Electronic Supplementary Information (ESI)

Surface state during activation and reaction of high-performing multi-metallic alkyne hydrogenation catalysts

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Experimental details

The preparation and characterization of the Cu_3Fe and $Cu_{2.75}Ni_{0.25}Fe$ catalysts was described in detailed elsewhere (B. Bridier and J. Pérez-Ramírez, *J. Am. Chem. Soc.*, 2010, **132**, 4321). Briefly, the precursors were prepared by continuous co-precipitation followed by calcination in static air at 873 K for 15 h using a heating rate of 5 K min^{-1}. The resulting mixed oxides (150 mg, sieve fraction 200-400 μm) were loaded in the 12 mm i.d. quartz micro-reactor (MicroActivity Reference set-up, PID Eng&Tech), heated in He to 773 K, reduced in 5 vol.% H_2 in He at 773 K for 30 min, and finally cooled down to the reaction temperature in He. The gas-phase propyne hydrogenation was carried out at 523 K and 1 bar using a feed mixture of $C_3H_4/H_2/He = 2.5/7.5/90$ and a total flow of 42 cm^3 STP min^{-1}. Propyne, propene, and propane were analyzed online using an Agilent GC6890N gas chromatograph equipped with a GS-GasPro column and a thermal conductivity detector. Propyne conversion was determined as the amount of reacted propyne divided by the amount of propyne introduced in the reactor. The selectivity to propene (propane) was determined as the amount of propene (propane) formed divided by the amount of reacted propyne.

(In situ) X-ray photoelectron (XPS) and X-ray absorption (XAS) spectroscopies, the latter in total electron yield mode, were performed simultaneously at the ISISS beam-line of BESSY II synchrotron facility of the Helmholtz Zentrum Berlin. Cu_3Fe and $Cu_{2.75}Ni_{0.25}Fe$ samples were investigated after they have been ex situ calcined and reduced. The powders were first pressed into a pellet and then placed on a sample holder, which could be heated from the rear by an infrared laser. Temperature was controlled by a K-type thermocouple fixed onto the sample surface; however at high temperatures (during in situ reductive treatment), a correction was taken into account as verified by reference experiments with a pyrometer. Gas flow into the analysis chamber was controlled via calibrated mass flow controllers. We performed in situ oxidative and reductive pretreatments as well as propyne hydrogenation experiments. For the latter, the feed gas contained a mixture of C_3H_4 and H_2 in a ratio of 1:3 at the total flow of 15 cm^3 STP min^{-1} and the pressure was set to 1 mbar (note the applied flow rate is equivalent to $15\times10^3\,cm^3\,min^{-1}$ at 1 mbar). Reaction temperature during hydrogenation was 523 K. A micro gas chromatograph (Varian CP-4900) was used to monitor reactant and reaction products simultaneously to the spectroscopic characterization of the surface. Before the catalytic experiment with the prereduced Cu_3Fe catalyst, we performed a refreshing reductive treatment at 650 K for 20 min at 1 mbar H_2. The atomic fraction of the main constituents was calculated upon excitation of the Cu/Fe/Ni 3p region and analysis of 450 eV kinetic energy photoelectrons. Photo ionization cross sections were taken from Yeh and Lindau (J. J. Yeh and I. Lindau, *At. Data Nucl. Data Tables*, 1985, **32**, 1).

