# Selective Hydrogenation of 1,3-Butadiene over Supported Nickel Catalyst Obtained from Nickel-Zirconia Solid Solution

**Jong-San Chang,* Jae Oak Ryu, Jong Min Lee, Sang-Eon Park,[†,*] Do-Young Hong, and Sung Hwa Jhung**

*Research Center for Nanocatalysts, Korea Research Institute of Chemical Technology (KRICT), Yuseong, Daejeon 305-600, Korea. \*E-mail: jschang@krict.re.kr*
*[†]Department of Chemistry, Inha University, Incheon 402-751, Korea. \*E-mail: separk@inha.ac.kr*
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Catalytic properties of Ni-ZrO₂ catalysts prepared by coprecipitation have been studied for the gas-phase hydrogenation of 1,3-butadiene to butenes. The coprecipitation method led to the solid solution of Ni-ZrO₂, which contains highly resistant Ni species to thermal reduction with H₂. Nickel species of the solid solution were highly dispersed in the ZrO₂ lattice, so that the reduced catalysts were selective for hydrogenation of 1,3-butadiene to butenes (99.9%) even in the presence of 1-butene.

**Key Words :** Ni-ZrO₂, Solid solution, Selective hydrogenation

## Introduction

Zirconia and its solid solutions are interesting materials of current technological and scientific fields.[1] In particular, they find applications as catalyst, support or electrode in environmental catalysis, high temperature fuel cell and electrochemical cells. In recent years, much work has been devoted to study chemically or physically modified ZrO₂ as a new generation catalyst.[2-5] Its superiority in catalytic application has been ascribed to the following two properties: (i) ZrO₂ gives rise to a unique interaction between the active catalytic phase and support and (ii) it is chemically more inert than classical support materials such as Al₂O₃, MgO, and SiO₂. Pure zirconia exists in a monoclinic phase at room temperature. Nevertheless, tetragonal and cubic phases can be formed at room temperature by adding adequate amounts of oxides of metals with similar radii to that of Zr. Numerous investigations on the phase stabilization process of ZrO₂ by doping alkali and rare-earth metal oxides have been carried out for several decades.[6] Moreover, the catalytically active components, such as transition metals and noble metals, can be incorporated into ZrO₂ matrix through several preparation methods.[7] The binary Ni-ZrO₂ system has the ability to form metastable solid solutions since the presence of nickel favors the formation of metastable tetragonal zirconia.[8] The state of nickel in the Ni-ZrO₂ system strongly depends on the preparation procedure. However, catalytic properties of the Ni-ZrO₂ solid solutions have not been studied in detail until now. This work concerns preparation of the Ni-ZrO₂ solid solution and its catalytic properties especially for hydrogenation reaction.

The versatility of catalytic hydrogenation allows the selective conversions of functionalized hydrocarbons.[9] Selective hydrogenation of diolefin to the corresponding monoolefin over supported Pd catalysts plays an important role in producing high purity alkene streams on an industrial scale.[10] In fact, modern industrial processes use the selective hydrogenation for the purification of petrochemical products generated from cracking units by removing acetylene and 1,3-butadiene in the ethylene-rich cut and butene-rich cut, respectively. A number of studies have been devoted to the selective hydrogenation of 1,3-butadiene to butene since the 1960s.[11] Although palladium is the most useful catalyst for the partial hydrogenation reactions of alkynes and dienes due to its outstanding intrinsic selectivity, the development of nickel-based catalysts for such reactions is highly promising due to the high cost and limited availability of noble metals. However, the application of nickel catalysts to the selective hydrogenation has been very rare due to low selectivity in general. In this work, we suggest the ZrO₂-supported nickel catalyst induced from Ni-ZrO₂ solid solution as a selective hydrogenation catalyst, especially, in partial hydrogenation reactions. The selective hydrogenation of 1,3-butadiene to butenes was investigated as a test reaction to evaluate catalytic activity and selectivity of reduced nickel species in the Ni-ZrO₂ system.

