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Organic syntheses by microwave selective heating of novel metal/CMC catalysts – The Suzuki–Miyaura coupling reaction in toluene and the dehydrogenation of tetralin in solvent-free media

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ABSTRACT

The present study examines carbon microcoils (CMCs) as a novel support for Pt and Pd nanocatalysts and compares it with activated carbon nanoparticles as support for Pt and Pd metal deposits in two model microwave-assisted organic syntheses: (i) the Suzuki–Miyaura coupling reaction between phenylboronic acid and 1-bromo-4-methylbenzene in toluene solvent to produce 4-methyl-biphenyl and (ii) the dehydrogenation of tetralin (1,2,3,4-tetrahydronaphthalene) in solvent-free conditions. The microwave absorption capacity of the CMCs was more effective than the ACs support from the viewpoint of dielectric parameters (dielectric constant, dielectric loss, and loss tangent). Possible generation of microplasma (i.e., hot spots) on both supports that can impact on the progress of the reactions was monitored visually and photographed with a high-speed camera. Conventional heating (oil bath or heating mantles) of the Pd(Pt)/CMCs and Pd(Pt)/ACs system led to significantly lower product yields.

1. Introduction

Carbon microcoils (CMCs) present unique physical characteristics, electric properties, electromagnetic properties, chemical properties, and bio-activation properties as expected of innovative materials [1]. As such, CMCs are good candidates as absorbers of electromagnetic waves, as field emitters, as microsensors, as hydrogen storage materials, and as electrode materials, among others. CMCs look like microsized springs made of carbon that has attracted considerable attention in the stealth technology of the military establishment owing to its high absorption of radio-waves. Particularly significant, these carbon microcoils display a double 3D-helix chiral structure with a coil diameter typically 1–10-μm and a 0.1–10-mm coil length. CMCs can effectively absorb electromagnetic waves in the 2–18 GHz microwave regions [2].

Recent studies on heterogeneous metal catalyst reactions have shown that microwave radiation as the heating source is particularly advantageous in many processes [3]. Microwave heating utilizes the polarization ability of molecules to transform electromagnetic energy into thermal energy. As such, in a heterogeneous catalyzed reaction system in a nonpolar solvent, it is possible to heat selectively only the catalysts by microwave irradiation [4]. Therefore, in the construct of the reaction system, the microwaves must interact solely with the solid catalyst, a feature that cannot be attained by existing conventional heating methods. To attain such a microwave/catalyst reaction system requires that the catalyst be supported on a material that is a strong absorber of microwave radiation. Activated carbon (AC) has proven in the past to be a good catalyst support and a useful microwave absorber.

In the present study, we examine the carbon microcoils as a microwave absorber and as a possible catalyst support. Features of the heat developed on microwave irradiation of CMCs are compared with those of the conventional activated carbon support. Palladium nanoparticles used as the metal catalysts were deposited on the CMC surface and used in the Suzuki–Miyaura coupling reaction as a model of an organic synthesis in toluene solvent; this solvent is a poor microwave absorber. As well, platinum nanoparticle deposits on the CMCs were examined in the dehydrogenation of tetralin as another model reaction and compared with the same deposits on activated carbon; tetralin is also a poor microwave absorber. Interestingly, in the hydrogen storage field, tetralin has been considered as a sort of cycloalkane material for hydrogen storage [5].

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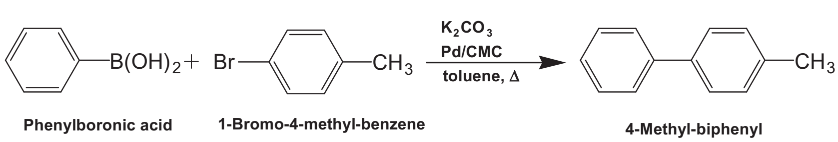
2. Experimental section

2.1. Preparation of metal deposits on carbon microcoils

A sample of carbon microcoils was a gift from Dr. Motojima of the Toyota Physical and Chemical Research Institute. CMCs were prepared by a thermal chemical vapor deposition (CVD) method at a temperature of 770 °C using Ni powder as the catalyst placed on a graphite substrate setting within a horizontal quartz reaction tube into which a gas mixture consisting of C_2H_2, H_2, H_2S, and N_2 was introduced that ultimately led to the growth of the carbon microcoils [6]. Granular activated carbon particles of ca. 0.95 mm in size were used for comparison with the CMCs. The particle size of the ACs was greater than the size of the CMCs (see Fig. 2 for the size of CMCs). BET measurements (Bel Japan, Micrometrics Tristar surface analyzer) revealed that the activated carbon sample had a specific surface area (ca. 1095 $m^2\,g^{-1}$) nearly fivefold greater than the surface area of the as-prepared CMCs (ca. 231 $m^2\,g^{-1}$).

