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Preparation of multi metal–carbon nanoreactors for adsorption and catalysis

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Abstract Metal–incorporated composite carbon materials have engendered great progress in the fields of catalysis, energy storage and material science because of their size and chemical and physical properties. In this study, a modern technique was applied for the development of multi metal–carbon nanoreactors (MCNRs) from a pristine carbon cage (CC) using template method with nano silica ball (NSB), pyrolysis fuel oil (PFO) and metal nanocrystals such as gold, copper, nickel, potassium and manganese. The newly prepared Au, Cu, Ni, K and Mn deposited carbon nanoreactors were fully characterized by various analytical techniques. Due to their easy fabrication protocols and broad potential applications, the MCNRs were used successfully for the chemisorptions of hydrogen and ethylene gases alongside the solvent–free heterogeneous catalytic oxidation of a secondary alcohol. The MCNRs have exhibited dynamic adsorption performance and excellent catalytic activity.

Keywords Adsorption · Heterogeneous catalysis · Metal–carbon · Nanoreactors · Pyrolysis fuel oil

1 Introduction

Nanocomposites of porous carbon and metals have revealed strong research interest due to the individual properties of metal and carbon materials and the emergence of new properties capable of supporting novel applications (Zhang et al. 2009). Among several methods available for the engineering of composite carbon materials, the template method can be easily used to develop a variety of porous networks with a wide range of pore sizes and well arranged morphology, along with combined chemical properties (Kao and Hsu 2008). Mesoporous siliceous materials (SBA-15 and MCM-41), various metal oxides (TiO_2, Al_2O_3, ZrO_2, MgO and SiO_2) and porous carbon have been recommended as solid support materials (Li et al. 2006; Zhang and Olin 2011; He and Hu 2012). Silica and carbon are the most widely used supports for metal composite materials (Rodríguez-reinoso 1998; Mayani et al. 2010, 2012c). Curiously, the nature of the catalyst supports plays an important role in synthesizing and maintaining the particle dispersity, enhancing the composite stability and raising the catalytic performance of the resulting composite material. These composite materials have driven considerable interest in various applications including biosensors, drug delivery, energy processing, methane combustion, heterogeneous catalysis and chemical synthesis with their commercial prospective viability (Grisel et al. 2000; Kapoor et al. 2002; Mohr et al. 2003; Figureiredo and Pereira 2010; Zhang and Olin 2011; Cabria et al. 2011; Shanahan et al. 2011).

In the approaching energy crisis, the storage of various gases is one of the key issues for the realization for energy conservation and reversing the ‘greenhouse’ effect. Some gases are believed to be major contributors to acid rain, global warming and the increased toxicity of breathing air (Finlayson-Pitts and Pitts 1986). The decreasing petroleum resources and rising environmental pollution awareness have initiated a search for alternate fuels and zero emission vehicles. Hydrogen gas is expected to play an important role in the future global energy balance. The effi-

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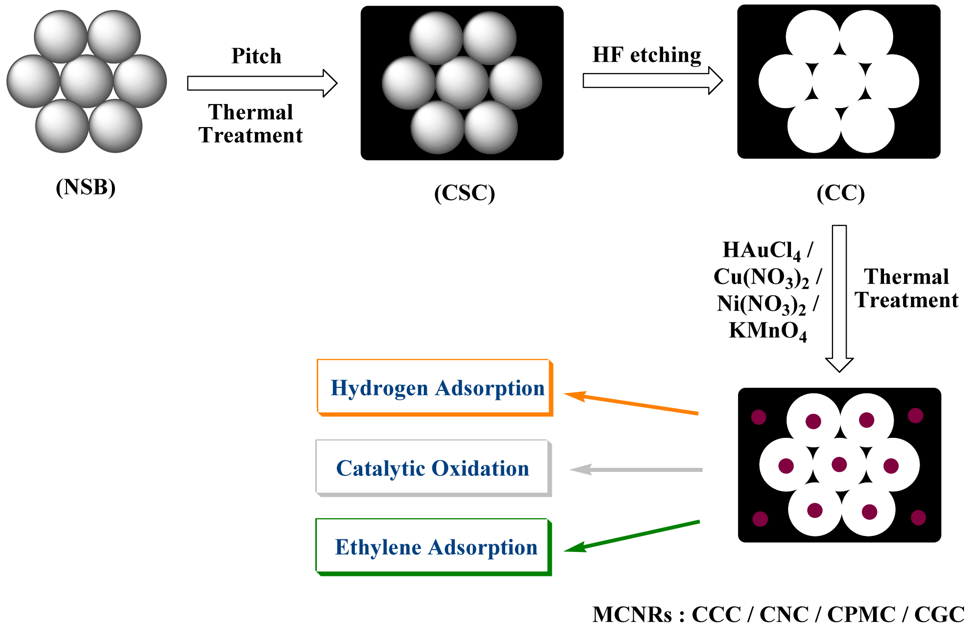


