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 $Rh_6(CO)_{16}$ 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 × 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 × (mol Rh)$^{-1}$ × 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 of desactivating 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 nanoparticular 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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catalytic reactions like hydroformylations [12], C—C bond forming reactions [13], Pauson–Khand type reactions [14] and hydrogenations [15,16].

2. Experimental

2.1. Materials and methods

$Rh_6(CO)_{16}$ was obtained by Acros, the ionic liquid (IL) 1-*n*-butyl-3-methylimidazolium tetrafluoroborate ($BMImBF_4$) from IoLiTec (H_2O content $\ll 100$ ppm; Cl^- content $\ll 50$ ppm).

New stirring bars with the dimensions (length × width) 20 mm × 6 mm were obtained from VWR International GmbH, Hilperstraße 20a, 64295 Darmstadt, Germany and had not been used for any reactions before. Solvents were of technical quality (acetone) or of p.a. quality (acetone, methanol, *iso*-propanol, tetrahydrofuran (THF), methylene chloride).

All manipulations were done using Schlenk techniques under nitrogen since the metal carbonyls salts are hygroscopic and air sensitive. The ILs were dried at high vacuum (10^{-3} mbar) for several days.

AAS (atomic absorption spectrometry) was performed with Perkin-Elmer AAnalyst 100 (flame AAS), using the software AA WinLab.

Transmission electron microscopy (TEM) photographs were taken at room temperature from a carbon coated copper grid on a Zeiss LEO 912 transmission electron microscope operating at an accelerating voltage of 120 kV. Samples were loaded on holey, carbon coated copper grids. The Rh-NP samples were prepared by cutting Teflon flakes from the stirring bar. Median Rh-NP diameters of Rh-NPs@stirring bar were 2.1 (±0.5) nm. The Rh-NPs@stirring bar after 10 hydrogenation runs of cyclohexene had a size of 1.7 (±0.3) nm (cf. Fig. 2). Particle diameters were measured manually using iTEM software tools for manual measurements. Completely automatic measurements, which can be easily performed for well separated particles, fail in the case of heavily clustered particles. For a better comparison of the samples also particles which would have allowed automatic detection were measured manually.

Scanning electron microscopy (SEM) samples were coated with a thin Au layer (~8 nm) and analyzed with a Quanta 250 FEG instrument. The measurements were performed at 3.20^{-4} Pa and at 10 kV voltage using an ETD detector.

2.2. Preparation of Rh-NP/IL dispersion

$Rh_6(CO)_{16}$ (41.42 mg, 3.89×10^{-5} mol) was dissolved/suspended (~1 h) under a nitrogen atmosphere at room temperature in dried and deoxygenated $BMImBF_4$ (2.0 mL, 2.4 g) to give a 1.0 wt.% dispersion. For the synthesis the mixture was placed in a CEM microwave type Discover under inert nitrogen atmosphere and the conversion was finished within 6 min at a power of 10 W. $Rh_6(CO)_{16}$ decomposes at 220 °C, so it can easily be handled at room temperature under inert atmosphere [17].

2.3. Preparation of Rh-NP@stirring bar

A brand-new (unused) magnetic stir bar was washed with dried acetone (10 mL) and dried under high vacuum prior to the Rh-NP deposition. Rhodium nanoparticle deposition on PTFE was obtained by stirring the magnetic stirring bar in the Rh-NP/BMImBF_4 dispersion at room temperature under nitrogen for different defined number of 2–8 days. The nanoparticle-loaded stirring bar was removed from the Rh-NP/BMImBF_4 dispersion and stirred in a washing solvent (20 mL) for 15 s to remove the IL, removed with a pincer and dried under vacuum for 30 min.

The solvents acetone, water, methanol, *iso*-propanol, tetrahydrofuran and methylene chloride were tested for the washing and removal of the ionic liquid film which adhered to Rh-NP@stirring bar. For each different washing solvent, a cyclohexene hydrogenation run (see Section 2.4) was carried out to test for the resulting activity. Activities for acetone (p.a.), THF or methylene chloride were similar and higher than for acetone (technical), methanol, *iso*-propanol or water. Eventually, THF (p.a.) was used as a standard washing solvent for the catalytic recycling experiments.

