Bimodal NdNiAl and NdFeB hybrid catalytic and magnetic nanoparticles laminated on Fe foam: catalytic conversion of CO + 3H₂ to CH₄

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Comparison of electron microscopy images of as-synthesized NdNiAl nanoparticles and as-fabricated NdFeB nanoparticles

As shown in S. Fig. 1a, the NdNiAl nanoparticles prepared by chemical synthesis exhibited a tendency toward severe agglomeration but weak bonding to the substrate. The SEM image (S. Fig. 1b) exhibits spherical NdFeB nanoparticles dispersed all over the substrate. The larger NdFeB nanoparticles exhibited less mutual agglomeration, but did show strong adhesion to the substrate. Compared to the morphology of the as-synthesized NdNiAl nanoparticles, the as-fabricated NdFeB nanoparticles coated on the substrate showed very weak agglomeration and had clear differences in dispersion morphology. This difference in agglomeration influenced morphology, dispersion, and adhesion to the substrate. As can be seen in S. Fig, 1c, the NdNiAl nanoparticles (the main catalysts) were well distributed over the surface of the NdFeB nanoparticles. Second, when NdFeB nanoparticles were applied to the surfaces of the NdNiAl nanoparticles, the agglomeration of the NdNiAl nanoparticles. Second, when NdFeB nanoparticles were applied to the surfaces of the NdNiAl nanoparticles, the agglomeration of the NdNiAl nanoparticles, the agglomeration of the NdNiAl nanoparticles were applied to the surfaces of the NdNiAl nanoparticles, the agglomeration of the NdNiAl nanoparticles were applied to the surfaces of the NdNiAl nanoparticles, the agglomeration of the NdNiAl nanoparticles were applied to the surfaces of the NdNiAl nanoparticles, the agglomeration of the NdNiAl nanoparticles were applied to the weak van der Waals interaction. The EDS spectrum (S. Fig. 1d) verified that when in the presence of NdFeB nanoparticles, the NdNiAl nanoparticles were composed

of each nominal element with trace amounts of O and C. The particle sizes of the NdFeB nanoparticles, measured by SEM analysis, were almost consistent with those determined in the particle size analysis (S. Fig. 1f); the average size of the NdFeB nanoparticles was 93.1 nm. As a result, the NiAlNd nanoparticles were coated by the magnetic force and van der Waals interaction onto the surfaces of the NdFeB nanoparticles. This process subsequently induced the formation of NdNiAl–NdFeB hybrid nanoparticles.

Fabrication of NdNiAl–NdFeB–Fe hybrid catalytic and magnetic foam using a combination of chemical, physical, and mechanical methods

Combined synthesis and fabrication approaches, using both chemical and physical methods, offer novel routes to produce catalytic and magnetic nanoparticles, while the template foam is made by a mechanical method. NdNiAl nanoparticles were prepared using a facile synthesis method. In fact, the most widely used catalysts for the hydrogenation of CO to CH₄ are usually based on Ni alloys. However, many of these catalysts undergo severe deactivation due to carbon deposition and oxide formation. Noble or rare earth metals have also been studied and are typically found to be much more resistant to deactivation than Ni catalysts but are generally uneconomical. Noble metals can also be used to promote the Ni catalysts in order to increase their resistance to deactivation. In this study, Nd is incorporated into a conventional NiAl Raney system to design a catalyst with minimum deactivation that can be involved in the conversion of CO to the production of CH₄. During this work, a method for the chemical synthesis of NdNiAl nanoparticles stabilized in mostly intermetallic compound formation was developed with the least possible oxidation of Nd and Al phases to form a spherical structure. Halide complexes, such as NiCl₂ and NdCl₃, were chosen as the precursors for synthesis of the catalyst; then, the synthesis route was based on the reaction of NiCl₂ and NdCl₃ with LiAlH₄ in non-aqueous media. This process generated intermediate species such as LiCl and AlCl₃, which were thermally labile and decomposed to leave only

pure NdNiAl at a heat treatment of 700 °C. Hydrogenation at such high temperature yielded a large amount of intermetallic NdAl₂ and Ni₃Al compounds as a purer catalyst. XRD results were used to analyze the crystallinity of the as-synthesized NdNiAl nanoparticles prior to, and after, heat treatment under H_2 .

