



Article CuO-Fe₂O₃ Nanoparticles Supported on SiO₂ and Al₂O₃ for Selective Hydrogenation of 2-Methyl-3-Butyn-2-ol

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Abstract: In this study, novel SiO₂- and Al₂O₃-supported Cu-Fe catalysts are developed for selective hydrogenation of 2-methyl-3-butyne-2-ol to 2-methyl-3-butene-2-ol under mild reaction conditions. TEM, XRD, and FTIR studies of adsorbed CO and TPR-H₂ are performed to characterize the morphology, nanoparticle size, and particle distribution, as well as electronic state of deposited metals in the prepared catalysts. The deposition of Fe and Cu metal particles on the aluminum oxide carrier results in the formation of a mixed oxide phase with a strong interaction between the Fe and Cu precursors during the calcination. The highly dispersed nanoparticles of Fe₂O₃ and partially reduced CuO_x, with an average size of 3.5 nm and with strong contact interactions between the metals in 5Cu-5Fe/Al₂O₃ catalysts, provide a high selectivity of 93% toward 2-methyl-3-butene-2-ol at complete conversion of the unsaturated alcohol.

Keywords: bimetallic Cu-Fe nanoparticle; selective hydrogenation; 2-Methyl-3-butyn-2-ol; 2-Methyl-3-butene-2-ol

1. Introduction

Selective catalytic hydrogenation of a C=C bond in unsaturated alcohols to the C=C bond is an important step in the production of fine chemicals and intermediates. One example is the catalytic hydrogenation of 2-methyl-3-butyn-2-ol (MBY) to 2-methyl-3-buten-2-ol (MBE), which is a key intermediate for the synthesis of vitamins A and E, biologically active compounds, linalool, aroma compounds, and agrochemicals [1]. Traditionally, the Lindlar catalyst (5–10% Pd/CaCO₃ inhibited by Pb complexes or quinoline) is highly effective in the selective hydrogenation of unsaturated compounds, however the instability of the CaCO₃ support, the suppression of hydrogenation by an excess of quinoline, and the toxicity of Pb limits its application, especially in view of the concept of "green" chemistry [2,3]. A number of scientific papers published over the last decade have been devoted to the development and research of palladium catalysts for the hydrogenation of acetylene compounds, the study of synergism in bimetallic Pd-Me systems in terms of the catalytic properties [4–8].

Today, special attention is focused on the study of catalytic systems with ultra-low loads of noble metals (Pd, Pt, Rh) or catalysts that contain non-noble metals, particularly those based on mono- and bimetallic nanoparticles of Fe, Cu, or Ni. Recently, a few reviews and articles summarizing the perspective applications of iron-containing catalysts in hydrogenation reactions of $-C=C-,-C\equiv C-, C=O$ bonds with molecular hydrogen have been published [9–15]. Catalysts based on supported iron and copper nanoparticles, and particularly on bimetallic Fe-Cu systems, are more preferred due to their low cost, high natural abundance of metals, and low toxicity [16–18].



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The application of the bimetallic Cu-Fe catalysts in the hydrogenation of furfural and levulinic acid to biofuels is known [16]. In the presence of Cu-Fe intermetallides, 2-methylfuran and γ -valerolactone were obtained with yields of 51% and 90%, respectively, under mild conditions. Cu-Fe catalysts were investigated [17] in the reaction of selective hydrogenation of furfural to furfuryl alcohol. It was shown that the Cu-Fe-Al catalyst exhibits the highest activity (the conversion reaches 96%) and the selectivity for furfuryl alcohol was 97%. The authors suggest that the high catalytic activity of the bimetallic Fe-Cu catalyst is probably due to the presence of stabilized highly dispersed copper particles. The catalytic activity of bimetallic iron-copper systems was described in the liquid-phase hydrogenation of p-dinitrobenzene to p-phenylenediamine in our previous work [18]. It was shown that the active phases in the complete reduction of nitro groups are ultrafine Cu oxide nanoparticles having strong interactions with Fe oxide nanoparticles or copper ions stabilized in the mixed phases of the Cu-Fe-O system. The observed synergistic effect between Cu^0 and FeO_x species in bimetallic Cu-Fe/SiO₂ catalysts [19] is the reason for the higher catalytic performance in comparison with monometallic Cu/SiO₂ in hydrogenation of diethylmalonate to 1,3-propanediol. Bimetallic Cu-Fe/SiO₂ catalysts were active in hydrogenation of phenylacetylene under mild reaction conditions, and their catalytic activity increased significantly when the size of Cu metal nanoparticles decreased to 13 nm, which were closely related to fairly large Fe crystallites [20]. However, it should be noted that Fe⁰ particles are very unstable in air and under reaction conditions, which leads to oxidation of the active surface and rapid deactivation of the catalyst.