The rhodium loading on the stirring bar and the rhodium leaching in the catalytic runs was analyzed by AAS. To dissolve the Rh-NPs from the Teflon-coating the stirring bar was placed into a conc. HCl/HNO_3 mixture (*aqua regia*, 50 mL) over night. The resulting solution was directly used for the AAS analysis. Repeated analyses of the Rh-NP content on a stirring bar from the above preparations reproducibly gave 32(±8) μg of rhodium (±8 is the standard deviation σ from multiple Rh-content determinations of different stirring bars). Hence, the Rh-NP loading does not depend on the time variation for deposition within 2–8 days. After the treatment with *aqua regia* the magnetic stirring bars lost their catalytic properties for the hydrogenation of cyclohexene or benzene.

2.4. Catalysis

2.4.1. General

Rh-NP@stirring bars were conditioned after their preparation by using the above-mentioned washing procedure with dried THF (20 mL) for 15 s before the first run to remove the ionic liquid.

An autoclave with a glass inlay was used. The hydrogenation reactions were carried out in the glass inlay. The autoclave was conditioned by evacuation and re-filling with nitrogen. All autoclave loading was carried out under nitrogen. Stirring rate was 850 rpm. The H_2 uptake over time was monitored with a Büchi pressflow gas controller (Büchi pbc). After quantitative or near quantitative conversion was reached (adjudged by the H_2 consumption) the reactor was depressurized, the volatile organic components were condensed under vacuum into a clean cold trap. The Rh-NPs@stirring bar was left behind in the glass inlay of the autoclave and was re-used by adding fresh substrate. Catalyst recycling was carried out ten times for cyclohexene and three times for benzene.

The cyclohexene or benzene to cyclohexane conversion was verified by gas chromatographic (GC) analysis of the product (Perkin-Elmer 8500 HSB 6, equipped with a DB-5 film capillary column, 60 m × 0.32 mm, film thickness 25 μm, oven temperature 40 °C, N_2 carrier flow 120 L/min and a flame ionization detector (FID), 250 °C detector temperature). The benzene or cyclohexene to cyclohexane conversion was analyzed by putting a drop of the mixture into a GC sample vial with 1 mL of water. The addition of water as a non-electrolyte can enlarge the activity coefficient of organic components, thereby increase their detection sensitivity through the increase in peak area. The FID does not detect the water itself [18].

2.4.2. Conditions for cyclohexene hydrogenation

Cyclohexene 0.69 mL, 6.8 mmol (density 0.811 g/mL, $M = 82.14$ g/mol); Rh metal (0.032 mg, 3.1×10^{-7} mol); 75 °C, 4 bar H_2.

2.4.3. Conditions for benzene hydrogenation

Benzene 0.60 mL, 6.8 mmol (density 0.88 g/mL, $M = 78.11$ g/mol); Rh metal (0.032 mg, 3.1×10^{-7} mol); 90 °C, 20 bar H_2. For the slower benzene hydrogenation the reaction was intentionally stopped at 90% conversion (adjudged by the H_2 consumption) as thereafter the decrease in benzene concentration lowered the reaction rate. Thus, the reactor was depressurized
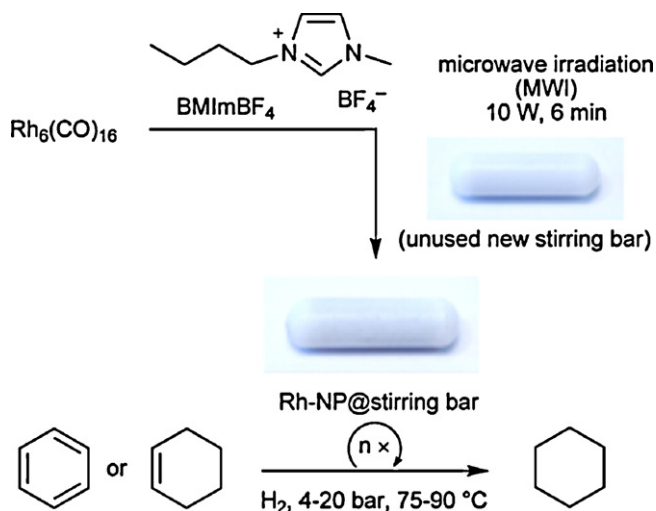
Fig. 1. Preparation of Rh-NP@stirring bar and repeated utilization as hydrogenation catalyst. The photographs show a standard commercial 20 mm × 6 mm magnetic stirring bar before and after Rh-NP deposition.

after 90% conversion and the liquid product removed under vacuum and fresh benzene (0.60 mL) was added.

