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Catalysts prepared from copper–nickel ferrites for the steam reforming of methanol

Yung-Han Huang [a], Sea-Fue Wang [a, *], An-Pang Tsai [b, c], Satoshi Kameoka [b]

[a] Department of Materials and Mineral Resources Engineering, National Taipei University of Technology, 1, Sec. 3, Chung-Hsiao E. Rd., Taipei 10608, Taiwan, ROC
[b] Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan
[c] National Institute for Materials Science, 1-2-1 Sengen, Tsukuba 305-0047, Japan

HIGHLIGHTS

- Fe_3O_4-supported Cu and Ni catalysts were prepared via reduction of Ni–Cu ferrites.
- Catalysts contained nano-size Cu or Ni (5–32 nm) and mesopores (5–30 nm) on Fe_3O_4.
- Reduced $CuFe_2O_4$ showed the max H_2 production rate, while reduced $NiFe_2O_4$ the least.
- Formation of Fe–Ni alloy amplified the CO formation and poisoned the H_2 production.

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ABSTRACT

In this study, Fe_3O_4-supported Cu and Ni catalysts are prepared through reduction of Cu–Ni ($Ni_{1-x}Cu_xFe_2O_4$) ferrites. The Cu–Ni ferrites, synthesized using a solid–state reaction method, are reduced at temperatures from 240 °C to 500 °C in a H_2 atmosphere. All ferrites are characterized with granular morphology and a smooth particle surface before reduction. For the $CuFe_2O_4$, $Ni_{0.5}Cu_{0.5}Fe_2O_4$ and $NiFe_2O_4$ ferrites reduced at 240, 300, and 400 °C, respectively, nanosized Cu and/or Ni particles (5–32 nm) and mesopores (5–30 nm) are distributed and adhered on the surfaces of Fe_3O_4 supports. After increasing the reduction temperature of $NiFe_2O_4$ ferrite to 500 °C, the Ni particles and mesopores disappear from the Fe_3O_4 surfaces, which is due to the formation of a Fe–Ni alloy covering on the Fe_3O_4 surfaces. The $CuFe_2O_4$ ferrite after H_2 reduction at 240 °C exhibits the highest H_2 production rate of 149 ml STP/min g-cat at 360 °C. The existence of Ni content in the Cu–Ni ferrites enhances the reverse water gas shift reaction, and raises the CO selectivity while reducing the CO_2 selectivity. Formation of a Fe–Ni alloy exaggerates the trend and poisons the H_2 production rate.

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1. Introduction

In recent years, hydrogen has become valuable as an alternative energy source due to its cleanliness and potential applications in several conversion processes, such as fuel cells [1,2]. Pure hydrogen can be produced by steam reforming of methanol (SRM) which is an endothermic process according to the following reaction:

$$CH_3OH + H_2O \rightarrow 3H_2 + CO_2 \quad \Delta H^0_{298K} = 49.5\ \text{kJ/mol} \qquad (1)$$

To minimize the generation of carbon monoxide, which can poison the electrode and lead to a lower power density in fuel cells, it is desirable to use a catalyst with high catalytic performance for the SRM reaction at low temperatures [3–5].

Perovskite-type and spinel-type oxides have been employed to prepare oxide-supported catalysts. Small metal particles are highly dispersed by phase separation in the spinel-type or perovskite-type oxides during reduction, which leads to high activity. Kameoka et al. prepared Cu catalysts from $CuCrO_2$ and $CuFe_2O_4$ oxides using metallurgical methodology [20–22]. The high catalytic performance and good thermal stability of the composite structure comprised the nano-scale Cu particles that were homogeneously dispersed in the porous Cr_2O_3 and Fe_3O_4 matrices, which were generated by reductive decomposition of $CuCrO_2$ and $CuFe_2O_4$

* Corresponding author. Department of Materials and Mineral Resources Engineering, National Taipei University of Technology, 1, Sec. 3, Chung-Hsiao E. Rd., Taipei 106, Taiwan, R.O.C.
E-mail address: sfwang@ntut.edu.tw (S.-F. Wang).

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[20–22]. Although $NiFe_2O_4$ was reported to have a high performance for the preferential oxidation of carbon monoxide (PROX) [13], CO oxidation [14], water gas shift reaction (WGSR) [15–17] and methane combustion [18,19], it has not been evaluated for use in SRM reactions. It was reported in literature that the physical properties of ferrites could be improved by changing the cations [6–12]; however, the approach for improving the catalyst performance using spinel compounds with different metal ions has not been explored.

The aim of this work was to investigate the catalytic performance of Cu–Ni ferrite catalysts ($Ni_{1-x}Cu_xFe_2O_4$) after reduction treatment. The powder characteristics of the catalysts were characterized using X-ray diffraction (XRD), BET surface area, H_2 temperature program reduction (H_2-TPR) and scanning electron microscopy (SEM). The catalytic activity for the SRM reaction was evaluated by the H_2 production rate (ml STP min^{-1} g^{-1}-cat). The selectivity of the CO_2, CO and CH_4 gases was also calculated. The relationship among the Ni/Cu ratio, reduction conditions, the morphological and microstructure of the catalysts and the catalytic characteristics of the Cu–Ni ferrite for use in the SRM reaction was examined and discussed.

2. Experimental procedure

In this work, Cu–Ni ferrite compounds were prepared using a solid–state reaction technique [23]. Highly pure (>99.9% purity) CuO (Nikko Rica Corporation, reagent grade), α-Fe_2O_3 (Voestalpine company, reagent grade) and NiO (Seido Chemical Industry Co. Ltd., reagent grade) were used as the raw materials. Stoichiometric mixtures of the oxide powders were mixed in a methyl alcohol solution to form a homogeneous slurry followed by drying overnight at 80 °C in an oven. After drying, all of the powders were calcined in air at temperatures from 1000 to 1100 °C for 4 h, followed by re-milling in methyl alcohol for 24 h.