The fabrication of NdFeB nanoparticles was carried out through plasma treatment using an evaporation-condensation process. A physical fabrication method, instead of a chemical synthesis method, was used to allow for less oxidation; this prevented any possible oxidation in the inert atmosphere. It was very difficult to fully transform ionic Nd and Fe with metallic Nd and Fe nanoparticles because the Nd and Fe ions were easily oxidized in solution, and this limited their application in any synthetic process. However, because the NdFeB nanoparticles were prepared via a plasma treatment method with rapid solidification, the NdFeB nanoparticles exhibited an amorphous structure with weaker magnetic strength but with more exposure of the Nd phase for better catalytic activity in the presence of NdNiAl nanoparticles. The plasma-treated NdFeB nanoparticles also experienced phase separation due to the different levels of enthalpy of vaporization among the constitutional elements in the presence of the extremely high plasma temperature of 10,000 K.

A slurry coating process was used to make a porous Fe foam. In this method, a polyurethane sponge was sprayed with a slurry containing a mixture of Fe powders, polyvinyl alcohol binders, blowing agents, and reactive additives. The foam coated in this way was dried and calcinated to a temperature at which the polymers were burnt out and the Fe powders started to sinter, thus forming rigid cellular structures. Under the influence of the additives and the blowing agents, the slurry turned viscous and began to evaporate as it was reduced in the reactive H_2 gas. If a sufficient temperature and proper calcination time had been used, the expanded slurry was preserved and dried completely, after which it was sintered to yield Fe foam with considerable porosity. After, structures with the intended

sufficient quantities of pores and cracks on the surface of the porous Fe foam were obtained.

Uniform distribution of the NdNiAl nanoparticles, on a support of NdFeB nanoparticles over Fe foam, was performed using an electrospraying process. Thereafter, the consolidation approach of the as-synthesized NdNiAl and as-fabricated NdFeB nanoparticles over Fe foam during the heat treatment initiated the development of novel hybrid foam. As the concentration ratio of the NdNiAl nanoparticles to the NdFeB nanoparticles was changed in this system, the morphology of the hybrid foam was also systematically changed. The morphology seemed to be affected by the presence of magnetic nanoparticles. As a result, the morphology of the hybrid foam can be modified by the concentration ratio between catalytic nanoparticles and magnetic nanoparticles.

Microscopic characterization of NdNiAl-NdFeB hybrid nanoparticles on Fe foam

If the catalytic activity occurs on the heterogeneous interface between the catalytic nanoparticles and the $CO + 3H_2$ gases, a more dispersed catalyst could lead to better reactant gas absorption and product gas desorption, improving catalytic behavior. In this study, to lower the agglomeration of NdNiAl nanoparticles, NdFeB nanoparticles were used as an intermediate supporter, as a result inducing higher surface area of the catalytic nanoparticles. To even further increase the surface area of the NdNiAl nanoparticles through double dispersion, Fe foam was employed together with magnetic nanoparticles.

The surface microstructure and chemical composition of the Fe foam are presented in S. Fig. 6 and S. Fig. 7. Many pits and clusters were found on the surface of the Fe foam; these were attributed to the thermal evaporation of the polyurethane foam and the reciprocal necking between Fe powders. The Fe foam fabricated from slurry coating via sintering on polyurethane foam became extremely defective in most positions. However, defects such as pores and cracks were able to impart better nanoparticle filling capability due to their higher surface area. Overall, although many pits were observed adjacent to the cracks, and though

