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Bimetallic Fe-Ni/SiO₂ Catalysts for Furfural Hydrogenation: Respective roles of Fe and Ni

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PURPOSE OF THE ABSTRACT

Introduction

Noble metals have been widely employed for their catalytic performances in the hydrogenation and hydrogenolysis of biosourced molecules, but their cost is high and their abundance low. Substitutes are currently searched for among the more abundant and cheaper metals from the first period of transition metals. Among them, Fe-Ni bimetallic systems have been reported to be more selective than monometallic Ni, which often leads to hydrogenolysis or overhydrogenation side reactions. However, standard preparation methods, such as impregnation, usually produce poorly controlled Fe-Ni nanoparticles (disparities in size and metal content), so that it has been difficult to derive general correlations between the formulation of Fe-Ni nanoparticles and their catalytic properties. In the present work, Fe-Ni/SiO₂ catalysts (40 wt% in metals) have been prepared by deposition-precipitation with urea (DPU) and investigated using a combination of advanced characterization techniques (in situ X-ray absorption spectroscopy, XAS; in situ Mössbauer spectroscopy, MössS; STEM-EDX and EELS subnanometric mapping; low energy ion scattering spectroscopy, LEIS), making it possible to precisely evidence the interplay between Fe and Ni along the different stages of the catalyst preparation (precipitation, initial reduction, exposure to O₂, activation by H₂), and to link the surface composition of Fe-Ni nanoparticles to their catalytic properties in the hydrogenation of furfural.

Results and discussion

DPU from Fe and Ni sulfates over silica Sipernat-50 (Degussa) under inert atmosphere leads to a mixed Fe-Ni 1:1 phyllosilicate phase [1], that is reduced under diluted H₂ following several stages (in situ XAS, recorded simultaneously at the Fe and Ni K edges; MössS): reduction of Fe(III) to Fe(II) between 275 and 350°C; reduction of Ni(II) to Ni(0), which triggers the destruction of the phyllosilicate and the reduction of Fe(II) to Fe(0); formation of fcc Fe-Ni nanoparticles above 400°C. The reduction of Fe is complete at 700°C. The size distribution of the Fe-Ni nanoparticles is narrow (TEM: 4-7 nm, dispersion: 15-20%), while particles larger than 10 nm are observed on samples prepared by impregnation. The standard deviation of chemical compositions evaluated on individual particles (STEM-EDX) is low (8 at %).

Both Fe and Ni partly oxidize upon exposure to diluted O₂ simulating ambient air, in two stages: a rapid stage of 20 s, followed by a slower one that extends over 25 min (XAS). As a result, a 1 nm-thick Fe(III)-enriched mixed oxidic shell surrounds the fcc Ni-rich metallic core (STEM-EELS, XAS). A new activation step in H₂ brings the initial state back, with Ni being reduced between 100 and 300°C, before Fe.

Catalysts activated at 400°C under H₂ have been tested in furfural hydrogenation on the REALCAT platform (example shown on the accompanying figure: T = 150°C, solvent = isopropanol, P_{H2} = 20 bar, t = 2h, 0.6 mmol furfural). Among the 6 tested bimetallic formulations (from Fe₆₃Ni₃₇ to Fe₇Ni₉₃), Fe₃₁Ni₆₉/SiO₂ and Fe₂₅Ni₇₅/SiO₂ provide the highest yield in furfuryl alcohol (FFA) and in the associated isopropyl ether. Decreasing the amount of Fe leads to the hydrogenolysis of the C-O bond and the hydrogenation of the furan ring, predominant with monometallic Ni (2-methylfuran; tetrahydrofurfuryl alcohol and its isopropyl ether; 2-methyl THF). Rather than their global composition, it is the surface content in Fe resulting from the history of the Fe-Ni nanoparticles that determines their catalytic properties. MössS and LEIS analysis show that after activation in H₂, Fe remains the major metal at the surface of Fe₃₁Ni₆₉/SiO₂ nanoparticles, toning down the hydrogenating properties of Ni, while Fe is still significantly detected at the surface of Fe₁₄Ni₈₆ particles (figure, insert).

FIGURES

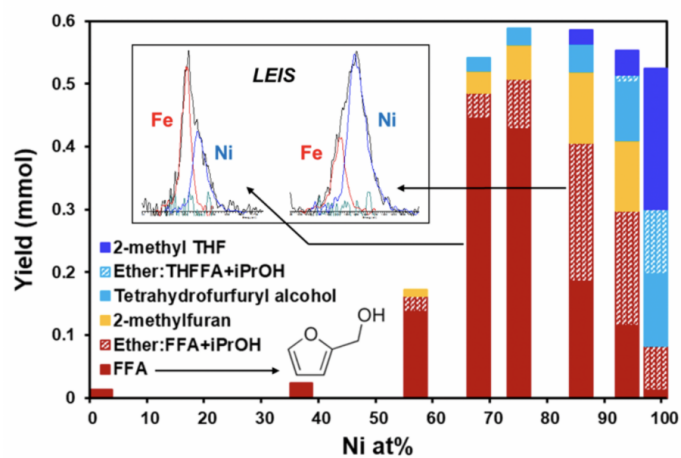


FIGURE 1

Yield in furfuryl alcohol (FFA) and in the associated isopropyl ether for 6 tested bimetallic formulations

FIGURE 2

KEYWORDS

BIBLIOGRAPHY

[1] D. Shi, Q. Yang, C. Peterson et al., Catal. Today, doi 10.1016/j.cattod.2018.11.041.