Agglomeration Suppression of a Fe-Supported Catalyst and its Utilization for Low-Temperature Ammonia Synthesis in an Electric Field

Ryuya Sakai, Kota Murakami, Yuta Mizutani, Yuta Tanaka, Sasuga Hayashi, Atsushi Ishikawa, Takuma Higo, Shuhei Ogo, Hideaki Tsuneki, Hiromi Nakai, and Yasushi Sekine*

1. INTRODUCTION

For various chemical reactions such as ammonia synthesis, Fischer–Tropsch reaction, and exhaust gas cleaning, Fe-supported heterogeneous catalysts are used widely. Activities of heterogeneous metal-supported catalysts depend on the metallic surface area of the supported metal. Therefore, higher dispersion and longer stability are required. To date, various attempts have been made for supporting Fe particles with high dispersion on the catalyst support, for example, using a support with a higher specific surface area such as CNF (Specific Surface Area; SSA = 150 m² g⁻¹), carbon material (SSA = 190 m² g⁻¹), using the CVD method for supporting Fe nanoparticles, and so on. Furthermore, using Al₂O₃ as a support is effective because of the strong interaction between Al₂O₃ and Fe particles. However, the supported Fe is known to be easily agglomerated during the high-temperature reaction; 3 nm diameter particles agglomerate to 13 nm in the case of CNF by annealing at 773 K in an N₂ atmosphere. Our group has succeeded in suppressing the agglomeration of base metal particles (Ni and Co) by doping into perovskite oxides i.e., anchoring effects. Therefore, elemental doping into oxide is a promising method for suppressing the agglomeration of Fe particles with high dispersion. After synthesizing such a finely Fe-supported catalyst, it can be used for various purposes. Recently, we have found that Fe-supported catalysts can show higher activity in an electric field, even at low temperatures. In this system, the N₂H intermediate is formed by protons so that N₂ dissociation is accelerated, which contributes to high performance at lower temperatures. It is impressive that the Fe-supported catalysts show higher turnover frequencies (TOF) than other catalysts, including Ru, in an electric field at low temperatures. This is true because intermediates (N₂H) are more likely to be formed at Fe particles than at Ru particles. Therefore, a finely dispersed Fe catalyst is promising for this purpose. Herein, we aimed at agglomeration suppression of a Fe-based catalyst by virtue of Al doping into a Ce–Zr–O oxide support. We used the best Fe-supported catalyst for low-temperature ammonia synthesis in an electric field.

2. RESULTS AND DISCUSSION

2.1. Suppression of Fe Particle Agglomeration by Al Doping into a Ce₀.₅Zr₀.₅O₂ Support

For suppressing the agglomeration of the supported Fe, we have prescreened for various element modifications. Among them, Al doping showed the best effect on enhancing the activities as presented
in Figure 1, which would be thanks to the suppression of the agglomeration by virtue of its strong interaction with Fe particles. To elucidate the anchoring effects of Al, Fe/Ce0.5−xAlxZr0.5O2−δ catalysts (x = 0, 0.05, 0.1, 0.15, 0.2; Fe loading amount is 5.0 wt %) were prepared and characterized by field emission transmission electron microscope (FE-TEM) measurement, X-ray diffraction (XRD) measurement, and Brunauer—Emmett—Teller (BET) measurement. Related FE-TEM images, energy-dispersive X-ray spectrometer (EDX) mappings, and the supported Fe particle size distribution for these catalysts are shown, respectively, in Figures S1−S10. As shown in Table 1, the Fe particle size after activity tests decreased concomitantly with increasing Al doping amounts. BET measurement revealed that the surface area did not show any relationship with Fe particle sizes. In addition, as shown in Figure S11 (XRD patterns), the crystal structure of Ce0.5−xAlxZr0.5O2−δ supports was attributed to the fluorite structure. Although the crystalline size decreased as the Al doping amount increased, we could not observe Al2O3 formation, and no peak shift was observed by introducing Al either. It is said that the limit of solubility for the doping concentration toward CeO2 is 20%, and no peak shift would be observed at the XRD pattern either.17 So, we conclude that Al is doped finely into Ce−Zr−O as well.