2.4.4. Special experiments

To investigate the possibility of mechanical abrasion or of leaching of Rh-NPs from the stirring bar the following special experiments were performed. In each case the hydrogenation was carried out at 75 °C and 4 bar H_2 and was stopped after 24 h to verify the conversion by GC.

Entry 14 in manuscript Table 1 – *test for mechanical abrasion:* Rh-NPs@stirring bar was stirred for 12 h at 75 °C in an empty glass inlay at 850 rpm under N_2. Afterwards this Rh-NPs@stirring bar was replaced by a brand-new (untreated) stirring bar. Cyclohexene (0.69 mL) was added and the autoclave was pressurized with H_2.

Entry 15 in manuscript Table 1 – *test for leaching into cyclohexene:* Rh-NPs@stirring bar was placed in and allowed to stand for 12 h at 75 °C in cyclohexene (0.69 mL) without stirring under N_2. Afterwards Rh-NPs@stirring bar was replaced by a brand-new (untreated) stirring bar and the autoclave was pressurized with H_2.

Entry 16 in manuscript Table 1 – *test for leaching into cyclohexene under hydrogenation conditions:* Using the general hydrogenation conditions, the hydrogenation of cyclohexene (0.69 mL) was run until 25% conversion (which was reached after 12 min). The cyclohexane/cyclohexene mixture was filtered hot at 60 °C under N_2 atmosphere into a new glass inlay equipped with a brand-new (untreated) stirring bar. The glass inlay was placed into the autoclave and hydrogenation was resumed.

3. Results and discussion

Deposition of Rh-NPs onto a standard Teflon (PTFE)-coated stirring bar is easily achieved by thermal decomposition of $Rh_6(CO)_{16}$ in $BMImBF_4$ through microwave irradiation [19] and immersion of the stirring bar into the Rh-NP/IL dispersion (Fig. 1).

Rh-NP deposition on the stirring bar is only slightly evident by visual inspection with a naked eye from some minor darkening (Fig. 1). Proof of the Rh-NP deposits is obtained by scanning electron microscopy (SEM) of the Teflon surface or transmission electron microscopy of Teflon flakes therefrom (Fig. 2). The amount of Rh-NP@stirring bar was quantified by AAS to 32(±8) μg per stirring bar. A Rh-NP size analysis was carried out by transmission electron microscopy (TEM) on Teflon flakes which were cut from the stirring

bar (Fig. 2d and e). Median Rh-NP diameters were 2.1 (±0.5) nm and 1.7 (±0.3) nm after the 10th hydrogenation run.

Syntheses and applications of transition-metal nanoparticles (M-NPs) are of contemporary interest in several areas of science [20–23] including catalysis [24]. The efficient stabilization of M-NPs requires surface-coordinating ligands [25,26] ionic liquids [27–30] or deposition onto solid surfaces [25,31,32]. There are wide ranges of supports described for M-NPs (see Supplementary data), however, very little is known for PTFE as a nanoparticle support [33–35]. The immobilization of Fe-NPs on the surface of PTFE nanogranules appears to be a singular example. The chemical properties of bulk PTFE were considered unsuitable for the stabilization of metal containing nanoparticles [36].

The caveat: It is evident that PTFE, albeit generally considered a chemically inert material with a non-sticking surface, can support nanoparticular metal deposits. Such nanoparticular deposits can originate from various uses of stirring bars in a laboratory. These M-NP deposits are also not easily removed by washing with common organic solvents or with water (see Section 2.3). If then such a stirring bar with a "colorful past" is used in catalysis experiments the metal nanoparticle deposits can exert an activity while the intended catalysis system is less active or even inactive (akin to the metal impurities in "intended" catalysts noted in the introduction). This possibility is especially problematic because such metal nanoparticle deposits cannot be visually detected.

