

## Short communication

## Novel heterogeneous Rh-incorporated graphitic-carbon nitride for liquid-phase carbonylation of methanol to acetic acid

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## ARTICLE INFO

## Keywords:

Liquid-phase carbonylation  
 Heterogeneous Rh-based catalyst  
 Graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>)  
 Acetic acid (AA)  
 Methanol

## ABSTRACT

A novel heterogeneous rhodium-incorporated graphitic carbon nitride (Rh-g-C<sub>3</sub>N<sub>4</sub>) was investigated for a liquid-phase carbonylation of methanol to acetic acid (AA) to overcome disadvantages of the commercialized Rh-based homogeneous catalysts. The heterogeneous Rh-g-C<sub>3</sub>N<sub>4</sub> catalyst showed a superior catalytic activity in a liquid-phase carbonylation with AA yield above 82% under the reaction conditions of 413 K and CO pressure of 4.0 MPa, where the initially formed MA intermediate can be easily hydrolyzed to form AA. A higher dispersion of the incorporated rhodium nanoparticles in the g-C<sub>3</sub>N<sub>4</sub> matrix with a small crystallite size was responsible for a higher catalytic activity with a less leaching degree of active rhodium metals. The novel Rh-g-C<sub>3</sub>N<sub>4</sub> with rhodium content of 1–3 wt% can be a candidate to substitute the commercial homogeneous Rh complex catalyst for AA production by methanol carbonylation.

## 1. Introduction

Carbonylation of methanol to acetic acid (AA, CH<sub>3</sub>COOH) through the reaction of CH<sub>3</sub>OH + CO ↔ CH<sub>3</sub>COOH is one of the important industrial processes using the commercialized rhodium or iridium-based homogeneous catalysts. AA has been widely used as important petrochemical intermediates such as production of vinyl acetate monomer (VAM), acetic anhydride, acetate esters and terephthalic acid (TPA) [1]. Since the first commercial cobalt iodide-based catalyst was developed by BASF in the late 1950s, Monsanto process using homogeneous rhodium complex was developed with a high selectivity to AA at a mild liquid-phase reaction condition [2]. New commercial process named as Cativa™ by using homogeneous iridium complex was also commercialized by BP Chemicals [2,3]. On Cativa process, the iridium-based catalyst with ruthenium promoter showed a higher catalytic activity at much lower water content and a less formation of inactive precipitates [3]. Since the cost of recycling of the commercialized homogeneous catalysts are relatively high, there have been many attempts to develop efficient heterogeneous catalysts by immobilizing the rhodium complex on various solid supports such as polymers, metal oxides and zeolites and so on [4,5]. Chiyoda and UOP have recently commercialized heterogeneous homogeneous catalyst by anchoring the ionic rhodium-complex on polymeric ion exchanged resins, which has been well known as a commercialized Acetica™ process [6], by immobilizing the

active rhodium complexes on polyvinylpyridine (PVP) resin [7]. This rhodium-based Acetica catalyst exhibited a higher catalytic activity and stability with an insignificant loss of rhodium metals than that of Monsanto process. In case of the Monsanto process, there have been considerable efforts to improve the catalyst stability by incorporating different ligands such as phosphorus or nitrogen containing ligands into the coordination sphere of the rhodium complexes [2,8–10]. In addition, iodide cocatalysts were inevitably required for the liquid-phase carbonylation, however, it can cause a severe corrosion of the equipment. Some recent researches of halide-free heterogeneous catalytic systems using copolymeric materials mainly through an incorporation of active rhodium metals have been also reported for a selective production of methyl acetate [11]. Recently, metallic gold catalyst was also reported for the carbonylation of methanol in a vapor-phase carbonylation [12,13], and multistep reactions via dimethyl ether carbonylation to methyl acetate and subsequent hydration to AA without using these exotic halides were announced to be commercialized by BP, named as BP-SaaBre process [14,15].

In the present investigation, carbonylation of methanol to AA was investigated by using novel rhodium-incorporated graphitic carbon nitride (Rh-g-C<sub>3</sub>N<sub>4</sub>), where the carbon nitride has been widely used as an efficient photocatalysts [16] and supporting materials. Since a facile electron transfer nature of the g-C<sub>3</sub>N<sub>4</sub>, we investigated the g-C<sub>3</sub>N<sub>4</sub> as a supporting matrix for rhodium-incorporation. The home-made

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heterogeneous Rh-g-C<sub>3</sub>N<sub>4</sub> at optimal small amount of rhodium metal showed a superior catalytic activity in a liquid-phase carbonylation, which can solve the separation problems of the homogeneous Rh-based commercial catalysts in liquid products. The roles of rhodium metals on the g-C<sub>3</sub>N<sub>4</sub> matrix were explained using surface characterization tools such as surface area, electronic states of rhodium species with its crystallite size distribution.