Then, the ammonia synthesis rate of the prepared Fe/Ce0.5−xAlxZr0.5O2−δ catalysts in an electric field was evaluated at 473 K under 0.1 MPa (Figure S14). The ammonia synthesis rate increased concomitantly, up to 10%, with increased Al doping amounts. However, the rate decreased with further increasing Al doping amounts despite the decrement of the Fe particle size. These results suggest that Al doping contributed not only to the increase of the number of active sites (i.e., the suppression of Fe agglomeration) but also to the decrease of the activity of the active sites. Therefore, density functional theory (DFT) calculations were done to ascertain what factors contribute to this trend by Al doping.

2.2. Investigation of Al Doping Effects. To elucidate Al doping effects, atomic-scale considerations were conducted using DFT calculations. First, Fe single atoms were supported over Ce0.5Zr0.5O2 and Ce0.5−xAlxZr0.5O2−δ surfaces. Figures 2 and 3, respectively, show the adsorption sites and energies E(Feadsorption) of Ce0.5Zr0.5O2 (color code: Yellow is Ce, green is Zr, and red is O). and 3, respectively, show the adsorption sites and energies E(Feadsorption) of Ce0.5−xAlxZr0.5O2−δ (color code: yellow is Ce, green is Zr, red is O, and sky blue is Al).
surface of Ce$_{0.5}$Al$_{0.1}$Zr$_{0.5}$O$_{2−δ}$. Fe single atoms were strongly anchored at O$_{4a}$ around Al. Especially, the adsorption energies at site 3 and site 7 over Ce$_{0.5}$Al$_{0.1}$Zr$_{0.5}$O$_{2−δ}$ (−4.83 and −4.07 eV, respectively), which were between two doped Al, were much smaller than those over Ce$_{0.5}$Zr$_{0.5}$O$_{2−δ}$ (−0.22 and −0.87 eV). Here, it is reported that the interaction between the support–O–metal is crucial for the anchoring effect$^{18}$ providing the evidence that the Fe atom’s strong adsorption over O is thanks to the anchoring effect.

Furthermore, to elucidate the anchoring effect of Al not only for the Fe single atom but also for the Fe particle, the Fe$_{29}$ cluster was set over each support (Figure 4). As a result, the E(Fe$_{29}$ adsorption) decreased upon Al addition, demonstrating the Al anchoring effect even for the Fe particle. A shortcoming of Al doping was also inferred from the optimized structures of Fe$_{29}$ clusters. Al doping led to a marked distortion of the Fe$_{29}$ cluster. The Fe$_{29}$ cluster periphery was partially bonded with oxygen, as shown in the enlarged picture (Figure 4). This phenomenon was explained in an earlier report indicating that Al$_{2}$O$_{3}$ addition to Fe-based catalysts engenders Fe and Al complex oxides.$^{19}$ The results indicate that a part of the three-phase boundary (TPB), which is the reaction site for ammonia synthesis in an electric field,$^{14−16}$ cannot function as an active site because of the high coordination number of Fe atoms at that point. Therefore, we concluded that the tradeoff between the benefits and shortcomings of Al doping causes the volcano-type relation (Figure S14).

2.3. Utilization of Ce$_{0.4}$Al$_{0.1}$Zr$_{0.5}$O$_{2−δ}$ Support for Practical Ammonia Synthesis. As described above, we suppressed the agglomeration of Fe particles by doping appropriate amounts of Al. Therefore, optimization of the Fe loading weight was conducted (Table S1). Among the tested catalysts, 12.5 wt % Fe/Ce$_{0.4}$Al$_{0.1}$Zr$_{0.5}$O$_{2−δ}$ showed the highest activity at 473 K under 0.1 MPa. The Fe particle size over 12.5 wt % Fe/Ce$_{0.4}$Al$_{0.1}$Zr$_{0.5}$O$_{2−δ}$ was 24.8 nm, which was much smaller in spite of such a high Fe loading weight.

