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Fe-based multicomponent catalysts for organic syntheses 有機合成を目指した Fe 系複合金属触媒

Fe-based multicomponent catalysts for organic syntheses

(有機合成を目指した Fe 系複合金属触媒)

This doctoral thesis discussed the use of Fe multicomponent catalysts for various organic syntheses, e.g. chemoselective hydrogenation of unsaturated carbonyls to unsaturated alcohols using Ni-Fe-based alloy catalysts; acceptorless dehydrogenation of alcohols to carbonyl compounds over Cu-Fe catalysts prepared from layered double hydroxides (LDHs) feature; and application of the Cu-Fe catalysts for one-pot synthesis of N-alkylation of aniline with benzyl alcohol. Accordingly, this thesis is basically divided into five chapters, namely chapter 1, introduction; chapter 2, selective hydrogenation of unsaturated carbonyls over Ni-Fe alloy-based catalysts; chapter 3, acceptorless dehydrogenation: Cu-Fe catalysts prepared from Cu-Fe LDHs; chapter 4, direct N-alkylation of aniline with benzyl alcohol using Cu-Fe Catalysts from LDHs feature; and chapter 5, summary.

[Chapter 1. Introduction]

In this chapter, the potential capability of multicomponent catalyst for a variety of organic reaction is discussed. Besides, the previous work from other research groups which has a relevance to the application of multicomponent catalysts for various reactions, such as selective hydrogenation of unsaturated carbonyl compounds, and acceptorless dehydrogenative reactions was also reviewed to construct the appropriateness of hypothesis and research objectives.

It has been widely known that the multicomponent catalysts can produce multiple functionalities on the catalysts and enhance catalytic performance in terms of activity, and selectivity, due to the synergistic catalysis. The cooperative catalysis may proceed through bifunctional catalysis, dual activation, electronic activation, and cascade catalysis.[1] As results, Xiaofeng et al[2] and Yuan et al[3] have proven that multicomponent Pt-Co and Au-Ag metal catalysts improved the selectivity toward carbonyl compound on the selective hydrogenation of unsaturated carbonyls and improved catalytic activity of alcohol dehydrogenation, respectively. Previously, our research group found that Ni-Sn alloy catalyst was effective for this hydrogenation of unsaturated carbonyl.[4] Herein, we investigate the potential application of nickel-iron alloy for selective hydrogenation of carbonyls to produce the corresponding unsaturated alcohols.

Generally, the multicomponent metal catalysts formed from the corresponding monocomponent catalysts prepare through co-precipitation, vapor deposition (via chemically ➔ CVD or physically ➔ PVD), and sol gel. In consequence, there are several mixing models in the bimetallic catalyst summarized by Fernando et al,[5] such as (a) core-shell structures, where a core of metal atoms are surrounded by a shell composed of a second metal atom with different types; (b) sub-cluster structure, that the two metal components have a pseudo-planar interface between them; (c) alloy that intimately mixed in either an atomically ordered or a statistically random manner, and (d) multi-shell nanoalloys where concentric shell covered by the other core metal forming “onion like” structure.

Recently, the preparation of multicomponent metal catalysts from LDHs protocols has been attracting a considerable attention due to its high metal dispersion, and compositional flexibility. The LDHs material is a layered material consisted of divalent metal cation (M^{2+}) coordinated with trivalent metal (M^{3+}) octahedrally with water and some exchangeable anion species located in interlamellar galleries, having the general formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}[A^{n-}]_{x/n}\cdot yH_2O$.[6] Moreover, the formation of intermetallic catalysts from LDHs precursor is an interesting strategy due to its flexibility on controlling particle size and acid-base property so the synergistic catalysis between two-metal species can optimize the catalytic activity. In the present thesis, we tried to synthesize the Cu-Fe catalyst from LDHs precursors for catalytic acceptorless dehydrogenation of alcohols and direct N-alkylation of aniline with benzyl alcohol through borrowing hydrogen pathway.

Therefore, the objectives of our study are: (a) to evaluate the performance of Ni-Fe alloy catalysts in selective carbonyl hydrogenation, (b) to investigate the catalytic activity of Cu-Fe catalyst prepared from Cu-Fe LDH feature for dehydrogenation reaction, and (c) to demonstrate the capability of the Cu-Fe catalysts for direct N-alkylation of aniline with benzyl alcohol.

[Chapter 2. Chemoselective Hydrogenation of Unsaturated Carbonyls over Ni-Fe Alloy-based Catalysts]

