Effects of Al promoter on novel heterogeneous mesoporous Rh-C_3N_4 for liquid-phase carbonylation of methanol to acetic acid

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Abstract: The roles of Al promoter on the heterogeneous Rh-incorporated mesoporous graphitic carbon nitride (Rh-mpg-C_3N_4) were investigated for a liquid-phase carbonylation of methanol to acetic acid (AcOH). The Al modified Rh-mpg-C_3N_4 at an optimal amount of Al below 3.0 wt% showed a higher AcOH yield above 60% compared to the unmodified Rh-mpg-C_3N_4. A highly dispersed Lewis acidic Al species on the Rh-mpg-C_3N_4 seems to increase the reverse esterification reaction rate of methyl acetate (MeOAc) intermediate to AcOH, and the increased hydrolysis of MeOAc was responsible for a higher AcOH yield.

Keywords: Liquid-phase carbonylation; Al promoter; mesoporous graphitic carbon nitride; Acetic acid.

1. Introduction

Carbonylation of methanol (MeOH) with CO to acetic acid (AcOH) using rhodium-based homogeneous catalyst with methyl iodide and water as co-catalyst has been known to be one of the most well-known methods to synthesize AcOH.[1,2] To solve the separation problems of the commercial homogeneous catalysts from products, some heterogenized-homogeneous catalysts have been enormously investigated using supporting materials such as zeolite,[3] metal oxides and P4VP (poly 4-vinyl pyridine) polymer (ACETICA process).[2] The graphitic carbon nitride (g-C_3N_4) shows semi-conductive properties and it is widely used as catalysts such as the activation of CO, trimerization, and photocatalysis and so on,[4,5] where the g-C_3N_4 can be an alternative supporting material for noble metals for efficient heterogeneous catalytic systems.[6]

2. Experimental sections

To prepare the Al-modified Rh-incorporated mesoporous graphitic carbon nitride (AlRh-mpg-C_3N_4) [**7**], SBA-15, aluminum precursor (nitrate) and rhodium precursor (nitrate) were dissolved in distilled water with the addition of hexamethylenetetramine (HTM) as carbon nitride source. The resulting yellowish solid powder was dried overnight and heated under N_2 flow up to 750 °C for 5h. The hard-template of SBA-15 was removed using 2M NaOH solution for 0.5 h at 90 °C and dried again for 12 h at 80 °C. The as-prepared heterogeneous catalysts were denoted as Al(x)Rh-mpg-C_3N_4, where x represents the aluminum contents (wt%) at a fixed rhodium content of 2.0 wt%. The catalytic activity for carbonylation of methanol was carried out in a high-pressure batch reactor with Teflon liner at the reaction conditions of $T = 463 \pm 5$ K, $P = 4.0$ MPa (90mol% CO balanced with N_2) and reactant molar ratio of methanol/methyl iodide/water = 47/28/26 with 0.40 g catalyst at the stirring speed of 300 rpm for 3 h. The liquid products were analyzed using an off-line gas chromatography (YoungLin, GC) with DB-WAX capillary column connected to a flame-ionized detector (FID).

3. Results and discussion

The catalytic activities for carbonylation of methanol (MeOH) to acetic acid (AcOH) on the AlRh-mpg-C_3N_4 according to the Al contents are summarized in **Table 1**. Compared to the Al-unmodified pristine Rh-mpg-C_3N_4, the Al(2.0)Rh-mpg-C_3N_4 showed the most higher yield of AcOH, and no further enhancements of AcOH yield were observed above 2.0 wt%Al on the heterogeneous AlRh-mpg-C_3N_4 at the present reaction conditions. As shown in **Figure 1(A)**, the catalytic activities were increased with an increase of Al content above the AcOH yield of 61 % with similar surface areas of AlRh-mpg-C_3N_4 above 800 m^2/g and ordered mesoporous pore size distributions as shown in **Figure 1(B)**. We believe that the highly dispersed Lewis acidic Al species on the Rh-mpg-C_3N_4 increased the reverse esterification reaction rate of MeOAc to AcOH, and the increased hydrolysis of MeOAc can be responsible for a higher AcOH yield. The highly dispersion of the Al promoter and active Rh species seems to be originated from the ordered mesoporous structures of mpg-C_3N_4 as confirmed by TEM images in **Figure 1(C)**. Therefore, the novel heterogeneous AlRh-mpg-C_3N_4 can be an efficient catalytic system to solve the commercialized homogeneous Rh-based catalysts for the carbonylation of MeOH to AcOH as well.