## Results and Discussion

It has been reported that the tetragonal phase can be obtained by the addition of foreign metal species with a suitable preparation method since the presence of foreign species plays an important role to derive the zirconia structure.[12] Likewise, for Ni-ZrO₂ system a chemical precipitation method leads to the formation of a metastable tetragonal ZrO₂. Using the precipitation method the tetragonal phase ZrO₂ in the NiO-ZrO₂ system is dominantly obtained in the range of 1-7 wt.% NiO loading. Figure 1 illustrates the XRD patterns for the 1 wt% and 3 wt% Ni-doped ZrO₂ catalysts, which clearly indicate the formation of a dominant tetragonal phase in the ZrO₂ matrix. It is noted that no crystalline peaks related to NiO in XRD patterns were detected up to 7 wt.% NiO loading. This means that NiO in the NiO-ZrO₂ is highly dispersed in a zirconia matrix or exists as an amorphous state. In the tetragonal zirconia,
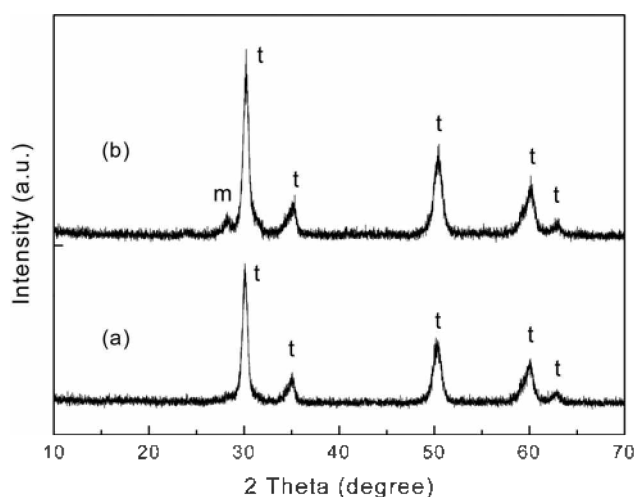
**Figure 1.** XRD patterns of (a) 1 wt% and (b) 3 wt% Ni-ZrO₂ catalysts. Notation: t, tetragonal ZrO₂; m, monoclinic ZrO₂.



**Figure 2.** TPR profiles of (a) 1 wt% and (b) 3 wt% Ni-ZrO₂ catalysts. Ramping rate: 10 °C/min.

nickel species can be incorporated in the zirconia structure so that they form the solid solution with the zirconia framework. As mentioned above, the tetragonal Ni-ZrO₂ phase is formed even at room temperature by adding nickel cations to have similar radius to that of $Zr^{4+}$ (0.69 Å for $Ni^{2+}$ vs. 0.72 Å for $Zr^{4+}$). The incorporation of Ni into zirconia lattice to form solid solution was also confirmed by EXAFS analysis.[13] For Ni K-edge EXAFS of NiO-ZrO₂, the spectrum displayed the first coordination shell of Ni-O with octahedral environment while there was a trace of the second-neighboring nickel atoms, indicating that nickel cations are almost atomically dispersed in the framework. XPS analysis of Ni-ZrO₂ revealed higher binding energy (855.7 eV) in Ni $2p_{3/2}$ core level as compared to that of bulk NiO (854.0 eV), indicating strong interaction between nickel and zirconia matrix. In addition, the concentration of the surface $Ni^{2+}$ ions determined by the ratio of photoelectron peak area of Ni $2p_{3/2}$ to that of Zr 3d ($R_{Ni/Zr}$) showed $Ni^{2+}$ surface content in tetragonal ZrO₂ was much lower than bulk Ni content. These supplementary results suggest that nickel species of the solid solution are highly dispersed in the lattice of tetragonal zirconia. Until some threshold concentration, the solid solution of Ni-ZrO₂ prevents the aggregation of nickel oxide on the zirconia surface because nickel in a dispersed state of nickel oxide enters the solid solution of zirconia lattice.[8]

TPR experiment has been carried out to determine the reducibility of Ni and interaction between nickel and support. As shown in Figure 2, Ni-ZrO₂ catalysts show reduction peaks at temperature higher than 400 °C and the reduction peaks shift to higher temperature at lower Ni loading. Considering reduction temperature (250-350 °C) of bulk NiO, these peaks at higher temperatures are ascribed to much strong interaction of nickel oxide and tetragonal zirconia. TPR profiles of these catalysts verify that the reduction of $Ni^{2+}$ or NiO in the solid solution is strongly hindered.