Thereafter, for practical applications, the performance of the optimized catalyst was evaluated at various temperatures and total pressures (0.1, 0.5, and 0.9 MPa) with or without the electric field. As presented in Figure 5, under 0.9 MPa with the electric field, a markedly high ammonia synthesis rate was obtained as 2.3 mmol g$^{−1}$ h$^{−1}$, even at 464 K. The obtained ammonia synthesis rate is the highest value achieved to date under such mild conditions. Consequently, using the optimized Fe-based catalysts with the electric field resulted in a high rate of ammonia synthesis under mild conditions, which is suitable for on-site/on-demand production.

3. CONCLUSIONS

We prepared a highly dispersed Fe-supported catalyst through Al doping into a Ce$_{0.4}$Zr$_{0.5}$O$_{2−δ}$ support. From activity tests conducted in an electric field, a volcano-type relation was observed between the ammonia synthesis rate and Al doping amounts. We identified Ce$_{0.4}$Al$_{0.1}$Zr$_{0.5}$O$_{2−δ}$ as the best support for low-temperature ammonia synthesis in an electric field. DFT calculations revealed that the anchoring effect of doped Al suppressed the agglomeration of Fe. A part of Fe atoms anchored by Al cannot work as an active site because of bonding with oxygen atoms. Therefore, excess amounts of Al doping decrease the number of active sites. The optimized catalyst, 12.5 wt % Fe/Ce$_{0.4}$Al$_{0.1}$Zr$_{0.5}$O$_{2−δ}$ shows a high ammonia synthesis rate of 2.3 mmol g$^{−1}$ h$^{−1}$ under 464 K and 0.9 MPa. In fact, the ammonia formation rate is the highest value achieved to date under such mild conditions.

This study revealed that Al doping into a Ce$_{0.4}$Zr$_{0.5}$O$_{2−δ}$ support under various catalyst bed temperatures and total pressures. Catalyst, 400 mg; reactant gas, N$_2$/H$_2$ = 1:3; total flow rate, 960 SCCM; current, 6 mA.

4. EXPERIMENTAL AND COMPUTATIONAL SECTIONS

4.1. Catalyst Preparation. For the catalyst support of ammonia synthesis in an electric field, Ce$_{0.5}$Zr$_{0.5}$O$_{2}$ is known to
be a good candidate. Modification of the catalyst support with other elements including Al and other base metals is investigated. For Al, Ca, and Ba doping, various doped Ce0.8Zr0.2O2−δ oxide samples are prepared using a complex polymerization method: Ce0.5−xAlxZr0.5O2−δ (x = 0, 0.05, 0.1, 0.15, 0.2), Ce0.4Ca0.1Zr0.5O2−δ, and Ce0.4Ba0.1Zr0.5O2−δ. First, ethylene glycol (Kanto Chemical Co., Inc.) and citric acid monohydrate (Kanto Chemical Co., Inc.) were dissolved in distilled water and stirred. Then, stoichiometric amounts of Ce(NO3)3·6H2O (Kanto Chemical Co., Inc.), ZrO(NO3)2·2H2O (Kanto Chemical Co., Inc.), Al(NO3)3·9H2O (Kanto Chemical Co., Inc.), Ca(NO3)2·4H2O (Kanto Chemical Co., Inc.), and Ba(NO3)2·9H2O (Kanto Chemical Co., Inc.) were added to the solution and stirred. The solution was heated at 343 K in a water bath overnight. Subsequently, the reaction mixture was dried into a powder on a hot plate. The obtained powder was calcined at 773 K for 5 h (5 K min−1).