The chance: The ease of support of metal nanoparticles on a readily available and thermally stable PTFE surface can open new vistas for metal nanoparticle and catalysis research, especially in view of the easy separation of a catalytically active magnetic stirring bar akin to the recovery of magnetic nanoparticle catalysts [37–39].

As a proof-of-concept the Rh-NP@stirring bar supported magnetic stirring bars were tested for their re-usable catalytic activity in the known hydrogenation of cyclohexene or benzene to cyclohexane under organic-solvent-free conditions where comparative literature data is available (Fig. 1, Table 1 and Tables S1 and S2 in Supplementary data). The hydrogenation reactions were carried out in a stainless steel autoclave equipped with a glass inlay. The autoclave was heated to 75 °C or 90 °C and pressurized with the hydrogen consumption monitored by a Büchi pressflow gas controller (H_2 uptake over time, see Figs. S3 and S4 in Supplementary data). Near quantitative conversion the reactor was depressurized and the volatile organic components were condensed under vacuum into a clean cold trap. To test for recycling the Rh-NPs@stirring bar was left behind in the autoclave and was re-used by adding fresh substrate. Catalyst recycling was carried out ten times for cyclohexene and three times for benzene. There is an initial increase in activity with recycling from entry 1 to 3 in Table 1 which was also seen in other hydrogenations with Rh-NP/IL systems [19,40]. This is probably due to a slow surface restructuring and not due to the rapid formation of Rh–hydride or Rh–heterocyclic carbene (NHC) [41] surface species [42].

Activities for cyclohexene hydrogenations with Rh-NP@stirring bar were 5–10 times higher than for other supported Ru-, Rh-, Pd- or Pt-NP catalysts in ILs [19,43–45] or on supports [46–50] (Table S1 in Supplementary data). For benzene hydrogenation the activity was higher than for most M-NP literature systems [16,43,46,51,52] and only surpassed by Rh-NP/carbon nanofibers [53] (Table S2 in Supplementary data). The lower hydrogenation activities of Ru- and Rh-NPs in ILs are traced to the IL diffusion barrier for H_2 and the substrate. For the supported Rh-NP catalysts the average nanoparticle size deposited here on the stirring bar was found to be considerably smaller (2.1 ± 0.5 nm) than the size given for other supports (2.8–5 nm) [46–48] (Table S1 in Supplementary data).

In general in M-NP catalysis the active species can be either "heterogeneous" M-NPs in a dispersion or on a surface or

Table 1
Hydrogenation of cyclohexene or benzene to cyclohexane with Rh-NP@stirring bar.[a]

| Entry	Substrate and run	Conversion [%]	Time [min]	Activity (TOF) [mol product $\times$ (mol Rh)$^{-1}$ $\times$ h^{-1}]
1	Cyclohexene[b]	>99	88	14.9×10^3
2	2nd run	>99	49	26.8×10^3
3	3rd run	>99	40	32.8×10^3
4	4th run	>99	48	27.3×10^3
5	5th run	>99	68	19.3×10^3
6	6th run	>99	132	9.9×10^3
7	7th run	87[d]	139	8.2×10^3
8	8th run	>99	139	9.4×10^3
9	9th run	>99	161	8.1×10^3
10	10th run	80[d]	160	6.6×10^3
11	Benzene[c]	85[d]	1474	750
12	2nd run	90	1607	730
13	3rd run	90	2553	460
14	Cyclohexene[e]	78	1440	
15	Cyclohexene[e]	20	1440	
16	Cyclohexene[e]	53	1440	

