1. Introduction

Light alkenes such as ethene and propene are major building blocks in the petrochemical industry. Nowadays, ethene and propene are produced by the endothermic steam cracking of naphtha and/or the heavy fraction of natural gas. However, these processes have drawbacks, in that they are carried out at high temperatures, consuming a large amount of energy with a low selectivity to products and with inevitable coke formation.

Oxidative dehydrogenation of ethane (ODHE) (1) is an attractive alternative to the current steam cracking processes. Since the ODHE is an exothermic reaction, it can be carried out at a lower temperature than those involving steam cracking. The first ODHE was reported by Lunsford et al. over MoO3 on SiO2 using N2O as an oxidant (4). Since then, a large number of researchers developed various catalysts, using O2, CO2, and N2O as oxidants. The catalysts are classified into reducible and non-reducible metal oxide catalysts.

As reducible metal oxides, vanadium oxide-based catalysts have been used in the ODHE with O2 as an oxidant; for example, vanadium oxide has been loaded on metal oxides such as SiO2 (5~7), MgO (6,7), TiO2 (8), Al2O3 (8,9), MCM-41 (10~12), microporous alumina, and aluminophosphates (13,14).

In general, the reactivity of these catalysts is consistent with both kinetically relevant steps involving the dissociation of C-H bonds and with a Mars-van Krevelen redox mechanism involving lattice oxygen. However, the main drawback of V-containing catalysts is that they do not always maintain their structure if high V contents are incorporated. Furthermore, the incorporated V species may sometimes be easily separated from the original structure during the reaction (3).

Supported MoO3 catalysts have been investigated (15~17). However, supported MoO3 catalysts are less active than supported V2O5 catalysts on the ODHE, regardless of the supports used (5).

Catalysts based on Mo-V binary oxides (18,19) and Mo-V-additives ternary or quaternary oxides (18,20~25) have exhibited high activities at low temperatures for the ODHE. On these catalysts, the ODHE reaction proceeds via the redox cycle and/or acid-base properties. Xie et al. (25) have reported that a high conversion of ethane (ca. 90%) and a high selectivity to ethene (ca. 87%) were obtained with a MoVTeNb mixed oxide catalyst at 400°C. In general, the reaction was conducted

Keywords
Zirconium oxide, Nickel oxide, Phosphoric oxide, Ethane, Oxidative dehydrogenation

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C2H6 + 1/2O2 → C2H4 + H2O  ΔH = −149 kJ/mol (1)

In one of the recent reviews of the oxidative dehydrogenation of ethane and propane (17~3), Cavani et al. (23) compiled over 400 papers in this field and came to a disappointing conclusion regarding the industrialization of ODHE.

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under dilution of ethane with an inert gas such as N2 to prevent the side reactions, leading to the formation of CO2 and H2O (2–4). From a practical perspective, dilution with inert gases must be avoided.

\[
\begin{align*}
\text{C}_2\text{H}_6 + 7/2\text{O}_2 & \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O} & \Delta H = -1560 \text{ kJ/mol} \\
\text{C}_2\text{H}_4 + \text{O}_2 & \rightarrow 2\text{CO} + 2\text{H}_2\text{O} & \Delta H = -136 \text{ kJ/mol} \\
\text{C}_2\text{H}_4 + 3\text{O}_2 & \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O} & \Delta H = -1411 \text{ kJ/mol}
\end{align*}
\]

(2) (3) (4)

As a non-reducible metal oxide catalyst, Li-Mg catalyst has been reported to be active at above 600°C. Wang et al. have reported that an ethene yield of 58% (75% conversion and 77% selectivity) was maintained for 50 h using Cl-doped Li-MgO catalyst.

Complex metal oxide catalysts such as La1−xSrFeO3−δ(39), La1−xSrFeO3−δCl, La1−xSrFeO3−δF(30), Lα1+δSrFeO3−δC1, Nd1−xCe0.5Cu0.5O4−δF, and Nd1−xCe0.5Cu0.5O4−δCl(31) have given high performance for the ODHE. However, these catalysts are functional at reaction temperatures higher than 650°C.

ZrO2 or sulfated ZrO2 supports have been reported to be effective in the ODHE(22)−(36). Deng et al. have reported that the acid/base properties of the catalyst also play an important role in the ODHE with CO2. Strong acid-base pairs are reported to promote the reforming and cracking reactions(36).

