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Communication

NiCu bimetallic catalysts derived from layered double hydroxides for hydroconversion of *n*-heptane

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NiCu bimetallic catalyst with uniform NiCu dispersion has been demonstrated to provide higher activity than Pt catalyst while with similar selectivity in the reforming reaction of n-heptane. The synergies between homogeneously dispersed Ni and Cu sites account for the enhancement of activity and selectivity.

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ABSTRACT

Article history: Received 9 May 2021 Received in revised form 29 July 2021 Accepted 23 August 2021 Available online xxx Supported NiCu bimetallic catalysts have been produced *in-situ* on commercial Al_2O_3 by using layered double hydroxides as precursors. The resulting catalysts show a uniform Ni and Cu distribution, thus providing good activity and selectivity in the reforming reaction of *n*-heptane. The catalytic performance has been found to depend on the Cu/Ni ratio, revealing the synergic catalysis between homogeneously dispersed Ni and Cu sites. The good catalysis of NiCu

Keywords: n-Heptane reforming NiCu bimetallic catalysts Synergic catalysis Uniform distribution Layered double hydroxides bimetallic catalysts makes it possible to partly or even completely replace Pt with NiCu bimetallic catalysts.

Supported Pt is a common catalyst for the catalytic reforming reaction [1-4]. Considerable efforts have recently been dedicated to the development of low-cost and highly efficient non-platinum reforming catalysts, and great progress has been made with tungsten carbide [5], Mo-based catalysts such as Mo₂C [6], MoO_xC_y [7] and MoO_x [8-10], as well as supported Ni [11-13] and Co [13] catalysts. The great challenges with non-platinum reforming catalysts originate from substantial hydrogenolysis and cracking reactions [14], which result in low isomerization selectivity. Increasing the dispersion of supported metals has been found to contribute to isomerization selectivity [15]. For example, Ni-La/HY catalyst exhibits higher isomerization selectivity than Ni/HY in the hydroconversion of n-C₈ because the metal dispersion has been improved by rare earth addition [15]. Yet the reforming performance of non-noble metal catalyst has not been reported to reach that of Pt catalyst. The bimetallic catalyst, in which small amount of platinum is used together with non-noble metal components such as Ni [16,17] or Cu [18], is till now a good choice to obtain good activity and selectivity while reduce the cost of catalysts. For example, with proper Pt proportions, the Ni-Pt bimetallic catalysts afford higher activity and are more selective to di-branched alkanes than Pt monometallic catalyst in the hydroconversion of $n-C_6$ reaction [17]. The complete replacement of platinum with transition metals in the paraffin reforming process remains a great challenge.

In this work, the feasibility to partly or even completely replace Pt with NiCu bimetallic catalyst has been demonstrated, with Ni and Cu in a highly homogeneous dispersion by using Ni and Cu containing layered double hydroxides as precursors. Layered double hydroxides (LDHs), a hydrotalcite-like compound, have been demonstrated to be excellent precursors for supported metal catalysts [19-23]. This work reports the homogeneously dispersed Ni and Cu centers, which affords good activity and selectivity in the reforming reaction of *n*-heptane. The NiCu bimetallic catalyst even provides higher activity than Pt catalyst while with comparable selectivity.

The Ni and Cu containing ZnAl-LDHs precursors were prepared *in situ* on γ -Al₂O₃ support according to the reported method [24]. The Cu/Ni molar ratios were controlled as 0.61, 1.19, 2.11 and 3.17 as determined by inductively coupled plasma optic emission spectrometer (ICP-OES) analysis (Table S1 in Supporting information). The Ni and Cu containing ZnAl-LDHs precursors were activated in the reactor by first calcining in the air at 550 °C and then reducing with H₂ flow at 500 °C. The resulting sample was denoted NiCu_x-ZnAl-LDO@Al₂O₃ (x represents the Cu/Ni molar ratio). The reaction was initiated by introducing *n*-C₇ into the reactor, and the products were analysed on-line with a gas chromatograph. For comparison, the supported NiCu bimetallic catalyst with a Cu/Ni molar ratio of 1.14 was also prepared by incipient wetness impregnation method (denoted NiCu_{1.14}/ZnAl-LDO@Al₂O₃), followed by the same calcination and reduction process as for $NiCu_x$ -ZnAl-LDO@Al₂O₃.

