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Priority Communication

Silver nanoparticles encapsulated by metal-organic-framework give the highest turnover frequencies of 10^5 h^{-1} for three component reaction by microwave-assisted heating

Di Li [a,1], Xiaoping Dai [a,1], Xin Zhang [a,*], Hongying Zhuo [b], Yan Jiang [b], Yan-Bing Yu [b], Pengfang Zhang [b], Xingliang Huang [b], Hai Wang [b]

[a] State Key Laboratory of Heavy Oil Processing, College of Chemical Engineering, China University of Petroleum, Beijing 102249, China
[b] National Institute of Metrology, Beijing 100013, China

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ABSTRACT

Microwave (MW)-assisted heating, due to its unique properties has been used for synthesis of metal, oxide, zeolite, and metal-organic framework (MOF), and even to carry out organic reactions. However, less attention has been paid to integration of two or more functional components into advanced materials by MW-assisted strategy. We report herein for the first time for controllable integration of silver nanoparticles (NPs) and IRMOF-3 as a core-shell Ag@IRMOF-3 nanostructures into highly efficient catalysts by a facile one-pot MW irradiation method. Impressively, the uniform core-shell Ag@IRMOF-3 nanostructures can be fabricated as short as 5 min and are highly active for three-component coupling reaction of amine, aldehyde and acetylene (A^3-coupling) by MW-assisted heating strategy. Specifically, the Ag@IRMOF-3 with average size of Ag NPs of 5.2 nm and IRMOF-3 of 91.5 nm exhibited the highest turnover numbers and turnover frequencies of 3052 and 149,004 h^{-1} reported up to date, respectively, for the A^3-coupling reaction. Thanks to the MOF shell coating, the Ag@IRMOF-3 can be recycled at least for 8 runs without losing any activity; furthermore, the size-selective catalysis was also successfully achieved due to the size selective for propargylamines with different sizes.

Controllable integration of two or more functional components is of significant importance in design and synthesis of advanced composite materials with collective properties and improved performance [1]. Recently integration of metal/metal oxide nanoparticles (NPs) and metal-organic framework (MOF) into core-shell NPs@MOF nanostructure has been the subject of intense research. [1–3] Two approaches including "ship-in-a-bottle" and "bottle-around-ship" for the encapsulation of NPs into MOF have been reported [2a]. These approaches usually consist of two or multi steps by using conventional solvothermal synthesis. Tang's group has prepared Au@MOF-5 in one-pot solvothermal synthesis. And the solvothermal synthesis took 3 h and the obtained Au nanoparticles were larger than 30 nm [2e]. So far most of reported synthesis was from several hours to multiday and the core size of NPs or shell thickness of MOF was in large sizes. Therefore the development of a rapid, efficient and straightforward synthetic strategy to prepare metal NPs@MOF with tunable nano-sizes is highly desired.

Microwave (MW)-assisted heating due to its unique advantages such as fast crystallization, high dispersion, decreasing reaction time, and narrow particle size distribution has been used to synthesis of metal and metal oxide, zeolite as well as MOF, respectively [4]. However, there are few reports to integrate two or more functional components into advanced composite materials by MW-assisted strategy. We report herein a facile one-pot synthesis to prepare Ag@IRMOF-3 nanostructures with uniform shape and tunable sizes through a rapid MW-assisted methodology. Distinguished with the earlier metal NPs@MOF, the well-defined Ag@IRMOF-3 can be fabricated as short as 5 min. The core size of Ag NPs and the shell size of IRMOF-3 can be tuned in the range of 5.2–45.9 nm and 24.0–174.9 nm, respectively.

We propose that the uniform core-shell Ag@IRMOF-3 could be used as the high-efficient catalyst for three-component coupling reaction. The coupling reaction of amine, aldehyde and acetylene (A^3-coupling) is designed as the model reaction [5a]. The reason to study this A^3-coupling is that the target products of propargylamines are versatile synthetic intermediates organic

* Corresponding author.
E-mail address: zhangxin@cup.edu.cn (X. Zhang).
[1] These authors contributed equally.