We have reported that the use of CO2 as an oxidant promotes the ODHE over Ga2O3-loaded TiO2(37) and Cr2O3-loaded oxidized diamond catalysts(38). However, with an increase in the reaction time, the ethene yield decreases due to carbon deposition. As a result, the use of oxygen as an oxidant is necessary to avoid carbon formation.

Recently, NiO-loaded catalysts such as NiO/Al2O3(38),(39),(40) and Ni–Nb–O(31)−(44) have been reported to exhibit high activity for ODHE. Zhang et al. have reported that the yield of ethene is approximately proportional to the pore volume/surface area ratio of the support, and that highly dispersed NiO on Al2O3 tends to convert ethane to ethene and that large crystallites of NiO on Al2O3 tend to convert ethane to carbon dioxide(40).

We have reported that NiO loaded on MgO with high surface area shows high performance in the ODHE without dilution of ethane and O2 with an inert gas, with ethane conversion of 68.8%, a high ethene selectivity of 52.8%, and an ethene yield of 36.3% at 600°C. The productivity of this catalyst corresponds to ethene space time yield of 6.35 g/h per 1.0 g of catalyst, and this value is the highest one in the table compiled by Cavaney et al.(3)

In addition, the highest ethene productivity of catalytic activity was kept constant for at least 10 h(35).

However, one of the important objective of developing ODH catalysts is to reduce the reaction temperature of the process to minimize energy consumption in the process. From this perspective, ODHE processes run above 600°C seem not to be practical. From such view point, we have explored a more favorable support material for NiO in the ODHE at lower temperatures, and an HSZ was found to be a good support for the ODHE. In this paper, we will describe the development of efficient NiO-based HSZ-supported catalysts for the ODHE without the dilution of ethane and O2 at a lower temperature.

2. Experimental

2.1. Materials

Zr(C6H5O2)4 in butanol with concentration of 27.2% was supplied from Matsumoto Chemical Industry Co., Ltd. C3H8NaO4S was supplied from Acros Organics Ltd. ZrO2·xH2O and La(NO3)3·6H2O were supplied from Nacalai Tesque Inc. Ni(CH3COO)2·H2O, NH4H2PO4, Co(NO3)2·6H2O, Cu(NO3)2·3H2O, Nd(NO3)3·6H2O, Ce(NO3)3·6H2O, (NH4)6Mo7O24·4H2O and Bi(NO3)3·5H2O were supplied from Wako Pure Chemical Ind., Ltd. Sb(CH3COO)3 was supplied from Sigma-Aldrich Co.

2.2. Catalyst Preparation

The catalyst supports used were HSZ and low surface area ZrO2 (LSZ). HSZ (surface area = ca. 140 m²/g) was prepared by the following procedure. A 2.0 g of C3H8NaO4S was dissolved into 60 ml of 0.5 M (1 M = 1 mol·dm⁻³) HCl at 0°C. Then 6.5 g of Zr(OCl)4 was added by dropping into this solution, and the mixture was aged at 60°C for 2 days under stirring. The mixture was filtered off and washed with H2O. The white filtered cake was dried overnight in an oven at 60°C, and the dried powder was calcined at a heating rate of 5°C/min from a room temperature to 600°C and kept at 600°C for 5 h. LSZ (surface area = ca. 40 m²/g) was prepared by calcination of ZrO2·xH2O at the same heating rate as above.

NiO was loaded onto the supports by the conventional impregnation method with Ni(NO3)2 or Ni(OAc)2 as a precursor. Catalysts containing 25 wt% of Ni as metal, were prepared by co-impregnation or two-step impregnation methods: into an aqueous solution of Ni(CH3COO)2 and (NH4)6Mo7O24·4H2O, NH4VO3, Sb(CH3COO)3, Bi(NO3)3, Cu(NO3)2·3H2O, Co(NO3)2·6H2O, Ce(NO3)3·6H2O, La(NO3)3·6H2O, Nd(NO3)3·6H2O or NiH2PO4, HSZ was added, followed by evaporation-to-dryness under vacuum. The additive/Ni molar ratio was kept constant at 0.1 in all the samples. Supported catalyst precursors were calcined at 600°C and kept at 600°C for 5 h in an air prior to the reaction. After the calcination, the catalysts were crashed and sieved to pass a 100 mesh screen.

