

Catalysis

Design of Efficient Noble Metal Free Copper-Promoted Nickel-Ceria-Zirconia Nanocatalyst for Bio-Fuel Upgrading

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A new series of noble metal free bimetallic Cu–Ni supported ceria-zirconia catalysts (Cu–Ni/CZ) has been developed with various Cu/Ni ratios by a simple co-precipitation/impregnation method. Aqueous-phase hydrodeoxygenation (HDO) of vanillin a typical compound of lignin-derived bio-oil, in promoting biomass refining was carried out to investigate catalytic performances under 25 bar of H₂ pressure at 160°C. All the as-synthesized catalysts were thoroughly characterised employing powder XRD, Raman spectroscopy, H₂-TPR, HR-TEM, HAADF-STEM, EDS Mapping, and XPS. It was found that 15 wt% Cu on Ni/CZ (Cu–Ni/CZ–B) nanocomposite enhanced activity significantly in comparison with other bimetallic or monometallic catalysts, exhibiting ~98% of vanillin conversion and ~94% of selectivity toward 2-methoxy-4-methylphenol as a desired

product. The Cu–Ni/CZ–B catalyst shows ~4-fold increase in activity compared with Cu–Ni/CeO₂ and Cu–Ni/ZrO₂, the mono oxide supported counterparts. The superior catalytic performance with improved stability were explained by synergistic effects at the interfaces of each species, in which electron interactions between Ni, Cu, and ceria-zirconia support generated novel active sites. XRD and HR-TEM revealed that Cu–Ni bimetallic phases were created on the ceria-zirconia, which were responsible for enhancement of catalytic performance with no significant drop in catalytic activity with desired product selectivity for eleven successive catalytic cycles demonstrating the excellent stability and reproducibility of this catalyst system.

Introduction

Currently, a world faces many serious problems, due to the rapid growth of global population and urbanization, inducing tremendous consumption of energy.^[1] Fossil resources have accounted as the world's primary energy source, however the depletion of them along with increasing environmental problems motivates researchers to focus on renewable biomass resources for the production of fuels and valuable chemicals.^[2,3] To meet the global energy demands, a biomass have been attracted much attention as a sustainable and alternative energy source by replacing fossil fuels.^[1,4,5] Bio-oils, produced by fast pyrolysis of biomass, emerged as a second-generation renewable energy carrier and potential resource for replacing fossil fuels. However, due to the high oxygen components (up to 45 wt% O), instability, and immiscibility with conventional fuels, the direct usage of bio-oils with a low calorific value is

not feasible and they must be up-graded to meet the necessities of the current infrastructure.^[4,6,7] In this regard, elimination of oxygen from the pyrolytic bio-oils is the key parameter for production of bio fuels. In order to eliminate oxygen from the pyrolytic bio-oils, hydrodeoxygenation (HDO) is necessary for upgrading and effective utilization of bio-oils. Hence, effective HDO catalysts with high activity, selectivity, and stability should be developed.^[8] Various noble metal based catalysts such as Pt–Ni/ γ -Al₂O₃,^[9] Pt–Co/ γ -Al₂O₃,^[9] Pd/ γ -Al₂O₃, Pd/TiO₂, Pd/MgO, Pd/CeO₂, and Pd/C with various carbon supports (N-doped carbon mesoporous carbon, and porous organic polymer)^[10,11] have been employed for HDO of biomass compounds. However, serious coke deposition, higher cost and low selectivity toward C–O bonds are obstacles to be overcome.^[7] Sulfided Ni–Mo and Co–Mo are commonly used catalysts for the HDO of pyrolytic bio-oils as well. Because sulfur from the hydrogenated products should be removed, non-sulfur containing, noble metal free HDO catalysts are highly demanding. Ni based catalysts are good candidates which activate dihydrogen under reaction conditions.^[12] Very recently, Xia and co-workers have designed promising catalyst cobalt, nickel nanoparticles supported on nitrogen-doped carbon, and explored their catalytic performance in the hydrodeoxygenation of vanillin.^[13,14] Cu loading to Ni-based catalysts further increases the catalytic activity by decreasing the reduction temperature of Ni species, preventing the formation of carbon and limiting the sintering of active phases.^[15] Very recently, supported Ni and Cu metal oxides as HDO catalysts are developed by many research groups.^[5–8] However there are serious leaching problems with noble metal and transition

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metal (Ni, Cu) supported catalysts during catalytic processes, because of weak interactions between metal nanoparticles (NPs) and support, resulting in a significant decrease in the catalyst recyclability accompanied with poor dispersion of NPs on the support. For the development of highly active and stable HDO catalysts, Mo, W, Co, Mn, Zr, Ce, Y, Sr and La have been used for the activation of oxygen-containing compounds.^[16,17] For the activation of C–O bonds ceria (CeO₂) can be used to provide vacancies for redox properties.^[18] Very recently, it was reported that doped ceria supported metal oxides exhibited high hydrogenation and HDO activity without leaching, due to the strong synergistic effect between metal and support.^[19,20] By doping, the redox properties of CeO₂ were enhanced by tuning the redox cycle with changing oxidation states from the 3+ to 4+ ($2\text{CeO}_2 \rightleftharpoons \text{Ce}_2\text{O}_3 + \text{O}$).^[19,20] Recent reports also demonstrated that doped ceria with zirconia increased the number of oxygen vacancies, lowered the reduction temperature of metals by dissociate hydrogen.^[21,22] Ceria-zirconia mixed oxides regarded as efficient supports for hydrogenation reaction by preventing carbonaceous formation due to their specific redox properties. As well as active metal species, a nature of support plays a crucial role by determining catalytic performances for the hydrogenation reactions. Postole *et al.*^[23] reported that doping also influenced surface acid-base properties of ceria-zirconia in HDO process. The incorporation of Ni²⁺ into the ceria-zirconia structure was proven to enhance activity in hydrogenation reaction with retarded deactivation to the single ceria and other commercial supports.^[24,25] Introduction of second metals such as Fe, Cu, Co, and Pd to Ni further enhanced catalytic performances, creating strong metal support interactions and redox properties of the catalysts. Q. Guo *et al.* reported that HDO efficiency of algae bio-oils over bimetallic Ni–Cu/ZrO₂ catalysts can be tuned with the amount of Cu.^[21] Transition metal alloys such as Ni–Cu are widely used in hydrogenation and HDO reactions, due to their unique structural and redox properties, as compared to pure transition metals.

Herein we developed noble metal free Cu promoted Ni supported ceria-zirconia catalysts (Cu–Ni/CZ) for aqueous phase HDO of vanillin. Vanillin, as a typical compound of lignin derived from bio-oils is converted catalytically through hydrogenation and hydrogenolysis. Catalytic HDO of vanillin is considered as one of a key reaction in many bio refinery schemes. In particular, Cu on Ni/CZ catalyst was well-known for significantly high HDO activity in comparison with other bimetallic, monometallic, and the single support (Cu–Ni/CeO₂ and Cu–Ni/ZrO₂) counterparts. In this study, bimetallic Cu–Ni/CZ catalysts with various Cu/Ni ratios prepared by co-precipitation followed by impregnation were designed for the catalytic HDO of vanillin under 25 bar of H₂ at 160°C. Powder X-ray diffraction (XRD), Raman, H₂-temperature programmed reduction (TPR), high resolution-transmission electron microscopy (HR-TEM), high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM), electron dispersive spectroscopy (EDS)-Mapping, and X-ray photoelectron spectroscopy (XPS) were utilized to characterize the Cu–Ni/CZ catalysts. The combined results of characterization and catalytic

HDO provide insights of active sites in novel Cu–Ni/CZ catalysts, which improved stability as well as activity by a synergistic interfacial effect of bimetallic mixed oxides. To the best of our knowledge, the developed bimetallic mixed oxide catalysts in this study are considered as the most efficient catalyst with high stability of HDO catalysts.

