Controllable synthesis of Ru nanocrystallites on graphene substrate as a catalyst for ammonia synthesis

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Abstract: Controllable synthesis of Ru nanocrystallites on graphene substrate using polyol methods was reported herein. The zeta potential of graphene oxide dispersed in polyols is found to play a key role in tailoring the morphology and oxidation state of Ru nanocrystallites on graphene substrate.

Keywords: Graphene, Ruthenium nanocrystallites, Ammonia synthesis.

1. Introduction

Controllable synthesis of supported metal nanocrystallites is crucial for designing heterogeneous catalysts with high performance [1-3]. Ruthenium has been extensively investigated as the second-generation catalyst for ammonia synthesis. Its catalytic activities have been found to be structurally and electronically dependent on the nature of supports and/or promoters, thus tailoring the shape and size of Ru nanocrystallites grown on appropriate substrates is of great importance for developing novel catalytic systems for ammonia synthesis.

2. Experimental

Graphite oxide (GO) was prepared by a modified Hummers method. The Ru/graphene catalysts were synthesized with polyol method. Appropriate amount of $RuCl_3.5H_2O$ (Ru 0.001 mol/L) was dissolved in 200 mL polyols (ethylene glycol (EG), 1,3-propanediol (PD)) under stirring. Then, a portion of the lyophilized GO (1.0 g) was dispersed into the polyol solution of Ru^{3+}. The mixture was first stirred at room temperature for 30 min and then sonicated for 2 h to exfoliate the GO into graphene oxides. Subsequently, the mixture was transferred into a three-necked flask, the flask was immersed into an oil bath preheated at 508 K. After being heated at 453 K for 30 min in a reflux system, the reaction mixture was immediately poured into an ice bath. The obtained product was then filtered and water-washed five times. Finally, the Ru/graphene catalyst was dried in vacuum at 453 K overnight.

3. Results and discussion

The morphology of Ru crystallites supported on graphene depended on the species of polyols utilized in the synthetic procedures. The TEM images (Fig. 1) of the Ru/graphene catalysts obtained by heating the mixtures at 453 K and 0.1 MPa for 30 min demonstrates that only the PD-derived Ru/graphene catalyst (Fig.1b) shows a uniformly dispersed Ru nanocrystallites with a hexagonal shape of 3-5 nm in size, which must have more abundant B_5 sites (necessary for the rate-limiting N_2 dissociation step) than spherical particles [5, 16, 21, 32, 33]. The Ru nanocrystallites on other three samples agglomerate into particles with a size of 50-100 nm (Fig.1a,c,d).

For the sake of evaluating the activities of the Ru/graphene catalysts, we chose $Ba(NO_3)_2$ (molar ratio of Ba: Ru = 1:1) as promoter precursors for the samples. The catalytic activities for ammonia synthesis over the Ba-Ru/graphene catalysts (0.10 g) were measured at 673 K and 0.1 MPa in a tubular continuous plug flow system. Fig. 2a shows the catalytic activities of the Ba-Ru/graphene catalysts. The PD-derived Ba-Ru/graphene catalyst exhibit the highest activity for ammonia synthesis, which is significantly higher than that of Ba-Ru/MgO (15 mmol NH_3 g^{-1}_{Ru} h^{-1}) [16]. The rate of ammonia synthesis over PD-derived Ba-Ru/graphene as a function of temperature is shown in Fig.2b. The figure shows that the rate of ammonia synthesis over PD-derived Ba-Ru/graphene increased progressively with an increase in temperature, reaching a maximum at 673 K.

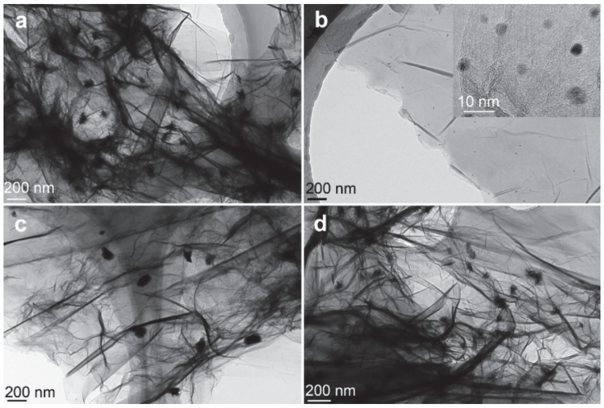

Figure 1. TEM images of the Ru/graphene catalysts prepared by heating 0.001 mol/L Ru^{3+} and 5.0 mg/L graphite oxide in (a) EG, (b) PD, (c) EG+OA, and (d) EG (the initial concentration of Ru^{3+} was 0.002 mol/L) at 453 K and 0.1 MPa for 30 min.

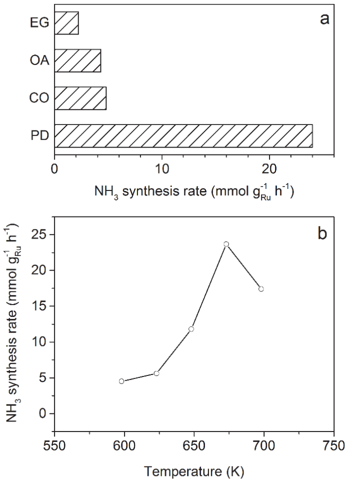

Figure 2. Catalytic activities for ammonia synthesis over (a) Ba-Ru/graphene (Ba: Ru = 1:1 in mole) catalysts based on specific mass of Ru at 673 K and (b) PD-derived Ba-Ru/graphene catalyst at 598 to 698K. Ammonia synthesis conditions: 0.10 g catalyst, 60 mL min^{-1} (STP) synthesis gas ($N_2 + 3H_2$) under 0.1 MPa.

4. Conclusions

Polyol methods are effective ways for controllable synthesis of Ru nanocrystallites as well as graphene supported nanostructured Ru catalysts. The size and shape of Ru nanocrystallites can be successfully tailored by varying the reduction ability of polyols, initial concentration of precursors, or by adding capping agents. The morphology and oxidation state of ruthenium nanocrystallites are influenced by the interaction between carboxylic acid groups and the Ru^{3+} precursors. Flat and hexagonal ruthenium particles of 3-5 nm bonded to the graphene substrate via C-O-Ru bonds epitaxially grow in PD, which shows satisfactory catalytic performance for ammonia synthesis.

References

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