## 2. Experimental

### 2.1. Synthesis of Rh-based heterogeneous catalysts and activity measurement

(1) Preparation of prototype Rh-3BP/PVP: To synthesize the rhodium-3benzoyl pyridine complex (denoted as Rh-3BP), Dichlorotetracarboxyldirrhodium precursor ([Rh(CO)<sub>2</sub>Cl]<sub>2</sub>), 3-benzoyl pyridine (3-BP) and poly(4-vinylpyridine) (P4VP) polymer were used (provided from Alfa Aesar). The obtained solid rhodium complexes were washed with hexane solvent and dried at room temperature according to the previous report [9]. A comparative heterogenized homogeneous catalyst, which has a similar chemical composition with the Acetica process, was prepared by wet impregnation method of the rhodium complex on the P4VP and it was denoted as Rh-3BP/PVP.

(2) Preparation of comparative RhCl<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>: To prepare a heterogeneous RhCl<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>, rhodium chloride hydrate (RhCl<sub>3</sub>·xH<sub>2</sub>O) precursor was used (provided from Alfa Aesar). The graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) was previously synthesized by a well-known preparation method [16]. The yellowish solid powder was obtained, and RhCl<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> was prepared by wet impregnation method with 5 wt% Rh metal using rhodium chloride (RhCl<sub>3</sub>) precursor.

(3) Preparation of novel rhodium-incorporated g-C<sub>3</sub>N<sub>4</sub> (Rh-g-C<sub>3</sub>N<sub>4</sub>): Melamine as the g-C<sub>3</sub>N<sub>4</sub> precursor and active rhodium metal precursor (rhodium nitrate, Rh(NO<sub>3</sub>)<sub>3</sub>) were used to synthesize rhodium-incorporated graphitic carbon nitride (Rh-g-C<sub>3</sub>N<sub>4</sub>) at a various rhodium content from 0 to 5 wt%. The resulting yellowish solid powder was dried overnight and heated under N<sub>2</sub> flow up to 873 K for 10 h [17,18]. The as-prepared heterogeneous catalysts were denoted as Rh(x)-g-C<sub>3</sub>N<sub>4</sub>, where x represent the rhodium content in wt%. In addition, the more detailed preparation procedures such as temperature profiles of the pure g-C<sub>3</sub>N<sub>4</sub> and rhodium-incorporated g-C<sub>3</sub>N<sub>4</sub> are presented in Supplementary Fig. S1.

(4) Activity measurements: The catalytic activity tests were carried out using a high-pressure batch reactor system equipped with pyrex liner at the following reaction conditions with 0.1 g of the as-prepared catalysts; T = 413 ± 5 K, CO partial pressure = 4.0 MPa (90 mol% CO balanced with N<sub>2</sub>), molar ratio of methanol/methyl iodide/water = 43/34/23 (molar ratio of methyl iodide/methanol = 0.79) and methanol/methyl iodide/water = 51/21/29 (molar ratio of methyl iodide/methanol = 0.40). The liquid products were sampled and analyzed by off-line gas chromatography (YoungLin 6500 GC) equipped with DB-WAX capillary column with a flame ionization detector.

### 2.2. Characterization

Powder X-ray diffraction (XRD) patterns of the fresh Rh-g-C<sub>3</sub>N<sub>4</sub> were collected by Bruker D8 Advance X-ray diffractometer with Cu Kα (λ = 1.5406 Å) irradiation from Ge(111) monochromator to verify the crystalline structures of Rh-g-C<sub>3</sub>N<sub>4</sub>. The specific surface area, pore volume and average pore diameter of the fresh Rh-g-C<sub>3</sub>N<sub>4</sub> were characterized by N<sub>2</sub> adsorption-desorption isotherms at a vacuum level of 10<sup>-6</sup> Pa. The surface area was calculated by Brunauer-Emmett-Teller (BET) method obtained at 77 K using TristarII 3020 instrument. The pore size distribution was determined by Barrett-Joyner-Halenda (BJH) method from the desorption branch. X-ray photoelectron spectroscopy (XPS) spectra were obtained by a VG Multilab 2000 instrument using a monochromatic Al Kα X-ray source. All binding energies