Results and Discussion

The prepared catalysts were tested for selective HDO of vanillin which was converted to 2-methoxy-4-methylphenol as a major product. Cu–Ni/CZ-A catalyst (10 wt% Cu on Ni/CZ) was tested first with a solution of vanillin (300 mg, 1.8 mmol) in water (70 mL) under 25 bar of hydrogen at 160°C. The Cu and Ni contents in the catalysts are measured by inductive coupled plasma-optical emission spectroscopy (ICP-OES) analysis (Table S1, SI). The monometallic Cu/CZ and Ni/CZ catalysts along with the bimetallic catalysts Cu–Ni/CZ-B (15 wt% Cu on Ni/CZ) and Cu–Ni/CZ-C (20 wt% Cu on Ni/CZ) were also evaluated under identical reaction conditions in HDO of vanillin for comparison study (Figure 1a). The contents of products and reactants were determined by using a GC/MS based on authentic samples. The corresponding Cu–Ni/CZ-B catalyst exhibited superior catalytic performance in HDO reaction of vanillin with ~98% of conversion and ~94% of selectivity toward 2-methoxy-4-methylphenol as a desired product. On the other hand, 91% and 84% of conversion with 98% and 86% of selectivity toward 2-methoxy-4-methylphenol was achieved after 12 h for Cu–Ni/CZ-A and Cu–Ni/CZ-C catalysts, respectively (Figure 1a). On the contrary, substantially lower catalytic activities were found for monometallic Cu/CZ and Ni/CZ catalysts with 58% and 54%, respectively. When the bare Cu–Ni bimetallic catalyst was tested for vanillin HDO reaction under optimized reaction conditions, the conversion was drastically decreased to 28% with a selectivity of 85%. Conversion of vanillin and product selectivity profiles are presented for all monometallic and bimetallic catalysts in Figure 1b. The highly improved catalytic performance of the Cu–Ni/CZ-B catalyst could be attributed not only due to its higher degree of metal NPs dispersion but also the support effect from mixed oxides and Synergetic effects or the bifunctional effect, including the electronic effect, geometric and other interfacial effects caused by the interaction of the two metal components present may contribute to the enhanced catalytic performance in bimetallic catalysts.^[21] Homogeneous dispersion of bimetallic NPs without agglomeration and hydrophilic nature combined with CeO₂-ZrO₂ support facilitated strong interaction between reactant and catalyst during the reaction. In particular, existence of ceria by having electron-rich/electron-deficient states ($2\text{CeO}_2 \rightleftharpoons \text{Ce}_2\text{O}_3 + \text{O}$) created strong electronic interaction between Ni and Cu bimetallic NPs on CeO₂-ZrO₂ support, favouring preferential hydrogenation which was consistent with the previous reports by Srinivas *et al.*^[26] Ratnasamy *et al.* also observed that interactions between ceria-zirconia support and metal NPs prepared by the deposition/co-precipitation was responsible for the enhanced catalytic activity in steam reforming of methane.^[26] Very recently, diminishment of

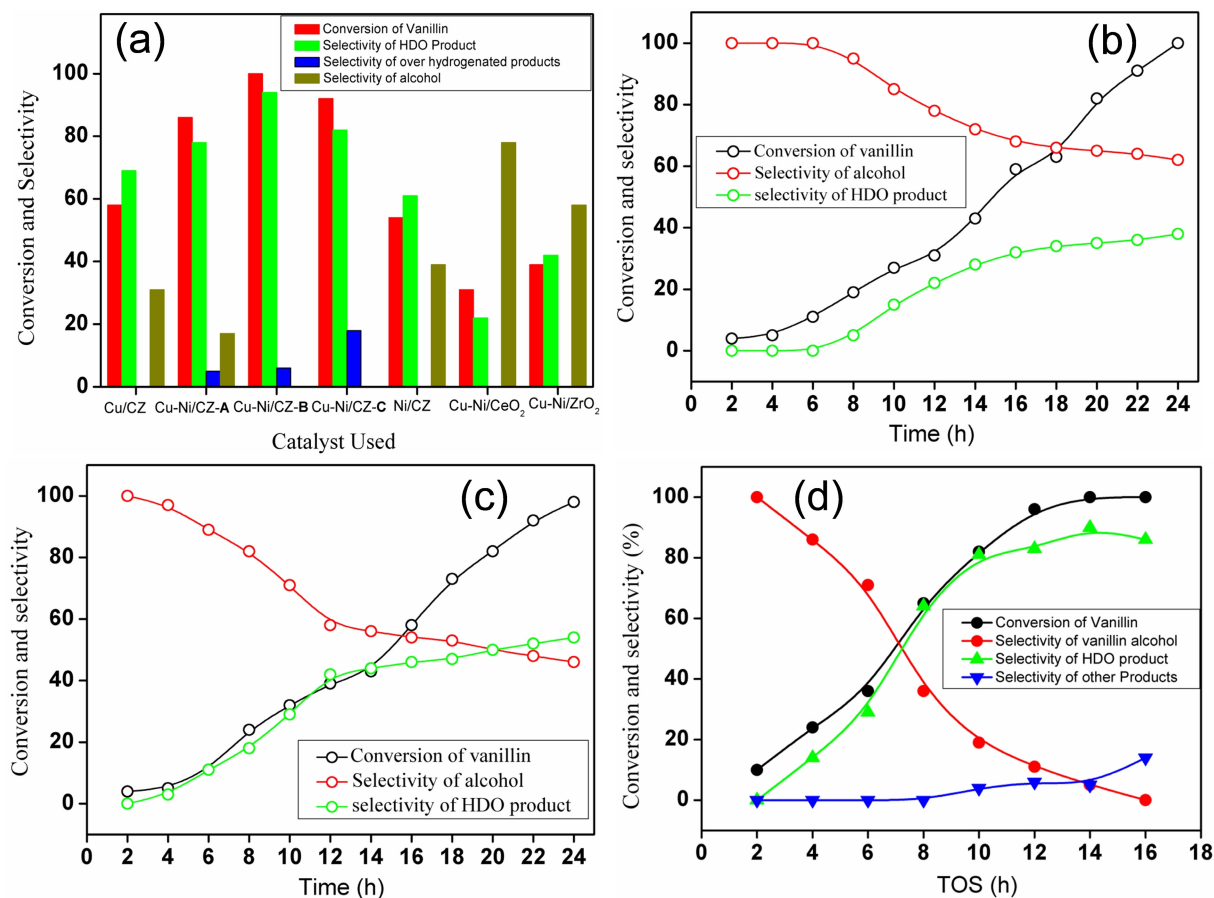


Figure 1. (a) Comparison study of as-synthesised catalysts for vanillin HDO. Reaction Conditions: vanillin (200 mg, 1.31 mmol), catalyst (100 mg), water (75 mL), H₂ pressure (25 bar), reaction temperature (160°C) and time (12 h). Comparison in catalytic activity as a function of time (b) HDO of Vanillin over Cu-Ni/CeO₂ (c) Cu-Ni/ZrO₂ (d) Cu-Ni/CZ-A; Reaction Conditions: vanillin (200 mg, 1.31 mmol), catalyst (100 mg), water (70 mL), 25 bar H₂ pressure, 160°C at 24 h and 16 h^d.

catalytic activity in bimetallic Ni-Cu/ZrO₂ catalyzed vanillin HDO reaction has been identified by Q. Guo *et al.* for the higher percentage of Cu addition.^[23] In addition, Yates and co-workers also demonstrated that increased Cu content to Ni alloy was responsible for the activity in hydrogenolysis of ethane.^[27] These weakly bounded hydrogen content is increasing proportionally with amount of copper introduction up to a certain level (10 wt%) and no significant variation is found beyond range from 12 to 70 wt% of Cu content to Ni catalyst. Similar results were demonstrated by Yang and co-workers that the superior catalytic activity and higher redox properties were accomplished with promotion of Cu to Ni on Al₂O₃ support.^[28] They reported that catalytic activity and redox properties were drastically decrease with the increase of the Cu content up to 20 wt%. Following these observations, we can emphasize that amount of Cu content plays a decisive role for such higher activity which resembles for the superior catalytic activity in Cu-Ni/CZ-B catalyst compared with the other catalysts. The impressive catalytic performance of the Cu-Ni/CZ-B catalyst may possibly due to the presence of large contents of active Ni-Cu bimetallic sites on the external unit surface of the catalyst per unit area for reaction substrate, exposing a greater extent of the crystalline facets to the surface, thereby

enhancing the catalytic activity among three tested bimetallic catalysts. The H₂ consumption of Cu-Ni/CZ-A, Cu-Ni/CZ-B and Cu-Ni/CZ-C catalysts was measured by H₂-TPR as shown in the Figure 5b. Calculated total H₂ consumption (4.93 mmol g⁻¹) of the Cu-Ni/CZ-B catalyst was higher than that of Cu-Ni/CZ-A (4.68 mmol g⁻¹) and Cu-Ni/CZ-C (4.37 mmol g⁻¹) catalysts, respectively. This result clearly indicates that Cu-Ni active sites of the Cu-Ni/CZ-B were more exposed by providing a preferential interaction with the reactants. In order to find the role of CeO₂-ZrO₂ support, we carried out vanillin HDO reaction over Cu-Ni/CeO₂ and Cu-Ni/ZrO₂ catalysts. Figure 1a shows that Cu-Ni/CeO₂-ZrO₂ catalyst exhibited highest catalytic activity compared to pure CeO₂ and ZrO₂ supported Cu-Ni based catalysts (Fig 1b, 1c).

