1. Introduction

Hydrogenation is one of the important processes used to refine intermediate compounds in the petrochemical industry, and has mainly depended on precious palladium-based catalysts for a long time. Recently, an intermetallic NiZn catalyst has been developed as a fascinating alternative because of the lower cost and availability of the component metals. This selective hydrogenation catalyst was identified in 2008 based on density functional calculations and experimental verification. Intermetallic NiZn has a definite tetragonal crystal structure (P4/mmm) except in amorphous Ni-Zn alloys. The ordered structure is important for the unique catalytic performance. Conventionally, the intermetallic NiZn nanostructures are prepared in a bulk or supported form by reducing the oxide precursors at high reduction temperature of 500-750 °C in a hydrogen flow. However, most reported NiZn catalysts contain an impurity phase of Ni metal, indicating incomplete synthesis of the single phase intermetallic NiZn. The main reason for the high temperature requirement and the difficulty in perfect preparation is the high thermal stability of ZnO, which is difficult to reduce.

This study successfully prepared a single phase intermetallic NiZn bulk nanopowder at temperatures as low as 360 °C. The combination of molten LiCl-KCl and CaH₂ was used as a reducing agent to completely reduce ZnO at low temperature. Previously, we have reported successful formations of single phase Ni₃Al, NiAl, LaNi₅Si₂ and YNi₅Si₂ from the oxide precursors at 600 °C in molten LiCl and CaH₂. The mixed CaH₂ was considered to act as a strong reducing agent in the high temperature molten salt to totally reduce refractory oxides, such as La₂O₃ and Y₂O₃. The temperature was chosen because the melting point of LiCl is around 600 °C. However, this temperature can be lowered by mixing with other salts because the melting point of a mixture of LiCl and KCl with a
molar ratio of LiCl/KCl = 6/4 is 355 °C. Here, we took advantage of the molten salt for synthesizing intermetallic NiZn bulk nanopowder at lower temperatures. The Ni-Zn precursor consisting of Ni, ZnO, and Ni3ZnC was totally reduced at 360 °C with a mixture of LiCl, KCl, and CaH2, resulting in formation of a single phase intermetallic NiZn without impurity phases.

2. Experimental

2.1. Preparation of NiZn Bulk Nanopowder

Intermetallic NiZn bulk nanopowder was prepared by reducing the Ni-Zn precursor in LiCl-KCl-CaH2 mixture at 360 °C. The precursor was prepared by the following sol-gel method. First, Ni(NO3)2·6H2O (Wako Pure Chem. Ind., Ltd.), Zn(NO3)2·6H2O (Wako Pure Chem. Ind., Ltd.) and citric acid (Wako Pure Chem. Ind., Ltd.) were dissolved in distilled water in a molar ratio of Ni/Zn/citric acid = 1.0/1.0/2.4. A small amount of 28% ammonia solution (Wako Pure Chem. Ind., Ltd.) was added to the solution to adjust the pH value to about 5. The solution was well-mixed at 50 °C for 3 h before drying at 110 °C overnight to obtain a dried gel. The gel was crushed in a mortar, preheated in air at 200 °C for 2 h, and finally heated at 500 °C in air for 3 h to obtain the Ni-Zn precursor, named NiZn(Pre). Next, the precursor, CaH2 (Junsei Chemical Co., Ltd.), LiCl (Wako Pure Chem. Ind., Ltd.) and KCl (Wako Pure Chem. Ind., Ltd.) were mixed in a mortar in a weight ratio of precursor/LiCl/KCl/CaH2 = 0.3/0.14/0.16/0.6. The mixed powder was then loaded in a stainless-steel reactor connected with an Ar or H2 gas flow system and heated at 360 °C for 5 h. The reduced precursor was crushed in a mortar. The obtained powder was rinsed with 0.1 M NH4Cl aqueous solution to remove any calcium-related impurities, especially CaO dissolved in the solution, and finally with distilled water to remove water-soluble compounds. The dried final products reduced under Ar and H2 were named NiZn(RDT-ALKC) and NiZn(RDT-HLKC), respectively. For comparison, NiZn(Pre) without LiCl/KCl/CaH2 was simply treated in a H2 gas flow at 360 °C for 5 h, and the obtained powder was named NiZn(RDT-H). The abbreviated sample names are listed in Table 1 with the preparation conditions.