Thus, the design of novel and ecofriendly catalysts at a low cost for the efficient transformation of the C=C bond in unsaturated alcohols to the C=C bond is a very promising approach. In our previously published work [21], monometallic oxide catalysts FexOy/SiO₂ were first investigated in the selective hydrogenation of phenylacetylene, which showed high catalytic activity and selectivity toward styrene under relatively mild reaction conditions (80–100 °C and 1.3 MPa H₂). It has been shown that an increase in the temperature of calcination of the samples from 250 to 500 °C led to the oxidation of Fe₃O₄ to Fe₂O₃, with a twofold increase in the catalytic activity and a high selectivity of styrene formation (68%) at the complete phenylacetylene conversion.

The goal of the present work is the investigation of the catalytic properties of ecofriendly and noble metal-free Cu-Fe catalysts prepared from inexpensive metal nitrates in the selective hydrogenation reaction of 2-methyl-3-butyn-2-ol (MBY) to 2-methyl-3-butene-2-ol (MBE) under relatively mild reaction conditions. The catalytic properties of bicomponent Cu-Fe oxide nanoparticles are compared with the properties of monocomponent Fe and Cu samples while varying the composition of the samples and the nature of the carriers (SiO₂ and Al₂O₃). The influence of the method of synthesis of bimetallic Cu-Fe nanoparticles on their catalytic properties will be also discussed.

2. Results and Discussion

2.1. Physicochemical Characterization

The state of the metals in the catalysts was estimated using the DRIFTS-CO spectroscopic study and XRD analysis.

Figure 1 shows the XRD profiles of different Cu-Fe catalysts after calcination at 300 °C for 4 h. The X-ray profile of the bimetallic sample deposited on SiO₂ shows two main reflections at $2\theta = 35.6^{\circ}$ and 38.7° and low-intensity reflection at 48.4° , which correspond to the characteristic diffraction lines of crystaline CuO, in agreement with the JCPDS card no. 45-0937. No iron-containing phases were detected for either sample, probably due to the high dispersion of iron oxide particles or their amorphous nature. For the sample deposited on γ -Al₂O₃, only main diffraction lines are present at 2 θ values of 37.5°, 45.8°, and 67.2°, as well as the rarely observed line at 39.5°, which can be attributed to the γ -Al₂O₃ structure according to the JCPDS card no. 51–0769. The reason for the absence of any deposited metal oxide phases on this sample may be the overlapping of the carrier reflections with the reflections of copper and iron oxide phases.



Figure 1. XRD profiles of the calcined 5%Cu-5%Fe/carrier catalysts and alumina carrier.

To study the electronic states of Cu and Fe, some representative catalysts were further characterized by DRIFTS using CO as a probe molecule. Figure 2 shows DRIFT-CO spectra as a function of time when calcined Cu-Fe samples are exposed to 16 Torr CO. A band of very weak intensity at 2360 cm⁻¹ arises in the spectra of this sample, which is characteristic of adsorbed CO₂ and indicates CO oxidation with lattice oxygen on Fe³⁺ sites, which are thereby reduced to Fe²⁺ ions [22]. Obviously, a high-frequency band at 2127 cm⁻¹ was observed on the calcined 5%Cu-5%Fe/SiO₂ sample, which corresponds to CO linearly adsorbed on the copper species Cu⁺ [23–25].



Figure 2. FTIR spectra of CO adsorbed at a pressure of 16 Torr and at room temperature on the 5%Cu-5%Fe/SiO₂ and 5%Cu-5%Fe/Al₂O₃ samples.

For the catalyst 5%Cu-5%Fe/Al₂O₃, the intensity of the band was enhanced substantially, and the position shifted to a low wavenumber, namely to 2118 cm⁻¹, compared with that on the 5%Cu-5%Fe/SiO₂ sample (Figure 2). The band at 2118 cm⁻¹ characterizes linear carbonyl on electron-deficient copper cations (Cu^{δ +}-CO) [26]. The presence of this band likely indicates strong interaction of copper and iron species in the 5%Cu-5%Fe/Al₂O₃ sample, which is also consistent with the TPR-H₂ results for this catalyst (to be discussed below). The band position at 2190 cm⁻¹ agrees with the assignment to CO adsorbed on Al³⁺ cations [27].