Fe was loaded on the prepared supports by a liquid-phase reduction method using Fe(NO3)3·9H2O (Kanto Chemical Co., Inc.) as a Fe precursor. First, the support was dispersed in an aqueous solution of the Fe precursor and was stirred for 1 h. Subsequently, the slurry was heated at 393 K on a hot plate by stirring for 1 h. Then, a 10% N2H4 aqueous solution as an aqueous solution of the Fe precursor and was stirred for 1 h. The Fe-loaded catalyst was dried overnight. Subsequently, the Fe-loaded catalyst was calcined at 773 K for 5 h before activity tests. The reaction gas was N2:H2 = 1:3 (total flow rate: 240 or 960 SCCM). Pretreatment to activate the catalyst was conducted at 773 K for 1 h before activity tests. The reaction gas was N2:H2 = 1:3 (total flow rate: 240 or 960 SCCM). Pretreatment to activate the catalyst was conducted at 773 K for 1 h before activity tests.

4.2. Characterization. X-ray diffraction (XRD) measurement was conducted using an X-ray diffractometer (SmartLab 3; Rigaku Corp.) with a Cu Kα radiation source at 40 kV and 40 mA in the 2θ range of 10–90° at a scan rate of 20° min−1. The supported Fe particles were observed using a field emission transmission electron microscope (FE-TEM; HF-2200; Hitachi Ltd.) with an energy-dispersive X-ray spectrometer (EDX). The Brunauer–Emmett–Teller (BET) method (Gemini VII 2390a; Micromeritics Instrument Corp.) was used to obtain the specific surface area by nitrogen adsorption. All samples were pretreated at 473 K for 1 h under an N2 atmosphere.

4.3. Activity Tests. Catalytic activity tests were conducted using a fixed-bed flow-type reactor equipped with a quartz tube under 0.1, 0.5, and 0.9 MPa. The catalyst was sieved into particles of 355–500 μm sizes. Then, 100 or 400 mg of it was charged to the reactor. After stainless steel (SUS304) rods were inserted into the catalyst bed as electrodes, 6 mA of direct current was applied using a DC power supply. The catalyst bed temperature was measured directly using a thermocouple attached to the bottom of the catalyst bed. A digital phosphor oscilloscope (TDS2001; Tektronix Inc.) was used to detect the response voltage. The reaction gas was N2:H2 = 1:3 (total flow rate: 240 or 960 SCCM). Pretreatment to activate the catalyst was conducted at 773 K for 1 h before activity tests. The produced ammonia was trapped into distilled water. An ion-chromatograph (IC-2001; Tosoh Corp.) was used to quantitate ammonia.

4.4. Computational Details. 4.4.1. Electronic Structure Calculations. Density functional theory (DFT) calculations were conducted using the Vienna ab initio simulation program (VASP) 5.4.4.20−23 The generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) version was adapted for the exchange-correlation functional.24 The projector-augmented wave (PAW) method was used for the representation of ion-core electron interactions. A plane-wave basis set with 400 eV energy cutoff was used for representing the valence electrons. All calculation results included the effects of spin polarization. Monkhorst–Pack grids with (5 × 5 × 5) and (1 × 1 × 1) were adapted for the bulk and slab models Ce0.8Zr0.2O2. Furthermore, the (10 × 10 × 10) grid was used for the bulk Fe calculation, which contains two Fe atoms in a unit cell. The geometry optimization threshold was set to 10−5 eV. The van der Waals forces were corrected using the DFT-D3 method of Grimme.25 We used the DFT + U method to correct the localization of Ce 4f orbitals, as reported earlier.26

4.4.2. Computational Models. Calculation models were constructed in a manner similar to our reported model.25 First, the lattice constant of Ce0.8Zr0.2O2 was optimized using the bulk structure. Then, the surface was expressed as (4 × 4) with O−Ce−O (or O−Zr−O) tri-layers (Figure S15). Each slab was separated by 20 Å vacuum layers. For Al doping models, two uppermost surface Ce atoms were replaced. The element portion of the surface used in calculations was as follows: Ce:Zr:Al = 0.33:0.5:0.17. This is almost the same as that of supports used in actual experiments. The atomic configuration options are presented in Figure S16. Two Al atoms favorably sit side-by-side. In addition, the oxygen vacancy formation for the charge compensation was an endothermic reaction. These trends showed great agreement with those over the Al-doped CeO2(111) surface.26 Therefore, the model without oxygen vacancy (shown in Figure S17) was used for the following considerations. During geometry optimization, the bottom layer was fixed, and the isolated O2 was arranged in a 10 × 10 × 10 Å cubic box. The energy of the O2 molecule and bcc-Fe bulk was calculated at the Γ point. The calculated models were depicted using Visualization for Electronic and Structural Analysis (VESTA).27 The size of the Fe cluster was restricted by the surface area of the slab model. In the calculation, as shown in Figure S18, the cluster was constructed by slicing Fe bulk structures along with the Miller indexes (010) and (111). From top to bottom of the cluster, the Fe atom numbers were 4, 9, and 16, and its total was 29.
Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c00170