Table 1. Catalytic activities on the Al-modified Rh-incorporated mesoporous graphitic carbon nitride (AlRh-mpg-C_3N_4)

Notation	Surface area (m^2/g)	Conv. (MeOH mol%)	Selectivity (mol%)		Yield (AcOH mol%)
			AcOH	MeOAc	
Al(0)Rh-mpg-C_3N_4	832	92.9	61.8	38.2	57.4
Al(1.0)Rh-mpg-C_3N_4	990	90.3	49.9	50.1	45.1
Al(1.25)Rh-mpg-C_3N_4	861	94.5	60.5	39.5	57.1
Al(1.5)Rh-mpg-C_3N_4	822	95.1	60.7	39.3	57.7
Al(2.0)Rh-mpg-C_3N_4	843	95.5	65.2	34.8	62.3
Al(2.5)Rh-mpg-C_3N_4	884	95.8	64.3	35.7	61.7
Al(3.0)Rh-mpg-C_3N_4	832	96.0	63.9	36.1	61.4

Reaction conditions: T = 463 ± 5 K, P = 4.0 MPa (90mol% CO balanced with N_2) and reactant molar ratio of methanol/methyl iodide/water = 47/28/26 with 0.40 g catalyst

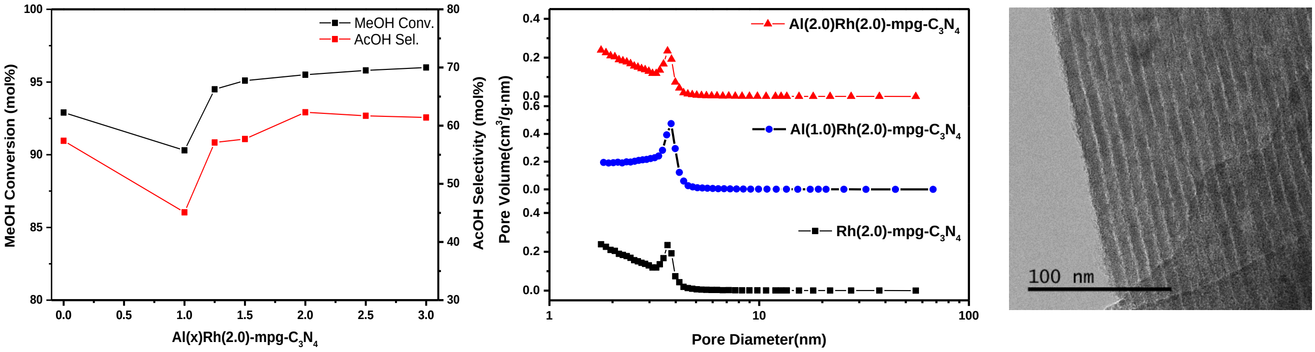

Figure 1. (A) Catalytic activity for carbonylation of methanol (MeOH) to acetic acid (AcOH) on the AlRh-mpg-C_3N_4, (B) Pore size distribution of the fresh AlRh-mpg-C_3N_4, and (C) TEM images of the of the fresh mpg-C_3N_4

4. Conclusions

The novel heterogeneous Al-modified Rh-incorporated mesoporous graphitic carbon nitride (AlRh-mpg-C_3N_4) revealed a superior catalytic activity for the carbonylation of methanol to acetic acid at an optimum aluminum content at 2.0wt%Al (Al(2.0)Rh-mpg-C_3N_4). The observed higher carbonylation activity with higher yield of acetic acid seems to be attributed to the positive roles of Al promoter by enhancing the reverse esterification of methyl acetate formed to acetic acid on the highly dispersed Lewis acid sites originated from the Al species on the AlRh-mpg-C_3N_4.

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