2.3. Catalytic Reaction

The ODHE was carried out with a fixed-bed flow-
type quartz reactor (8 mm I.D. × 350 mm L) at 450-600°C under an atmospheric pressure. Typical reaction conditions are as follows: After placing a 60 mg of the catalyst with an equal amount of quartz sand in the reactor, O₂ and ethane were introduced at a molar ratio of 1 : 2. A total gas flow rate was fixed at 30 ml/min by using mass flow controllers. Products (H₂, CO, CO₂, CH₄, C₂H₄, C₂H₆, and O₂) were analyzed with an online high speed gas chromatograph equipped with thermal conductivity detectors (TCD, GL Science Inc., Micro GC CP-2002) using Molecular Sieve 5A and Poraplot Q columns.

2.4. Catalyst Characterization

Powder X-ray diffraction (XRD) patterns were obtained with a Shimadzu XRD-6000 using monochromatized Cu-Kα radiation.

Temperature programmed reduction (TPR) was done by an on-line quadrupole mass spectrometer (Hiden Analytical Ltd., HAL201), fitted with an outlet of a fixed-bed quartz reactor (4 mm I.D. × 200 mm L). After placing a 100 mg of catalyst into the reactor, 10 ml/min of H₂ and 20 ml/min of Ar were introduced. Before the reaction, the catalyst was pretreated under Ar flow for 20 min at 150°C to eliminate adsorbed H₂O on the catalyst. Mass spectrometer was scanned corresponding parent peaks of following 4 compounds, H₂, H₂O, CO, CO₂, within 1 s, and repeated scans were collected in a personal computer.

X-ray photoelectron spectroscopy (XPS) was done with a JEOL model JPS-9000MX using Mg-Kα radiation as the energy source with the reference of C₁S at 285.0 eV.

3. Results and Discussion

3.1. Effects of Reaction Temperature and ZrO₂ Surface Area on the ODHE

In order to confirm the crystal structures of HSZ and LSZ, XRD measurements of the catalyst supports were carried out and the XRD patterns are shown in Fig. 1. The HSZ (Fig. 1(a)) and LSZ (Fig. 1(b)) showed different diffraction peaks assigned to different morphologies of ZrO₂. The HSZ exhibited the tetragonal phase of ZrO₂ (t-ZrO₂), and the LSZ had a monoclinic phase of ZrO₂ (m-ZrO₂).

Table 1 compares the effect of reaction temperature and the ZrO₂ surface area on the ODHE at 400-500°C. Over NiO/HSZ catalyst, with an increase in the reaction temperature, ethane conversion and ethene selectivity increased from 7.2 to 30.0% and from 51.6 to 59.6%, respectively (Runs 1-3). In contrast, over NiO/LSZ catalyst, with an increase in the reaction temperature from 400 to 500°C, ethane conversion increased from 23.2 to 30.4% and ethene selectivity decreased from 24.5 to 0.3% (Runs 4-6). Complete oxidation of ethane seems to have occurred predominantly at 400°C on the catalyst. With an increase in the reaction temperature, reforming reaction of ethane with H₂O and CO₂ to give CO and H₂ proceeded (after complete oxidation); consequently the ethene yield and selectivity decreased to nearly nil.

Figures 2 and 3 compare the effects of the ZrO₂ surface areas on the ODHE behavior against time on stream at 450°C. The results obtained here indicate

![XRD Patterns of ZrO₂](image)

(Left) HSZ, (Right) LSZ.

**Fig. 1** XRD Patterns of ZrO₂
that NiO-loaded HSZ afforded ethane conversion of 23.6% and ethene selectivity of 55.4% at the early stage of the reaction, and during the run for 60 min the conversion of ethane slightly increased to 25.1%, with an increase in the ethene selectivity of 57.5%. In contrast, with LSZ, a small initial increase in ethane conversion was observed, while a slight decrease in ethane conversion was observed for the run for 60 min. However, selectivity to ethene rapidly decreased from 45.9 to 9.6% when the reaction proceeded from 15 to 60 min, together with increases in CO2, CO, and H2 selectivities, and carbon formation on the catalyst surface was observed. In addition, the selectivity to CO2 was predominant with NiO/LSZ after the run for 60 min. This result seems to indicate that NiO on LSZ would be reduced to metallic Ni active for the complete oxidation of ethane.