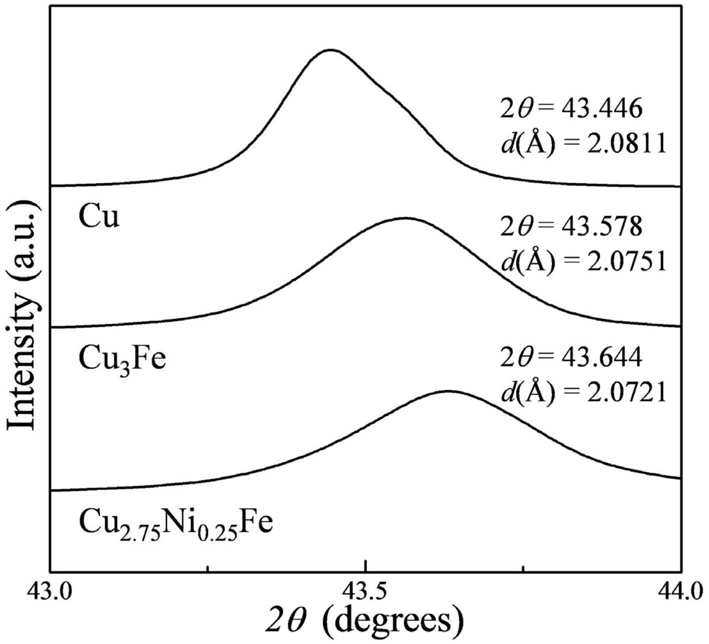

Fig. ESI 1 X-ray diffraction patterns of pure metallic copper and the reduced Cu_3Fe and $Cu_{2.75}Ni_{0.25}Fe$ samples, focusing on the Cu(111) reflection. The three reflections are described by their 2θ position and corresponding d value. The shift to higher diffraction angles is in agreement with the increment of the metallic interaction. The patterns were measured in an X'Pert PRO-MPD diffractometer using a step size of 0.033° and a counting time of 14 s per step.

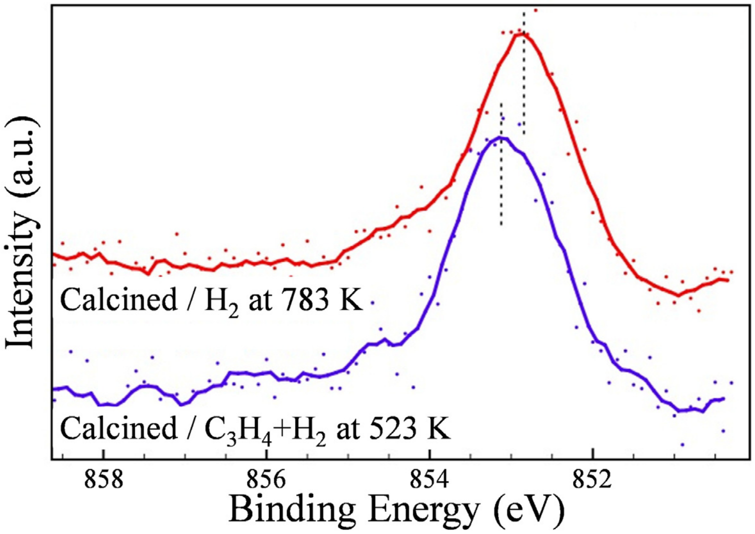

Fig. ESI 2 Ni 2p region of the calcined $Cu_{2.75}Ni_{0.25}Fe$ in 1 mbar H_2 at 783 K and under C_3H_4 hydrogenation (1 mbar) at 523 K.

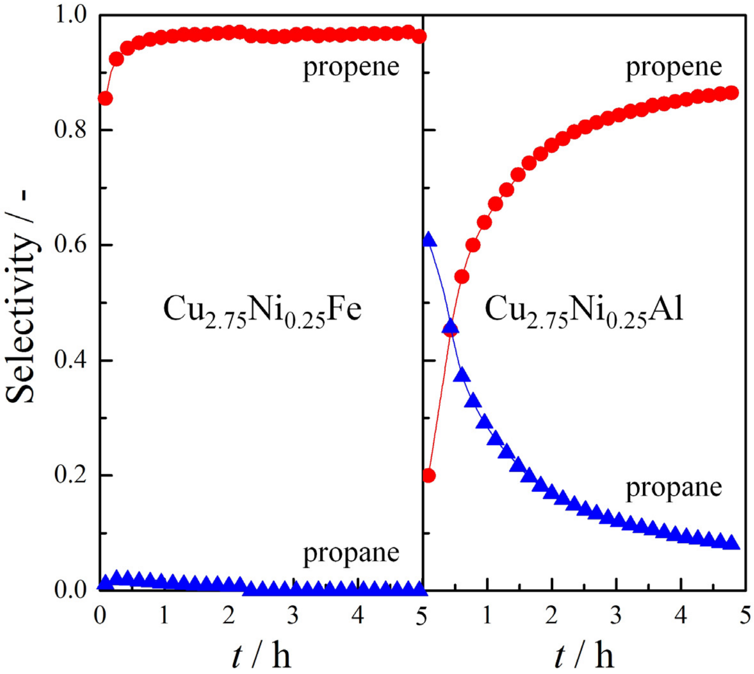

Fig. ESI 3 Selectivity to propene and propane versus time-on-stream during propyne hydrogenation at 1 bar over $Cu_{2.75}Ni_{0.25}Fe$ and $Cu_{2.75}Ni_{0.25}Al$ catalysts.