In order to validate the reaction pathway for vanillin HDO over Cu promotional Ni/CZ catalysts, we examined distribution of the substrate and product selectivity as a function of reaction time, temperature, and hydrogen pressure. Product distributions with the progress of the reaction as a function of reaction time over the Cu-Ni/CZ-A, Cu-Ni/CZ-B, and Cu-Ni/CZ-C catalysts are shown in Figure 1d, 2a and 2b. Vanillin alcohol selectivity was reached to ~75–90% within 4 h, indicating that vanillin was hydrogenated to vanillin alcohol as a major

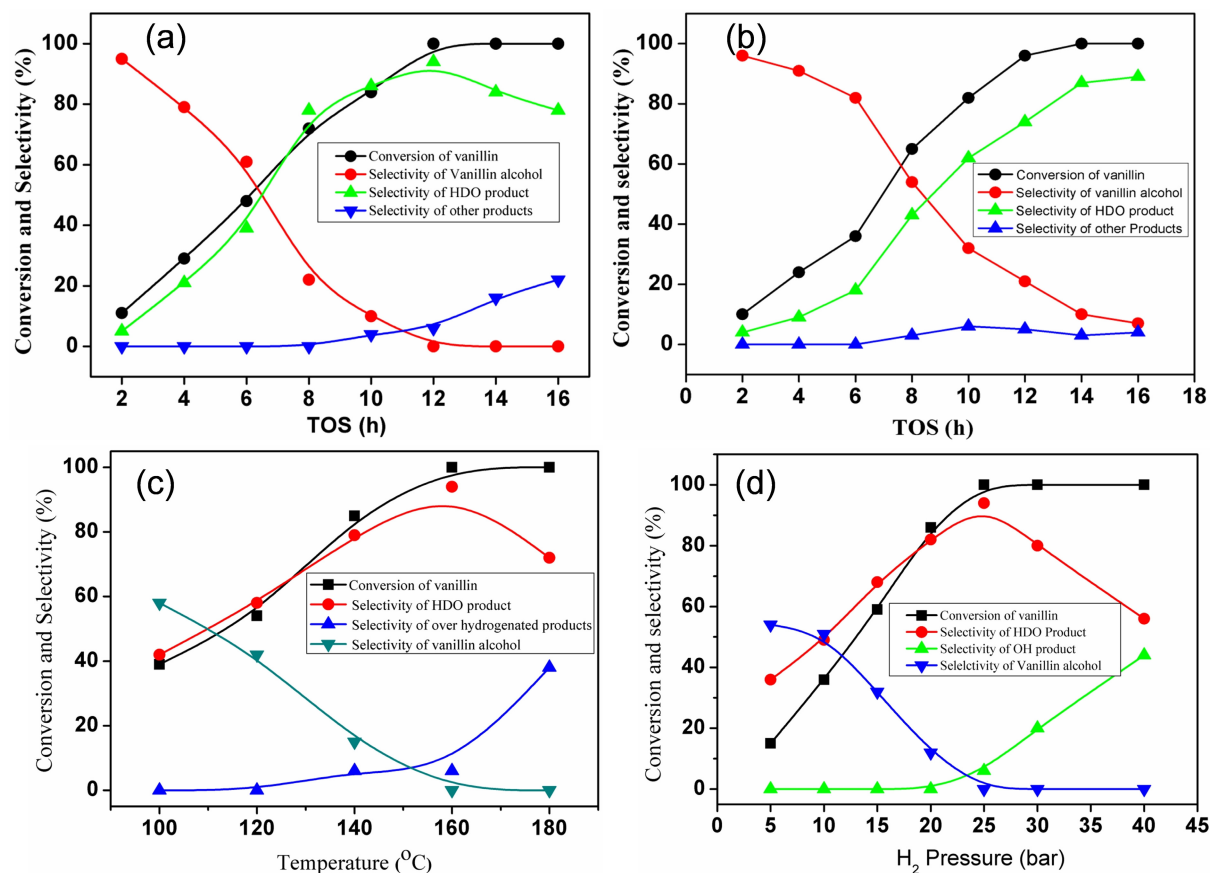


Figure 2. Evolution product distributions as a function of time over (a) Cu–Ni/CZ–B, (b) Cu–Ni/CZ–C, Influence of (c) reaction temperature and (d) H₂ pressure over CuNi/CZ–B catalyst in the vanillin HDO reaction catalysts, respectively. Reaction Conditions: vanillin (200 mg, 1.31 mmol), catalyst (100 mg), water (75 mL), H₂ pressure (25 bar), and reaction temperature (160°C) on 12 h (c, d). In hydrogen pressure effect the selectivity of –OH products refer to the production of cyclohexanol and *p*-cresol.

product in the first step. Further hydrogenolysis of vanillin alcohol produced 2-methoxy-4-methylphenol (~20%) as a major HDO product over the Cu–Ni/CZ–B (Figure 2a). A trace amount of 2-methoxy-4-methylphenol within 3 h was detected over Cu–Ni/CZ–A, Cu–Ni/CZ–B and Cu–Ni/CZ–C catalysts (Figure 1d, 2a and 2c). When the reaction time prolonged, the conversion of vanillin was reached to 96.7% with the gradual decrease of vanillin alcohol, producing 2-methoxy-4-methylphenol concentration. The transformation of vanillin to 2-methoxy-4-methylphenol is achieved by the hydrogenation of vanillin to vanillin alcohol and subsequent hydrogenolysis of the vanillin alcohol to HDO products over Cu–Ni/CZ catalysts, which was consistent with the recent study by Xia *et al.*^[29]

The role of reaction temperature and H₂ pressure in vanillin HDO over Cu–Ni/CZ–B was examined at the temperature range from 100°C to 180°C under 5–40 bar of H₂. Figure 2c reveals that reaction temperature had a significant impact on chemo-selectivity. Vanillyl alcohol and 2-methoxy-4-methylphenol are appeared to be the major products at 100 and 140°C. The Cu–Ni/CZ–B catalyst improved significant vanillin conversion (~96%) and selectivity 2-methoxy-4-methylphenol (a HDO product) (>94%) at the temperature range from 100 to 160°C. However, Cu–Ni/CZ–A (from 38 to 87%) and Cu–Ni/CZ–C (from

35 to 84%) catalysts required much higher temperature than the Cu–Ni/CZ–B catalyst. The selectivity of 2-methoxy-4-methylphenol selectivity decreased gradually (from 87 to 65%) on Cu–Ni/CZ–A, (from 94 to 71%) on Cu–Ni/CZ–B and (from 89 to 75%) on Cu–Ni/CZ–C catalysts, respectively, at 180°C, with expense of the production of guaiacol, *p*-cresol, phenol, cyclohexanol, benzene and cyclohexane (Scheme S1, SI). The decarbonylation of the aldehyde group was promoted at high temperature and some undesired side reactions occurred including demethoxylation and HDO/demethylation by catalyst deactivation.^[30] It was reported that elevated temperature accelerated the reaction and deactivated the catalyst, due to the sintering or coalescence of metal NPs, producing undesired products.^[31] We also conducted vanillin HDO over Cu–Ni/CZ–B with various solvents including isopropanol, water, and isopropanol/water mixture (Figure S1, SI).

We carried out vanillin HDO under different hydrogen pressures (5–30 bar) at 160°C (Figure 2d). Figure 2d indicates H₂ pressure affected significantly the HDO of vanillin over the Cu–Ni/CZ–B catalyst. Conversion of vanillin was achieved at 25 bar (99%) which was three times higher than normal condition in this study. The selectivity towards 2-methoxy-4-methylphenol also increased considerably from 14% to 98%