X-ray diffraction (XRD) measurements were performed for the phase identification of the powders, and recorded with Mac science M03XHF22 using Cu Kα (λ = 1.542 nm) radiation. High-resolution XRD measurements, using high brilliant synchrotron radiation in BL15XU (λ = 0.65297 Å) on SPring-8 at the Japan Synchrotron Radiation Research Institute, were also performed. The SEM (Hitachi SU8000) technique was employed to determine the morphology and nature of the agglomerates in the catalysts. The particle size and particle size distribution of the compounds after calcination were measured by light scattering (Zeta 1000). The surface area of the particles was determined using BET analysis. Pore structure and pore size distributions of the samples were determined using the Barrett–Joyner–Halenda (BJH) method from N_2 adsorption–desorption isotherms at 77 K (BELSORP-mini, BEL JAPAN, Inc.) with the corrected Kelvin equation (Eq. (2)) as follows:

$$R_P = \left(\frac{-2\gamma V_P}{RT}\right) \times \ln\left(\frac{P}{P_0}\right) \quad (2)$$

where R_P is the radius of the capillary, γ is the surface tension of liquid nitrogen and V_P is the liquid molar volume of nitrogen [24].

H_2 temperature-programmed reduction (H_2-TPR) measurements were performed in a conventional flow system. Samples (approximately 15 mg) were heated from room temperature to 800 °C at a heating rate of 10 °C/min and reduced in a 5% H_2-95% Ar gas mixture at a volume flow rate of 30 cm^3/min. The quantity of H_2 consumption caused by the reduction reaction of spinel compounds was recorded. Steam reforming of methanol (SRM: $CH_3OH + H_2O \rightarrow 3H_2 + CO_2$) reactions was carried out in an *in situ* conventional flow reactor at 100 kPa. The Cu–Ni ferrites were reduced in a hydrogen atmosphere at 240–500 °C prior to the reaction. The inlet partial pressures of methanol, water and nitrogen (used as a dilutant) were controlled at 35.5, 52.7, and 13.2 kPa, respectively (LHSV of CH_3OH/H_2O mixture: 25 h^{-1}, CH_3OH/H_2O = 2/3). The reaction products were analyzed by an on-line gas chromatograph (Shimadzu GC 14A) equipped with a Shincarbon column (H_2, CO, CO_2 and CH_4) under an Ar carrier gas. The data from GC equipment were recorded when the reaction was maintained at a stable state after 30 min at each temperature. The catalytic activity for the SRM reaction was evaluated by the H_2 production rate (ml STP min^{-1} g^{-1}-cat). The selectivity of the CO_2, CO and CH_4 gases was calculated using the following equations:

$$CO_2\ Selectivity(\%) = [CO_2]_{Out}/([CO_2]_{Out} + [CO]_{Out} + [CH_4]_{Out}), \quad (3)$$

$$CO\ Selectivity\ (\%) = [CO]_{Out}/([CO_2]_{Out} + [CO]_{Out} + [CH_4]_{Out}), \quad (4)$$

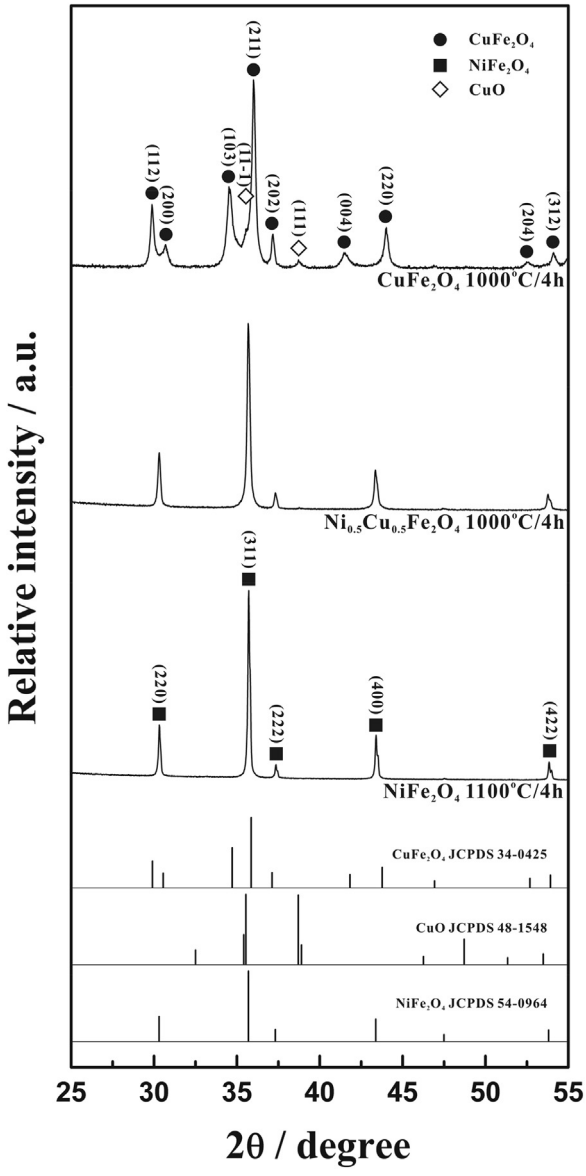

Fig. 1. XRD patterns of the Cu–Ni ferrites after calcination at different temperatures.

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