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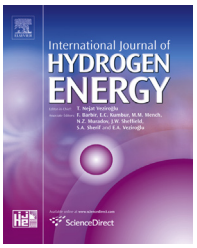

Highly selective doped Pt–MgO nano-sheets for renewable hydrogen production from APR of glycerol

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ABSTRACT

A series of M-doped Pt–MgO (M = Pd, Ir, Re, Ru, Rh and Cr) sheet-shaped nano-catalysts were synthesized by the controlled co-precipitation method. The effects of M-doping on both the physicochemical and the chemisorption characteristics of Pt–MgO catalysts were examined. The performance of the catalysts for the aqueous phase reforming (APR) of glycerol was also investigated. The APR activity of Pt–M–MgO catalysts depended on the type of the M dopant used. The APR activity varied in the following order: Rh > Pd > Cr > Ir > undoped ≈ Ru > Re, with the Rh-promoted catalyst having an activity of about one order of magnitude higher than the Re-promoted catalyst at 250 °C. It was found that M-promotion had a significant effect on the reducibility of the Pt–MgO catalysts thus affecting their APR activity.

Introduction

The ever-increasing world energy demand along with the decreasing fossil fuel reserves has resulted in concentrated efforts for developing alternative sustainable energy sources. Hydrogen generation from renewable biomass sources is one such alternative that has received much attention. The main industrial process for hydrogen production is the high temperature reforming of hydrocarbons originated from fossil fuels. Alternatively, hydrogen could be produced from the more sustainable sources such as biomass using catalytic processes that employ milder temperature and pressure conditions. In aqueous phase reforming (APR) that was pioneered by Dumesic and co-workers [1–5], biomass derived oxygenates including ethanol, ethylene glycol, glycerol, sorbitol, and glucose are converted to hydrogen in a single step catalytic reaction.

Among different potential feeds for APR, glycerol is particularly attractive since it is the most abundant by-product of the transesterification process for biodiesel production [6]. Glycerol also has a relatively simple structure making it a suitable model molecule for investigations on biorefinery schemes [7]. Hydrogen generation from APR of glycerol is achieved by the reforming reaction (1) followed by the water-gas shift (WGS) reaction (2):

$$C_3H_8O_3 \rightarrow 4H_2 + 3CO \quad (1)$$

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$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (2)$$

The suitable catalyst for the APR process should, therefore, have a high activity for both C–C bond cleavage and WGS reactions. Platinum is therefore considered as the best active metal for APR reaction especially when supported on porous basic materials that have a high oxygen storage capacity. Even the best known catalysts for APR reaction, however, have low selectivities for hydrogen and suffer from low stabilities as a result of sintering, change of the support's phase, and carbon deposition. Further studies are therefore required to develop the promising catalysts. In this regard, intensive studies on APR of polyols have been performed employing Pt-based multi-metallic catalysts including Pt–Re [8–10], Pt–Co [11,12], Pt–Ni [12–18], and Pt–Ce–Zr [19]. Alloying of Pt with Re was shown to improve C–C bond cleavage and glycerol conversion albeit with lower H_2 selectivity [8–10]. Pt–Co bimetallic catalyst [11], however, exhibited a high H_2 production rate of 4.6 mmol g_{cat}^{-1} min^{-1} when ethylene glycol was used as the feed for the APR process. Furthermore, Pt–Ni bimetallic catalysts also demonstrated higher H_2 and lower alkane formation from APR of glycerol compared with the monometallic Pt catalyst [13]. In our previous work [19], we showed that $Pt_{0.05}Ce_xZr_{0.95-x}O_2$ ternary solid solution catalysts are highly active and selective under APR reaction conditions.

Support properties are also crucial factors affecting both catalytic activity and selectivity. Pt-catalyzed APR of glycerol on different oxide supports such as Al_2O_3, SiO_2, ZrO_2, MgO, CeO_2, SAPO-11, HUSY, and carbonaceous material has been reported by various investigators [20–28]. MgO and ZrO_2 stood out among other supports since they exhibited high hydrogen production rates as well as low hydrocarbon formation rates due to their strong electron donating behaviour which is an important characteristic of basic supports. Basic supports have shown both a high activity and a high selectivity for hydrogen production although their poor stability under hydrothermal conditions restricts their applications as conventional supports [29].

Further improvement in both activity and selectivity of monometallic catalysts can be achieved by the addition of a second metal as a promoter. Alumina-supported Pt catalysts

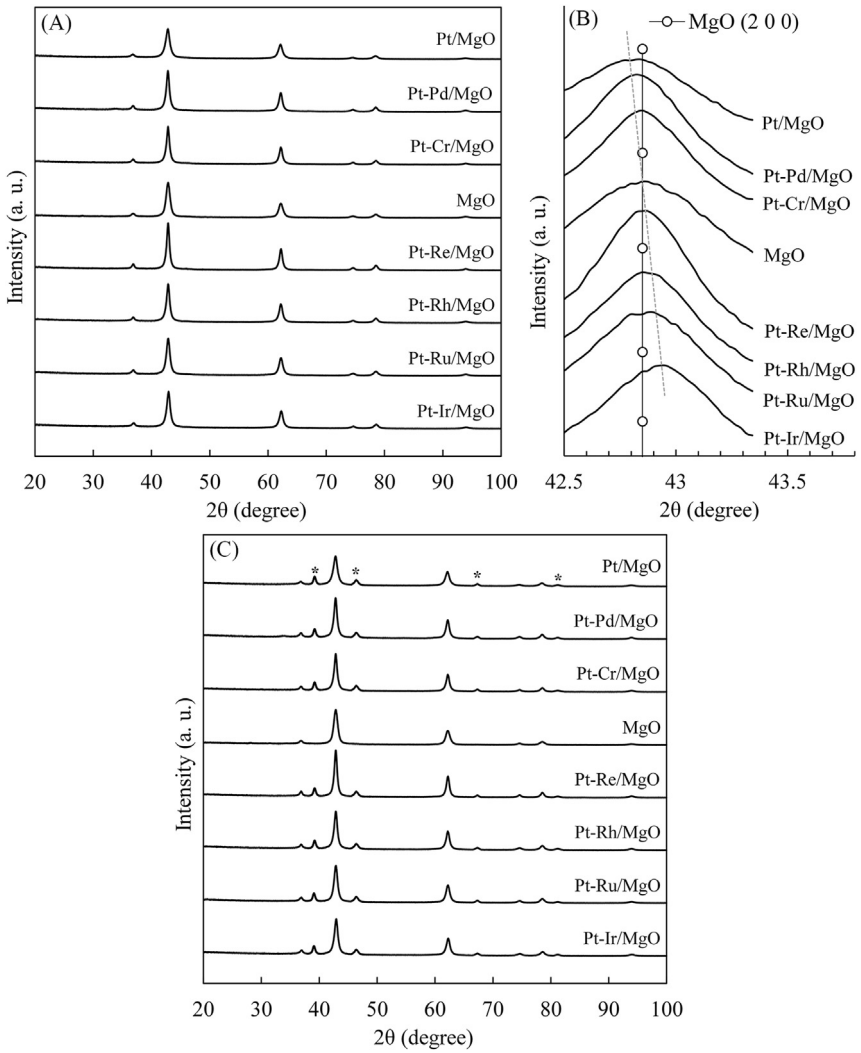

Fig. 1 – (A) XRD patterns and (B) comparison of XRDs in 42.5–43.5° region for calcined catalysts, and (C) XRD patterns of reduced catalysts.

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