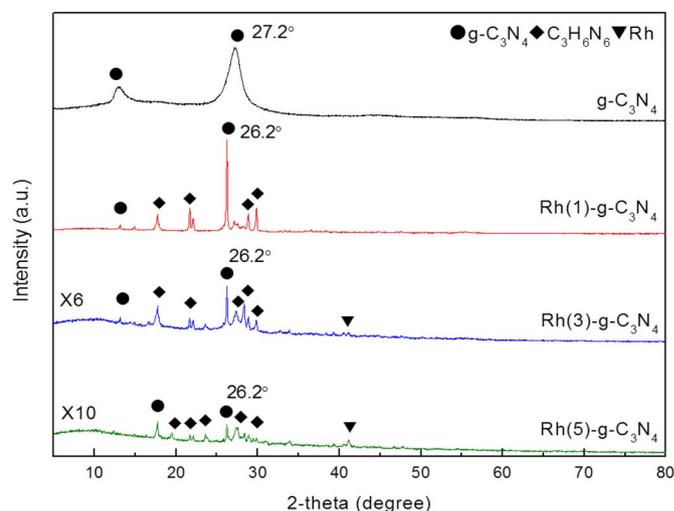


Fig. 1. XRD patterns of the fresh Rh-g-C<sub>3</sub>N<sub>4</sub>.

form the XPS spectra were corrected by using a binding energy of C 1s at 286.4 eV. CO chemisorption was performed using an ASAP 2020 instrument at an adsorption temperature of 50 °C. Transmission electron microscopy (TEM) images were obtained by a Tecnai G<sup>2</sup> T-20S instrument with an operating voltage of 200 kV. The leaching amount of rhodium metal after a liquid-phase carbonylation reaction was measured by inductively coupled plasma-auger electron spectroscopy (ICP-OES) using a CIROS CCD ICP spectrometer using the liquid product mixtures. The more detailed preparation methods and characterization of the Rh-g-C<sub>3</sub>N<sub>4</sub> are precisely included in Supplementary material.

## 3. Results and discussion

### 3.1. Characteristics of the fresh Rh-g-C<sub>3</sub>N<sub>4</sub>

XRD patterns of the fresh Rh-g-C<sub>3</sub>N<sub>4</sub> prepared by using melamine and Rh(NO<sub>3</sub>)<sub>3</sub> precursors are displayed in Fig. 1. The detailed preparation procedures of the pure g-C<sub>3</sub>N<sub>4</sub> [17,18] and the Rh-g-C<sub>3</sub>N<sub>4</sub> are presented in Supplementary Fig. S1. The characteristic diffraction peaks, especially with large peak intensities at 2θ = 13.1 and 27.2°, were clearly observed on the fresh Rh-g-C<sub>3</sub>N<sub>4</sub>. These peaks are generally assigned to an in-plane structure and interlayers of the g-C<sub>3</sub>N<sub>4</sub>, respectively [17]. This observation strongly suggests that the g-C<sub>3</sub>N<sub>4</sub> structures were well synthesized even in the metal-incorporated Rh-g-C<sub>3</sub>N<sub>4</sub>. A slight shift of the major diffraction peak corresponding to the inter-planar stacking structures of the pure g-C<sub>3</sub>N<sub>4</sub> at 2θ = 27.2° was observed after rhodium incorporation especially at a lower content of rhodium metal on the Rh [1]-g-C<sub>3</sub>N<sub>4</sub> at 2θ = 26.2° and this observation supports the possible rhodium-incorporation to the matrix of the g-C<sub>3</sub>N<sub>4</sub>. This also suggests that a host-guest interaction and polymeric condensation were strongly controlled by rhodium-incorporations on the pure g-C<sub>3</sub>N<sub>4</sub> structures [17,18]. The crystallinity of the g-C<sub>3</sub>N<sub>4</sub> can be dramatically decreased with an increase of rhodium content as shown in Fig. 1.

However, the characteristic g-C<sub>3</sub>N<sub>4</sub> structures were preserved even after the introduction of rhodium species, and the characteristic peaks of rhodium metals were clearly observed as increasing the amount of the incorporated rhodium species such as the Rh [5]-g-C<sub>3</sub>N<sub>4</sub>. Since the diffraction peak observed at 2θ = 41.1° represents the (111) diffraction plane of the metallic rhodium species [19], the incorporated rhodium species seems to exist in the matrix of g-C<sub>3</sub>N<sub>4</sub> with a highly dispersed small size below 1 nm at a lower rhodium amount, especially on the Rh [1]-g-C<sub>3</sub>N<sub>4</sub>. However, at a high rhodium content on the Rh [5]-g-C<sub>3</sub>N<sub>4</sub> as summarized in Table 1, the metal crystallites seem to be mainly

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