2.2. Characterization

X-ray diffraction (XRD) measurements were conducted to investigate the crystal structure using a SmartLab (3 kW, Rigaku Corp.) with CuKα radiation at 40 kV and 45 mA. Nitrogen adsorption/desorption experiments were performed at −196 °C to examine the porosity using a BELLSORP mini-II (MicrotracBEL Corp.). The sample was pretreated at 200 °C for 30 min in N2 flow before the measurement. The pore size distribution was analysed from the measured isotherms using the Barrett, Joyner, and Halenda (BJH) method. The morphology was observed with a scanning electron microscope, (JSM-7800F, JEOL Ltd.) with energy dispersive X-ray spectroscopy (EDS) for elemental analysis. Surface analysis by X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) used a JEOL JPS-9010TR with MgKα radiation at 10 kV and 20 mA. The spectra were corrected using a C 1s peak (284.6 eV). Commercial Ni powder (Wako Pure Chem. Ind., Ltd.) and ZnO (Aldrich) were used for comparison. The surface oxide layer of the sample was removed with an Ar+ etching ion gun (JEOL X-PS-HSIG, 600 V, 12 mA, 60 s). Data analysis was conducted using XPSPEAK4.1 software.

3. Results and Discussion

Figure 1 shows the XRD patterns of NiZn(Pre), NiZn(RDT-H), NiZn(RDT-ALKC), and NiZn(RDT-HLKC). Table 1 summarizes the observed crystal structures and the crystallite sizes calculated by the Scherrer equation. NiZn(Pre) consisted mainly of Ni, ZnO, and Ni3ZnC. NiZn (RDT-H) consisted partially of intermetallic NiZn phase, but Ni, ZnO, and Ni3ZnC still remained. Formation of intermetallic NiZn from a Ni/ZnO precursor starts at ~550 °C, so the partial formation was probably due...
to insufficient reduction of ZnO at such a low temperature. Co-existence of NiZn and Ni is not preferable for selective hydrogenation catalyst because Ni actually has low selectivity. In contrast, NiZn(RDT-ALKC) and NiZn(RDT-HLKC) contained only intermetallic NiZn. These results indicate that addition of LiCl, KCl, and CaH₂ to the precursor is effective to decrease the reduction temperature of ZnO and improve the alloy formation. Note that the XRD pattern of NiZn(RDT-ALKC) consisted only of peaks assigned to intermetallic NiZn, so alloy formation was confirmed even in the Ar flow condition. Thus, we conclude that the reducing agent is not H₂ gas, but CaH₂. In addition, the calculated crystallite sizes were 35.6 nm and 26.9 nm for NiZn(RDT-ALKC) and NiZn(RDT-HLKC), respectively. Therefore, the low temperature synthesis approach allowed for the formation of nano-sized intermetallic NiZn powder without impurity phases.

Figure 2 indicates the nitrogen adsorption/desorption isotherms and the corresponding pore size distributions for NiZn(Pre), NiZn(RDT-H), and NiZn(RDT-HLKC). The calculated physical parameters are summarized in Table 1. No hysteresis between the isotherms was observed and the pore volumes were very small, so that all samples had extremely low porosities. The BET surface areas of NiZn(Pre) and NiZn(RDT-H) were relatively high at 45.9 m²/g and 40.6 m²/g, respectively. XRD measurements indicated that ZnO with crystallite sizes of 31.9-34.5 nm was present in both samples, so the high BET surface areas could be attributed to the nano-sized ZnO. On the other hand, the surface area of NiZn(RDT-HLKC) was low at 6.6 m²/g. In addition to crystal growth of the intermetallic NiZn phase, disappearance of ZnO could also decrease the surface area. Assuming that the NiZn(RDT-HLKC) sample consisted of intermetallic NiZn spheres, the average spherical diameter of 106 nm was estimated from the BET surface area (6.6 m²/g) and the bulk density (8.56 g/cm³). This calculated diameter is much larger than the crystallite size of 26.9 nm, so the obtained NiZn(RDT-HLKC) powder could contain polycrystalline particles formed by aggregation of a large number of single phase NiZn nanocrystals.

Scanning electron microscope (SEM) images in Figs. 3, 4, and 5 show the morphologies of NiZn(Pre), NiZn(RDT-H), and NiZn(RDT-HLKC). Similar irregularly-shaped morphologies were observed for NiZn(Pre) and NiZn(RDT-H), which seemed to consist of many nanoparticles contrasted by black and white colors that could correspond to a mixture of metals and oxides. However, NiZn(RDT-HLKC) appeared quite different from NiZn(Pre) and NiZn(RDT-H). The particle size distribution seemed broad, but many spherical particles of nanometer sizes were clearly observed, and small particles were interconnected to form the porous structure. Figure 6 shows the elemental mappings of Ni and Zn on NiZn(RDT-HLKC). The elements had homogeneous distribution on the interconnected particles and the positions overlapped, supporting the even formation of NiZn phase.

