Enhanced activity of Ru/TiO$_2$ catalyst using bisupport, bentonite-TiO$_2$ for hydrogenolysis of glycerol in aqueous media

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**Abstract**

A combination of bentonite-TiO$_2$ was used as support to enhance the activity of Ru/TiO$_2$ catalyst in hydrogenolysis of aqueous glycerol to 1,2-propanediol. A series of bentonite, TiO$_2$, SiO$_2$, and Al$_2$O$_3$ supported Ru catalysts were fabricated and characterized by XRD, XPS, BET, FESEM-EDX and TEM to establish some physicochemical properties of the catalysts. The activity of the catalysts was tested in glycerol hydrogenolysis reaction and were found to be in the following increasing order: Ru/SiO$_2$ < Ru/TiO$_2$ < Ru/Al$_2$O$_3$ < Ru/bentonite. In particular, Ru/bentonite catalyst recorded the highest conversion (62.8%) of glycerol (20 wt%) with 80.1% selectivity to 1,2-propanediol at 150 °C, 20-30 bar H$_2$ with a reaction duration of 7 h. The Ru/TiO$_2$ catalyst exhibited the highest selectivity (83.7%) for hydrogenolysis of glycerol to 1,2-propanediol and with 38.8% conversion only. The activity of Ru/TiO$_2$ catalyst was enhanced by adding bentonite to the titanias support at 1:2 ratio resulting in an 80% increasing the activity from 38.8% to 69.8% under the same optimum condition for Ru/TiO$_2$ while maintaining an 80% selectivity to 1,2-propanediol. TPD-NH$_3$ analysis found that mixed support could increase catalyst acidity. CO pulse chemisorption analysis revealed that Ru particles was well dispersed with the smallest average size particles (1.5 nm) which could contribute to high activity of Ru/TiO$_2$ catalyst for hydrogenolysis of glycerol.

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1. Introduction

The transesterification of triglycerides with methanol in the presence of basic or acidic catalysts produced biodiesel consisting of fatty acid methyl esters. Every 9 kg of biodiesel production gave out about 1 kg of crude glycerol as by-product [1]. Glycerol is one of the top 12 chemical building blocks that can be converted to more marketable products. The recent rapid development of biodiesel processes had caused some concern over the over supply of glycerol in the market. The glycerol market would likely be saturated because of limited utilisation of glycerol at present time [2]. Due to the concern on the over supply of the glycerol a suitable and viable conversion of glycerol to a more marketable product such as catalytic hydrogenolysis reaction had received considerable attention [3].

The hydrogenolysis of glycerol produced 1,2-propanediol (1,2-PDO) and ethylene glycol (EG) as major products that had a 4% annual market growth [4]. Typical uses of 1,2-propanediol were for production of unsaturated polyester resins, functional fluids, pharmaceutical products, cosmetic products and paints [5]. Selective hydrogenolysis of glycerol to 1,2-propanediol required a cleavage of the C–O bonds by H$_2$ insertion without attacking C–C bonds in the glycerol molecule. Several groups had reported hydrogenolysis of glycerol on different catalyst systems, including supported transition metal catalyst such as Rh, Ni, Ru, Pt, Pt–Ru and Cu catalysts [2,6–13]. Among the catalysts studied, supported Ru catalyst was the most active for the hydrogenolysis of glycerol [14].

Previous report had claimed that in acidic conditions glycerol was dehydrated to acetal as an intermediate product prior to hydrogenolysis [15]. Thus, acid catalyst could play an important role in the glycerol dehydration stage as well as working under milder reaction conditions that might increase the conversion and selectivity. The use of two support materials could provide an

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