The powder X-ray diffraction (XRD) patterns pattern for each NiCux-ZnAl-LDHs@Al2O3 sample (Fig. 1A and Fig. S1 in Supporting information) clearly illustrates the [003], [006] and [012] reflections characteristic of the structure of hydrotalcites [25], indicating the formation of LDHs on the γ -Al₂O₃ support. No other crystalline phases were detected in addition to γ -Al₂O₃ support and LDHs. Flake-shaped NiCuZnAl-LDHs crystallites can be observed from the SEM image (Fig. 1B) as growing in interlaced direction on the surface of Al₂O₃. As can be seen from the cross section of NiCuZnAl-LDHs@Al₂O₃ (Fig. 1C), LDHs phase grows on the Al₂O₃ surface in a thickness of about 292 nm, with the edges of LDH slabs tightly adhered to Al₂O₃ spheres. The growths of LDHs and the corresponding LDO results in the specific surface area increasing from 187 m²/g (for γ -Al₂O₃) to 218 m²/g (for NiCu_{1.19}-ZnAl-LDHs@Al₂O₃) or 212 m²/g (for NiCu_{1.19}-ZnAl-LDO@Al₂O₃), probably because the LDHs or LDO crystallites raise the surface roughness. The calcination and reduction cause no visible destruction of the LDH morphology or change in surface area on Al₂O₃ surface, and the resulting NiCu_{1.19}-ZnAl-LDO@Al₂O₃ well retains the interlaced arrangement of flake-shaped slabs (Fig. 1D).



Fig. 1. (A) XRD patterns of (a) γ -Al₂O₃, (b) NiCu_{1.19}-ZnAl-LDHs@Al₂O₃ with a Cu/Ni molar ratio of 1.19; (B) SEM images of the surface; (C) the cross section of the NiCu_{1.19}-ZnAl-LDHs@Al₂O₃; and (D) SEM images of NiCu_{1.19}-ZnAl-LDO@Al₂O₃ obtained from NiCu_{1.19}-ZnAl-LDHs@Al₂O₃.

The transmission electron microscopy (TEM) image (Fig. 2A) shows that the metal nanoparticles are homogeneously dispersed in NiCu_{1.19}-ZnAl-LDO@Al₂O₃. The particles are in a narrow size distribution from 1.9 nm to 4.2 nm with the maximum of around 3.0 nm, and the lattice spacing of the exposed NiCu (111) facet is 0.206 nm in the high-resolution TEM (HRTEM) image (inset in Fig. 2A). The high angle annular dark-field scanning