Fig. 1 Schematic illustration for the synthesis of metal–carbon nanoreactors (MCNRs)

cient storage of hydrogen is a crucial and challenging requirement necessary for its use as an automotive fuel. The advantages of hydrogen over electric battery cars and gasoline cars are twofold: as hydrogen can be produced from water by electrolysis, the only emission from its subsequent reaction with oxygen in the energy generating stage is water; and it has the highest energy (120 MJ/kg) content per mass (Psofogiannakis et al. 2011; Alonso et al. 2012). In agricultural production, the chemisorption of ethylene gas plays a significant role during transport, distribution or storage. Certain fruits and vegetables suffer a reduction in their quality and shelf-life due to such ethylene production. In recent years, numerous experimental investigations of the adsorption of ethylene on a range of metal–carbon nanoreactors (MCNRs) surfaces have been conducted using various methods. These nanoreactors preserve the fruit quality during transportation and storage (Palou et al. 2003; Mayani et al. 2012a). Porous carbon composites can also be used as catalyst supports or as catalysts on their own in the field of fine chemicals. Using an eco-friendly reaction system, the selective oxidation reaction of alcohol to the corresponding aldehyde is not only of commercial relevance in the industries of fine chemicals and pharmaceuticals but is also of specific interest (Bird 1987; Figueiredo and Pereira 2010; Shanahan et al. 2011; Mayani et al. 2012c).

Carbonaceous materials have attracted attention as potential adsorbent and heterogeneous catalysts. The advantages of carbonaceous materials for gas storage are fast adsorption/desorption kinetics and low weight. Thus, on-going research is focused on the development of advanced carbon based storage materials. The construction of porous carbon materials has been achieved by using low-cost pyrolysis oil (PFO) based pitch with advanced aromatic content from petroleum residue (Mayani et al. 2011, 2012b). Pitch residue was considered a cheap and suitable source for preparing diverse carbon materials due to its unique structural property and highly rich aromatic content (Korai et al. 1998; Charinpanitkul et al. 2009; Wazir and Kakakhel 2009). The performance of the metal–deposited nanoreactors depends on the availability of appropriate active sites that are capable of chemisorbing the reactants and forming surface intermediates of sufficient strength. Herein, newly designed multi MCNRs were prepared with metals precursors (gold, copper, nickel, potassium and manganese) loaded into a hierarchical carbon cage (CC) using an easy deposition method followed by controlled chemical or physical treatment. These MCNRs played an important role in the chemisorptions of hydrogen and ethylene gases and the heterogeneous catalytic oxidation reaction of secondary alcohol.

2 Experimental

2.1 Synthesis of metal–carbon nanoreactors (MCNRs)

The MCNR samples were fabricated by a nanocasting metal deposition process using pristine CC and metal nanocrystals such as gold, copper, nickel, potassium and manganese (Fig. 1). Four MCNRs composite materials (carbon copper composite (CCC), carbon nickel composite (CNC), carbon potassium manganese composite (CPMC) and carbon gold composite (CGC)) were synthesized following our earlier report (Mayani et al. 2012b, 2012c) with minor modification, which is briefly described below.