Temperature-programmed reduction studies (TPR- H_2) were performed to provide further information about the reducibility of the prepared catalysts. The TPR-H₂ studies revealed a different reduction behavior for the samples depending on the nature of the carrier (Figure 3). The TPR profile for bimetallic 5Cu-xFe/Al₂O₃ catalysts is represented by a main single intensive peak with a slight shoulder in the range from 100 to 250 $^{\circ}$ C and is shifted to the low-temperature region with a maximum at 208–218 °C (Figure 3a) as compared to the monometallic copper sample with the same Cu content. The TPR profile of 5Cu/Al₂O₃ shows the presence of a single symmetric peak centered at 229 °C; such a temperature is diagnostic of the presence of a highly dispersed copper oxide phase in a reducible state. The deconvolution of the first peak and the calculated H_2/Cu and H_2/Fe ratios for this area (Table 1) for the 5Cu-5Fe/Al₂O₃ catalyst indicate the accelerating effect of Cu^0 on the Fe_2O_3 reduction and formation of a mixed phase of copper and iron oxide. The shift of the maximum to lower temperatures may be explained by the smaller particle size featured and high dispersion of metal oxides for the bimetallic samples supported on Al₂O₃. The second peak on the TPR profiles in the range of 400–650 $^{\circ}$ C and the H₂/Fe ratio of 0.89 correspond to the partial reduction of Fe_2O_3 nanoparticles supported on alumina. The reduction of the monometallic 5Fe/Al₂O₃ sample proceeds in two steps: the conversion of Fe^{3+} to Fe^{0} via Fe^{2+} at high temperatures in the range of 380–750 °C [20,28].



Figure 3. TPR curves of the calcined Cu-Fe samples on Al₂O₃ (a) and SiO₂ (b).

The SiO₂-supported samples exhibited a different reduction behavior after calcination. The reduction temperatures for the Cu-Fe/SiO₂ catalysts are shifted to the high-temperature region in relation to alumina-supported catalysts. The double peak of a lower intensity was observed on the TPR curve of the sample 5%Cu-5%Fe/SiO₂ (Figure 3b) at the temperatures of 150–330 °C in the region of reduction of silica-supported CuO to Cu⁰ (maximum at 221 °C) and Fe³⁺ to Fe²⁺ (maximum at 260 °C). The peak in the range of 400–650 °C with a maximum at 492 °C corresponds to reduction of Fe²⁺ to Fe⁰. Thus, in a bimetallic iron-copper catalyst, there is a close contact interaction between the oxide phases of iron and copper, and the Cu⁰ phase contributes to an easier reduction of Fe₂O₃. A similar accelerating effect of copper on the reduction of Fe₂O₃ to Fe₃O₄ was described earlier [18,29].

Catalyst	Peak Temperature (°C)	H ₂ Uptake (mmol/g.cat)	H ₂ /Cu	H ₂ /Fe
5Cu/SiO ₂	255	0.89	1.13	-
5Cu/Al ₂ O ₃	230	1.52	1.97	-
5Fe/Al ₂ O ₃	416 628	0.23 0.51	-	0.83
5Cu-5Fe/SiO ₂	223 260 470	0.54 0.49 0.71	0.69	1.34
5Cu-5Fe/Al ₂ O ₃	218 486	1.24 0.33	1.01	0.88

Table 1. H₂ uptake and reduction of peak temperatures of catalyst samples.

TEM analysis was conducted on calcined samples to obtain information on the size and microstructure of metal particles (Figure 4). It is interesting to note the effect of the support on the metal dispersion. The TEM study of the 5Cu-5Fe/Al₂O₃ catalyst revealed the more homogeneous distribution of metal particles, with a smaller average size (3.5 nm) and aggregates of particles with a size of 10–13 nm, while the sample of the same composition supported on SiO₂ prepared by the impregnation method is characterized by the higher values with the mean particle size of 8.4 nm and particle aggregates above 20 nm. Additionally, in the 5Cu-5Fe/SiO₂ sample, there are agglomerates of larger particles up to 20 nm in size in addition to small particles. It appears that the metal interaction with alumina is stronger than with silica, which is consistent with XRD results and the discussion above. A similar dependence of the influence of the carriers on the nanoparticle size was discussed earlier [30]. Additionally, the 5Cu-5Fe/SiO₂ sample prepared by the DPU codeposition method provides the formation of particles with a narrow size distribution with an average size of 5 nm.



Figure 4. TEM images and particle size distribution of the calcined samples: (**a**) 5Cu-5Fe/Al₂O₃; (**b**) 5Cu-5Fe/SiO₂; (**c**) 5Cu-5Fe/SiO₂ prepared by the DPU method.

