

**NICKEL-CATALYZED REDUCTIONS AND DEOXYGENATIONS AT HYDROTHERMAL**

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**Introduction:** Reactions at the water/crystal interface are often considered an important aspect of the organic chemistry associated with the origins of life.<sup>1</sup> Catalysis of organic reactions under hydrothermal conditions (200-400°C, 2-100MPa) with minerals has been demonstrated (see, for example, refs 2-6), but much less work has been reported on catalysis at the water/metal crystal surface. Such reactions are of interest since pure metals are known to be among the most active and widely used catalysts in organic chemistry,<sup>7</sup> and so a low abundance of pure metals in natural systems could very well be compensated by a high catalytic activity. Nickel and iron, in the forms of minerals and alloys have been found in serpentinizing hydrothermal systems that are implicated as having a role in the origins of life.<sup>8,9</sup> Here we describe the results of experiments that explore the scope of pure crystalline metals, with particular emphasis on nickel, as catalysts for hydrothermal organic reactions. We have focused on reductions, using metallic iron as a sacrificial hydrogen donor.



Figure 1. Schematic representation of organic functional group transformations observed under hydrothermal conditions, catalyzed by crystalline metallic nickel.

We have now observed a wide variety of organic functional group transformations, several of which are components of the extensively studied pathway from carboxylic acids to alkanes.<sup>10</sup> For example, at 250°C and 40 bar in the presence of metallic nickel as the catalyst and metallic iron as a sacrificial hydrogen generator, simple alkenes such as cyclohexene are reduced with 90% conversion in an hour or less to form the corresponding alkanes. Under these conditions in the absence of nickel and iron, cyclohexene will add water

to form alcohols and isomeric alkenes, but with less than 1% conversion.<sup>11</sup> Although they react more slowly, aromatics are also reduced under these conditions, so that benzene is converted into cyclohexane with greater than 95% yield in 7 days. Hydrogen additions as alkene, aromatic, and carbonyl reductions, as well as hydrogenolysis, have also been studied. Compounds containing multiple oxygen atoms can be fully deoxygenated and reduced. The metal catalyzed versions of these reactions occur up to 10x faster than the corresponding reactions under non-catalyzed conditions.<sup>8</sup> In addition to conventional reactions, selective carbon-carbon and carbon-oxygen bond cleavage processes are observed. For instance, benzyl alcohol undergoes carbon-oxygen hydrogenolysis to toluene, while octanol undergoes carbon-carbon hydrogenolysis to heptane. This work allows us to assess the types of reactions that may be possible on other planets which may have analogous hydrothermal systems. Reduced Ni, while rare on Earth's surface more abundant than Al in the Universe.<sup>12</sup> It is a highly active catalyst, and even a small amount could have an impact on the fate of organic carbon at elevated temperatures. This is useful in determining how prebiotic organic compounds may have formed, and potentially their fate.

**References:**

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