Table 1 summarizes catalytic activities and selectivities of 1% and 3% Ni-ZrO₂ catalysts reduced at 400 °C for 1 h in
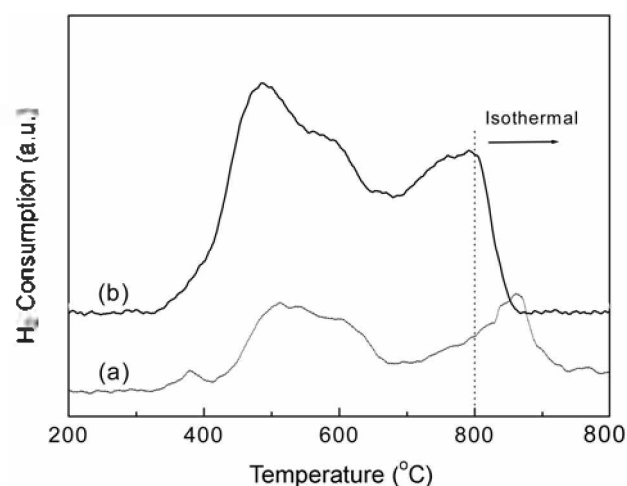
**Table 1.** Selective hydrogenation of 1,3-butadiene over Ni-ZrO₂ catalysts

| Ni loading (wt%) | BD Conv. (%) | $S_{Butenes}$ (%) | Selectivity (%) | | | |
|---|---|---|---|---|---|---|
| | | | n-C₄H₁₀ | 1-C₄H₈ | c-2-C₄H₈ | t-2-C₄H₈ |
| 1.0 | 5.4 | 96.3 | 3.7 | 35.2 | 20.4 | 40.7 |
| 3.0 | 70.9 | 99.7 | 0.3 | 40.4 | 16.4 | 42.9 |
| 3.0* | 51.7 | 99.9 | 0.1 | 50.4 | 13.2 | 36.3 |

Reaction conditions: Temp. = 100 °C, W/F = 0.6 g·min/mL, H₂:BD = 2 (molar ratio), P (BD) = 10.1 kPa. Time on stream: 1 h. Notation: BD, 1,3-butadiene. *Competitive hydrogenation of 1,3-butadiene in the presence of 1-butene: Temp. = 100 °C, W/F = 0.6 g·min/mL, P (olefins) = 15.1 kPa, H₂/BD = 1.5 (molar ratio), BD/1-butene = 0.312 (molar ratio).

the selective hydrogenation of 1,3-butadiene. Although 1 wt% Ni-ZrO₂ exhibits very poor activity for hydrogenation, 3 wt% Ni-ZrO₂ shows very high selectivity (99.7%) to butenes with moderate activity. It seems that the Ni content of more than 1 wt% is necessary for obtaining reasonable activity over the catalysts induced from the Ni-ZrO₂ solid solution.

For supported Pd catalysts high trans/cis ratios (4-12) of the 2-butenes in the products have been generally observed.[11] On the other hand, the reduced Ni-ZrO₂ catalysts give much lower trans/cis ratios (2.0-2.6), close to the equilibrium ratio. This suggests that an adsorption mode of the partially hydrogenated intermediate is different from that on Pd catalyst, which is assumed to be a π-allyl species. Butenes produced by the hydrogenation may either undergo desorption or subsequent hydrogenation. In general, 1,3-butadiene is more strongly adsorbed on group VIII metals than butenes formed by hydrogenation. The desorption rate of butenes on catalyst surface that is mainly determined by the relative difference in the adsorption strength of 1,3-butandiene and butenes depends markedly on the surface structure of the active nickel sites. The high butenes selectivity on the reduced Ni-ZrO₂ may be due to the high desorption rate of butene intermediates.