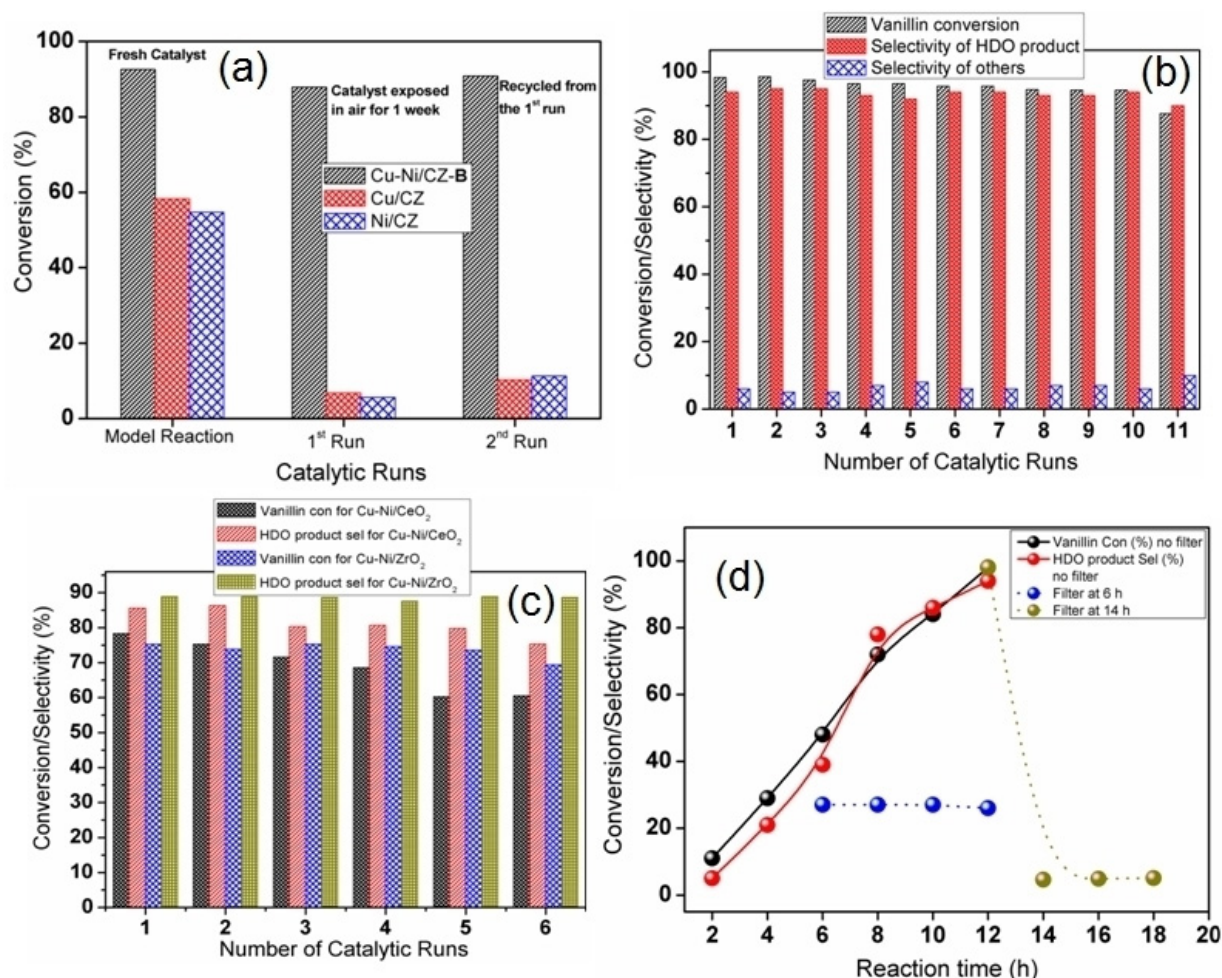


Figure 3. Investigation of the stability of Cu–CZ, Ni–CZ, and Cu–Ni/CZ–B catalysts (a), Recycling test of the Cu–Ni/CZ–B (b) and Cu–Ni/CeO₂, Cu–Ni/ZrO₂ (c) bimetallic catalysts, Hot filtration experiments in which Cu–Ni/CZ–B catalyst was removed after 6 h and 14 h (d).

with an increase in H₂ pressure from 5 to 30 bar. However, a prominent degradation in 2-methoxy-4-methylphenol selectivity was found under increased hydrogen pressure above 25 bar. The decrease in desired product selectivity was correlated with the subsequent formation of undesired side products (e.g. guaiacol, cyclohexanol, and anisole) following over-hydrogenation and decarbonylation in the presence of excessively high hydrogen concentration. This is in line with the findings of our previous work where we have noted same scenario for Pd based catalysts.^[5]

We investigated the stability for bimetallic Cu–Ni/CZ–B catalyst in vanillin HDO reaction in comparison with the monometallic Cu and Ni catalysts after exposing in air for 1 week (Figure 3a). Monometallic Cu/CZ and Ni/CZ catalysts provided 58.3% and 54.7% vanillin conversions, respectively, while the bimetallic Cu–Ni/CZ–B catalyst yielded 92.6% of 2-methoxy-4-methylphenol. After exposing in air for 1 week, three catalysts (A, B, and C) afforded 87.9%, 6.8% and 5.6% vanillin conversions, respectively. Surprisingly, a huge drop of conversion was found in monometallic Cu/CZ and Ni/CZ catalysts. The stability and resistant of bimetallic Cu–Ni catalyst

did not affected by air exposed. After recycling the catalysts for second run, catalytic performance did not improved over monometallic catalysts. For recyclability, Cu–Ni/CZ–B bimetallic catalyst was used through a 10th runs in vanillin HDO reaction (Figure 3b). The solid was recovered after the reaction, by simple washing and drying. Under these conditions, the bimetallic catalyst exhibited outstanding recyclability up to 10th runs preserving 2-methoxy-4-methylphenol selectivity and yield. After the 10th cycle, vanillin conversion and selectivity were dropped from 94.6 to 87.6% and 94 to 88% with increased selectivity toward alcohols as a hydrogenated product. In the control experiment, single metal catalysts of Ni and Cu could be recycled only for two times, because of accumulation of carbonaceous species on the catalyst surface which blocked active sites and detached metals from the supports. On the contrary, the bimetallic catalyst attained modulated electron properties by alloying.^[32,33] When Cu–Ni/CeO₂ and Cu–Ni/ZrO₂ catalysts was tested up to 6th runs (Figure 3c), the conversion and 2-methoxy-4-methylphenol selectivity were dropped from 78.3 to 60.5% and from 85.6 to 75.3% after 6th runs, respectively. The considerably less stable

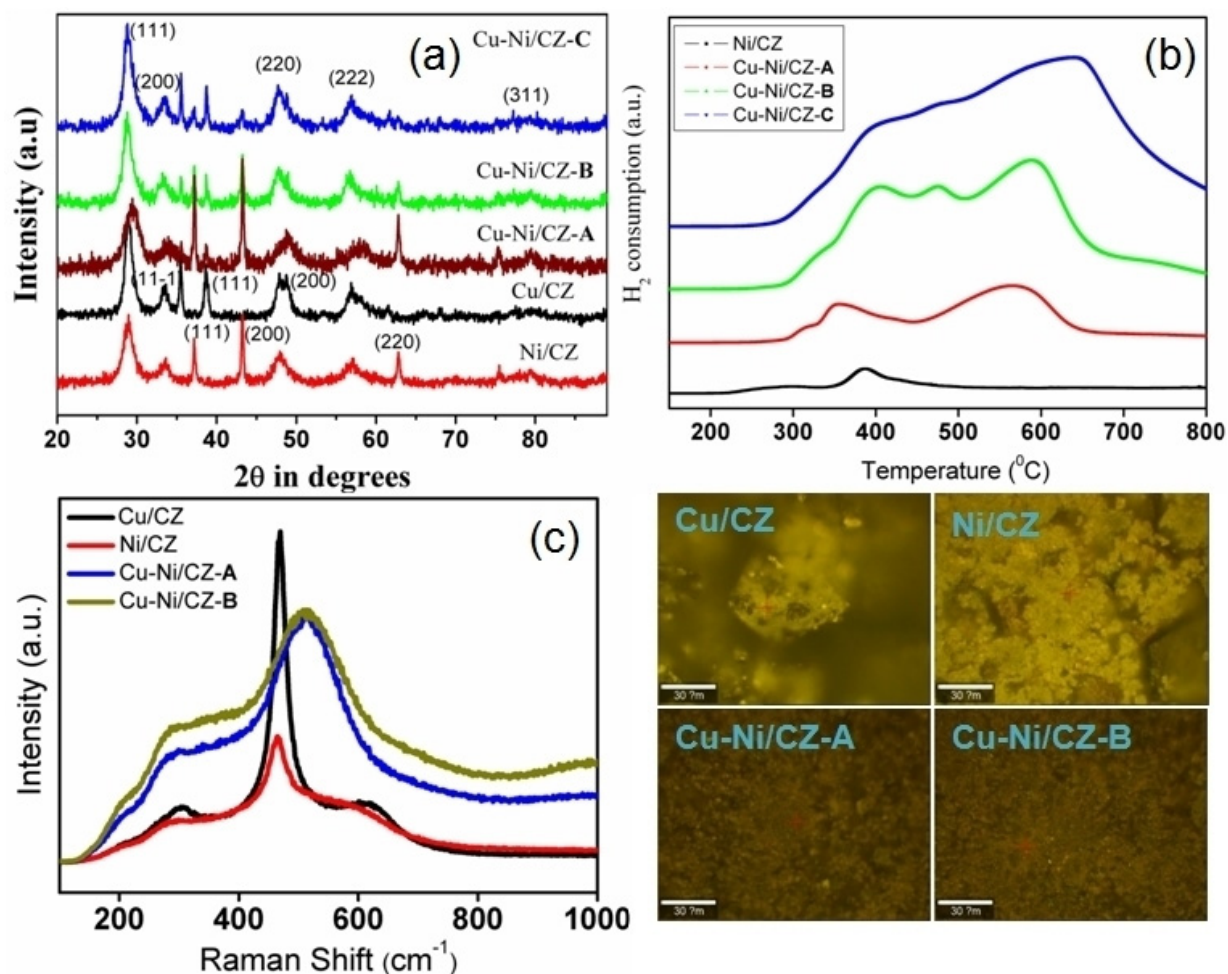


Figure 4. (a) Powder XRD pattern, (b) H_2 -TPR profiles, (c) Raman spectra, and (d) AFM images of Cu–Ni/CZ catalysts

feature of Cu–Ni/ZrO₂ catalyst was found after 6th runs, showing a conversion drop from 75.3 to 69.4%. On the other hand, bimetallic Cu–Ni/CZ-B proved to be practically active with less deactivation, by producing 2-methoxy-4-methylphenol with high yield up to 4th runs. When the both catalysts were regenerated by reduction at 500°C after six consecutive catalytic cycles, there was no improvement in vanillin conversion.^[34] The deactivation of the catalysts was attributed to metal NPs sintering, the over reduction of a support, and carbon formation. As a result, the stability of the bimetallic Cu–Ni/CZ catalyst was significantly improved up to 10th cycles of catalytic run without detectable significant deactivation due to their alloying. The strong interaction between metal and mixed oxide support was responsible for the novel stability against sintering.^[35] Through the hot filtration test (Figure 3d), it was found out that the bimetallic Cu–Ni/CZ-B exhibited limited leaching of active metal species (Cu & Ni content remained comparable with the fresh catalyst as measured by ICP-OES analysis) into the reaction mixture.

