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Effects of the pretreatment of $CuNi/SiO_2$ on ethanol steam reforming: Influence of bimetal morphology

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ABSTRACT

Previous research shows that bimetallic $CuNi/SiO_2$ catalysts prepared by $NaBH_4$ reduction perform well in ethanol steam reforming (ESR) compared to their monometallic counterparts. More importantly, these bimetallic catalysts yield simple products of only H_2, CO_2, CO, and CH_4, at high ethanol conversions. The as-prepared catalysts contain mainly alloy nanoparticles. This study shows that ESR performance can be further improved by catalyst pretreatment, i.e., calcination at 400 °C followed by reduction at 350 °C (coded hereafter as calc-CuNi-R350). Characterization using in situ X-ray diffraction (XRD) and X-ray absorption fine structure (XAFS) indicates that the calc-CuNi-R350 catalyst contains Cu-rich nanoparticles in close proximity to NiO nanocrystals. Compared to the uncalcined but reduced catalyst (asis-CuNi-R350), the calc-CuNi-R350 catalyst had higher turnover frequency for ethanol conversion and for acetaldehyde conversion and lower selectivity to CH_4 formation. Increasing the steam/ethanol (S/E) ratio from 6 to 9 significantly suppresses CH_4 formation from this calc-CuNi-R350 catalyst. The results of this study suggest that the interface between NiO and Cu-rich nanoparticles improves ASR/AD (acetaldehyde steam reforming/acetaldehyde decomposition) selectivity via stabilizing the methyl (or methylene) groups from the decomposition of acetaldehyde intermediate and consequently decreases the probability of CH_4 evolution. If CH_4 evolution is suppressed, the ESR reaction produces only H_2, CO, and CO_2. This makes ESR an attractive sustainable route for H_2 production.

1. Introduction

Currently, methane steam reforming is largely used for commercial hydrogen production and methanol steam reforming (MSR) is extensively studied for boosting devices such as fuel cells. Bioethanol is considered a carbon-neutral fuel and therefore ethanol steam reforming (ESR) is a sustainable method for producing hydrogen. ESR derives many side products other than the expected H_2 and CO_2 and its reaction pathways and mechanism have recently been reviewed [1]. The more complicated reaction pathway of ESR compared to MSR arises from the necessity to break the C—C bond of ethanol. The much-used Cu catalysts for MSR are ineffective to break the C—C bond while Ni, Co, Ir, and Rh are effective [2,3]. Ni is relatively inexpensive and therefore many tests of Ni catalysts for ESR have been reported. However, coke formation is severe in ESR over Ni catalysts. Two approaches are typically adopted to resolve this problem, namely, using bimetal (or multi-metal) catalysts and using active support such as CeO_2 which can contribute lattice oxygen to enhance steam reforming. Trimm [4,5] mentioned that CeO_2 support can decrease the coke formation over Ni catalysts during steam reforming. Choi et al. [6] reported that $Ni/CeO_2–Al_2O_3$ had a lower coking tendency than Ni/Al_2O_3 during isooctane autothermal reforming. When a second metal is used, the type of metal, the composition and the alloy formation are key factors determining the catalytic performance [7]. Different metals have been reported to cope with Ni for ESR, such as Co, Cu, Rh, Pt. Among these second metals, Cu is relatively inexpensive and it enhances ESR performance with decreased coking tendency [8–14]. In general, ESR performance can be rated by the ethanol conversion rate, the hydrogen yield and the coking tendency of catalyst. We reported previously that a Cu/Ni ratio of 1 resulted in better ESR performance than other Cu/Ni composition over the $CuNi/SiO_2$ catalyst prepared by $NaBH_4$ reduction [11]. However, the optimal Cu/Ni composition seems to depend on the type of support, the catalyst preparation method and even the operating temperature. For example, Fierro et al. [15] reported that Cu doped Ni/Al_2O_3 showed the highest H_2 selectivity for oxidative ESR at 923 K but it became the worst comparing to that doped with Zn, Fe, and Cr when operated at 1073 K. Mariño et al. [8–10] examined the effect of adding Cu to $4\%Ni/K–Al_2O_3$ and reported that 2% Cu addition showed the highest hydrogen yield. Wang reported that $10\%Ni–5\%Cu/MgO–Al_2O_3$ was superior to catalysts with different Cu/Ni ratio [16]. De Rogatis et al. [14] reported that the ESR

