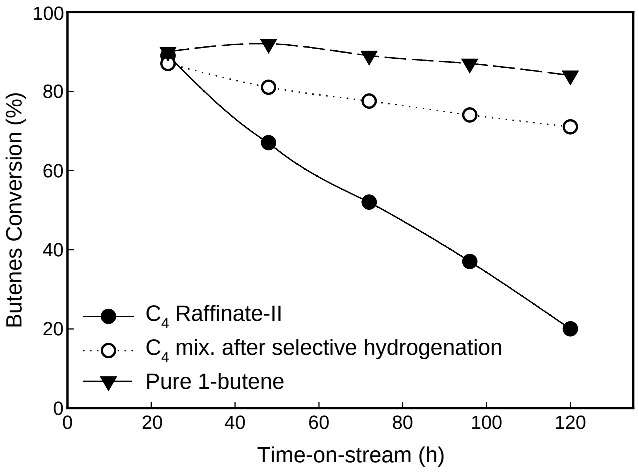

Fig. 1. Comparison of catalyst life for oligomerization over Ni/Al_2O_3 catalyst (catalyst: 10 g of 10 wt.% Ni/Al_2O_3; reaction condition: 70 °C, 700 psig; LHSV = $1.0\,h^{-1}$).

ture containing 71.8 wt.% butenes, 28.2 wt.% butanes and 0.004 wt.% 1,3-butadiene was obtained (Table 2). Through selective hydrogenation, 1,3-butadiene content could be reduced from 0.15 to 0.004 wt.%, while a small amount of butenes was lost to butanes through hydrogenation.

Fig. 1 shows the effects of 1,3-butadiene on catalytic performance in the oligomerization reaction. In the case of the pure 1-butene oligomerization reaction, C_4 conversion remained above 85% for 120 h of time-on-stream. When the C_4 mixture containing 0.004 wt.% 1,3-butadiene was used as a feed for the oligomerization reaction, C_4 conversion decreased slightly with time-on-stream. In the case of C_4 raffinate II containing 0.15 wt.% 1,3-butadiene, catalytic activity decreased drastically with time-on-stream. While C_4 raffinate II conversion at 24 h time-on-stream is similar to that of pure 1-butene and that of the C_4 mixture containing 0.004 wt.% 1,3-butadiene, C_4 raffinate II conversion at 120 h time-on-stream is only 20%, that is much lower than in other C_4 feeds. Podrebarac et al. suggested that deactivation was caused by butadiene irreversibly complexing with active nickel sites and by participating in the Diels–Alder reaction to form bulky cyclic products which block the catalyst pores in Y zeolite [11]. They reported that catalytic activity deceased linearly with a mole ratio of 1,3-butadiene/Ni. Nkosi et al. suggested that the longer chain oligomers were responsible for the fouling of the Y zeolite catalysts [9].

In this study, it was found that deactivation by butadiene could be mitigated by a reduction of 1,3-butadiene content from 0.15 to 0.004 wt.% through selective hydrogenation. In order to elucidate deactivation, the BET surface area of the spent catalysts was compared with the freshly calcined catalysts. The loss of BET surface area after oligomerization for 120 h time-on-stream by using pure 1-butene, C_4 mixture containing 0.004 wt.% 1,3-butadiene, and C_4 raffinate II containing 0.15 wt.% 1,3-butadiene was 2.3, 3.1, and 19.5%, respectively. In the case of C_4 raffinate II feed, conversion decreased from 89 to 20% after 120 h time-on-stream, even though the loss of BET surface was only 19.5%. Catalyst deactivation seemed caused by 1,3-butadiene irreversibly complexing with active nickel sites as well as blocking the catalyst pores with bulky cyclic products or longer chain oligomers.

3.2. Effects of phosphorous promoter

In order to enhance butene conversion and octene selectivity, phosphorous compounds were adapted as promoters for the Ni/Al_2O_3 catalyst. To evaluate the industrially produced C_4 raffinate II, oligomerization was conducted with a C_4 mixture containing 0.004 wt.% 1,3-butadiene obtained through selective hydrogenation of C_4 raffinate II, not pure 1-butene. Fig. 2 shows the effect of phosphorous compounds over the Ni/Al_2O_3 catalyst on the butene conversion and octene selectivity. The catalyst composition is 10 wt.% nickel and 1 wt.% phosphorous compound. It was found that the addition of phosphorous to the Ni/Al_2O_3 catalyst slightly increased the octene selectivity as well as the