In order to confirm the Ni species after the reaction, XRD patterns of the catalysts were obtained, as shown in Fig. 4. Both fresh NiO-loaded HSZ (Fig. 4(a)) and LSZ (Fig. 4(c)) catalysts showed diffraction peaks only ascribed to NiO. Even after the reaction, NiO/HSZ catalyst exhibited diffraction peaks of NiO (Fig. 4(b)). In contrast, mainly metallic Ni species were observed on the NiO/LSZ catalyst after the reaction (Fig. 4(d)). These results indicate that NiO on LSZ was mostly reduced to metallic Ni during the reaction and that complete oxidation of ethane to CO2 and H2O proceeded on
the metallic Ni together with the reforming of C2H4 to give CO and H2.

In order to examine differences in the reducibility of NiO on HSZ and LSZ, TPR profiles with ethane are presented in Fig. 5. As shown in Fig. 5, H2O was produced from NiO and ethane according to reaction (4).

\[
\text{NiO/ZrO}_2 + \text{C}_2\text{H}_6 \rightarrow \text{Ni/ZrO}_2 + \text{H}_2\text{O} + \text{C}_2\text{H}_4 \quad (4)
\]

In the case of NiO/LSZ, the response of H2O appeared at temperatures from 450 to 570°C (Fig. 5(a)). In contrast, for the NiO/HSZ, the response of H2O shifted to a higher temperature region of 500 to 670°C (Fig. 5(b)). This result clearly indicates that NiO was more stable on HSZ than on LSZ due to a stronger interaction between NiO and ZrO2 on HSZ. In contrast, weakly interacting NiO on the LSZ surface could easily be reduced to metallic Ni; as a result, complete oxidation proceeded over NiO-loaded LSZ at 450°C in the course of the ODHE. Similar behavior has been reported by Zhang et al.40. Highly dispersed NiO on Al2O3 prefers converting ethane to ethene while large crystalline NiO on Al2O3 prefers converting ethane to carbon dioxide.

Further studies were carried out using HSZ-supported catalysts.

3.2 Effects of NiO-loading Level on the ODHE

Figure 6 shows the effects of the NiO-loading level on the ethane conversion and product selectivities at 450°C. With an increase in NiO-loading levels from 5 to 25 wt%, ethane conversion increased from 5.9 to 24.8% and ethene selectivity was kept constant to values of ca. 60%, below the Ni loading level of 20%. However, above Ni loading levels of 20%, the ethene selectivity slightly decreased together with an increase in the CO2 selectivity. The maximum yield of ethene, 14.1%, was obtained with a NiO-loading level of 25 wt%. At higher NiO loading, the decreased dispersion of NiO on HSZ seems to have led to increase in the reducibility of NiO. Consequently, an increase in the CO2 selectivity was observed.

3.3 Effects of Various Additives to NiO/ZrO2 Catalyst on the ODHE

Although the ODHE proceeded at a moderate temperature of 450°C with NiO/HSZ catalyst, the ethene conversion was lower than that obtained with NiO/MgO catalyst45. To improve the catalyst, various additives to NiO/HSZ catalyst were tested. Table 2 illustrates the effects of several additives to NiO/HSZ on the ODHE. All the catalysts were prepared by the co-impregnation method. The addition of Mo, V, Sb, or Bi to NiO/HSZ (Runs 7-10) caused it to almost lose its activity of the ODHE, although some additives showed higher ethene selectivity. NiO-CuO/HSZ catalyst showed high selectivity to CO2 with a moderate ethene conversion (Run 11). The effect of the addition of Co, Ce, or La, on the performance of the catalyst was marginal (Runs 12-14) as compared to NiO/HSZ. The addition of P or Nd to NiO/HSZ catalyst increased ethane conversion...
conversion (Runs 15 and 16). Especially with the NiO-PO₅/HSZ catalyst, the ethane conversion increased from 24.8 to 29.1%, and the ethene selectivity increased from 55.6 to 61.7%. Maiti et al. have reported based on their first principle calculation of phosphorous-loaded SiO₂ or Al₂O₃ catalyst that activation barriers for the rate-limiting steps are lowered by ca. 42 kJ/mol in the presence of P over the SiO₂ surface in the ODHE. Takita et al. have reported that Ni₂P₂O₇ catalyst exhibits high activity for the oxidative dehydrogenation of isobutane. Furthermore El-Idrissi et al. have reported that the addition of phosphorous to Cr/TiO₂ leads to the formation of Cr-phosphate and increases the amount of isolated octahedral Cr³⁺ species exhibiting higher ethane conversion and ethene selectivity. Although a detailed mechanism for the promotion effect of phosphorous compound on Ni/HSZ catalyst has not been clarified, all these results are consistent with our NiO/HSZ catalyst.