The results of N₂ adsorption–desorption analysis are presented in Table 2. The surface area for all investigated catalysts increased slightly relative to the pure SiO₂ carrier. For the 5Cu-5Fe/SiO₂ catalysts synthesized by impregnation method, the total volume of pore of the size below 300 nm significantly decreased. Both facts probably indicate the formation

of metal oxides nanoparticles mainly inside the pores of the carrier. For the sample 5Cu- $5Fe/SiO_2$ -DPU prepared by co-deposition precipitation, the considerable increase in the specific surface area was observed. The increase in the pore volume indicates the formation and supported of porous aggregates mainly in the macropores or on the outer surface of silica.

Catalyst	S_{BET}/m^2g^{-1}	D _{pore} , nm	t-plot V _{micro} /cm ³ g ⁻¹	V_{total}/cm^3g^{-1} (at $P/P_0 = 0.99$)
SiO ₂	108	26	0.006	0.639
5Cu/SiO ₂	134	31	0.002	0.636
5Cu-5Fe/SiO ₂	124	24	0.005	0.560
5Cu-5Fe/SiO ₂ -DPU	169	22	0.006	0.676

Table 2. The results of nitrogen adsorption-desorption analysis.

2.2. Catalytic Activity

All synthesized samples exhibited the catalytic activity under relatively mild reaction conditions. In the present work, we conducted a study of the influence of the preparation method of the 5Cu-5Fe/SiO₂ sample on the catalytic properties. The Cu-Fe samples obtained by the DPU method showed a low catalytic activity with a low MBE selectivity compared to the catalysts prepared by the impregnation method, so the impregnation method is more promising for the synthesis of Cu-Fe catalysts for this reaction of selective hydrogenation (Figure 5). The results of catalytic tests of calcined Cu-Fe catalysts in selective liquid-phase hydrogenation of acetylene alcohol MBY showed a significant influence of the sample composition and the carrier nature on the catalytic properties (Figures 5 and 6). Figure 6 shows the results of MBY hydrogenation on the catalysts with low (0.5 wt%) iron content. The best catalytic properties among these samples were found for the 0.5Cu-5Fe/Al₂O₃ bimetallic catalyst, which provides a full MBY conversion in 2.75 h with the MBE selectivity of 87%. A remarkable change in the product selectivity was observed with an increase in the iron content by 10 times compared to the SiO₂-supported bimetallic catalysts with the same composition. Thus, the catalytic activity of the 5%Cu-5%Fe/Al₂O₃ catalyst was comparable to the 0.5%Cu-5%Fe/Al₂O₃ sample, however the selectivity was significantly higher than 92%. Therefore, in all cases where mono- and bimetallic nanoparticles were supported on Al₂O₃, the full MBY conversion was achieved several times faster as compared to the samples supported on SiO₂. The 5%Cu-5%Fe/Al₂O₃ catalyst remained stable for 3 cycles with intermediate washing of the catalyst in ethanol, while maintaining high selectivity of 92 and 90 for the 2nd and 3rd cycles, respectively. According to the TPR- H_2 analyses, the hydrogenation reaction temperature of 150 °C contributes to the initial partial reduction of copper oxide during the reaction occurring using the calcined bimetallic 5%Cu-5%Fe/Al₂O₃ catalyst. The reason for the high catalytic activity of the Al₂O₃-supported bimetallic catalyst is probably the high dispersion of Fe₂O₃, CuO, and Cu⁰ nanoparticles with strong contact interactions between the metals. For comparison, the reduced 5%Cu-5%Fe/Al₂O₃-Hcatalyst was prepared, which is supposed to contain Cu⁰ and Fe³⁺ phases based on the TPR studies. This sample was highly active under reaction conditions and the complete MBY conversion was achieved in 0.75 h, however the selectivity for the target product was only 11%. Thus, the reduction of catalysts in an H_2 flow is undesirable for the synthesis of Cu-Fe catalysts for selective hydrogenation of the triple bond in unsaturated alcohols.



Figure 5. Time dependence of the MBY conversion (**a**,**c**) and the selectivity to MBE (**b**,**d**) for the 5Cu-5Fe samples supported on Al_2O_3 and SiO_2 (*DPU method).



Figure 6. Time dependence of the MBY conversion (\mathbf{a} , \mathbf{c}) and the selectivity to MBE (\mathbf{b} , \mathbf{d}) for the 0.5Cu-5Fe samples supported on Al₂O₃ and SiO₂.