2.2 Synthesis of CCC, CNC and CPMC

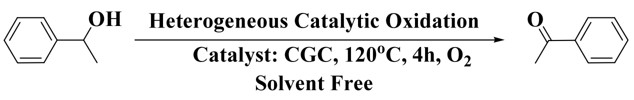
CC (1 g) and transition metals salts (copper (II) nitrate trihydrate/nickel (II) nitrate hexahydrate/potassium permanganate (0.1 g)) were shaken in a beaker containing distilled water (10 ml). The resulting suspension was exposed to ultrasonication for 1 h. The excess water was evaporated at 100 °C in an oven for 2 h (Fig. 1). The resultant metal carbon nanoreactors CCC, CNC and CPMC were obtained with yields of 1.08, 1.09 and 1.10 g, respectively.

2.3 Synthesis of CGC

To 250 ml of sodium citrate dihydrate solution was added 3.07 g of CC and the mixture was ultrasonicated for 5 min. The suspension of CC was then transferred to 250 ml of distilled water. The diluted suspension was refluxed with stirring for 5 min, followed by the addition of 1 % $HAuCl_4$ (100 ml) to the suspension containing CC. The resulting suspension was stirred at 100 °C for the next 5 min. The resulting solid particles were filtered with a Buchner funnel and washed with distilled water. The powder was dried in air at 100 °C. Finally, the solid was calcined at 900 °C for 1 h in nitrogen to yield 3.6 g of CGC (Fig. 1).

2.4 Characterization and analysis

The MCNR materials were fully characterized by powder X-ray diffraction (XRD, Phillips X'pert MPD diffractometer, Almelo, The Netherlands), Fourier transform infrared spectroscopy (Perkin-Elmer FTIR Spectrometer, Massachusetts, USA) using KBr self-supported pellet technique, scanning electron microscopy (SEM; LEO-1430, VP, UK) coupled with energy dispersive spectroscopy (EDS), transmission electron microscopy (TEM, JEM 2011, Jeol Corporation, Japan), elemental analyzer (CE instruments, UK), thermogravimetric analysis (TGA, SDT600, TA instrument, USA) and nitrogen adsorption–desorption isotherm (Micromeritics ASAP-2010, USA). The hydrogen adsorption experiments were carried out using gravimetric measurement with a Rubotherm magnetic suspension balance (MSB, Germany). Gas chromatography (GC, Hewlett Packard GC 5890 series-II) integrated Pyrex adsorbent cell and auto gas injectors were used for ethylene adsorption at room temperatures.



Scheme 1 Heterogeneous catalytic oxidation of 1-phenylethanol using CGC

2.5 Hydrogen adsorption using the MCNRs

The hydrogen adsorption isotherms were performed by using gravimetric measurement with a Rubotherm MSB in four steps: blank measurement, loading and reactivation of samples, buoyancy measurement and adsorption measurement. The adsorption measurement at 25 °C was done up to 60 bar pressure. The samples were activated in situ by controlled heating up to 400 °C (heating rage 1 °C/min) under high vacuum and the temperature and vacuum were maintained for 12 h before sorption measurements. The amount of activated adsorbent was determined from the weight of the absorbent before as well as after activation and prior to start of adsorption measurement. After activation, the samples were allowed to cool down to the desired temperature and the temperature was maintained during entire analysis using external water circulator. Hydrogen with a specific pressure steps was introduced into the sample chamber. The increase weight of the sample due to hydrogen adsorption was accurately measured using MSB connected to the sample holder. Typically, 0.2–0.7 g of samples were used in experiment. Adsorption isotherms of metal–carbon nanoreactors CCC, CNC, CPMC, CGC and non-metal CC were also conducted in order to evaluate the enhancement of the modified carbons. The hydrogen adsorption capacity of MCNR and non–meal CC are expressed in terms of wt% (weight of the hydrogen molecules/weight of the material × 100).

2.6 Ethylene adsorption using the MCNRs

The chemisorption of ethylene gas was measured on the MCNRs in a medium pressure auto gas adsorption system utilizing gas chromatography at room temperatures. Typically, 0.5 g of the four MCNR adsorbents (CCC, CNC, CPMC, CGC) and of non-metal CC was loaded into a Pyrex adsorption cell attached to the system and subjected to a standard pretreatment prior to ethylene (C_2H_4) adsorption measurement which included vacuum drying in a desiccator and thermal activation at 100 °C for 5 h in an oven.