Figure 7 shows the results of SEM-EDS analysis of
NiZn(RDT- HLKC) that was carried out at two different positions marked as 001 and 002, together with the corresponding SEM images. Nickel, zinc, oxygen, potassium, and chlorine were detected at both positions. The molar ratios of Ni/Zn were nearly 1 in both positions, consistent with the stoichiometric ratio in the NiZn phase observed by XRD. In addition, the residues on the samples were investigated by SEM-energy dispersive X-ray fluorescence spectrometer (EDX) (Fig. 7) and XPS (Fig. 8). The XPS spectra were calibrated by adjusting the peak of C 1s to 284.6 eV in

Fig. 3 SEM Images of NiZn(Pre)

Fig. 4 SEM Images of NiZn(RDT-H)

Fig. 5 SEM Images of NiZn(RDT-HLKC)

Fig. 6 Elemental Mapping of Ni and Zn on NiZn(RDT-HLKC)

Fig. 8(a). SEM-EDX detected some potassium and chlorine. However, the XPS spectra in Fig. 8(a) did not show any potassium on the surface. We considered that the amounts were actually negligible and could be removed totally by more thorough treatments. Calcium species, such as CaH₂, CaO, CaCl₂, etc., were not detected by SEM-EDS (Fig. 7) or XPS (Fig. 8(b)). Lithium species were not detected by XPS in Fig. 8(b). Therefore, any impurity species were efficiently washed out by the post-rinsing treatments.

Finally, the surface oxidation states of NiZn(Pre),
NiZn(RDT-HLKC) and the Ar\textsuperscript{+}-etched sample, denoted by NiZn(RDT-HLKC)-etch, were investigated by XPS/AES measurements. The separated peak top positions are summarized in Table 2. Figure 8(c) shows the Ni 2p\textsubscript{3/2} spectrum of NiZn(RDT-HLKC) as well as NiZn(RDT) had two peaks at 854 eV and 856 eV for NiO\textsuperscript{32} and Ni\textsubscript{2}O\textsubscript{3}/NiOOH\textsuperscript{32}, respectively. The spectrum of NiZn(RDT-HLKC)-etch contained an intense peak of metallic Ni at 852.6 eV\textsuperscript{33}. NiZn(RDT-HLKC) is likely to consist of Ni\textsuperscript{0} species surrounded by several Ni\textsuperscript{2+}/Ni\textsuperscript{3+} species.

Figures 8(d) and 8(e) show the Zn 2p\textsubscript{3/2} spectra of the samples were similar, with only a peak at ca. 1022 eV. We consider that the peak can be separated into two peaks at 1022.6 eV and 1021.3 eV only for NiZn(RDT-HLKC). These values will be discussed later. On the other hand, the Zn L\textsubscript{3}M\textsubscript{4.5}M\textsubscript{4.5} AES spectra (Fig. 8(f)) were different. The spectra of NiZn(RDT-HLKC) had two peaks at 988.3 eV and 988.7 eV, respectively. The spectrum of NiZn(RDT-HLKC) had two peaks at 986.9 eV and 989.0 eV. The spectrum of NiZn(RDT-HLKC)-etch had two peaks at 989.5 eV and 992.8 eV. Here, we discuss the Auger parameters of zinc species (\(\alpha\)) which can help us understand the surface oxidation states of zinc species. The \(\alpha\) values were calculated according to Eq. (1)\textsuperscript{34}, as summarized in Table 2.

\[
\alpha' [eV] = (\text{Binding energy of Zn 2p}_3/2 [eV] + (\text{Kinetic energy of Zn L}_3M_{4.5}M_{4.5}) [eV])
\] (1)