Characterization Studies

For structural characterization of the catalysts, powder XRD was used (Figure 4a). The XRD patterns exhibited characteristic diffraction peaks at 2θ values of 28.6, 33.2, 47.8, 57.2, and 79.3, which corresponded to the (220), (311), (400), (511), and (440) crystalline reflections, respectively, indicating cubic fluorite-type oxide structure of mixed CeO₂–ZrO₂ (PDF# 34–0394) with space group of $Fm\bar{3}m$.^[36,37] Two diffraction peaks appeared at 35.1 and 38.9° in all freshly prepared Cu containing catalysts which demonstrated successful formation of CuO crystalline phase. Similarly, for the all Ni containing catalysts, the small diffraction peaks for bulk NiO ($2\theta = 36.4^\circ$ and 44.3°) were identified. XRD pattern of Cu–Ni/CZ-B catalyst illustrated broad reflections compared with the other bimetallic catalysts which indicated that the cubic phase of individual copper oxide and nickel oxide species were either highly dispersed on CeO₂–ZrO₂ catalyst surface or formed a bimetallic solid solution in ceria through the bifunctional effect or synergetic effects.^[38] The average crystallite sizes (D) of the Cu/CZ and Ni/CZ catalysts as evaluated following the Debye-Scherrer equation are 19.3 and 16.3 nm, respectively. When the second metal atom was

introduced, slight reduction in crystalline size was observed for Cu–Ni/CZ-A (11.42 nm) and Cu–Ni/CZ-B (12.87 nm), respectively, suggesting that the Ni and Cu form the bimetallic alloy. The obtained crystallite size of the Cu–Ni/CZ-C catalyst was larger in comparison with other bimetallic catalysts and monometallic catalysts, presumably because of the growth of the Ni and Cu particles on CeO₂-ZrO₂ surfaces. In addition, an obvious diffraction peaks shift towards higher 2θ angles is observed with the co-incorporation of both Cu and Ni in CeO₂-ZrO₂ lattice^[39] (Figure 4a), revealing successful insertion of both Cu²⁺ and Ni²⁺ ions in to the CeO₂-ZrO₂ lattice with changing of the lattice parameters.^[40] Similarly, XRD peaks displacement towards higher 2θ value is identified by Doğ u *et al.*^[41] The reduction properties of the as-synthesized catalysts were investigated using TPR technique (Figure 4). The H₂-TPR of the Ni/CZ and Ni–Cu/CZ catalysts shown in Figure 4b that two reduction peaks were located at 260°C and 382°C, respectively. The less intense broad peak appeared at relative lower temperature and broad peak at higher temperature could be attributed to the reduction of weakly surface bounded NiO species and their interaction with CeO₂-ZrO₂ surface, respectively. In Figure 4b, the reduction temperature of Ni is increased with increasing Cu content. H₂ consumption of all as-synthesised samples was calculated on the basis of pure CuO as reference material (Table S1) from the H₂-TPR study. A significant difference was noticed in H₂ uptake with and without Cu catalyst, revealing higher H₂ uptake occurred with the Cu-loaded catalysts, particularly much higher for Cu–Ni/CZ-B. The order of H₂ consumption follows as Cu–Ni/CZ-B (4.93 mmol/g) > Cu–Ni/CZ-A (4.63 mmol/g) > Cu–Ni/CZ-C (4.37 mmol/g) > Ni/CZ (4.01 mmol/g) > Cu/CZ (3.86 mmol/g). Two peaks located at 352 and 572°C for Cu–Ni/CZ-A catalyst (Figure 4b) are assigned to CuO and NiO reduction, respectively. The reduction peak shifted toward the higher reduction temperature compared to the monometallic indicates the introduction of second metal promoter, enhancing the metal support interaction between Cu–Ni and CeO₂-ZrO₂. In case of Cu–Ni/CZ-B catalyst, shift of reduction temperature of NiO and CuO toward higher temperature with three characteristic reduction regions. Two regions belong to reduction of CuO and NiO on CeO₂-ZrO₂ surface, while another characteristic reduction temperature region is due to the formation of bimetallic phase weakly bounded on CeO₂-ZrO₂ surface.^[42] In the Cu–Ni/CZ-C catalyst, reduction peak is shifted toward the higher temperature with less H₂ consumption (Table S1, SI), compared with the other Cu promoted Ni/CZ catalysts due to the sintering, which is good agreement with XRD and TEM results. From these results, the Cu–Ni/CZ-B catalyst with higher catalytic efficiency and greater stability was from higher amount H₂ consumption than other catalysts.

UV- Raman spectra of Ni/CZ, Cu/CZ, Cu–Ni/CZ-A, and Cu–Ni/CZ-B catalysts are presented in Figure 4c. Three bands correspond to ceria based mixed oxides. There is one triply degenerate Raman active optical phonon located at around 300–360 cm^{−1} (F_{2g}). There are no other peaks corresponding to ZrO₂ in the as-synthesized samples, indicating that the CeO₂-ZrO₂ formed the solid solutions. The significant red shift of F_{2g}

peak is resulted from asymmetry induced by unsystematically oriented oxygen vacancies (2CeO₂ ⇌ Ce₂O₃ + O). Apart from that other two bands observed, one at 480–530 cm^{−1} indicates that the longitudinal optical band which allows a vibration mode by relaxation of selection rules. This band is more sensitive and relevant for the detection of oxygen vacancies created in the lattice cell, enabling the oxygen absorption and release from the surface.^[43] As impregnation of Cu and Ni on CZ solid solution, the F_{2g} mode turn into asymmetric and marginally shifted to lower wavenumber and the FWHM enlarged. This shift is the consequence of combine effects: diminution in the M–O vibrations as Cu and Ni metal ion are introduced into CZ lattice, lattice expansion, reduction in the crystallite size, and enhance of oxygen vacancies. The other second order longitudinal optical band at around 1100 cm^{−1} primarily associated to A_{1g} symmetry with little combination of E_g and F_{2g} symmetries is also observed.^[44] This band is mainly observed in UV-Raman spectra, alike to the 570 cm^{−1} band. The 1170 cm^{−1} band is also corresponding to defects created in the lattice. The activation of these two longitudinal optical bands is due to multi-phonon relaxation by the resonance Raman Effect.^[45] Increasing the amount second metal promoter of Cu, surface or subsurface positions of the lattice incorporation of Cu²⁺ and Ni²⁺ into the fluorite lattice must be accompanied by enhancing of oxygen vacancies. Evidence of little amount of Cu and Ni incorporation in the lattice for the CZ catalysts is given by the blue shift and broadening observed in the main longitudinal optical band at 500–600 cm^{−1}, which has been related to the enhancement of oxygen vacancies.^[46] Oxygen vacancies order is Cu/CZ < Ni/CZ < Cu–Ni/CZ-A < Cu–Ni/CZ-B. Figure 4c has shown increasing relative peak broadening with increasing the amount of Cu. These shifts are in accordance with XRD and XPS results. The cubic crystalline structure with oxygen vacancies is considered as a key role for increase in the oxygen absorb/release capacity, since these vacancies increase the bulk oxygen diffusion and thereby enhance reversible adsorption and desorption of oxygen. Due to this oxygen absorb capacity, hydrogenolysis was enhanced by the facile interaction of -OH group of alcohol with the CZ support, facilitating the stronger interaction between -OH group and CZ and weakening C–O bond strength for the production of the desired HDO product by C–O bond breaking.

