



Turning Teflon-coated magnetic stirring bars to catalyst systems with metal nanoparticle trace deposits – A caveat and a chance

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ABSTRACT

It could be an unintentional effect to deposit metal nanoparticles on a simple Teflon-coated magnetic stirring bar. Rhodium nanoparticles, as an example, were reproducibly deposited onto a standard, commercial Teflon-coated magnetic stirring bar by easy and rapid microwave-assisted decomposition of the metal carbonyl precursor $\text{Rh}_6(\text{CO})_{16}$ in the ionic liquid 1-*n*-butyl-3-methyl-imidazolium tetrafluoroborate. Such metal nanoparticle deposits are not easy to remove from the Teflon surface by simple washing procedures and present active catalysts which one is not necessarily aware of. Barely visible metal-nanoparticle deposits on a stirring bar can act as trace metal impurities in catalytic reactions. As a proof-of-principle the rhodium-nanoparticle deposits of 32 μg or less Rh metal on a 20 mm $\times$ 6 mm magnetic stirring bar were shown to catalyze the hydrogenation reaction of neat cyclohexene or benzene to cyclohexane with quantitative conversion. Rhodium-nanoparticle-coated stirring bars were easily handable, separable and re-usable catalyst system for the heterogeneous hydrogenation with quantitative conversion and very high turnover frequencies of up to 32,800 mol cyclohexene $\times$ (mol Rh)^{−1} $\times$ h^{−1} under organic-solvent-free conditions.

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1. Introduction

It has recently become more evident that not every component which was originally claimed as catalyst turned out to be the actual active ingredient. In some prominent cases trace metal impurities were eventually proven as the actual catalytic species [1,2]. In an early example, traces of nickel compounds which formed unintentional during the cleaning of a V2A steal autoclave and remained in there changed the Ziegler–Aufbau reaction (reaction of AlEt_3 with ethylene at 100 °C under pressure to long-chain Al-alkyls) to a clean ethylene dimerization to yield butene. The cause of this unexpected dimerization was at first unknown and later termed the “nickel effect” after its origin had become clear. In addition, the nickel compounds had required traces of acetylene which were present in technical ethylene for stabilization of the nickel catalyst [3,4].

More recently, a Suzuki cross-coupling which was thought to have occurred metal-free was indeed promoted by ppb Pd traces in the Na_2CO_3 or K_2CO_3 bases used for the reaction [5]. Suggested iron-catalyzed cross-coupling reactions with different FeCl_3 sources were eventually corrected to ppm-scale copper impurities

doing the catalysis [6]. Even with Pd in the ppb range it is possible to carry out a Sonogashira coupling with quantitative conversion [7].

On the other hand, metal traces or dopants are intentionally added to enhance or promote catalytic performance [8,9] or to assist catalyst regeneration [10].

Researchers in catalysis are aware that impurities left over from previous experiments in their (cleaned) vessels can give activating or deactivating effects which change the outcome of a catalytic reaction. Thus, catalytic reactions should be carried out more than once to ensure reproducibility. Surprisingly, a Scifinder search [11] combining the terms “memory effect”, “contamination” or “impurity” and “catalysis” did not give any relevant references.

Here we show that a common and frequently used laboratory commodity such as a Teflon-coated magnetic stirring bar can carry on its surface catalytically active metal nanoparticles which are not easily removed. On one hand this is “caveat” on the unintentional preparation of “catalytically active stirring bars” by nanoparticulate metal depositions from previous reactions. On the other hand our simple deposition of rhodium metal nanoparticles (Rh-NPs) on the Teflon surface of a stirring bar (Rh-NPs@stirring bar) yields an easily handable and re-usable hydrogenation catalyst. This proof-of-concept should be extendable to other metal nanoparticle catalysts. Rhodium was used here as a metal for the proof-of-principle because rhodium is used in many types of

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