3.4. Effects of Loading Levels of Phosphorous Compound on the ODHE

Figure 7 shows the effects of PO₅ loading levels on the ODHE. With a decrease in the PO₅ loading level from 2.6 to 0.52 wt% as P atom (P/Ni = 0.2-0.04), ethane conversion increased from 8.6 to 33.1%, keeping the ethene selectivity nearly constant at ca. 64%. However, a further decrease in the PO₅ loading level to 0.13 wt% (P/Ni = 0.01) decreased ethane conversion to ca. 25% with a slight decrease in ethene selectivity to ca. 55%. An excess amount of PO₅ on the catalyst significantly decreased the catalytic activity. The optimal PO₅ loading level was found to be 0.52 wt% (P/Ni = 0.04) to NiO/HSZ.

3.5. Effects of the Preparation Method of PO₅-loaded NiO/ZrO₂ Catalyst on the ODHE

Runs 16-18 in Table 2 compare the effects of the preparation method of PO₅-loaded NiO/HSZ catalyst on the ODHE. Catalysts were prepared by co-impregnation (Run 16) and two-step impregnation methods (Runs 17-18).

![Figure 7](image_url)

**Fig. 7** Effect of P Loading Level on the C₂H₆ Conversion and Product Selectivity over NiO-PO₅/HSZ in the ODHE

Table 2 Effect of Various Additives to NiO/HSZ on the ODHE

<table>
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<tr>
<th>Run</th>
<th>Catalyst</th>
<th>C₂H₆ conv. [%]</th>
<th>Selectivity [%]</th>
<th>C₂H₄ yield [%]</th>
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<td>1.7</td>
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**Table 2** Effect of Various Additives to NiO/HSZ on the ODHE

- a) Flow rate: C₂H₆/O₂ = 20/10 (m³/min); Reaction temperature: 450°C; Reaction time: 1 h; Catalyst: 60 mg.
- Space velocity: 30,000 m³/g-cat h; Molar ratio: Ni : Me = 10 : 1; Silica sand/catalyst = 1; Catalyst preparation method: co-impregnation method; Ni loading level: 25 wt%.
- c) H₂ reduction.

18) with different orders of impregnation. PO₈ loaded onto as-prepared NiO/HSZ catalyst, PO₈/NiO/HSZ (Run 18), afforded a higher selectivity of ethene as compared to that prepared by the co-impregnation method (Run 16). With the NiO/PO₈/HSZ catalyst (Run 17) where NiO was loaded onto PO₈/HSZ, the activity increased slightly as compared to the NiO/HSZ catalyst (Run 2). The activity order by preparation methods is as follows:

PO₈/NiO/HSZ > NiO-PO₈/HSZ > NiO/PO₈/HSZ > NiO/HSZ

These results indicate that the ethane conversion seems to increase with the surface concentrations of PO₈. In addition, except with PO₈/NiO/HSZ catalyst, carbon deposition during the run for 1 h was observed.

3.6 Effects of H₂ Reduction on the ODHE

Runs 18 and 19 in Table 2 illustrate the effects of H₂ pretreatment before the ODHE reaction on the ethane conversion and product selectivity. It was reported previously that when NiO-loaded on a high surface area MgO was reduced with H₂ prior to the reaction, the ethene selectivity decreased to nearly zero with increases in the selectivities to CO and H₂[45]. However, on the PO₈/NiO/HSZ catalyst, reduction of the catalyst with H₂ prior to the reaction did not affect the conversion of ethane and the ethene selectivity (Run 19). These results seem to indicate that metallic Ni, even if it is formed on PO₈/NiO/HSZ, would easily be re-oxidized to NiO in the presence of O₂.