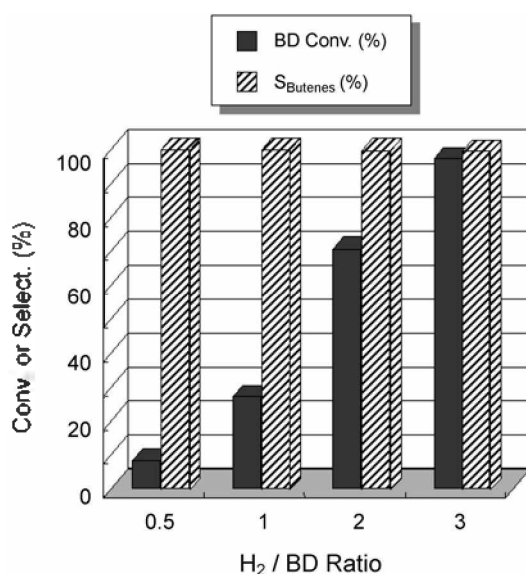In addition to high performance toward selective hydro-

**Figure 3.** Effect of $H_2$/BD ratio on catalytic activity and selectivity. Catalyst: 3 wt% Ni-ZrO$_2$. Reaction conditions: see Table 1.

genation, another characteristic of the Ni-ZrO$_2$ catalyst is insensitivity of its selectivity to hydrogen concentration, as illustrated in Figure 3. Its selectivity to partial hydrogenation is not changed significantly even when the ratio of hydrogen to butadiene increases from 0.5 to 3, as contrasted to the general behavior of hydrogenation catalysts that tends to lose their selectivities easily at higher hydrogen concentration (H$_2$/BD > 1).[9] Instead, the hydrogenation activity increases steadily with an increase of hydrogen concentration. It is also observed that the Ni-ZrO$_2$ catalysts are much selective for hydrogenation of 1,3-butadiene to butenes (50.4%) even in the presence of 1-butene. The catalytic results clearly suggest that Ni species incorporated into the zirconia framework are highly selective for partial hydrogenation of diolefins.

In summary, the coprecipitation method led to the solid solution of Ni-ZrO$_2$ to contain Ni species highly resistant against thermal reduction with H$_2$. Nickel species of the solid solution were highly dispersed in the ZrO$_2$ lattice, which were highly selective for hydrogenation of 1,3-butadiene to butenes. This work demonstrates that ZrO$_2$-supported Ni catalysts derived from the solid solution of Ni-ZrO$_2$ could be utilized for selective hydrogenation.

**Experimental Section**

Ni-doped zirconia (NiO-ZrO$_2$) materials were prepared by chemical precipitation method. Thus, synthesis of these materials with 1-7 wt% of NiO loading was carried out by hydrolyzing the solution of ZrO(NO$_3$)$_2$·H$_2$O (Fluka) and Ni(NO$_3$)$_2$·6H$_2$O (Aldrich) and neutralizing the resultant sol with aqueous ammonia solution (28%) to obtain a precipitate (pH~9) in continuous stirring, followed by aging at 30-40 °C for 6 h. The precipitate was washed with distilled water and dried at 100 °C. The as-prepared powder was calcined at 600 °C for 6 h in air. The selective hydrogenation of 1,3-butadiene to butenes was carried out with a conventional fixed-bed microreactor made of quartz at atmospheric pressure. Before catalytic measurement, the catalyst was reduced with 5% H$_2$/N$_2$ at 400 °C for 1 h. The reaction was carried out by introducing a mixture of 1,3-butadiene (purity: 99.0%+) and pure hydrogen in helium balance. The effluent stream from the reactor was analyzed by an on-line gas chromatograph (HP 5890 Series II) equipped with a capillary column (J&W, GS-Al$_2$O$_3$) and a flame ionization detector.

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