2.7 Catalytic oxidation using CGC

Heterogeneous catalytic oxidation of 1-phenylethanol was carried out at atmospheric pressure by solvent-free reaction condition using CGC as an eco-friendly catalyst (Scheme 1). Catalytic oxidation was carried out in a magnetically stirred 3-neck round-bottom flask under oxygen gas purging attached with a Dean–Stark trap and condenser to collect the water formed during the reaction. CGC (0.1 g) was added to 1-phenylethanol (41.4 mmol, 5.06 g) at room temperature. The reaction mixture was heated to 120 °C and continuously stirred for 4 h. The completion of the catalytic oxidation

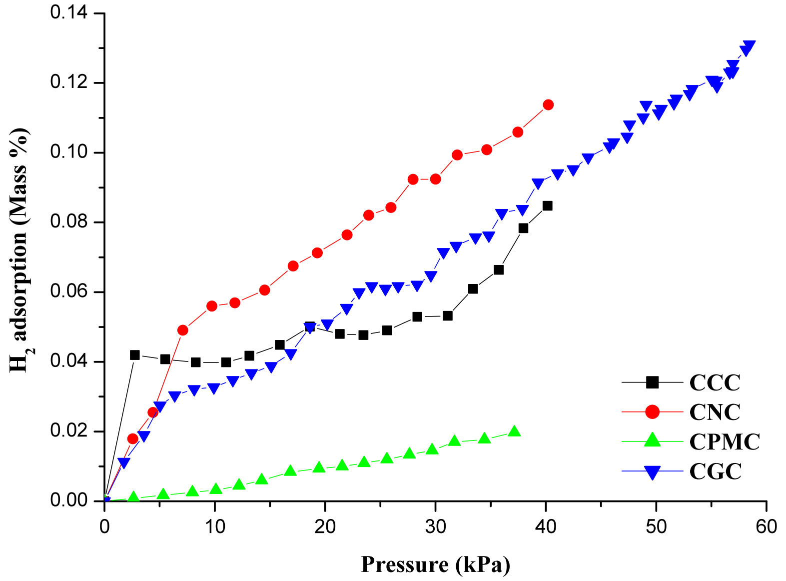


Fig. 2 Hydrogen adsorption isotherms of metal–carbon nanoreactors CCC, CNC, CPMC and CGC

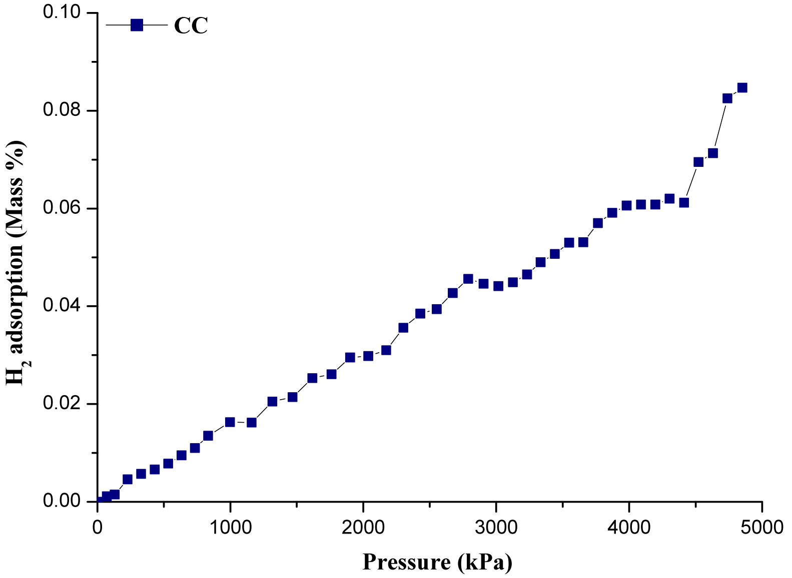


Fig. 3 Hydrogen adsorption isotherms of non-metal CC

was monitored by thin layer chromatography. The product was filtered and the residue was washed with dry ethanol. The solvent was removed from the combined filtrate and the residue was purified by column chromatography by using *n*-hexane/EtOAc (9:1) to give acetophenone (yield, 4.78 g).

