

Correction to “Chemoselective Hydrogenation of Benzoic Acid over Ni–Zr–B–PEG(800) Nanoscale Amorphous Alloy in Water”

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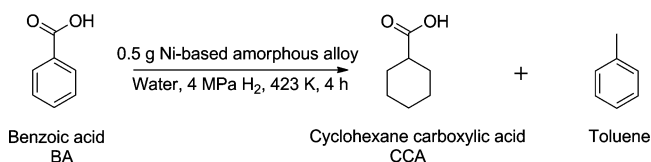
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We recently published a paper entitled “Chemoselective Hydrogenation of Benzoic Acid over Ni–Zr–B–PEG(800) Nanoscale Amorphous Alloy in Water”. Because of an oversight, the byproduct of this paper needs to be corrected to toluene. The following corrections should appear for the above-mentioned paper.

Page 2267: In section 2.3, the published Scheme 1 is incorrect. A corrected version of Scheme 1 has been presented below:

Scheme 1. Products from the Divergent Pathways of Hydrogenation of BA over Ni-Based Amorphous Alloy



Also, in the last sentence of section 2.3, the words “an Agilent 5975C spectrometer” should be replaced by “a Thermo Finnigan Polaris-Q spectrometer”.

Page 2269: The published version of Table 4 is incorrect. A corrected version of Table 4 is presented below.

Table 4. Hydrogenation of Benzoic Acid in Various Solvents over Ni–Zr–B–PEG(800)^a

entry	solvent	conversion of BA (%)	selectivity for CCA (%)	selectivity for toluene (%)	yield of CCA (%)
1	water	93.5	93.6	6.4	87.5
2	dioxane	99.7	69.2	30.8	69.0
3	tetrahydrofuran	87.8	56.1	43.9	49.3
4	cyclohexane	99.6	42.7	57.3	42.5
5	ethanol ^b	78.7	1.1	0.9	8.7
6	butan-2-ol ^c	72.7	58.6	5.9	42.6

^aReaction conditions: BA, 3.0 g; catalyst, 0.5 g; solvent, 60 mL; 423 K; initial $P(\text{H}_2) = 4$ MPa; and reaction time, 4 h. ^bOther byproducts (selectivity): ethyl benzoate (71.5%), ethyl cyclohexane carboxylate (26.6%); ^cOther byproducts (selectivity): butan-2-yl benzoate (12.8%), butan-2-yl cyclohexane carboxylate (22.7%).

Also, the first paragraph in section 3.3 should read as follows (altered text is highlighted in boldface italic font):

3.3. Effect of Solvents. The selective hydrogenation of aromatic compounds with both aromatic rings and other

reducible groups usually requires severe conditions over non-noble metal catalysts,^{45–47} with the potential to lead to the hydrogenation of the latter functionality. The chemoselective hydrogenation of BA was therefore studied in a series of solvents over Ni–Zr–B–PEG(800) to investigate the effect of solvents on the selectivity, and the results are shown in Table 4. As can be seen, in the case of water, a highly polar solvent, the selectivity for CCA reached 93.6%, whereas the selectivity decreased significantly with decreasing polarity of the solvents. For instance, in the cases of 1,4-dioxane and tetrahydrofuran, the selectivity for CCA decreased to 69.2 and 56.1%, respectively. Nevertheless our result in 1,4-dioxane was still superior to the observation of Anderson with only 3% yield of CCA over a Pd-based catalyst.⁴⁸ Thus, our catalytic system involving Ni–Zr–B–PEG(800) catalyst exhibits a better solvent profile with 99.7% conversion and 69.2% selectivity for CCA in 1,4-dioxane. In the case of the nonpolar solvent cyclohexane, the selectivity for CCA decreased to only 42.7% but the selectivity for **toluene** increased to 57.3%, in keeping with the results of Malyala when using *n*-hexane,⁴⁹ showing that production of **toluene** increases commensurate with the decrease of the polarity of the solvents. Thus, it can be concluded that the polarity of a solvent has a significant effect on the selectivity for CCA. However, it must be pointed out that this rule does not fit for solvents that can react with the substrate. Using ethanol, a moderately polar solvent, the selectivity for CCA was only 1.1%, much lower even than that of the nonpolar cyclohexane, with esterification rather than hydrogenation occurring under the reaction conditions, leading mainly to ethyl benzoate (71.5% selectivity). Furthermore, even the CCA formed reacted further with the ethanol to produce ethyl cyclohexane carboxylate (26.6% selectivity), resulting in the very low selectivity for CCA. In contrast, in the case of a sterically hindered alcohol, such as butan-2-ol, the selectivity for CCA improved notably to 58.6%, although butan-2-yl benzoate and butan-2-yl cyclohexane carboxylate were also obtained in relative amounts of 12.8 and 22.7%, respectively. Thus, water is the solvent of choice for BA hydrogenation due to the

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high selectivity of this combination as well as the green nature of the system.

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