Author Contributions
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. R.S., Y.M., Y.T., and S.H. conducted experiments, K.M. and A.L. performed computational calculations, T.H., S.O., H.T., H.N., and Y.S. discussed the results, and R.S., K.M., S.O., and Y.S. wrote the paper.

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Notes
The authors declare no competing financial interest.

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REFERENCES
(1) Erisman, J. W.; Sutton, M. A.; Galloway, J.; Klimont, Z.; Winjewarter, W. How a century of ammonia synthesis changed the world. Nat. Geosci. 2008, 1, 636–639.
(2) Stoltz, P.; Norskov, J. K. Bridging the “pressure gap” between ultrahigh vacuum surface physics and high-pressure catalysis. Phys. Rev. Lett. 1985, 55, 2502–2505.
(3) Park, J.; Lee, Y.; Khanna, P.; Jun, K.; Bae, J. W.; Kim, Y. H. Alumina-supported iron oxide nanoparticles as Fischer–Tropsch catalysts: Effect of particle size of iron oxide. J. Mol. Catal. A: Chem. 2010, 323, 84–90.
(4) Torres-Galvis, H. M.; Bitter, J. H.; Davidian, T.; Ruitenbeek, M.; Dugulan, A. L.; Jong, K. P. Iron Particle Size Effects for Direct Production of Lower Olefins from Synthesis Gas. J. Am. Chem. Soc. 2012, 134, 16207–16215.
(5) Bao, H.; Chen, X.; Fang, J.; Jiang, Z.; Huang, W. Structure-activity Relation of Fe2O3–CeO2 Composite Catalysts in CO Oxidation. Catal. Lett. 2008, 125, 160–167.
(6) Koutsooulos, S.; Barford, R.; Eriksen, K. M.; Fehrmann, R. Synthesis and characterization of iron-cobalt (FeCo) alloy particles supported on carbon. J. Alloys Compd. 2017, 725, 1210–1216.
(7) Li, Y.; Liu, J.; Wang, Y.; Wang, Z. Preparation of Monodispersed Fe–Mo Nanoparticles as the Catalyst for CVD Synthesis of Carbon Nanotubes. Chem. Mater. 2001, 13, 1008–1014.
(8) Mukai, D.; Tochiya, S.; Murai, Y.; Imori, M.; Hashimoto, T.; Sugiyama, Y.; Sekine, Y. Role of support lattice oxygen on steam reforming of toluene for hydrogen production over Ni/ La2/5Sr3/5AlO3 catalyst. Appl. Catal., A 2013, 453, 60–70.
(9) Sekine, Y.; Mukai, D.; Murai, Y.; Tochiya, S.; Izutsu, Y.; Sekiguchi, K.; Hosomura, N.; Arai, H.; Kikuchi, E.; Sugiyama, Y. Steam reforming of toluene over perovskite-supported Ni catalysts. Appl. Catal., A 2013, 451, 160–167.
(10) Sugiyama, Y.; Mukai, S.; Murai, Y.; Tochiya, S.; Sekine, Y. Oxidation resistance of Ni/La2/5Sr3/5AlO3 catalyst for steam reforming of model aromatic hydrocarbon. Int. J. Hydrogen Energy 2013, 38, 7822–7829.
(11) Takise, K.; Manabe, S.; Muruguchi, K.; Higo, T.; Ogo, S.; Sekine, Y. Anchoring effect and oxygen redox property of Co/La2/5Sr3/5AlO3 perovskite catalyst on toluene steam reforming reaction. Appl. Catal., A 2017, 538, 181–189.
(12) Murakami, K.; Tanaka, Y.; Sakai, R.; Toko, K.; Ito, K.; Ishikawa, A.; Higo, T.; Yabe, T.; Ogo, S.; Ikeda, M.; Tsuneki, H.; Nakai, H.; Sekine, Y. The important role of N2H formation energy for low-temperature ammonia synthesis in an electric field. Catal. Today DOI: 10.1016/j.cattod.2018.10.055, in press.