3. Experimental

3.1. Catalyst Synthesis

Supported oxide Cu-Fe nanoparticles were synthesized via (i) deposition of Cu and Fe precursors inside the pores of the support (SiO₂ and Al₂O₃) using the sequential incipient wetness impregnation with an aqueous solution of nitrates Fe(NO₃)₃ and Cu(NO₃)₂ and (ii) co-deposition–precipitation of Fe and Cu salts mainly on the outer surface of the SiO₂ support by thermal hydrolysis of urea (DPU).

SiO₂ (S_{BET} = 108 m² g⁻¹; D_{por} = 26 nm; V_{por} = 1.05 cm³ g⁻¹) and γ -Al₂O₃ (S_{BET} = 270 m² g⁻¹; V_{mesopore} = 0.46 cm³ g⁻¹; V_{micropore} = 0.005 cm³ g⁻¹) were used as a support.

The synthesis procedure (i) was performed as follows. At the first step of synthesis, the monometallic Fe/SiO₂ and Fe/Al₂O₃ samples were prepared by incipient wetness impregnation with a Fe(NO₃)₃ solution, dried at 60 °C, and then calcined in air at 300 °C for 4 h. Then, the copper precursor was deposited by incipient wetness impregnation with a Cu(NO₃)₂ solution, followed by drying at 80 °C and calcination in air at 300 °C for 4 h. The monometallic supported Cu and Fe catalysts were prepared by the incipient wetness impregnation of SiO₂ and Al₂O₃ for comparison of catalytic properties. Additionally, the calcined bimetallic 5Cu-5Fe/Al₂O₃ sample was reduced in a hydrogen flow at 400 °C for 2 h to compare the catalytic activity.

To study the effect of the method of synthesis of catalysts, Cu-Fe samples were obtained using the method (ii). A detailed synthesis procedure is presented in our previously published work [17]. Briefly, a silica suspension in a solution containing Cu(NO₃)₂, Fe(NO₃)₃, and urea was heated under vigorous stirring and kept at 92 °C for 9 h. The resulting solid was separated from the mother solution by centrifugation and washed three times with distilled water using intermediate centrifugation. Then, it was dried consequently on a rotary evaporator (40 °C, 40 mbar for 4 h) and in an oven at 110 °C for 16 h. The dried sample was calcined in air at 300 °C for 4 h.

The Fe loading in the samples was varied in the range of 0.5–5 wt.%, while the Cu loading was 5 wt.%. The synthesized catalysts were designated as 5Cu-xFe/S, where x is the Fe loadings and S is the used support.

3.2. Catalyst Characterization

The synthesized catalysts were investigated using TPR-H₂, DRIFTS-CO, XRD, and TEM methods.

The morphology of the samples and the particle size distribution were studied using a JEM-2100 (JEOL, Tokyo, Japan) transmission electron microscope. Before measurements, the samples were deposited on 3 mm carbon-coated copper grids from a suspension in isopropanol. Images were acquired in the bright-field TEM mode at a 200 kV accelerating voltage. The average particle size was calculated by analyzing 300 nanoparticles of various sizes and shapes using the Gatan Microscopy Suite[®] program.

The specific surface area, pore diameter, and pore volume in the SiO₂ carrier and SiO₂supported catalysts were investigated by nitrogen adsorption–desorption measurements at 77 K using a Micromeritics ASAP 2020 V1.02 E ("Micromeritics", Norcross, GA, USA) instrument.

DRIFT spectra were recorded using a Nicolet Protege 460 spectrophotometer («Thermo Electron Corporation», Madison, WI, USA) in transmittance mode in the interval range of 6000–400 cm⁻¹ (spectral resolution 4 cm⁻¹). Powdered materials were pressed into self-supporting wafers (25–35 mg·cm⁻²) and placed in a vacuum infrared quartz cell equipped with CaF₂ windows. Before the experiments, the samples were evacuated at 300 °C in a vacuum for 2 h. Carbon monoxide was adsorbed on the calcined samples at the equilibrium pressure of 16 Torr at ambient temperature.

The method of temperature-programmed reduction with hydrogen (TPR-H₂) (I was used on the lab constructed device to investigate the Fe-Cu interaction. The materials were studied via the TPR-H₂ method using the setup described elsewhere [20,31]. Before TPR runs, the samples (0.10 \pm 0.01 g of the fraction 0.25–0.35 mm) were kept in an Ar flow at 300 °C for 1 h, then they were cooled to 20 °C. Subsequently, the samples were

heated from 20 to 800 °C with a heating rate of 10 °C min⁻¹ in a flow (30 mL min⁻¹) of a reducing mixture (5% H₂ in Ar) and reduced at 800 °C until H₂ consumption became negligible. The reduced catalyst sample was cooled down to room temperature in an Ar flow. A thermal conductivity detector (TCD) was used in order to record changes in the H₂ concentration and to measure the H₂ uptake and release. Hydrogen consumption (release) was determined based on the measured values of the area for peaks on the time dependence of TCD curves and the preliminary calibration with CuO (Aldrich-Chemie GmbH, 99%, New Jersey, NJ, USA) pretreated in an Ar flow at 300 °C. The presented TPR profiles were normalized per 1 gram of the material.