In the case where the Pd/CMCs catalyst was used in the reactions, the surface of the CMCs (1 g) was washed in an aqueous HNO_3 solution (10 M, 100 mL) with stirring for 3 h at an 80 °C temperature. Note that CMCs were synthesized using nickel as the catalyst, such that the initial CMCs contained 1.2% nickel that upon washing with the HNO_3 solution fell to 0.095% Ni content. The microcoils were subsequently washed further with ultrapure water and quantities of NaOH (2 M, 50 mL) for 24 h under room temperature conditions, after which the CMCs were washed once again with ultrapure water and dried for a few hours at 100 °C. The so-washed CMCs (1 g) were introduced into an aqueous $PdCl_2$ (0.034 g) and HCl (1 M) solution (50 mL), following which the solution was brought to pH 14 by addition of NaOH. Subsequently, $NaBH_4$ (0.016 M) was added to the solution and stirred for 3 h; stirring was then continued for an additional 2 h at 60 °C. Finally, the colloidal Pd/CMC solids in the solution were filtered, washed with ultrapure water, and then dried at 100 °C overnight. In the preparation of Pt/CMCs, the aqueous 50 mL solution contained $H_2PtCl_6{\cdot}H_2O$. The quantity of Pd deposited on the CMC and on the AC was ca. 0.7 and 1.5 wt.%, respectively, ascertained by atomic emission spectroscopy using the Shimadzu ICPE-9000 apparatus.



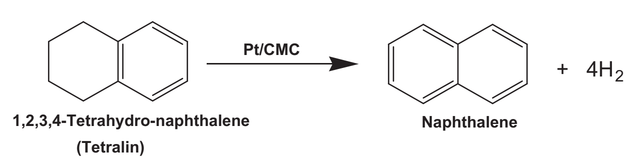
(1)

2.2. Chemical model reactions and microwave apparatus

2.2.1. Suzuki–Miyaura coupling reaction

The synthesis of 4-methylbiphenyl by the Suzuki–Miyaura coupling reaction was carried out by a procedure similar to the one given earlier [7]. The Pd/CMCs and Pd/ACs catalyst (150 mg), phenylboronic acid (0.80 mmol; 0.0975 g), 1-bromo-4-methylbenzene (0.60 mmol; 0.1026 g), K_2CO_3 as the base (1.2 mmol; 0.165 g), and the nonpolar toluene solvent (5 mL) were mixed and subsequently added under an Ar atmosphere to a quartz cylindrical reactor (height, 24 mm; diameter, 16 mm). Since the dielectric loss factor of toluene (ε'' = 0.07) is significantly smaller than that of pure distilled water (ε'' = 9.4), so that by comparison, toluene solvent was not heated by the microwave radiation. Nonetheless, microwaving the toluene solution in the absence of the catalyst led to a 7 °C increase in temperature after 30 min of irradiation. Therefore, this reactive system can be taken as a solvent-free system from the viewpoint of absorption of microwave radiation. A condenser was connected to the microwave cylindrical reactor. Reaction yields of 4-methylbiphenyl (reaction (1)) were determined by gas chromatographic analyses (Shimadzu model 2014 equipped with Ultra alloy-1 capillary columns) from samples appropriately prepared from the various dispersions; a sample of 4-methylbiphenyl was used as the calibration standard (Wako Pure Chemical Industries, Ltd., 100% GC standard).

Tetralin dehydrogenation: The dehydrogenation of tetralin (1,2,3,4-tetrahydronaphthalene; reaction (2)) was carried out by a procedure similar to the one given earlier [8]. Accordingly, the Pt/CMCs powder (150 mg) and a pure tetralin sample (5 mL) were introduced, under an Ar atmosphere, into a quartz cylindrical reactor (height, 24 mm; diameter, 16 mm). Note that since the dielectric loss factor of tetralin (ε'') is 0.12, it too is a poor microwave absorber when compared to water. Microwave irradiation of the tetralin system in the absence of the Pt/CMCs catalyst increased the temperature by only 33 °C after a 30-min period. The extent of tetralin conversion was also determined by gas chromatography using a Shimadzu Model 2014 Chromatograph equipped with a Zebron ZB-624 column.



(2)

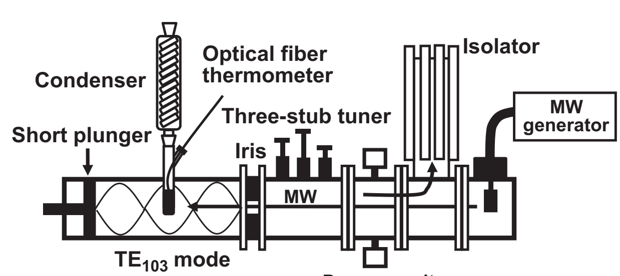


Fig. 1. Details of the experimental setup and position of the reaction samples in the single-mode microwave resonator. Sample set at the maximal *E* field position.