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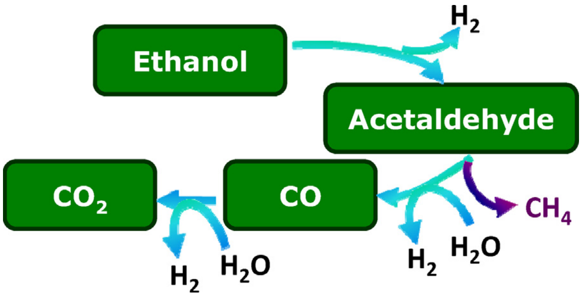
product distribution was not significantly changed by the Cu/Ni ratio of Al_2O_3-supported CuNi catalysts. The formation of Cu–Ni alloy was considered beneficial for ESR [12,14,17]. However, the different Cu/Ni ratios reported in these references imply a need to resolve the active bimetallic structure such that the catalyst can be improved further.

The other approach utilizes the metal–support interaction to enhance the ESR performance and the stability of Ni catalysts. Support can have significant influence on the catalytic performance; for example, using acidic support can cause more dehydration and dehydrogenation during ESR which lead to high coking tendency. Additives such as K, Mg, and La are frequently used to modify Al_2O_3 support where an optimal amount of basic additives is frequently sought after. Youn et al. [18] reported that the best oxidative ESR performance can be obtained when using an intermediate acidity support for Ni catalysts, whereas Furtado et al. [19] reported that the acidity of support had no effect on the oxidative ESR over NiCu catalysts. Additives not only change acid–base property but can also influence Ni dispersion [20,21], create a carbon reservoir [22], or provide high-temperature stability [21,23]. The multiple roles that the additive may play make its optimization a complex issue. Another type of supports used for suppressing coke formation is reducible oxides, where surface oxygen from oxide may participate and consequently enhance reaction performance. Xu et al. examined Ni/CeO_2 for ESR and proposed that Ce(III) at Ni-CeO_2 interface can provide OH groups to react with the methyl groups from C—C bond breaking over Ni metal [24]. However, formation of CH_4 and coke are still present under their test conditions. Similar uses of reducible oxide support for mono- and bi-metallic catalysts have been reported for enhancing ESR reaction. For example, $Ce_xZr_{1-x}O_2$ has been examined as the support for Ni [25] and CeO_2 [26], $Ce_xZr_{1-x}O_2$ [27], and $CeGdO_x$ [28] for CuNi catalysts. In such cases of using reducible oxide support, increasing metal–support interface is usually the primary concern in catalyst preparation and the promoting effect is usually attributed qualitatively to the participation of surface oxygen.

Although different catalysts have been reported for ESR, ESR is not as efficient a hydrogen production reaction as MSR. ESR usually runs at a much higher steam ratio and a much higher reaction temperature than MSR. Though high reaction temperatures increase cracking activity, they also lead to coke formation and high energy consumption. The reverse water gas shift reaction is also favored at high temperatures, resulting in increased CO/H_2 ratio that may not be suitable for downstream uses such as fuel cells. Palma and co-workers [29–32] recently addressed the advantages of decreasing the reaction temperature of ESR and Pt/CeO_2 and Pt-Ni/CeO_2 were reported as effective catalysts. Approaches such as using membrane reactor to promote ESR were also reported [33,34] for decreasing the reaction temperature of ESR. Lower reaction temperatures are desirable and ideally, ESR products should include only H_2, CO, and CO_2, as in the case of MSR. If successful, this would make ESR an effective and sustainable route for H_2 production. Our previous report demonstrated that using Cu–Ni bimetallic catalysts can limit the ESR products to include only H_2, CO, CO_2, and CH_4 [11], and a reaction scheme (Scheme 1) was proposed. Reducing CH_4 formation is a prerequisite to simplifying Scheme 1 and improving ESR performance for H_2 production. This study reports that CH_4 formation can be reduced, though not eliminated, by changing the pretreatment of 5% Cu_1Ni_1/SiO_2 catalyst. Morphology characterization by TPR, XRD, and EXAFS suggests that mixed phases in Cu_1Ni_1/SiO_2 achieve more efficient ESR than the alloy phase. This is attributed to the enhanced acetaldehyde steam reforming and the enhanced water gas shift pathways of Scheme 1 by the presence of alloy–NiO interface.