The phase composition of the materials and the particle size were estimated by X-ray diffraction (XRD) analysis. X-ray diffraction patterns were recorded using an ARL X'TRA diffractometer (ThermoScientific, Ecublens, Switzerland) with CuK α radiation (40 kV, 40 mA), with a scanning rate of 1.2° per minute over the scanning range of 20 < 2 θ < 60°. ICCD data were used for identification purposes.

3.3. Catalytic Activity Tests

The catalytic properties of the calcined bimetallic Cu-Fe and monometallic Fe and Cu nanoparticles were characterized in the reaction of the liquid-phase hydrogenation of 2-methyl-3-butyn-2-ol (MBY) to 2-methyl-3-buten-2-ol (MBE) with molecular hydrogen in the batch mode. The liquid-phase hydrogenation was carried out in a 100 mL autoclave equipped with a probe-withdrawing valve. The reaction conditions of MBY hydrogenation were as follows: a 0.2 M DMY solution in ethanol (15 mL) with undecane as an internal standard, 150 °C, H₂ pressure 1.3 MPa. The time dependences of the MBY conversion and selectivity to MBE were investigated. Samples of the reaction mixture were analyzed by GLPC with an internal standard method. Only 2-methyl-3-buten-2-ol (MBE) and 2-methyl-2-butanol (MBA) were detected as reaction products and the carbon balance was better than 99%. The results are shown as the time dependences of the MBY conversion and selectivity to the products.

4. Conclusions

In this study, novel supported Cu-Fe catalysts for the selective hydrogenation of alkynes to alkenes were described. The catalytic properties of the bimetallic catalysts depend on the composition of the samples, type of support, and conditions of thermal treatment of the samples. The calcined samples were the most promising catalysts in selective hydrogenation under mild reaction conditions.

The change of the support affects the interaction of the oxide phases of iron and copper and consequently the selectivity toward MBE. When using γ -Al₂O₃ instead of SiO₂ as a support of the bimetallic 5Cu-5Fe catalyst, the catalytic activity and selectivity greatly increased. These results suggest that the intrinsic properties of the support have a significant influence on the catalytic performance of Cu-Fe catalysts. The observed contrasting behavior of the catalysts depending on the support nature was explained in terms of a higher dispersity of the metals on the alumina support, which was induced by stronger interaction of the support and the metal oxides, as evidenced by DRIFTS-CO, TPR-H₂, and TEM characterization. The best catalytic properties in the selective liquid-phase hydrogenation of acetylene alcohol were obtained on the bimetallic 5%Cu-5%Fe/Al₂O₃ catalyst with a 93% selectivity toward MBE at full MBY conversion for 2.75 h.