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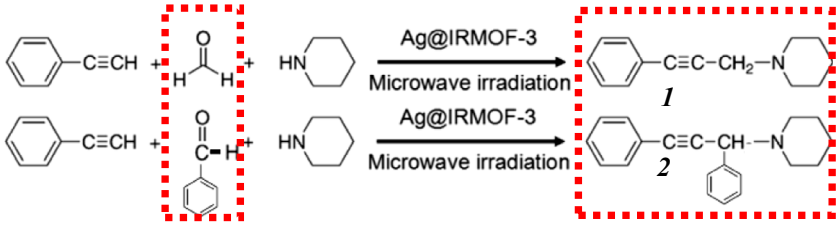
synthesis and are also important structural elements in natural products and therapeutic drug molecules [5b]. These compounds were usually synthesized by lithium acetylides or Grignard reagents in stoichiometric amounts, or recently by homogenous gold, silver, and copper salt [5c–5g]. But these reagents and homogeneous catalysts are difficult to recycle and cannot be reused. Recent progress in this area has been reported using gold, silver nanoparticles and heterogeneous gold and copper catalysts [5a,6]. However the catalytic performance especially stability of these heterogeneous gold catalysts is still not satisfactory. Encouraged by the novel synthesis of the core-shell Ag@IRMOF-3 nanoparticles, the three-component coupling reaction of acetylene (benzacetylene), aldehyde (formaldehyde or benzaldehyde), and amine (piperidine) (A^3-coupling) was carried out by MW and conventional heating by oil-bath, respectively (Scheme 1). Particularly, such a novel type of core-shell Ag@IRMOF-3 catalyst exhibited the highest turnover numbers and turnover frequencies of 3052 and 149,004 h^{-1} up to date, respectively, for the A3-coupling reaction. To the best of our knowledge, this is the first example to engineer silver nanoparticles (NPs) and IRMOF-3 as core-shell Ag@IRMOF-3 nanostructures into highly efficient catalysts by a facile one-pot MW irradiation method.

Different from the conventional two-step method to synthesize NP@MOF composites by adding the pre-synthesized NPs into the MOF precursors [2d,7], we prepared the core–shell Ag@IRMOF-3 nanostructures by directly mixing the Ag with MOF precursors of $AgNO_3$, $Zn(NO_3)_2{\cdot}6H_2O$, and 2-aminoterephthalic acid (NH_2-H_2BDC) in the reaction solution containing N,N-dimethylformamide (DMF), and polyvinylpyrrolidone (PVP) under MW irradiation method. By controlling the reaction conditions, the formation rates of Ag NPs and IRMOF-3 in the solution could be adjusted effectively and thus a series of core-shell Ag@IRMOF-3 crystals with different nano-sizes were obtained (see Experimental sections of the Supporting Information).