Surface composition and oxidation states of monometallic and bimetallic catalysts were evaluated by XPS analysis. Partial surface oxidation of metals took place by air, when catalysts were transferred from the reduction reactor to the XPS chamber. Figure 5a shows the Cu-2p_{3/2} XPS spectra for pre-reduced monometallic Cu and bimetallic Cu–Ni catalysts on CeO₂-ZrO₂ support. The high-resolution deconvoluted XPS spectra in Cu-2p region (Figure 5a) show two characteristic binding energy doublets at 933.7–938.0 eV and 930.1–935.4 eV, respectively, accompanied with their two satellite peaks, due to the existence of Cu²⁺ and Cu⁰ oxidation states.^[47] The decrease in intensity of the satellite peaks in the bimetallic Cu–Ni/CZ catalysts refers to the reduction of Cu²⁺ to metallic state (Cu⁰) after mixing with Ni. Cu⁺ peak was not taken into account in this XPS spectra, owing to overlap with

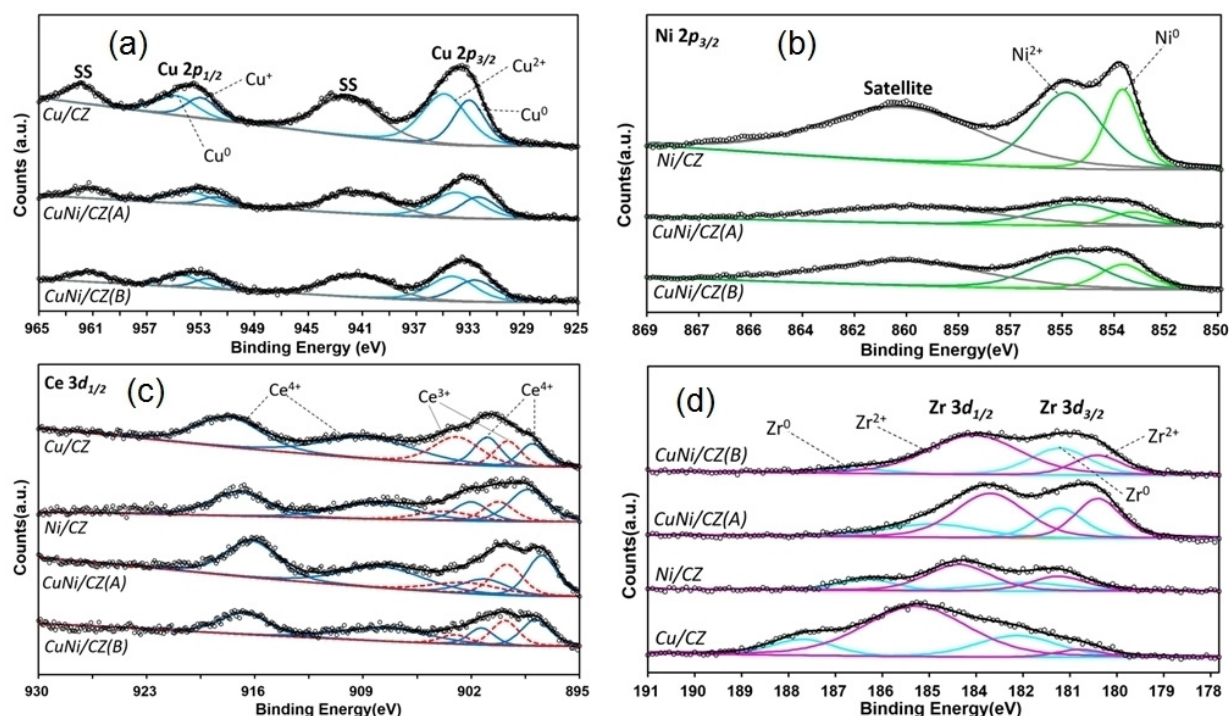


Figure 5. XPS spectra in Cu-2p (a), Ni-2p (b), Ce-3d (c), and Zr-3d (d) regions of Cu/CZ, Ni/CZ, CuNi/CZ-A, and CuNi/CZ-B catalysts, respectively.

the Cu⁰ peak. The relative ratio of Cu⁰/Cu²⁺ in the catalysts is follows Cu/CZ (1.494) < CuNi/CZ-A (1.307) < CuNi/CZ-B (1.722). For CuNi/CZ-B, the relative proportion of Cu⁰ species with respect to Cu²⁺ was greatly enhanced compared with the Cu/CZ and CuNi/CZ-A catalysts. The binding energy (BE) displacement of the Cu⁰ could be attributed to the weaker interactions between Cu and CZ in CuNi/CZ-B, in contrast to the monometallic Cu/CZ. The observed XPS BE displacement is attributed to the modification of the electronic status of Cu caused by the intrinsic synergistic effect between Cu and Ni by charge transfer of electrons from Ni to Cu.^[48] The Ni-2p_{3/2} XPS spectrum for monometallic Ni/CZ catalyst shows three characteristic peaks with the BE located at 851.9 and 854.9 eV, along with a satellite peak at higher BE of the metallic Ni⁰ and NiO species, respectively.^[49] The reduction of the catalysts were conducted at 450 °C, because the catalysts were reduced below 450 °C, based on the TPR study. Re-oxidation of Ni⁰ metals during sample preparation, formation of Ni²⁺ or Ni⁺ species and small amounts of NiO species that were not entirely reduced with the appearance of Ni²⁺ BE peaks in XPS spectra.^[50] The binding energy shift of the Ni⁰-2p_{3/2} peak for bimetallic Cu–Ni/CZ catalysts in comparison with monometallic Ni/CZ was more significant than that observed for the Cu⁰-2p_{3/2} peak in the monometallic Cu/CZ catalyst.^[51–54] The relative order of Ni⁰/Ni²⁺ follows as Ni/CZ (0.534) < CuNi/CZ-A (0.387) < CuNi/CZ-B (0.504), which plays a role for hydrogenation of aldehyde in to alcohols.

Figure 5c presents the Ce-3d core-level XPS spectra of the reduced monometallic (Cu/CZ & Ni/CZ) and bimetallic (Cu–Ni/CZ-A & Cu–Ni/CZ-B) catalysts, respectively. The high resolution

deconvoluted Ce-3d XPS spectra exhibit three characteristic BE peaks as well as their concomitant shake-up lines of the 3d_{3/2} and 3d_{5/2} for Ce⁴⁺ and Ce³⁺ species. The XPS spectra indicate the formation of fairly complex structure owing to the presence of both Ce⁴⁺ and Ce³⁺ derived modes, which deviated from their ideal stoichiometry.^[16,17,18,55] A notable BE shifts in Ce-3d core-level toward the higher region are shown in the reduced bimetallic Ni–Cu/CZ catalysts as compared to the pure CZ mixed oxide. The incorporation of Ni and Cu species into CZ lattice resulted in the discrepancy of electric charge and lattice distortion of CZ.^[38] In the case of bimetallic Ni–Cu/CZ catalysts, BE displacement of the Ce³⁺ and Ce⁴⁺ species toward the lower value compared to monometallic counterparts is assigned to the relatively rich electron density of CeO₂, indicating better reducibility of surface metal atoms by strong metal support interaction. Pérez-Vidal *et al.* reported similar kind of negative BE shift for Ag/ZrO₂-(20%)-CeO₂ catalysts, indicating abundant Ce³⁺ species, after silver doping.^[56] These results are clearly correlated with the H₂-TPR results. It was concluded that the shift of the reduction temperature toward lower value was caused by the presence of both Ni and Cu in the CeO₂-ZrO₂ lattice (Figure 4b). The Zr-3d XPS spectra profile was fitted to two doublets at around 184.8 (3d_{3/2}) and 181.9 eV (3d_{5/2}), which is a good agreement with the known ZrO₂ (IV).^[57] In addition, there is another significant observation referred to BEs shift of Zr-3d core level of the Cu–Ni/CZ samples by the possible electron transition from metal to support. The actual Ce, Zr, Ni, and Cu content were also determined *via* ICP-OES analysis which was in close agreement with the nominal values from the synthesis (Table S2).