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References

- Chen, B.; Dingerdissen, U.; Krauter, J.; Rotgerink, H.L.; Möbus, K.; Ostgard, D.; Panster, P.; Riermeier, T.; Seebald, T.; Tacke, T.; et al. New developments in hydrogenation catalysis particularly in synthesis of fine and intermediate chemicals. *Appl. Catal. A* 2005, 280, 17–46. [CrossRef]
- Garcia-Mota, M.; Gomez-Diaz, J.; Novell-Leruth, G.; Vargas-Fuentes, C.; Bellarosa, L.; Bridier, B.; Perez-Ramirez, J.; Lopez, N. A density functional theory study of the 'mythic' Lindlar hydrogenation catalyst. *Theor. Chem. Acc.* 2011, 128, 663–673. [CrossRef]
- 3. Rapeti, S.K.; Kasina, K.C.; Gundepaka, P.; Birudaraju, S.; Sailaja, B.B.V. Efficient insitu palladium nano catalysis for Z-selective semi transfer hydrogenation of internal alkynes using safer 1, 4-butanediol. *Tetrahedron Lett.* **2020**, *61*, 151395. [CrossRef]
- González-Fernández, A.; Pischetola, C.; Cárdenas-Lizana, F. Gas Phase Catalytic Hydrogenation of C4 Alkynols over Pd/Al₂O₃. Catalysts 2019, 9, 924. [CrossRef]
- Delgado, J.A.; Benkirane, O.; Claver, C.; Curulla-Ferré, D.; Godard, C. Advances in the Preparation of Highly Selective Nanocatalysts for the Semi-Hydrogenation of Alkynes Using Colloidal Approaches. *Dalton Trans.* 2017, 46, 12381–12403. [CrossRef]
- Mashkovsky, I.S.; Markov, P.V.; Bragina, G.O.; Baeva, G.N.; Rassolov, A.V.; Bukhtiyarov, A.V.; Prosvirin, I.P.; Bukhtiyarov, V.I.; Stakheev, A.Y. PdZn/α-Al₂O₃ Catalyst for Liquid-Phase Alkyne Hydrogenation: Effect of the Solid-State Alloy Transformation into Intermetallics. *Mendeleev Commun.* 2018, 28, 152–154. [CrossRef]
- Vernuccio, S.; Goy, R.; Meier, A.; Rudolf von Rohr, P.; Medlock, J. Kinetics and mass transfer of the hydrogenation of 2-methyl-3butyn-2-ol in a structured Pd/ZnO/Al₂O₃ reactor. *Chem. Eng. J.* 2017, *316*, 121–130. [CrossRef]
- Okhlopkova, L.B.; Prosvirin, I.P.; Kerzhentsev, M.A.; Ismagilov, Z.R. Capillary microreactor with PdZn/(Ti, Ce)O₂ coating for selective hydrogenation of 2-methyl-3-butyn-2-ol. *Chem. Eng. Process.* 2021, 159, 108240. [CrossRef]
- 9. Shesterkina, A.A.; Kustov, L.M.; Strekalova, A.A.; Kazansky, V.B. Heterogeneous Iron-Containing Nanocatalysts—Promising Systems for Selective Hydrogenation and Hydrogenolysis. *Catal. Sci. Technol.* **2020**, *10*, 3160–3174. [CrossRef]
- 10. Fu, F.; Dionysiou, D.; Liu, H. The use of zero-valent iron for groundwater remediation and wastewater treatment: A review. *J. Hazard. Mater.* **2014**, *267*, 194–205. [CrossRef]
- Reddy, A.V.B.; Yusop, Z.; Jaafar, J.; Reddy, Y.V.M.; Aris, A.B.; Majid, Z.A.; Talib, J.; Madhavi, G. Recent progress on Fe-based nanoparticles: Synthesis, properties, characterization and environmental applications. *J. Environ. Chem. Eng.* 2016, *4*, 3537–3553. [CrossRef]
- 12. Redina, E.A.; Kirichenko, O.A.; Shesterkina, A.A.; Kustov, L.M. Unusual Behavior of Bimetallic Nanoparticles in Catalytic Processes of Hydrogenation and Selective Oxidation. *Pure Appl. Chem.* **2020**, *92*, 989–1006. [CrossRef]
- Shesterkina, A.A.; Kirichenko, O.A.; Kozlova, L.M.; Kapustin, G.I.; Mishin, I.V.; Strelkova, A.A.; Kustov, L.M. Liquid-Phase Hydrogenation of Phenylacetylene to Styrene on Silica-Supported Pd–Fe Nanoparticles. *Mendeleev Commun.* 2016, 26, 228–230. [CrossRef]
- Huang, X.; Liu, K.; Vrijburg, W.L.; Ouyang, X.; Dugulan, I.A.; Liu, Y.; Verhoeven, M.W.G.M.T.; Kosinov, N.A.; Pidko, E.A.; Hensen, E.J.M. Hydrogenation of levulinic acid to γ-valerolactone over Fe-Re/TiO₂ catalysts. *Appl. Catal. B Environ.* 2020, 278, 119314. [CrossRef]
- Tejeda-Serrano, M.; Cabrero-Antonino, J.R.; Mainar-Ruiz, V.; Lopez-Haro, M.; Hernandez-Garrido, J.C.; Calvino, J.J.; Leyva-Perez, A.; Corma, A. Synthesis of Supported Planar Iron Oxide Nanoparticles and Their Chemo- and Stereoselectivity for Hydrogenation of Alkynes. ACS Catal. 2017, 7, 3721–3729. [CrossRef]
- 16. Yan, K.; Chen, A. Selective hydrogenation of furfural and levulinic acid to biofuels on the ecofriendly Cu–Fe catalyst. *Fuel* **2014**, *115*, 101–108. [CrossRef]
- 17. Shesterkina, A.A.; Shuvalova, E.V.; Kirichenko, O.A.; Strelkova, A.A.; Nissenbaum, V.D.; Kapustin, G.I.; Kustov, L.M. Using Fe–Cu nanoparticles applied to silica gel in the reaction of the selective hydrogenation of p-Dinitrobenzene to p-Phenylenediamine. *Russ. J. Phys. Chem. A* 2017, *91*, 201–204. [CrossRef]
- He, L.; Gong, X.; Ye, L.; Duan, X.; Yuan, Y. Synergistic effects of bimetallic Cu-Fe/SiO₂ nanocatalysts in selective hydrogenation of diethyl malonate to 1,3-propanediol. *J. Energy Chem.* 2016, 25, 1038–1044. [CrossRef]
- 19. Nitta, Y.; Matsugi, S.; Imanaka, T. Partial hydrogenation of phenylacetylene on copper-promoted iron catalyst. *Catal. Lett.* **1990**, *5*, 67–72. [CrossRef]