If \(\alpha'\) is about 2014 eV, the zinc species must be metallic zinc\textsuperscript{35}. On the other hand, if \(\alpha'\) is about 2010 eV, the zinc species must be Zn\textsuperscript{2+}, such as ZnO and Zn(OH)\textsubscript{2}\textsuperscript{36}. Therefore, the zinc species of NiZn(Pre) was ZnO. For NiZn(RDT-HLKC), the zinc species were ZnO (2010.3 eV = 1021.3 eV of Zn 2p\textsubscript{3/2} + 989.0 eV of Zn L\textsubscript{3}M\textsubscript{4.5}M\textsubscript{4.5} and Zn(OH)\textsubscript{2} (2009.7 eV = 1022.8 eV of Zn 2p\textsubscript{3/2} + 986.9 eV of Zn L\textsubscript{3}M\textsubscript{4.5}M\textsubscript{4.5}). For NiZn(RDT-HLKC)-etch, the zinc species were ZnO (2011.0 eV = 1021.5 eV of Zn 2p\textsubscript{3/2} + 989.5 eV of Zn L\textsubscript{3}M\textsubscript{4.5}M\textsubscript{4.5}) and Zn\textsuperscript{0} (2014.3 eV = 1021.5 eV of Zn 2p\textsubscript{3/2} + 992.8 eV of Zn L\textsubscript{3}M\textsubscript{4.5}M\textsubscript{4.5}). Therefore, we can conclude that NiZn(RDT-HLKC) consists of Zn\textsuperscript{0} species surrounded by ZnO/Zn(OH)\textsubscript{2}.

These results for NiZn(RDT-HLKC) indicate the presence of Ni-Zn alloy, which could be an intermetallic NiZn phase, below the oxide/hydroxide surface layer. The XPS spectra of O 1s (Fig. 8(g)) support this speculation. For NiZn(RDT-HLKC), the spec-
trum had a strong peak of hydroxides (532.6 eV)\textsuperscript{37} with small shoulders of oxides (531.5 eV and 530.1 eV)\textsuperscript{37}). For NiZn(RDT-HLKC)-etch, two weak peaks of oxides were observed. Therefore, the Ar\textsuperscript{+}-etching treatment removed the oxide/hydroxide layer from the surface of NiZn(RDT-HLKC).

### 4. Conclusions

Single phase NiZn bulk nanopowder was successfully prepared from Ni-Zn precursor by a simple chemical method at temperatures as low as 360 °C. The Ni-Zn precursor was reduced by CaH\textsubscript{2} in molten LiCl-KCl.
to obtain the nanopowder. The obtained powder had BET surface area of 6.6 m²/g with crystallite size of 26.9 nm. Simple hydrogen flow treatment did not reduce ZnO in the precursor, but our approach could reduce ZnO at temperatures as low as 360 °C. Therefore, the mixtures decrease the reduction temperatures (500-750 °C) down to 360 °C. The proposed reduction method is effective to prepare intermetallic bulk nanopowders from oxide precursors difficult to reduce at lower temperatures, so is a promising scalable method to prepare single phase intermetallic powders for industrial application.

Acknowledgment

A part of this work was conducted at Advanced Characterization Nanotechnology Platform of the University of Tokyo, supported by “Nanotechnology Platform” of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. We acknowledge the Center for Instrumental Analysis, Ibaraki University for the XPS measurements.

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要  旨

溶融 LiCl-KCl と CaH₂還元剤を用いた NiZn 金属間化合物ナノ粉末の低温合成

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近年、水素化プロセスにおいて、Pt 系触媒に代わり、NiZn 金属間化合物が注目されている。結晶性の良い NiZn 金属間化合物の得るには、前駆体 ZnO の難還元性のため、高温処理（500 〜 750 ℃）が必要となる。しかしながら、高温処理を行っても NiZn 金属間化合物の単一相を得るのは困難であり、NiZn と Ni が共存する結果を示す報告が多い。本研究では、より低温で NiZn 金属間化合物の単一相を得ることを目的に、LiCl-KCl 混合溶融塩中で CaH₂還元剤を用いた合成手法を検討した。溶融塩中で合成するメリットは、難還元性酸化物の還元を阻害する酸素・水分がない最適な合成条件を生み出すことにある。得られた粉末の XRD 測定の結果より、不純物相は観測されず NiZn 金属間化合物の単一相のみが観測された。水素流通下においてはアルゴン流通下の両合成条件において単一相の NiZn が得られたことから、CaH₂が還元剤として作用していることが示唆された。算出した結晶子サイズは 26.9 nm、BET 表面積は 6.6 m²/g であった。SEM 観察から、ナノサイズの粒子の存在が明確に示された。EDS と XPS 測定の結果より、サンプルに含まれる Ca や Li、K の割合は微妙である。NH₄Cl 水溶洗洗浄処理によって不純物を適切に除去されることが示唆された。結論として、ZnO の熱力学的安定性のために通常の水素還元処理では不可能な 360 ℃（LiCl-KCl 溶融塩温度近傍）という低温条件下において、単一相の NiZn 金属間化合物ナノ粒子を得ることに成功した。低温溶融塩中で CaH₂が優れた還元剤として作用することが示された。