The morphology and structure of as-prepared Ag@IRMOF-3 nanocomposites were in-depth investigated by different characterization techniques. Clearly the well-defined core-shell structure of Ag@IRMOF-3 can be obtained at 5 min by using the one-pot synthesis assisted by MW heating at 120 °C (Fig. 1A). By prolonging the reaction time from 5 to 15, and 30 min, the average sizes of core were increased from 7.4 to 18.6, and 45.9 nm, respectively, and the shell size of IRMOF-3 also increased from 24.0 nm to 97.4 and 174.9 nm, respectively (Fig. 1A–C). It is evident that the feature of core-shell structure was well preserved, and the core size of Ag NPs and the shell size of IRMOF-3 are significantly increased by increasing the reaction time. The Ag loadings measured by ICP-AES also increased from 2.06% to 2.10% and 2.63%, respectively, with increasing the reaction time from 5 to 15, and 30 min. By decreasing the $AgNO_3$ amount from 0.014 mmol to 0.0014, and 0.0005 mmol at 15 min with MW at 120 °C, the corresponding Ag content decreased from 2.10% to 0.25%, and 0.09%, respectively. The well-defined core-shell Ag@IRMOF-3 nanostructures were still remained. The core size of Ag nanoparticles was decreased from 18.6 to 11.9 and 5.2 nm, respectively, while the shell sizes of IRMOF-3 remained almost intact (92–97 nm) (Fig. 1B, D, and E). Analysis of the cores by high-resolution transmission electron microscopy (HRTEM) imaging of 2.06% Ag@IRMOF-3 indicated that the spacing between two adjacent lattice planes was about 0.24 nm (Fig. 1F). This value was in agreement with the spacing of (111) planes of cubic Ag, demonstrating that the cores were Ag NPs. The high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image (Fig. 1G) further clearly demonstrated the core–shell structure. And the energy-dispersive X-ray (EDX) elemental mapping showed that the Ag element was distributed only in the core and that the elements of C, N, O, and Zn of IRMOF-3 were homogenously distributed throughout the whole shell, suggesting that the Ag NP core was surrounded with a uniform IRMOF-3 shell (Fig. 1H–L).

Crystal structure analysis from powder X-ray diffraction (XRD) patterns revealed a typical phase of IRMOF-3 for all Ag@IRMOF-3 nanocomposites. Only a very weak diffraction pattern centered at 38.1° ascribed to face-centered cubic (fcc) phase of Ag was found on 2.06% and 2.63%Ag@IRMOF-3 samples while no diffraction pattern of fcc phase of Ag was found on 0.09%Ag@IRMOF-3. The relative crystalline degree in terms of the intensity of classic peak centered at $2\theta = 6.8°$ of IRMOF-3 was significantly increased with the reaction time increased from 5, 15 to 30 min (Fig. 2A). Fourier transform infrared (FTIR) spectra (Fig. S1) indicated that the characteristic —OH stretching frequency in the carboxylic acid group of the NH_2-H_2BDC linker centered at 2670 cm^{-1} disappeared after formation of the Ag@IRMOF-3 nanocomposites, suggesting occurrence of the coordination interaction between Zn^{2+} ions and carboxylic acid group of NH_2-H_2BDC to form IRMOF-3. The characterization by X-ray photoelectron spectroscopy (XPS) showed that there were not any Ag signals, indicating that Ag nanoparticles were completely covered with IRMOF-3 shells that shielded the underlying Ag surface (Fig. 2B). The UV/Vis spectra showed that the vibration of Ag NPs at 400 nm wavelength became weaken when the reaction time increased from 5 to 15 min, and it was completely disappeared at 30 min due to the shield of the larger length of the shell (Fig. 2C). These results further demonstrated the core-shell nanostructure of Ag@IRMOF-3. Hydrogen-temperature-programmed reduction (H_2-TPR) experiments showed that only one peak centered at ca. 455 °C which was assigned to the decomposition of IRMOF-3, and no hydrogen consumption peak ascribed to the reduction of cationic silver species. The result indicated that the silver species in Ag@IRMOF-3 samples were in metallic state (Fig. 2D). The features of the MOF shells, especially the porosity, determine the properties of the core–shell NPs. The representative of Ag@IRMOF-3 nanostructures determined by nitrogen adsorption-desorption experiments featured a classic Type 1 nitrogen sorption isotherms with the steep increase in N_2 uptake at low relative pressure (<0.01), indicating Ag@IRMOF-3 possesses microporous pore. The average pore size was ca. 1.9 nm calculated according to Saito-Foley method based on molecular modulation (Fig. S2). And the BET surface areas were



Scheme 1. The A^3 coupling reaction of phenylacetylene, formaldehyde or benzaldehyde, and piperidine on Ag@IRMOF-3 nanostructures.