3 Results and discussion

3.1 Characterization of MCNR composite materials

The four MCNR composite materials CCC CNC, CPMC and CGC were synthesized by simple template method using nano silica ball (NSB) and PFO based pitch followed by easy deposition of metal nano crystals on hierarchical CC. Inexpensive, non toxic and commercially available PFO is extensively suitable as a carbon source because it contains a higher aromatic content and can be easily carbonized. All the MCNRs were fully characterized by XRD, TGA, N_2 adsorption–desorption isotherm, SEM coupled with EDS, TEM and FT-IR. The detailed characterizations are given in our earlier paper (Mayani et al. 2012b, 2012c).

3.2 Hydrogen adsorption study

The adsorption of hydrogen in pristine CC and its metal doped MCNRs were investigated using static gravimetric adsorption system. The experimental hydrogen uptake capacities at 25 °C up to 60 bar pressure for various MCNRs (CCC, CNC, CPMC and CGC) and non-metal CC are shown

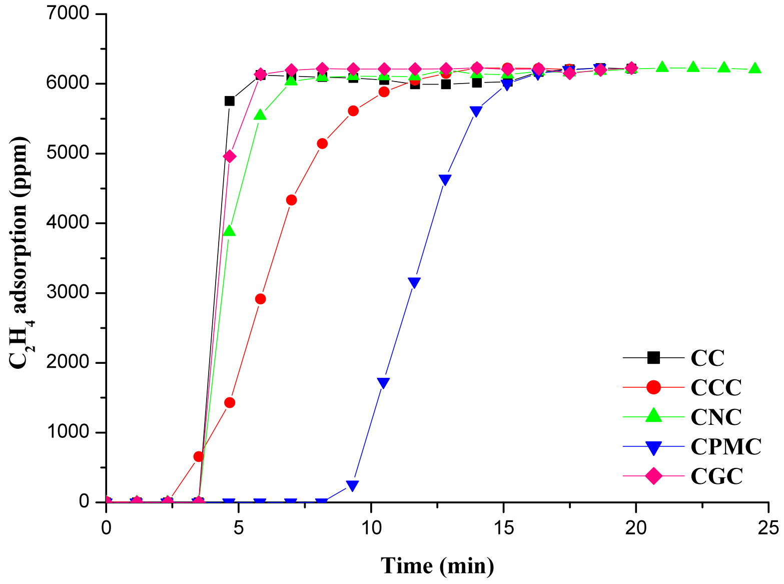


Fig. 4 Ethylene adsorption of metal–carbon nanoreactors CCC, CNC, CPMC, CGC and non-metal CC

in Figs. 2 and 3, respectively. The adsorption of hydrogen took place in a potential region which restrained the hydrogen adsorption domain. The hydrogen adsorption of CCC and CNC showed a maximum hydrogen adsorption capacity of 0.08 wt% and 0.11 wt% at 40.2 kPa, respectively. The adsorption of hydrogen at 25 °C in the CGC increased with increasing pressure (0.13 wt% at 58.5 kPa). The CPMC isotherm showed negligible hydrogen uptake with increasing pressure (0.02 wt% at 37.1 kPa) compare to other MCNRs. On the other hand, hydrogen adsorption was absent for pristine CC at pressures up to 5000 kPa. In general, the experimental results illustrate that the hydrogen adsorption ability of the MCNRs was greatly improved compared to that of the non-metal CC base, in terms of percentage mass uptake per unit pressure. The entire MCNR isotherms revealed moderate to excellent hydrogen adsorption with pressure.