- Kirichenko, O.; Kapustin, G.; Nissenbaum, V.; Strelkova, A.; Shuvalova, E.; Shesterkina, A.; Kustov, L. Thermal decomposition and reducibility of silica-supported precursors of Cu, Fe and Cu–Fe nanoparticles. *J. Therm. Anal. Calorim.* 2018, 134, 233–251. [CrossRef]
- Shesterkina, A.A.; Shuvalova, E.V.; Redina, E.A.; Kirichenko, O.A.; Tkachenko, O.P.; Mishin, I.V.; Kustov, L.M. Silica-supported iron oxide nanoparticles: Unexpected catalytic activity in hydrogenation of phenylacetylene. *Mendeleev Commun.* 2017, 27, 512–514. [CrossRef]
- Šmit, G.; Strukan, N.; Crajé, M.W.J.; Lázár, K. A comparative study of CO adsorption and oxidation on Au/Fe₂O₃ catalysts by FT-IR and in situ DRIFTS spectroscopies. J. Mol. Catal. A Chem. 2016, 252, 163–170. [CrossRef]
- Lu, R.; Mao, D.; Yu, J.; Guo, Q. Enhanced activity of CuFe/SiO₂ catalyst for CO hydrogenation to higher alcohols by pretreating the support with ammonia. J. Ind. Eng. Chem. 2015, 25, 338–343. [CrossRef]
- 24. Xu, R.; Ma, Z.; Yang, C.; Wei, W.; Li, W.; Sun, Y. The effect of iron on the adsorption properties of CuMnZrO₂ catalysts studied by temperature-programmed desorption and FTIR spectroscopy. *J. Mol. Catal. A Chem.* **2004**, *218*, 133–140. [CrossRef]
- 25. Fisher, I.A.; Bell, A.T. In Situ Infrared Study of Methanol Synthesis from H₂/CO over Cu/SiO₂ and Cu/ZrO₂/SiO₂. J. Catal. **1988**, 178, 153–173. [CrossRef]
- Sun, C.; Mao, D.; Han, L.; Yu, J. Effect of impregnation sequence on performance of SiO₂ supported Cu-Fe catalysts for higher alcohols synthesis from syngas. *Catal. Commun.* 2016, 84, 175–178. [CrossRef]
- 27. Larrubia Vargas, M.A.; Busca, G.; Costantino, U.; Marmottini, F.; Montanari, T.; Patrono, P.; Ramis, G. An IR study of methanol steam reforming over ex-hydrotalcite Cu–Zn–Al catalysts. *J. Mol. Catal. A Chem.* **2007**, *266*, 188–197. [CrossRef]
- Lingaiah, N.; Babu, N.S.; Gopinath, R.; Reddy, P.S.S.; Prasad, P.S.S. Hydrodechlorination of chlorobenzene over supported metal catalysts. *Catal. Surv. Asia* 2006, 10, 29–39. [CrossRef]
- 29. dos Santos Monteiro, D.; da Guarda Souza, M.O. Thermal decomposition of precursors and iron oxide properties. *J. Therm. Anal. Calorim.* **2016**, *123*, 955–963. [CrossRef]
- 30. Pino, N.; Sitthisa, S.; Tan, Q.; Souza, T.; López, D.; Resasco, D.E. Structure, activity, and selectivity of bimetallic Pd-Fe/SiO₂ and Pd-Fe/γ-Al₂O₃ catalysts for the conversion of furfural. *J. Catal.* **2016**, *350*, 30–40. [CrossRef]
- Kirichenko, O.; Kapustin, G.; Nissenbaum, V.; Mishin, I.; Kustov, L. Evaluation of Stability of Silica-Supported Fe–Pd and Fe–Pt Nanoparticles in Aerobic Conditions Using Thermal Analysis. J. Therm. Anal. Calorim. 2014, 118, 749–758. [CrossRef]