Short Communication

Synthesis of Ru nanoparticles confined in magnesium oxide-modified mesoporous alumina and their enhanced catalytic performance during ammonia decomposition

Hua Tan [a,*], Kun Li [b], Salim Sioud [a], Dongkyu Cha [b], Maan H. Amad [a],
Mohamed Nejib Hedhili [b], Zeyad A. Al-Talla [a]

[a] Analytical Core Lab, 4700 King Abdullah University of Science and Technology, Thuwal, 23955-6900, Saudi Arabia
[b] Imaging and Characterization Lab, 4700 King Abdullah University of Science and Technology, Thuwal, 23955-6900, Saudi Arabia

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ABSTRACT

In this work, Ru nanoparticles confined in the channels of ordered mesoporous alumina (MA) and magnesium oxide-modified ordered MA are prepared for the first time via a two-solvent technique, combined with the amorphous citrate route. Structural characterizations reveal that uniform 2–3 nm Ru nanoparticles are highly dispersed in the blockage-free channels of mesoporous supports. The Ru nanoparticles confined in MA modified with 20% molar ratio magnesium oxide exhibited a high catalytic activity and stability during ammonia decomposition due to the optimized particle size, basic support, lack of chlorine, and confined space provided by the channels of the mesoporous supports.

1. Introduction

The proton exchange membrane fuel cell (PEMFC) is currently emerging as an efficient and environmentally friendly power source because it uses hydrogen as a fuel source [1]. Since the hydrogen produced from the steam reforming of hydrocarbons inevitably contains CO_x ($x = 1, 2$) impurities that poison cell electrodes [2], the catalytic decomposition of ammonia to produce CO_x free hydrogen has attracted considerable amount of attention [3]. In the past, extensive studies have been conducted on catalytic ammonia decomposition over various metals on different supports [4–14]. It is generally accepted that Ru supported on conductive graphitized carbons and carbon nanotubes have been the most efficient catalysts for this catalytic reaction [15]. However, the methanation reaction of the carbon supports usually occurs at temperatures as low as 423 °C, which has an adverse effect on the catalyst stability [14]. For the non-carbon supports, previous studies have revealed that a support of strong basicity is highly beneficial for catalytic ammonia decomposition [15].

Recently, many studies have been conducted exploring the use of ordered mesoporous materials as supports to confine metal/metal oxide catalysts within the mesopores for catalysis, because the mesopores provide a confined space that not only can prevent the sintering of nanoparticles, but can also enhance the catalytic performance. However, there are two limitations to this type of catalyst; first, most of the

work was focused on using silica-based or carbon-based materials as catalyst supports. It is well known that alumina is the more important catalyst support in catalysis because silica and carbon are chemically inert and lack acid/base active sites [16]; second, pore blockage is usually encountered after poor filling of catalytically active materials into the confined space. To address the second limitation, Cheng et al. [17] reported a novel amorphous citrate route to prepare highly-dispersed and thermally-stable NiO nanoparticles confined in the blockage-free nanochannels of SBA-15, which showed high activity on the methanation reaction. In this study, ordered mesoporous alumina (MA) modified with magnesium oxide was used as a basic catalyst support. Ru nanoparticles confined in the channels of this catalyst support are prepared by a two-solvent method combined with the amorphous citrate route [17,18]. The catalytic activity and stability are tested for ammonia decomposition.

2. Experimental

2.1. Catalyst preparation

Ordered MA and MgO-modified MA were prepared according to the procedure reported by Morrs et al. [19]. After solvent evaporation, the samples were calcined at 600 °C with airflow for 4 h in a tube furnace with a heating rate of 1 °C/min.

The Ru precursor was prepared by mixing Ru(acac)$_3$ with an aqueous solution of citric acid with a mole ratio of 3:1 of Ru:citric acid. The suspension was heated to 40 °C. Since Ru(acac)$_3$ is not soluble in water, hydrogen peroxide (30%) was added slowly to this suspension, a clear dark red solution was obtained [20]. The final ruthenium concentration of this

stock solution was kept at 0.1 mol/L to achieve a 2% Ru loading in the catalysts.

To synthesize the catalysts, 20 mL of cyclohexane was added to 1.0 g of MA or MgO-modified MA while stirring. A 2 mL precursor solution was added dropwise with stirring. After the supernatant was decanted, the solid was dried at 100 °C overnight, and then reduced by 10% H_2 in Ar at 400 °C for 4 h at a ramping rate of 2 °C/min. For the purpose of comparison, 2 mL of 0.1 mol/L $RuCl_3$ solution was also used as a Ru precursor to prepare the catalysts by the conventional two-solvent method.