3.3 Ethylene adsorption study

Another possible growth area for MCNRs is in the adsorption of ethylene gas. Due to the excellent characteristics of carbon materials, the ethylene gas adsorption capacities of the MCNRs were accomplished by gas chromatography at room temperature. Figure 4 represents the isotherm for ethylene adsorption on the four MCNRs and non-metal CC. The corresponding ethylene adsorptions on the pure adsorbents (CC, CCC, CNC and CGC) have been increased noticeably from 0 to 6000 ppm in 3–15 min. CPMC showed a corresponding ethylene adsorption rise from 0 to 6000 pm in 8–15 min. The ethylene adsorption was relatively similar on the adsorbent MCNRs and non-metal CC samples, and it looks relatively similar with each other with an increment in ethylene adsorption and more or less constant upon saturation with time (Fig. 4). The four MCNRs and pristine CC showed a noticeable capacity for ethylene adsorption at room temperature. The MCNR had a pore size less than 170 nm and a metal affinity which allows them to trap and adsorb the smaller molecules such as ethylene (3.14 Å). Due to this exceptional characteristic of the MCNRs, they exhibited excellent ethylene adsorption compatibility with active ethylene adsorption sites. These non-metal CC and MCNRs can be used extensively as effective and inexpensive adsorbents during the transport and storage of fruits and vegetables in order to conserve the agro-product quality by adsorbing any ethylene production.

3.4 Heterogeneous catalytic oxidation using CGC

Although, gold is the most inert of all metals, it has interesting properties and the large pores of the CGC composite material render it a potential heterogeneous catalyst. We carried out the solvent-free oxidation of 1-phenylethanol with CGC in the presence of oxygen gas at 120 °C. CGC provided the oxidation product in ∼96 % yield (Table 1, entry 1). An attempt was made to recycle the CGC catalyst in the catalytic oxidation reaction under the optimized reaction condition. After the first catalytic run, the product was isolated by filtration and the solid mass underwent was Soxhlet extraction with ethanol. The recovered CGC was then activated, dried in a vacuum desiccator overnight and subjected to the next catalytic cycle. Four catalytic cycles were completed successfully without any observed loss of catalytic performance (Table 1, entries 1–4). The pristine CC support failed to catalyze the oxidation reaction under same reaction condition (Table 1, entry 5). The microwave–assisted reaction was fast

Table 1 Heterogeneous catalytic oxidation of 1-phenylethanol using CGC and its recycling study[a]

Entry	Materials[b]	Yield[d] (%)	Catalytic run
1	CGC	96	1
2	CGC	94	2
3	CGC	95	3
4	CGC	95	4
5	CC	–	–
6	CGC + MW[c]	–	–

[a] The reaction was carried out by using 1-phenylethanol (5.06 g) and CGC (0.1 g) in presence of O_2 at 120 °C for 4 h

[b] Two composite materials (CC/CGC) were used as catalyst

[c] The reaction was carried out by using 1-phenylethanol (5.06 g) and CGC (0.1 g) was irradiated for 1 min in a microwave oven

[d] Isolated yield after column chromatography

and convenient but CGC failed to catalyze the oxidation reaction under microwave irradiation (Table 1, entry 6). This catalytic study clearly attributed the entire catalytic activity to the Au supported on the CGC material.

4 Conclusions

Four MCNRs were newly synthesized and characterized with various combinations of metal and carbon foundation. The collective chemical and physical properties of these nanocomposites allow new kinds of scientific application. The prepared MCNRs and non-metal CC have potential applications in adsorption and catalysis due to their significant capacities for ethylene and hydrogen gas adsorption. The highest adsorption capacity for hydrogen in CGC and CNC were obtained to be 0.13 and 0.11 mass%. CGC showed remarkable catalytic activity and selectivity for solvent-free heterogeneous catalytic oxidation of 1-phenylethanol to acetophenone, along with the added advantage of catalyst recycling. These MCNRs materials revealed excellent adsorption, high catalytic conversion and reasonable stability under our experimental condition. These materials can be used as solid catalysts in different catalytic reactions and as adsorbents for the adsorption of various molecules using MCNRs for energy storage and reverse 'greenhouse' effect. Furthermore, we are expanding new spillover techniques that will allow us to scrutinize the MCNRs and enhance their adsorption and storage capacities with characteristic tailored property.

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