[a] Conditions: Rh metal 32 µg, 3.1×10^{-7} mol.
[b] Cyclohexene 0.69 mL, 6.8 mmol, 75 °C, 4 bar H$_2$.
[c] benzene 0.6 mL, 6.8 mmol; 90 °C, 20 bar H$_2$.
[d] Conversion ceased.
[e] See Section 2.4.4 for further details.
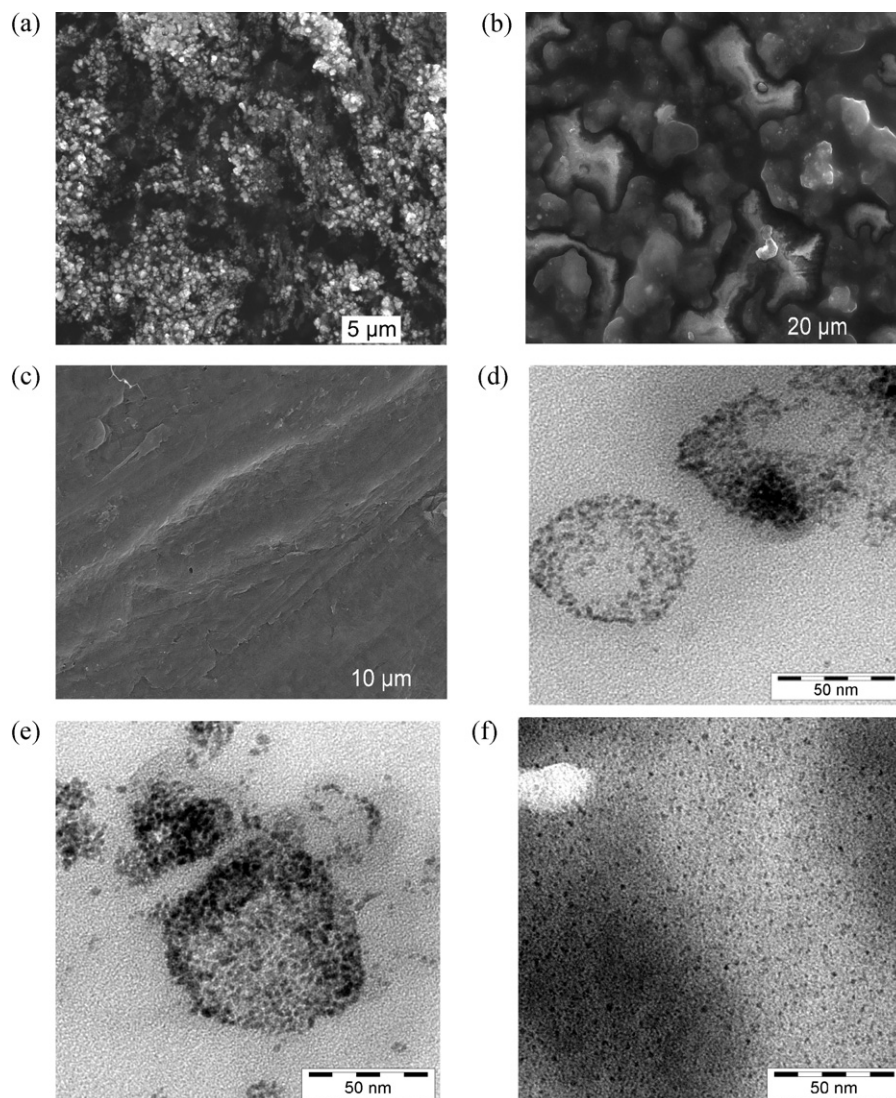
Fig. 2. SEM-pictures of Rh-NPs on a Teflon-coated magnetic stirring bar (Rh-NP@stirring bar) (a) and after 10 hydrogenation runs (b) in comparison to the blank Teflon surface (c). TEM of Teflon flakes from the stirring bar coating for Rh-NP size analysis before catalysis (d, e) and after the 10th catalytic hydrogenation run of cyclohexene (f).
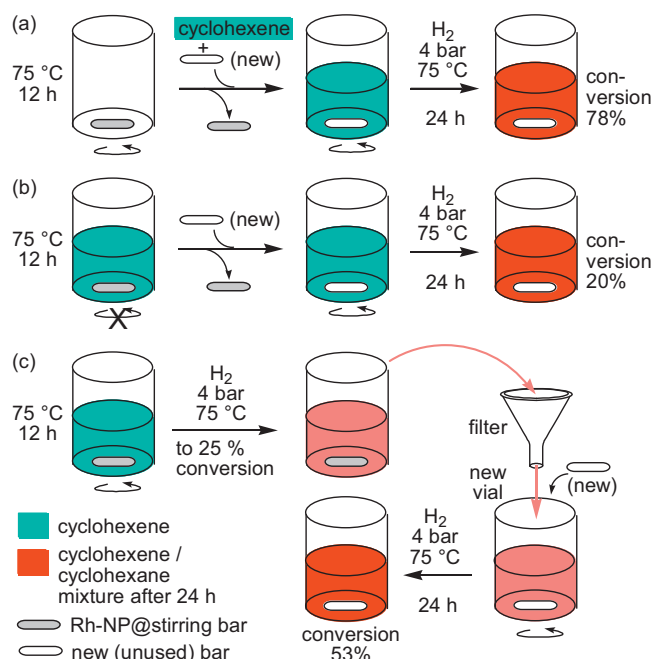
Fig. 3. Experiments to attest the abrasion or leaching from Rh-NPs@stirring bar (carried out twice to ensure reproducibility within experimental error). (a) (Entry 14, Table 1) Stirring of Rh-NP@stirring bar in the empty glass inlay at 75 °C for 12 h under N₂, followed by removal of the stirring bar, addition of a new (unused) stirring bar, cyclohexene and H₂. A conversion of 78% is reached after 24 h (cf. > 99% with Rh-NP@stirring bar in 1–2 h, entry 1–5) and indicates some, but little mechanical abrasion of the Rh-NPs from the PTFE surface. (b) (Entry 15, Table 1) Allowing Rh-NP@stirring bar to stand in cyclohexene at 75 °C for 12 h under N₂, followed by removal of the stirring bar, addition of a new stirring bar and H₂. A conversion of only 20% after 24 h indicates little leaching from the stirring bar into the cyclohexene substrate. (c) (Entry 16, Table 1) Cyclohexene hydrogenation was run to 25% conversion (within 12 min, monitored by gas uptake). Then, Rh-NP@stirring bar was removed, the cyclohexene/cyclohexane mixture filtered under argon into a new glass inlay, equipped with a new stirring bar and re-pressurized. Conversion proceeded very slowly to 53% in 24 h, attesting little leaching even under the reaction conditions.