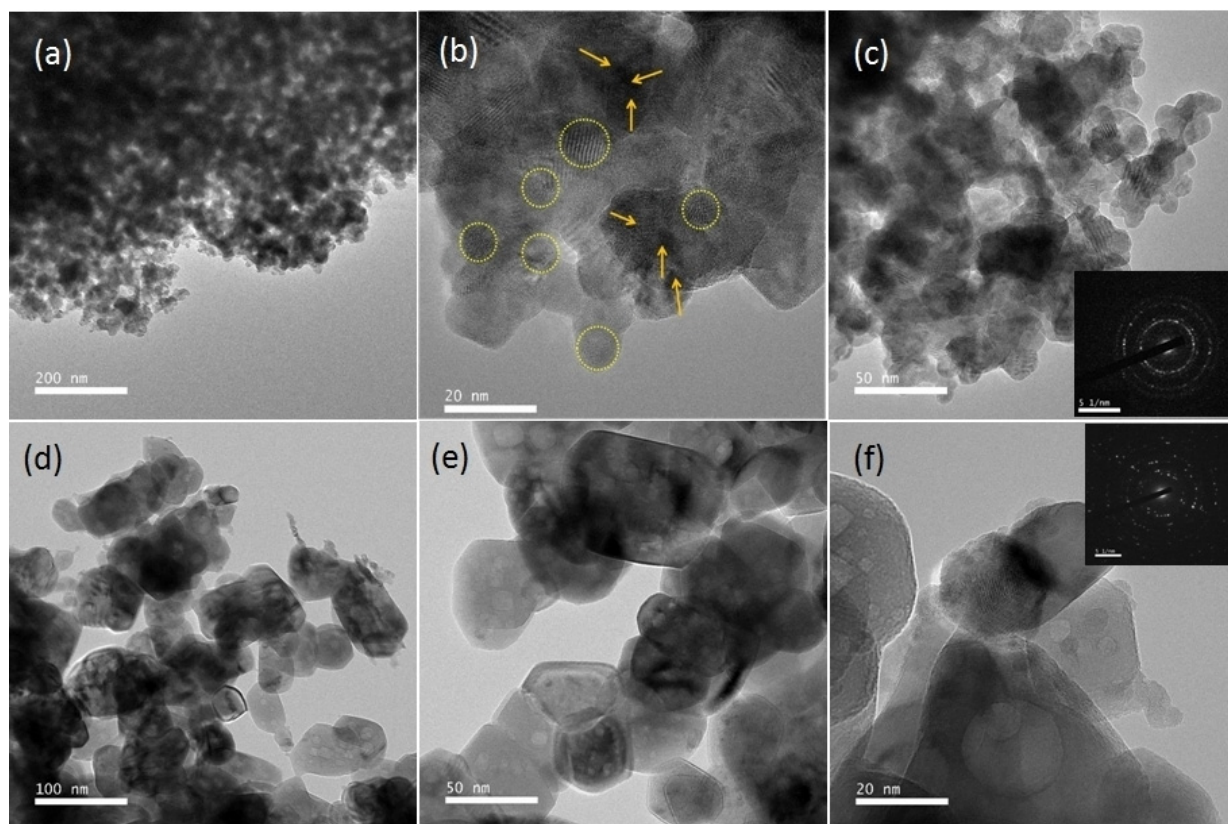


Figure 6. TEM Images (a, b, and c) of Cu/CZ and (d, e, and f) of Ni/CZ catalysts, respectively. Selected area electron diffraction (SAED) patterns are provided in the inset of Figures c and f.

Structural characterization of both monometallic and bimetallic Ni CeO₂-ZrO₂ based catalysts were investigated by TEM analysis. Agglomerated particles with relatively homogeneous distribution was found in the Cu/CZ catalysts (Figure 6 a-c). The average crystal sizes of the as-synthesized Cu/CZ and Ni/CZ were 22.6 ± 1.9 and 19.9 ± 0.9 nm, respectively. The grains of Ni/CZ catalyst are clearly shown by their transparent irregular opaque shape, which is not homogeneous in nature with a dual distribution having mean sizes of 42.9 ± 0.4 and 60.3 ± 0.9 nm, respectively.^[58] HR-TEM images along with the SAED (Figures 6c and 6f insets), demonstrates polycrystalline nature of the Cu/CZ and Ni/CZ catalysts. HR-TEM images also confirm interfacial microstructures of catalysts. Crystalline lattice fringes marked in yellow (Figure 6b) clearly distinguish metal/metal oxide from the support particles. The metal/oxides with densely black interfaces marked by yellow arrows (Figure 6b) are clearly shown, suggesting metal particles were immersed into the surroundings of CZ particles with a partial encapsulation.^[59] The lattice fringe was calculated to be 0.336 nm (Figure 6b), which corresponded to the (111) plane of CeO₂ shown in XRD patterns. A close observation of Ni/CZ catalyst in TEM image (Figure 6e) reveals the existence of some small void space in the crystal, caused by a detachment of some NiO NPs from the support during the synthesis in high temperature. The lattice fringes of metal particles on CeO₂-ZrO₂ support are not clearly seen. HAADF-STEM images of the

respective Cu/CZ and Ni/CZ catalysts (Figure 7) with the corresponding elemental mapping clearly revealed that both Cu and Ni were coexisted in an individual NP, surrounded by CeO₂-ZrO₂.

TEM images of Cu-Ni/CZ-A (Figure 8 a-c) indicate that the each particle is octahedral in shape with 17.4 ± 1.2 nm of the size without any large pores or cracks. However, the Cu-Ni/CZ-B catalyst has a distorted square shape with rough surface with 19.1 ± 0.6 nm of the size (Figure 8 d-f). A considerable decrease in the average particle size of Cu-Ni bimetallic is observed due to the introduction of second metal promoter Cu into Ni/CeO₂-ZrO₂ lattice. An enriched distribution with comparatively smaller size of bimetallic Cu-Ni NPs on CZ surface is attributed to the strong interaction between the Ni and Cu. Di *et al.* reported a similar result on the basis of morphological changes, due to the interactions between the Cu and Pd by introducing second metal promoter which facilitated stability, enhanced the redox properties of catalyst and inhibited leaching of active metal centres.^[60] The disorderly arranged mixed metal/oxides interface is also identified (Figure 8) in Cu-Ni/CZ-A and Cu-Ni/CZ-B catalysts, indicating the inter diffusion of the correlative phases. Lattice fringes with 0.341 nm of a *d*-spacing in HR-TEM image (Figure 8a) of Cu-Ni/CZ-A catalyst correspond to the (111) crystalline lattice plane of CeO₂. The polycrystalline features of the bimetallic particles on CeO₂-ZrO₂ are validated with the SAED patterns in the HR-TEM images (Figures 8c and 8f, insets).

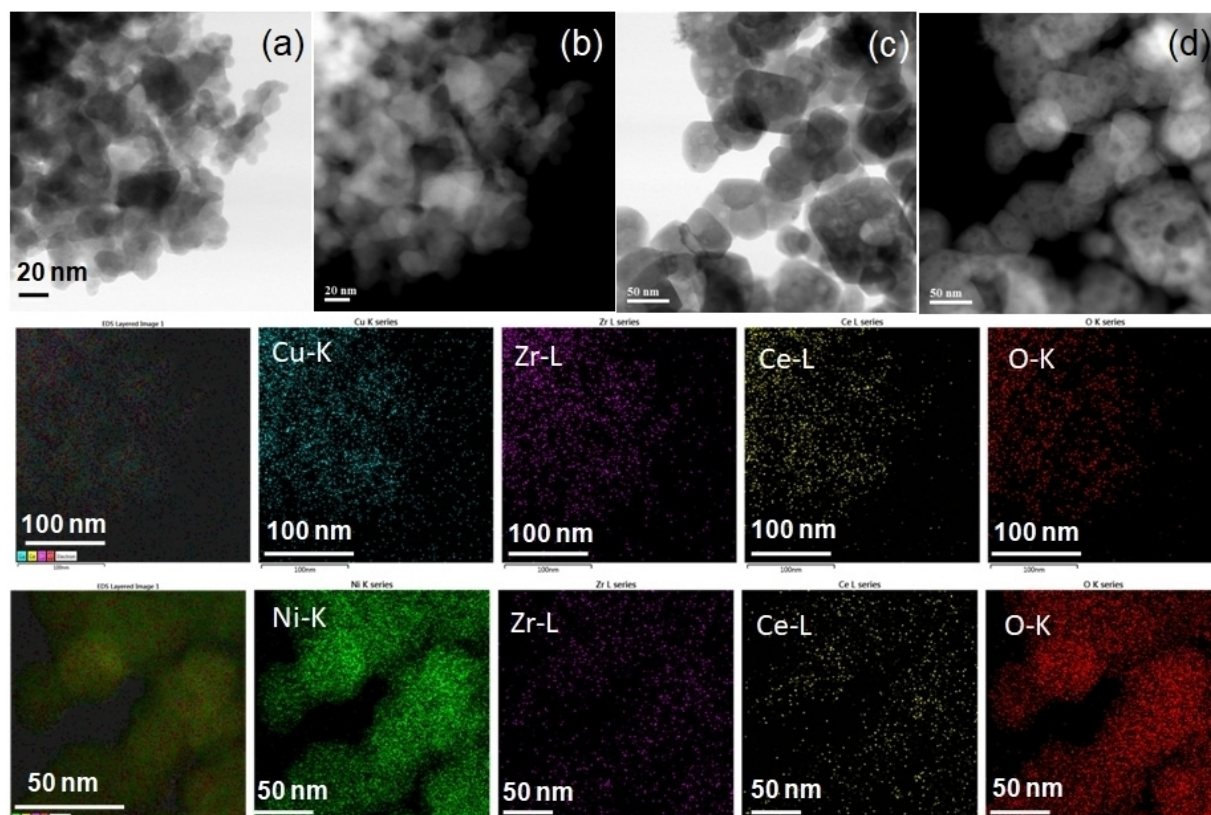


Figure 7. HAADF-STEM images (a & b) of Cu/CZ and (c & d) of Ni/CZ catalysts with the corresponding elemental mapping presented with different colors.