Scheme 1. A simple ESR reaction pathway.

2. Experimental

2.1. Preparation of catalysts

Supported 5 wt.% Cu, Ni, and bimetallic Cu–Ni (1/1) catalysts were prepared [11] by incipient-wetness impregnation of metal (Cu and Ni) nitrate (Aldrich, 98%) aqueous solution on SiO_2 support (Davison 952, 300 m^2/g, used after calcinations at 550 °C). After impregnation, catalysts were dried at 25 °C under rough vacuum generated by a rotary pump. Each catalyst was then dispersed in H_2O and stirred for 10 min. A 5% $NaBH_4$ (diluted from Aldrich, 98.5%) solution was then added drop-by-drop at room temperature until $NaBH_4$/metal = 5 (molar ratio) [11]. After additional stirring for 30 min, the solid was recovered by centrifugation, washed thoroughly with H_2O and then vacuum dried at room temperature. The supernatant was examined by ICP-AES and no loss of Cu or Ni was evident. The as-prepared catalysts (denoted as asis-) were then calcined in air at 400 °C for 5 h (denoted as calc-).

2.2. Characterizations

Temperature-programmed reduction (TPR) analysis was performed at 5 °C/min using 10% H_2 in nitrogen and a TCD detector; the H_2O formed during TPR was trapped by a molecular sieve column installed prior to the detector. The catalyst was typically purged by He at 50 °C till TCD became stable and then switched to H_2/N_2 flow and the temperature was ramped. For metal surface area analysis, the catalyst was pretreated by H_2 flow at the target temperature for 1 h, cooled to 25 °C under He, and then subjected to N_2O flow (50 mL/min) at 25 °C for 30 min. The catalyst bed was then purged with He and the O_{ad} from N_2O adsorption was quantitatively analyzed by the H_2 consumption in a subsequent TPR experiment. Metal dispersion was calculated by assuming an O_{ad}/M_S ratio of 1/2, where M_S represents the surface atoms of either Cu or Ni. This O_{ad}/M_S stoichiometry of 1/2 is typically used for the evaluation of Cu_S but it was doubted for Ni_S due to the possible exchange of surface and subsurface oxygen over Ni [35]. However, the metal dispersion obtained by assuming $O_{ad}/M_S = 1/2$ is close to the calculated dispersion of Cu (or Ni) particles based on the average size obtained from XRD and TEM [11].

In situ XRD was performed using the beamline BL01C at the National Synchrotron Radiation Research Center (NSRRC) in Hsinchu, Taiwan. The electron storage ring operated at 1.5 GeV with a beam current of 200 mA. The XRD pattern was recorded using a wavelength of 0.5167 Å for limited angular regions at room temperature. The recorded diffraction was corrected to that of Cu Kα1 radiation at a wavelength of 1.5418 Å. Diffraction patterns were obtained at a scan rate of 10°/min with steps of 0.05° in the 2θ range from 20° to 90°. EXAFS experiments were also performed using the BL17C beamline at the NSRRC. The Ni K-edge and Cu K-edge absorbance were measured sequentially in transmission mode at room temperature. In situ analysis was carried out in a stainless