In order to understand the effects of PO₈ on the increase in the selectivity to ethene in the ODHE, C₂H₆-TPR patterns are compared as shown in Fig. 5. The reduction peak of NiO in the PO₈/NiO/HSZ catalyst shifted to 500-700°C (Fig. 5(c)). The result indicates that the reducibility of NiO/HSZ catalyst decreased with the addition of PO₈, keeping Ni species to a higher valence state of NiO during the reaction. The amounts of H₂O evolved from the three catalysts were almost the same, and these amounts correspond to that of observed for TPR with H₂, although the reduction of NiO was observed at a much lower temperature of 350°C with sharper H₂O response.

In order to confirm the oxidation state of Ni species, XPS of various NiO-loaded catalysts are compared, and they are shown in Fig. 8. It is well known that the binding energies of the Ni(2p½) peak of bulk NiO and that of metallic Ni appear at 853.5 eV and 852.9 eV, respectively. On the surface of the fresh NiO/HSZ and PO₈/NiO/ZrO₂ catalysts (Fig. 8(a) and (d)), only NiO was observed at 853.5 eV, and by H₂ reduction, NiO was reduced to metallic Ni (Fig. 8(b) and (e)), as evidenced by the smaller binding energy of 852.9 eV. After the ODHE reaction, NiO/HSZ catalyst afforded two overlapping peaks composed primarily of NiO and a minor amount of metallic Ni (Fig. 8(c)). On the other hand, PO₈/NiO/HSZ catalyst gave only the NiO peak after the ODHE reaction (Fig. 8(f)). These results indicate that PO₈ co-loaded on NiO/HSZ catalyst kept Ni species as NiO during the ODHE, or that even if NiO was reduced to metallic Ni, it was immediately re-oxidized to NiO. As a result, a high yield of ethene, 20.6% with a STY of 4.8 g-C₂H₄/g-cat-h, was obtained.

3.7 Stability of PO₈/NiO/ZrO₂ Catalyst in the ODHE

The catalytic performance of PO₈/NiO/HSZ catalyst was tested for a prolonged run at 450°C. Figure 9 shows the conversion of ethane and the selectivity of ethene, CO₂, and CO as a function of time on stream. PO₈/NiO/HSZ catalyst exhibited stable catalytic activity for 12 h, indicating that the catalyst is durable for the ODHE reaction.

4. Conclusions

For the ODHE to ethene, NiO/HSZ catalyst showed ethane conversion of 24.8% and ethene selectivity of 55.6% without dilution by inert gas at ethane/O₂ = 2/1.
and 450°C. The addition of PO₆₈ (0.52 wt%) to NiO/HSZ increased the catalytic activity to ethane conversion of 32.1%, ethene selectivity of 64.2%, and ethene yield of 20.6%, and STY reached 4.8 g-C₂H₄/g-cat·h at 450°C. The addition of PO₆₈ to NiO/HSZ catalyst could keep the Ni species oxidized to a NiO state during the ODHE reaction without reduction to metallic Ni.

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References

要旨

高比表面積酸化ジルコニウム担持酸化ニッケル触媒を用いるエタンの酸化的脱水素反応

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固定床流通反応系により高比表面積 ZrO₂に担持した NiO-POₙ触媒を用いてエタンの酸化的脱水素反応を450℃ 常圧下で検討した。エタンを不活性ガスで希釈することなく、エタン酸素比 2:1 で行い、エタン転化率32.1%、エチレン選択率64.2%、エチレン収率20.6%を示した。触媒活性は少なくとも12時間は一定の値を示した。X線光電子スペクトルにより、NiO/ZrO₂触媒を用いると NiO が反応中に Ni 金属に還元されるのに対し、POₙを添加した触媒では反応後も NiO の状態であった。高いエチレン選択性を得るためには、脱水素反応中に NiO が Ni に還元されないことが重要で、POₙの NiO/ZrO₂触媒への少量添加は NiO の還元を抑制し、高いエチレン選択性に寄与した。