Cu–Ni/CZ-A and Cu–Ni/CZ-B catalysts have a similar morphology in HAADF-STEM images (Figures 9 a-d). The corresponding elemental mapping images revealed that Cu, Ni, Ce, and Zr are homogeneously distributed in an individual crystalline particle, confirming the formation of hetero-di nuclear CeO₂-ZrO₂ based mixed oxide lattice rather than the physical mixture.

Conclusions

In summary, we investigated a series of CuNi/CZ catalysts for HDO of vanillin into 2-methoxy-4-methylphenol. The different ratio of Ni–Cu/CZ catalysts exhibited outstanding catalytic activity and selectivity through tandem hydrogenation-deoxygenation of vanillin into 2-methoxy-4-methylphenol. The high catalytic activity and stability of the CuNi/CZ catalyst were proven to be the characteristic nature of mixed ceria-zirconia and bimetallic Cu and Ni NPs compare to the corresponding monometallic counterparts. The role of Cu in the CuNi/CZ catalyst was faster consumption of intermediate products, generating HDO product. In particular, the bimetallic Cu–Ni/CZ-B exhibited the highest catalytic TOF, due to the synergistic effect between metal active centres (Cu–Ni) and support, which was confirmed by H₂-TPR and XPS studies. Through the kinetic study, it was revealed that the Cu–Ni/CZ-B catalyst induced hydrogenation of vanillin into vanillin alcohol and the subsequent hydrogenolysis of vanillin alcohol into 2-methoxy-4-methylphenol. In addition, the Cu–Ni/CZ-B catalyst was proven

to be recyclable for at least ten times without any significant loss in catalytic activity and selectivity toward desired products. The high catalytic efficiency of the newly designed Cu–Ni/CZ-B catalyst holds promising alternative to noble-metal catalysts for the biofuel upgrading process.

Supporting Information Summary

Detail Experimental section including catalyst synthesis procedure, catalysis, characterization techniques, influence of solvent, H₂ consumption values, scheme for the possible formation of products in hydrodeoxygenation (HDO) of vanillin are available in the Supporting Information Section.

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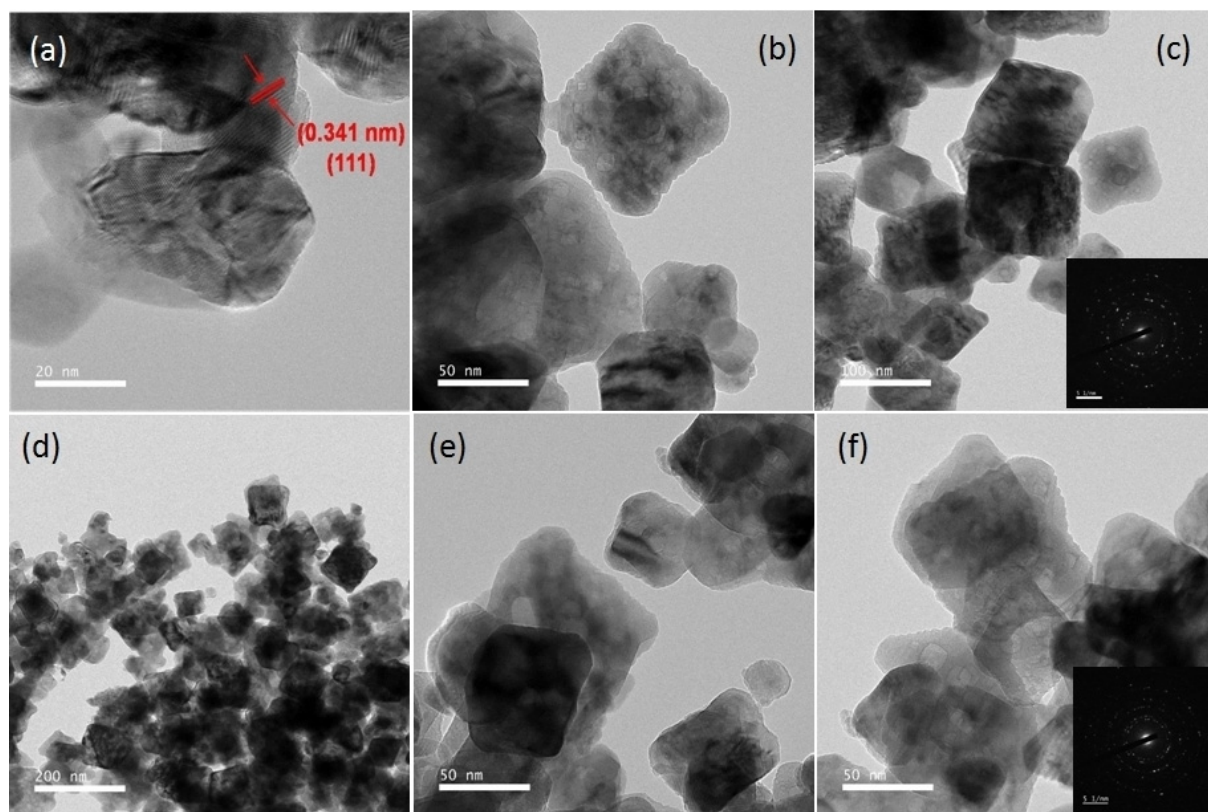


Figure 8. TEM Images (a, b, and c) of Cu–Ni/CZ-A and (d, e, and f) of Cu–Ni/CZ-B catalysts, respectively. SAED patterns are provided in the inset of Figures c and f.

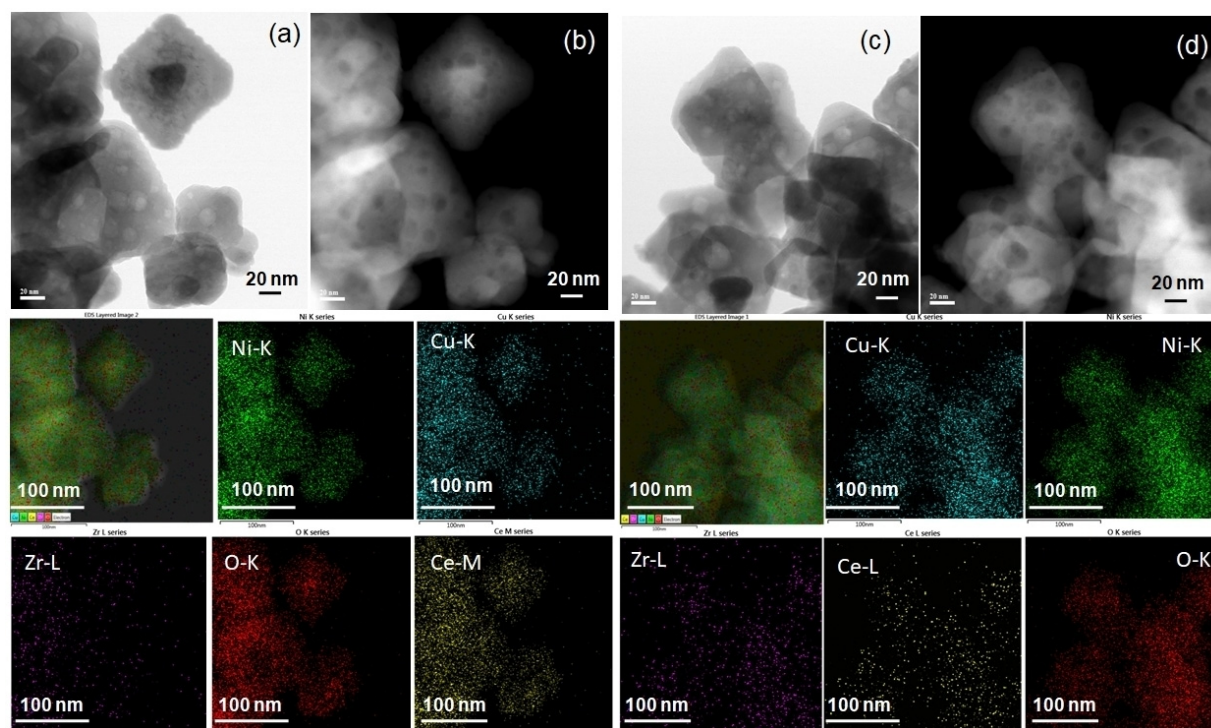


Figure 9. HAADF-STEM images (a and b) of Cu–Ni/CZ-A and (c and d) of Cu–Ni/CZ-B catalysts with the corresponding elemental mapping presented with different color, respectively.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Biomass • Ceria-zirconia mixed oxides • Cu promoted Ni catalyst • Hydrodeoxygenation (HDO) • Vanillin • 2-Methoxy-4-methylphenol

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