Ni-Fe alloy catalysts were simply synthesized by hydrothermal method with a subsequent reduction process by using H_2 treatment at range temperature of 523 K – 723 K. The formation of Ni-Fe alloy

was confirmed by XRD measurement that the indicated Ni-Fe alloy peaks shifted to lower angle (ca. ~ 0.3 degree) relative to the Ni(111) peak. The Ni-Fe alloy catalysts exhibited the highest activity for the hydrogenation of biomass-derived furfural among the examined second metals, such as Al, Ga, In, Co, and Ti. We also found that decreasing temperature of H_2 treatment (i.e decreasing crystallite size); e.g. Ni-Fe(2)HT-573 K (TOF = 7.93 h^{-1}) increased the activity compared to that over Ni-Fe(2)HT-673 (TOF = 3.03 h^{-1}) for furfural hydrogenation. This result suggests that low-coordinated Ni-Fe alloy was imperative for catalytic cycle. This work reveals that the alloying Ni and Fe is a key in achieving highly selective hydrogenation of C=O moiety in unsaturated carbonyl substrates. Vibrational studies using FT-IR measurement informed that furfural was physically adsorbed on the surface of Ni-Fe alloy catalyst via η^1(O) configuration. Moreover, the effect of metal/supports interface was critical; despite the high catalytic performance of Ni–Fe/TiO_2, Ni–Fe/Al_2O_3, and Ni–Fe/CeO_2, Ni–Fe alloy supported on SiO_2, and ZrO_2 catalysts were ineffective. The synthetic scope of the Ni–Fe catalyzed system has been very broad; various types of unsaturated carbonyls, such as unsaturated aromatics, unconjugated aliphatic, and a large substituent were selectively converted into the corresponding alcohols. The low selectivity for the hydrogenation of conjugated carbonyls might be due to the isomerization of unsaturated alcohols. With these results, we envision that future work with more precise control over the isomerization process would further boost the catalytic selectivity over Ni–Fe-based catalyst systems.

[Chapter 3. Acceptorless Dehydrogenation: Cu-Fe Catalysts prepared from Cu-Fe LDHs]

In the catalytic dehydrogenation, the synergic catalysis between metal and acid-base sites is crucial for the catalytic cycle. Intermetallic (IMC) catalysts derived from layered double hydroxides (LDHs) feature offers an attractive alternative since acid-base property of the IMC catalysts is controllable. Herein, inexpensive and environmentally friendly Cu-Fe catalysts prepared from LDHs structure exhibited high catalytic activity for acceptorless dehydrogenation of alcohols and indole derivatives. The catalytic reaction was performed in liquid phase condition under N_2 atmosphere. It was also confirmed that reaction was carried out under atmospheric O_2 or air decreased the catalytic activity due to the formation of CuO species which is inactive for this catalytic reaction. It was also confirmed by XRD that The Cu-Fe catalysts consisted of Cu(0) metal and mixed iron oxide allowed a remarkable dehydrogenation of 1-phenylethanol to corresponding acetophenone with a yield of 97% at 388 K for 20 h reaction under atmospheric N_2 condition. These Cu-Fe catalysts also showed outstanding activity and selectivity for an AD of various secondary alcohols under oxidant- and base-free conditions with 70 ~ 97% of yield range. The secondary unsaturated alcohols (2-cyclohexene-1-ol) was selectively dehydrogenated to unsaturated carbonyl (2-cyclohexene-1-one) with no product of C=C bond hydrogenation (cyclohexanone). These magnetically responsive Cu-Fe catalysts were also recyclable up to five consecutive runs with no loss of activity.

[Chapter 4. Direct N-alkylation of aniline with benzyl alcohol using Cu-Fe Catalysts from LDHs feature]

Cu-Fe catalysts prepared from Cu-Fe LDH precursor were subsequently applied for the direct N-alkylation of aniline with benzyl alcohol with base- and oxidant-free condition. It was found that the Cu-Fe catalysts also showed high catalytic performance to produce N-phenylaniline (amine product) and benzylaniline (imine product) at low temperature with base and oxidant-free condition. It was also observed that the product distribution was greatly influenced by changing reaction temperature, the use of a solvent, addition of a base, and amine/alcohol ratio. The optimum Cu-Fe catalyst was tolerable to proceed the one-pot N-alkylation of various aniline-based compounds with a series of alcohols to produce the amine and imine products almost exclusively. These results confirmed that the multicomponent metal catalysts prepared from LDHs protocols could significantly improved the catalytic reaction of dehydrogenative feature.

[Chapter 5. Summary]

In this thesis, we have proven that the multicomponent metal catalyst enhanced the catalytic selectivity toward carbonyl groups on the selective hydrogenation of unsaturated carbonyls, increased the catalytic activity of acceptorless alcohols dehydrogenation, and promoted the one-pot N-alkylation of anilines with alcohols.

[References]

[1] C. Sci, A. E. Allen, D. W. C. Macmillan, *Chem. Sci.* **2012**, *3*, 633–658.

[2] X. Wang, Y. He, Y. Liu, J. Park, X. Liang, *J. Catal.* **2018**, *366*, 61–69.

[3] J. Zheng, J. Qu, H. Lin, Q. Zhang, X. Yuan, Y. Yang, Y. Yuan, *ACS Catal.* **2016**, *6*, 6662–6669.

[4] Rodiansono, S. Khairi, T. Hara, N. Ichikuni, S. Shimazu, *Catal. Sci. Technol.* **2012**, *2*, 2139–2145.

[5] R. Ferrando, J. Jellinek, R. L. Johnston, *Chem. Rev.* **2008**, *108*, 845–910.

[6] C. Li, Y. Chen, S. Zhang, S. Xu, J. Zhou, F. Wang, M. Wei, D. G. Evans, X. Duan, *Chem. Mater* **2013**, *25*, 3888–3896.