transmission electron microscopy (HAADF-STEM) image (Fig. 2B) indicates a uniform distribution of the metal nanoparticles, just as observed from the TEM image. The STEM-energy dispersive X-ray (EDX) elemental mapping (insets in Fig. 2B) displays that the Ni and Cu elements are distributed homogeneously and almost in the same position. The observations from HRTEM image and EDX mapping illustrate a NiCu alloy structure, which is consistent with an earlier report [26]. As a comparison, the metal particles in the NiCu_{1.14}/ZnAl-LDO@Al₂O₃ are diverse in morphology (Fig. 2C), with a broader size distribution from 1.7 nm to 6.0 nm, as observed in TEM image. Separated Ni and Cu particles with both (111) facet exposed are observed in HRTEM image (inset in Fig. 2C). The HAADF-STEM image provides a more obvious difference in the metal distribution between NiCu_{1.14}/ZnAl-LDO@Al₂O₃ and NiCu_{1.19}-ZnAl-LDO@Al₂O₃). The metal particles are observed to be in a continuous and more chaotic distribution in the HAADF-STEM image of NiCu_{1.14}/ZnAl-LDO@Al₂O₃, with visible aggregation (Fig. 2D). The EDX image (insets in Fig. 2D) exhibit a discrepant Ni and Cu element distribution. In the XPS spectra (Fig. 3), the binding energies of Ni^0 and Cu^0 [27,28] are measured as 852.7 and 932.8 eV for NiCu_{1.19}-ZnAl-LDO@Al₂O₃ (Fig. 3A), 0.2 and 0.3 eV higher than that for NiCu_{1.14}/ZnAl-LDO@Al₂O₃ (Fig. 3B), consistent with better NiCu dispersion in NiCu_{1.19}-ZnAl-LDO@Al₂O₃. The adjacent binding energy at 855.8-856.9 eV in the Ni 2p3/2 XPS spectra originates from a high-spin divalent state of Ni²⁺ in the sample [27]. When nickel is alloyed with copper, changes in the electronic properties of nickel result in displacement of BEs to lower values depending on the copper content.



Fig. 2. TEM image (A) and HAADF-STEM image (B) of catalyst NiCu_{1.19}-ZnAl-LDO@Al₂O₃; TEM image (C) and HAADF-STEM image (D) of catalyst NiCu_{1.14}/ZnAl-LDO@Al₂O₃. Insets in (A) and (C) are the HRTEM images and the particle size frequency distribution histograms. Insets in (B) and (D) are the elemental mapping images of Ni and Cu for the corresponding sample, Scale bar: 20 nm.



Fig. 3. Ni (A) and Cu (B) 2p XPS spectra for (a) NiCu_{1.14}/ZnAl-LDO@Al₂O₃, (b) NiCu_{1.19}-ZnAl-LDO@Al₂O₃, and (c) 0.17% Pt/ NiCu_{1.19}-ZnAl-LDO@Al₂O₃.

In the hydro-conversion of heptane $(n-C_7)$ (Table 1), NiCu_{1.19}-ZnAl-LDO@Al₂O₃ as the catalyst (Table 1, entry 1) shows visibly higher n-C7 conversion, higher specific activity, higher i-C₇ selectivity, and lower C₁-C₄ selectivity than NiCu_{1.14}/ZnAl-LDO@Al₂O₃ (Table 1, entry 2). The n-C₇ conversion over NiCu_{1.19}-ZnAl-LDO@Al₂O₃ is even higher than over Pt/ZnAl-LDO@Al₂O₃ with a 0.32% Pt loading (Table 1, entry 3), while with almost the same selectivity. The better apparent activity and isomerization selectivity of NiCu1.19-ZnAl-LDO@Al2O3 is supposed to owe to the well-alloyed structure with NiCu uniform distribution. As revealed by the XPS results, the in situ exsolution of NiCu from LDHs layers provides stronger metalsupports interactions that leads to Ni and Cu centers more electron-deficient, which well accounts for the higher activity of NiCu_{1.19}-ZnAl-LDO@Al₂O₃ than NiCu_{1.14}/ZnAl-LDO@Al₂O₃. According to previous observation [29], more highly are metal centers dispersed, more is C-C cleavage inhibited. So the better selectivity of NiCu_{1.19}-ZnAl-LDO@Al₂O₃ than NiCu_{1.14}/ZnAl-LDO@Al₂O₃ could also be well explained. The use of Pt in 0.17% loading together with NiCu_{1.19} bimetallic catalyst promotes both of $n-C_7$ conversion and $i-C_7$ selectivity, while largely reduces the C_1 - C_4 selectivity (Table 1, entry 6). The specific activity on 0.17% Pt/NiCu_{1.19}-ZnAl-LDO@Al₂O₃ is 268% higher than that on 0.32%Pt/ZnAl-LDO@Al2O3. The significant increase in specific activity (normalized by moles of Pt) can be attributed to the contribution of NiCu. The ICP results and TEM/STEM images show that the Pt loading makes no visible impact on components of Ni or Cu and the homogeneous distribution of NiCu elements (Table S1 and Fig. S2 in Supporting information). The NiCu particles retain narrow distribution sized from 3.8 nm to 6.3 nm. In the XPS spectra (Fig. 3), a visible increase in the BEs of Ni $2p_{3/2}$ and Cu $2p_{3/2}$ is observed with Pt loaded, illuminating the electron transfer from NiCu to Pt atoms. Therefore, the promotion of catalysis observed with 0.17%Pt/NiCu1.19-ZnAl-LDO@Al2O3 could originate from the synergies of NiCu and Pt centers. Similar synergy effect of the metal active sites was previously observed for the Ir-Pt/Al₂O₃ catalyst prepared by organometallic grafting method in the ring opening reaction of methyl-cyclopentane [30].