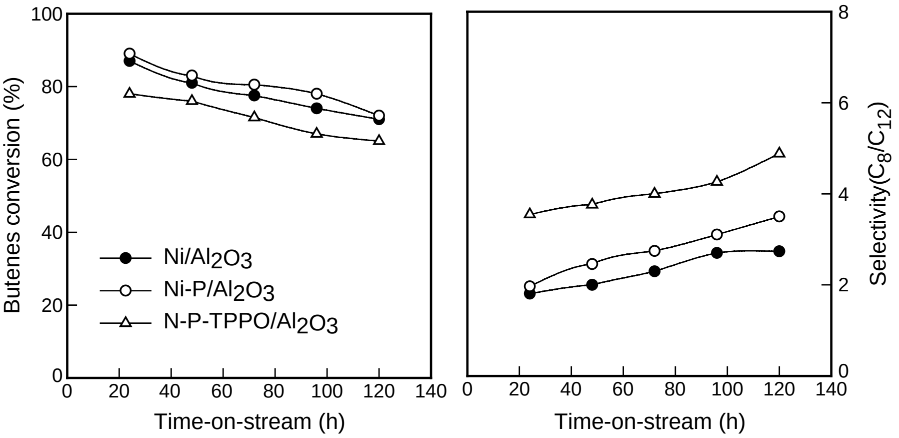

Fig. 2. Effect of phosphorous promoters on butene conversion and C_8 selectivity over Ni/Al_2O_3 catalyst (catalyst: 10 g, 10 wt.% Ni, 1 wt.% P, 1 wt.% TPPO; reaction conditions: 70 °C, 700 psig; LHSV = $1.0\,h^{-1}$).

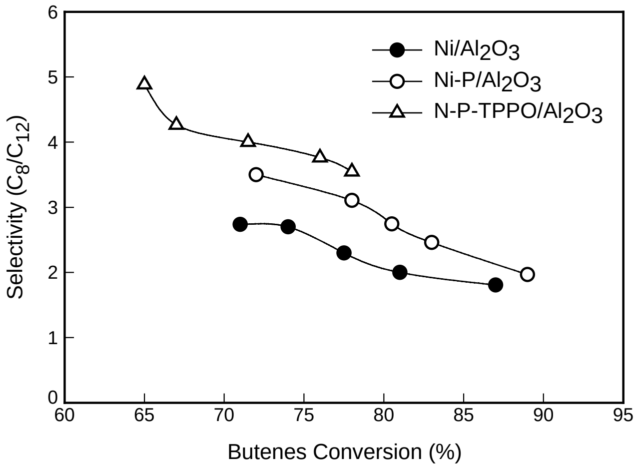

Fig. 3. Butene conversion vs. C_8 selectivity over Ni/Al_2O_3 catalyst with phosphorous promoters (catalyst: 10 g, 10 wt.% Ni, 1 wt.% P, 1 wt.% TPPO; reaction condition: 70 °C, 700 psig; LHSV = $1.0\,h^{-1}$).

butene oligomerization activity. At the same level of butene conversion, the octene selectivity over the $Ni–P/Al_2O_3$ catalyst is higher than that of the phosphorous-free catalyst, as shown in Fig. 3.

When TPPO was added to the $Ni–P/Al_2O_3$ catalyst, butene conversion was lower but the octene selectivity was much higher than that over the Ni/Al_2O_3 catalyst without TPPO. Consequently, the octene yield over the $Ni–P–TPPO/Al_2O_3$ catalyst remained almost the same as that over the Ni/Al_2O_3 catalyst. Since dodecenes synthesis is a consecutive reaction that takes place after the formation of intermediate octenes, a higher octene selectivity was observed at lower conversions. It has been reported that it is desirable to keep the butene conversion low to reduce catalyst deactivation [11]. When using a TPPO-free catalyst, the primary products seem to remain partly adsorbed, favoring secondary reactions such as trimerization and thus leading to the production of heavy oligomers. However, the presence of a basic TPPO may allow an easier desorption of octenes and thus increase the selectivity for dimerization.

From Table 3, it can be seen that the branching index of the product over the $Ni–P–TPPO/Al_2O_3$ catalyst is higher than that over other catalysts. As branched octane isomers have higher octane numbers (Table 1), it is highly desirable to increase the branching index by using octenes as a raw material for high-octane additives.

Table 3
Composition of octene isomers in butene dimerization

C_8H_{16}	Catalyst		
	Ni/Al_2O_3	$Ni–P/Al_2O_3$	$Ni–P–TPPO/Al_2O_3$
Dimethylhexene	26.2 wt.%	28.5 wt.%	30.9 wt.%
Methylheptene	62.0 wt.%	61.9 wt.%	61.5 wt.%
n-Octene	11.8 wt.%	9.6 wt.%	7.6 wt.%
Branching index	1.14	1.19	1.23

Lepetit et al. discussed a reaction mechanism for propene dimerization that consisted of a concerted coupling of two monomer molecules and proceeded via metallacyclic intermediates [13]. The effect of TPPO on butene dimerization seemed consistent with the analysis by Lepetit et al. This analysis of metallacyclic intermediate mechanisms leads us to suggest modifying the dimer distribution by steric effects of TPPO. Bulky TPPO induces a strong steric hindrance between the two methyl groups of the metallacyclic intermediate and the phenyl substitutes of the phosphorous. The head–head and head–tail couplings are thus disfavored, limiting the percentage of less-branched octenes. On the contrary, the selectivity to more-branched octenes increases, as it results from tail–tail coupling for which steric hindrance is minimum.

4. Conclusions

Catalytic deactivation by butadiene in oligomerization of industrially produced C_4 raffinate II could be mitigated by a reduction of 1,3-butadiene content from 0.15 to 0.004 wt.% through selective hydrogenation.

The octene selectivity could be enhanced by using some phosphorous compounds as a promoter for the Ni/Al_2O_3 catalyst. The branching index of the product over the $Ni–P–TPPO/Al_2O_3$ catalyst was higher than that over other catalysts.

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