these might cause severe faults from a mechanical perspective, more catalytic nanoparticles were able to adhere and be consolidated in these defective spaces on the Fe foam. Thus, they became advantages in terms of the catalytic aspect. However, direct deposition of only the NdNiAl catalytic nanoparticles on the Fe foam was a problem in some instances, as shown in S. Fig. 8. These included poor adhesion and shell peeling, even though Nd was doped to increase the magnetic bondability of the nanoparticles. As shown in S. Fig. 9, significant surface changes occurred in the sintering process; thus, a clumped surface appeared. The results were confirmed by direct elemental measurement using EDS analysis. The specific coating layers, marked with a white arrow, were found in the morphology of the clumped structure on the Fe foam with one impregnation. Similar layers were observed for the other struts of the foam. Furthermore, the coating layers were found to be thicker at the ends of a strut over the foam. A possible explanation for this difference in coating thickness could be the unequal agglomeration of the magnetic nanoparticles according to disproportional magnetic strength. As shown in S. Fig. 10, the bondability of the NdNiAl layers to the Fe foam seemed to have been enhanced after the addition of the NdFeB nanoparticles and the subsequent necking formation during the sintering process. Previously, it was determined that the dispersion extent and geometric shape of the NdNiAl nanoparticles were dependent on the presence of the NdFeB nanoparticles over the Fe foam when compared with the surface morphology of each single set of nanoparticles. Due to the high magnetic strength of the NdFeB nanoparticles, the agglomeration of the NdNiAl nanoparticles collapsed when the mixture of nanoparticles was dispersed over the Fe foam. As a result, the surface morphology was stabilized at the microscopic scale.

Overall, the SEM image (S. Fig. 8) reveals that when catalytic foam composed of only NdNiAl nanoparticles was integrated closely to form catalytic layers, peeled-off shells occurred due to the difference in thermal conductivity between the NdNiAl nanoparticles and the Fe foam. Their microstructure was very different from the rough, coarse surface of the original Fe foam (S. Fig. 7). After thermal reduction in H_2 gas, the agglomerated morphology of the NdFeB nanoparticles changed (S. Fig. 9), leaving thick flakes on the surface of the Fe foam. In S. Fig. 10, however, surface areas outside of the NdFeB nanoparticles are able to be seen, and the NdNiAl nanoparticles are evenly distributed after blending and sintering the mixture of both nanoparticles. This knowledge was significant for the practical application of the hybrid nanoparticles on templates for feasibility and durability tests.



S. Fig. 1. SEM images of NdNiAl nanoparticles (a), NdFeB nanoparticles (b), bimodal NdNiAl and NdFeB hybrid nanoparticles (c), EDS result (d) of the bimodal NdNiAl and NdFeB hybrid nanoparticles, with B K_{α}, O K_{α}, Fe L_{α}, Ni L_{α}, Nd M, and Al K_{α}, as well as B: 0.183, O: 0.525, Fe: 0.705, Ni: 0.851, Nd: 0.978, Al: 1.486 keV, and particle size analysis results of NdNiAl nanoparticles (e) and NdFeB nanoparticles (f).



S. Fig. 2. TEM image and elemental mapping results of NdNiAl nanoparticles.



S. Fig. 3. TEM image and elemental mapping results of NdFeB nanoparticles: The NdFeB nanoparticles exhibited phase separation among the constitutional elements due to the extremely high plasma temperature.



S. Fig. 4. A comparison of XRD analysis results for the fresh and deactivated hybrid NdNiAl–NdFeB nanoparticles after 100 h at 260.0 °C with product gases (CH₄ and H₂O).



S. Fig. 5. XPS results for (a) survey scan, (b) Nd scan, (c) Fe scan, and (d) B scan of NdFeB nanoparticles.



S. Fig. 6. Photograph (a) and SEM images of Fe template foam at low (\times 20, b), intermediate (\times 150, c), and high (\times 500, d) magnifications.



S. Fig. 7. SEM images and elemental mapping results of Fe foam at low (\times 30, a) and intermediate (\times 100, b) magnifications; with Fe phase (c) and O phase (d).



S. Fig. 8. SEM image (a) and elemental mapping results of NdNiAl nanoparticles coated on the surface of Fe foam; Al phase (b), Fe phase (c), and Nd phase (d).



S. Fig. 9. SEM image (a) and elemental mapping results of NdFeB nanoparticles coated on the surface of Fe foam; B phase (b), Fe phase (c), and Nd phase (d).



S. Fig. 10. SEM image (a) and elemental mapping results of bimodal NdNiAl and NdFeB hybrid nanoparticles coated on the surface of Fe foam; Ni phase (b), Fe phase (c), and Nd phase (d).