(13) Manabe, R.; Nakatsubu, H.; Gondo, A.; Murakami, K.; Ogo, S.; Tsuneki, H.; Ikeda, M.; Ishikawa, A.; Nakai, H.; Sekine, Y. Electrocatalytic synthesis of ammonia by surface proton hopping. Chem. Sci. 2017, 8, 5434–5439.
(14) Murakami, K.; Tanaka, Y.; Hayashi, S.; Sakai, R.; Hisai, Y.; Mizutani, Y.; Ishikawa, A.; Higo, T.; Ogo, S.; Gil Seo, J.; Tsuneki, H.; Nakai, H.; Sekine, Y. Governing factors of supports of ammonia synthesis in an electric field found using density functional theory. J. Chem. Phys. 2019, 151, No. 064708.
(15) Murakami, K.; Manabe, R.; Nakatsubu, H.; Yabe, T.; Ogo, S.; Sekine, Y. Elucidation of the role of electric field on low temperature ammonia synthesis using isotopes. Catal. Today 2018, 303, 271–275.
(16) Gondo, A.; Manabe, R.; Sakai, R.; Murakami, K.; Yabe, T.; Ogo, S.; Ikeda, M.; Tsuneki, H.; Sekine, Y. Ammonia Synthesis over Co Catalyst in an Electric Field. Catal. Lett. 2018, 148, 1929–1938.
(17) Willmont, Y.; Hernandez, M. A.; Centeno, F. R. S.; Jose, A. O. Synthesis and Characterization of Ce1−xEuxO2 Mixed Oxides and Their Catalytic Activities for CO Oxidation. J. Phys. Chem. A 2009, 113, 5629–5635.
(18) Shinjoh, H.; Hatana, M.; Nagai, Y.; Tanabe, T.; Takahashi, N.; Yoshida, T.; Miyake, Y. Suppression of Noble Metal Sintering by the Support Anchoring Effect and its Application in Automotive Three-Way Catalysis. Top. Catal. 2009, 52, 1967–1971.
(19) Fagherazzi, G.; Galante, F.; Garbassi, F.; Peronne, C. Structural study of Al2O3-promoted ammonia synthesis: 2. Reduced state. J. Catal. 1972, 26, 344–347.
(20) Kresse, G.; Hafner, J. Ab initio molecular dynamics for liquid metals. Phys. Rev. B 1993, 47, 558.
(21) Kresse, G.; Hafner, J. Ab initio molecular-dynamics simulation of the liquid-metal-ammorphous-semiconductor transition in germanium. Phys. Rev. B 1994, 49, 14251.
(22) Kresse, G.; Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. Comput. Mater. Sci. 1996, 6, 15–50.
(23) Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys. Rev. B 1996, 54, 11169.
(24) Perdew, J.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. Phys. Rev. Lett. 1996, 77, 3865–3868.
(25) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, S. A consistent and accurate ab initio parameterization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. J. Chem. Phys. 2010, 132, No. 154104.
(26) Murakami, K.; Ogo, S.; Ishikawa, A.; Takeno, Y.; Higo, T.; Tsuneki, H.; Nakai, H.; Sekine, Y. Heteroatom doping effects on interaction of H2O and CeO2 (111) surfaces studied using density functional theory: Key roles of ionic radius and dispersion. J. Chem. Phys. 2020, 152, No. 014707.
(27) Momma, K.; Izumi, F. VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *J. Appl. Crystallogr.* **2011**, *44*, 1272–1276.