Table 1

Catalytic results for the hydroconversion of $n-C_7^a$.

| Entry | Catalyst ^b | Conversion |
|-------|---|------------|
| | | (%) |
| | | |
| 1 | NiCu _{1.19} -ZnAl-LDO@Al ₂ O ₃ | 33.8 |
| 2 | NiCu _{1.17} /ZnAI-LDO@Al ₂ O ₃ | 24.9 |
| 3 | 0.32%Pt/ZnAl-LDO@Al ₂ O ₃ | 22.2 |
| 4 | 0.15%Pt/Ni-ZnAl-LDO@Al ₂ O ₃ | 44.6 |
| 5 | 0.16%Pt/NiCu _{0.61} -ZnAI-LDO@Al ₂ O ₃ | 39.7 |
| 6 | 0.17%Pt/NiCu _{1.19} -ZnAl-LDO@Al ₂ O ₃ | 42.6 |
| 7 | 0.17%Pt/NiCu _{2.11} -ZnAl-LDO@Al ₂ O ₃ | 65.7 |
| 8 | 0.17%Pt/NiCu _{3.17} -ZnAl-LDO@Al ₂ O ₃ | 85.0 |
| 9 | 0.14%Pt/Cu _{1.21%} -ZnAI-LDO@Al ₂ O ₃ | 27.0 |
| 10 | 0.16%Pt/Cu _{3.91%} -ZnAI-LDO@Al ₂ O ₃ | 44.4 |

^a Reaction conditions: 500 °C, 0.7 MPa, H₂/*n*-C₇ = 6, WHSV = 4 h⁻¹.

^b The loadings of Ni and Cu are shown in Table S1.

^c The specific activities representative moles of *n*-heptane conversion on per mol metal per hour; specific activities are normalized by moles of (Ni + Cu) for NiCu-containing samples (without Pt), and are normalized by moles of Pt for Pt-containing samples.

To better understand why the reforming catalysis of Ni and Cu even better than supported Pt, the Cu/Ni molar ratios (Table S1) have been varied in this work. As shown in the XPS spectra (Fig. 4), in comparison with Ni-ZnAl-LDO@Al₂O₃, Cu introduction decreases the binding energy (BE) of Ni $2p_{3/2}$ (Fig. 4A) slightly, and meanwhile the BE of Cu⁰ in NiCu_{0.61}-ZnAl-LDO@Al₂O₃ rises in comparison to Cu-ZnAl-LDO@Al₂O₃ (Fig. 4B), consistent with the electron transfer from Cu to Ni. With increasing Cu/Ni ratio, both of Ni⁰ and Cu⁰ BEs successively increases. But the reason for the increase in the BEs needs more investigations. Similar trends are observed on Pt-containing samples (Figs. 4C and D).