The amorphous citrate route involves mixing solutions of a metal precursor and an organic polyfunctional acid, such as citric acid, which results in complexation of the metal by citric acid. After complete removal of the solvent by heat-treatment, a rigid Ru-citrate gel with molecule-level homogeneity is formed [17]. In this study, $Ru(acac)_3$ is used to replace $RuCl_3$ as the precursor to avoid the
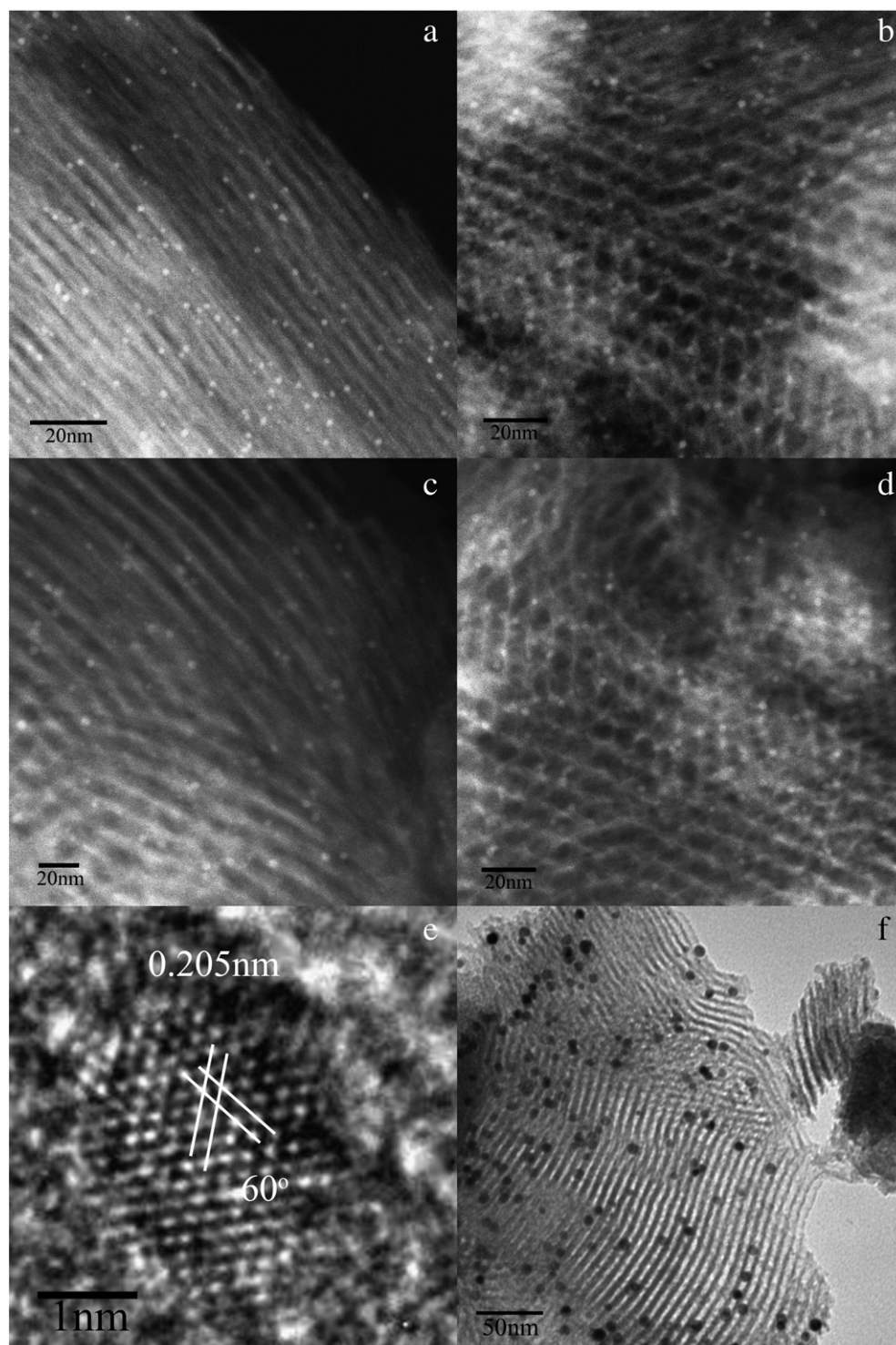

Fig. 1. HAADF STEM images of Ru/*m*-Al (a, b) and Ru/*m*-Al–20 Mg (c, d), (e) shows the HRTEM of a single Ru nanoparticle in Ru/*m*-Al–20 Mg; the scale bar is 1 nm; (f) conventional TEM image of $RuCl_3$/*m*-Al.