Low-temperature conversion of methane to methanol using carbon nanotubes supported catalyst

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1. Introduction

Conversion of methane to methanol is performed by a two-step process under harsh reaction conditions in industry. The direct synthesis process of methanol from partial oxidation of methane has been studied for a few decades. However, it remains one of the considerable challenges in the sector of methane utilization. [1] Herein, we report carbon nanotubes (CNTs) supported palladium-gold (Pd-Au) nanoparticles catalyst for this direct synthesis, which shows outstanding methanol selectivity and productivity at low temperature. [2), 3)]

2. Experimental

2.1 Catalyst preparation

Commercial CNTs were pretreated by various acids to modify its surface properties. The supported Pd-Au catalysts were prepared by an incipient wetness impregnation method. The Pd and Au amount were 2.5 % wt respectively without explain.

2.2 Catalyst characterization

XRD, XPS, H_2-TPR, CO-PULSE, FE-SEM, HR-TEM measurements were performed to analyze the physical and chemical properties of our catalysts.

2.3 Catalytic tests

Catalyst tests for direct synthesis of methanol from methane were accomplished in a stainless-steel autoclave. The motor was vigorously stirred at 1200 rpm, the temperature was raised to 50 °C to start the reaction at the same time. After the 30 min reaction, the vessel was cooled by ice (< 10 °C), to avoid volatilization of the products.

3. Results and Discussion

The carbon materials such as carbon nanotubes (CNTs), activated carbon (AC), and reduced graphene oxide (rGO) are employed as the catalyst support, and the palladium-gold (Pd-Au) nanoparticles are used as active center. By using oxygen/hydrogen mixture as oxidant in the direct synthesis, it is found that Pd-Au/CNTs catalyst shows outstanding methanol selectivity and productivity.

Table 1 Catalytic performance with different carbon supported Pd-Au nanoparticles catalyst

Catalyst	Total product ($mmol/kg_{cat.}$)	MeOH Selectivity (%)	TON of MeOH [b]
Pd-Au/rGO	33.2	54.2	76.5
Pd-Au/AC	156.0	65.6	435.1
Pd-Au/CNTs	190.1	73.2	591.7
Pd-Au/CNTs-a	149.5	71.2	452.6
Pd-Au/CNTs-n	98.0	90.0	375.0

a: Reaction conditions: Time 30 min; Temp. 50 °C; Solvent H_2O 10 mL; Catalyst weight 30 mg; Feed gas $CH_4/O_2/H_2/Ar$; Total pressure 3.3 MPa.
b: mmoles of MeOH formed by per mole Pd metal.

Compared with the Pd-Au/CNTs, the Pd-Au/CNTs-n catalyst with a treatment of nitric acid on the CNTs support enhances the methanol selectivity obviously (Table 1), due to the changed surface oxygen species on the supports. In addition, our characterization results reveal that a weak interaction between Pd-Au nanoparticles and CNTs support is in favor of methanol productivity and selectivity.

This work offers a simple and effective strategy to directly synthesize methanol from methane partial oxidation under the mild conditions.

1) Hammond C, Forde M. M, Ab Rahim M. H, et al.; *Angew. Chemie - Int. Ed.*, **51**, 5129 (2012).
2) He Y, Luan C, et al.; *Catalysis Today*, **339**, 48 (2020).
3) He Y, Liang J, et al.; *Catalysis Today*, **352**, 104 (2020).