"homogeneous" atoms or small clusters which leach from the M-NP into the solution [25]. Hence, we cannot exclude, that the Rh-NP@stirring bar functions as a reservoir of such "homogeneous" active atoms or clusters. There is only a minor amount of mechanical abrasion or of leaching of Rh-NPs from the stirring bar during each catalytic run as was attested by three reproducible experiments outlined in Fig. 3. Abrasion onto the glass surface appears to be more prominent than simple leaching when comparing the resulting activities from stirred (Fig. 3a, entry 14 in Table 1) versus non-stirred preparations (Fig. 3b, entry 15 in Table 1) before applying the hydrogen pressure. Sizeable conversion can be attested from the abrasion, albeit at prolonged reaction times (24 h, entry 14) when compared to the conversion versus time of Rh-NP@stirring bar under otherwise identical conditions (entry 1–10). If one would want to avoid abrasion the stirring bar could be loaded into containments of a mechanical stirrer, such as designed by Mouljin, van Leeuwen et al. for loading catalyst-impregnated monolith blocks to give an immobilized homogeneous rotating catalyst (ROTACAT) [54,55].

4. Conclusions

Metal nanoparticle traces can easily be deposited – intentional or un-intentional – on the PTFE surface of magnetic stirring bars. Activating or desactivating effects can derive from un-intentional deposits when such stirring bars are employed in catalytic reactions. At the same time we show that a lab commodity such as a Teflon-coated magnetic stirring bar can be easily turned into a re-usable, smoothly handable and magnetically removable catalyst system. "Traces" of 32 µg or less of Rh-nanoparticles on the stirring bar surface exert very high hydrogenation activities for cyclohexene or benzene under mild conditions.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcata.2012.03.017.

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