In the hydro-conversion of $n-C_7$, in comparison with Ni catalyst without Cu (Table 1, entry 4), the introduction of Cu in a Cu/Ni ratio of 0.61 decreases the n-C₇ conversion while improves the isomerization selectivity visibly (Table 1, entry 5). With the Cu/Ni ratio increasing, n-C7 conversion, specific activity, and toluene selectivity all increase, while the isomerization selectivity shows a first increasing and then decreasing change (Table 1, entries 5 to 8). The dependence of catalytic activity and selectivity on the Cu/Ni ratio of NiCu bimetallic catalyst indicates the synergic catalysis between highly homogeneous Ni and Cu sites [31]. The introduction of Cu in a Cu/Ni ratio of 0.61 increases the electronic density of Ni site, accounting for the on Pt/NiCu_{0.61}-ZnAl-LDO@Al₂O₃ activity reduction in Pt/Ni-ZnAl-LDO@Al₂O₃. comparison to The activity enhancement with increasing Cu/Ni ratio is well consistent with the successive decreases in the electronic density of both Cu and Ni sites.

The introduction of Cu inhibits the hydrogenolysis and/or cracking reactions, giving a reduced C_1-C_4 selectivity (Table 1, entries 4 to 8). But a visible inhibition of C_1-C_4 selectivity needs a higher Cu loading when no Ni is present (Table 1, entries 9 and 10). The toluene selectivity increases with Cu/Ni ratio (Table 1, entries 5 to 8), but not with the amount of single Cu (Table 1, entries 9 and 10), indicating the role of synergic catalysis between Cu and Ni sites in the improvement of toluene selectivity. When a small amount of Cu added, the XPS show that the binding energy of Ni shifts toward a low energy of 0.3 eV, and the binding energy of Cu increases 0.3 eV (Fig. 4). The changes of electronic structure of the metals result in a slight decrease in catalytic activity. Further increases successively. The activities of catalysts show an increasing trend and the selectivity

of toluene increase in sequence. The dehydrogenation ability of the metals is enhanced with the binding energy of metals increasing. The selectivity of isomerization increases at first and then decreases, while the cleavage selectivity shows an opposite trend, but the magnitude of the change is relatively small.

In the H₂-TPR profiles (Fig. S3 in Supporting information), the reduction temperature for Ni (II) gradually decreases from 596 °C to 481 °C with increasing Cu/Ni ratio, while the reduction temperature of Cu (II) decreases from 341 °C to 254 °C. Additional hydrogen consumptions are observed at 325 °C for NiCu_{1.19}-ZnAl-LDO@Al₂O₃ and 288 °C for NiCu_{2.11}-ZnAl-LDO@Al₂O₃, which suggests the possible formation of NiCu alloy phase. But the hydrogen consumption at 287 °C almost diminishes for NiCu_{3.17}-ZnAl-LDO@Al₂O₃.

The isomerization selectivity on 0.16%Pt/Cu_{3.91%}-ZnAl-LDO@Al2O3 is 142% higher than on 0.15% Pt/Ni-ZnAl-LDO@Al₂O₃. The isomerization reaction rate has been reported highly dependent on the acidic property of catalysts [4]. But there is no significant difference in the amount and strength of acidic sites between 0.16%Pt/Cu_{3.91%}-ZnAl-LDO@Al₂O₃ and 0.15% Pt/Ni-ZnAl-LDO@Al2O3, based on NH3-TPD profiles (Fig. S4 in Supporting information). So it can be deduced that the Cu promote isomerization selectivity by inhibiting sites hydrogenolysis reaction. The synergies of Ni and Cu sites on alloy phase is mainly responsible for the higher isomerization selectivity observed with NiCu_{1.19}-ZnAl-LDO@Al₂O₃ and NiCu_{2.11}-ZnAl-LDO@Al₂O₃ than with other catalysts.

In summary, NiCu bimetallic catalyst with uniform NiCu dispersion has been demonstrated to provide higher activity than Pt catalyst while with similar selectivity in the reforming reaction of *n*-heptane. The synergies between homogeneously dispersed Ni and Cu sites account for the enhancement of activity and selectivity.

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Declaration of Competing Interest

The authors declare no competing financial interest.

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