



Direct catalytic conversion of glycerol to liquid-fuel classes over Ir–Re supported on W-doped mesostructured silica



Fengbo Li^{a,*}, Fei Xue^{a,b}, Bingfeng Chen^{a,b}, Zhijun Huang^{a,b}, Yin Yuan^{a,b}, Guoqing Yuan^{a,*}

^a Beijing National Laboratory of Molecular Science, Laboratory of New Materials, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, PR China

^b Graduate University of Chinese Academy of Sciences, Beijing 100049, PR China

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ABSTRACT

Glycerol was converted to liquid fuels through a one-pot process catalyzed by mesostructured Ir–Re–W/SiO₂. The reaction was performed over 0.4 g of catalyst suspended in an aqueous solution of glycerol (4.72 mmol/ml) at 553 K under a hydrogen pressure of 6.0 MPa for 50 h. A hydrocarbon-enriched organic phase was self-separated from the aqueous solution after the reaction. The total yield of oil products was greater than 40%, and the selectivity toward hydrocarbons was approximately 90%. The conversion proceeds through a complicated mechanism that involves a C–C coupling reaction and hydrodeoxygenation. Doped tungsten oxide species in a silica matrix are active acidic sites for acid-catalyzed dehydration. Supported iridium species are catalytic active sites for hydrodeoxygenation and C–C coupling reactions. The evolution of their chemical states during the catalytic process was detected by X-ray photoelectron spectroscopy. Rhenium species are important co-catalysts for iridium species. These active catalytic species work together to achieve the direct conversion of glycerol in aqueous solution to liquid fuels under a hydrogen atmosphere.

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1. Introduction

Diminishing fossil fuel reserves and environmental concerns about CO₂ release have stimulated research into sustainable fuel production from biomass-based resources. Many breakthroughs were pioneered by Dumesic's group [1–4]. Biomass-based carbon sources consist mainly of sugars and polyols. Deoxygenation and C–C coupling are two key reactions in the conversion of biomass to liquid fuel. The direct conversion of glycerol to liquid fuels may involve complicated C–C coupling and hydrodeoxygenation (as shown in Scheme S1), which provides a new route for the production of liquid fuels from renewable sources.

The increased production of biodiesel has resulted in a large surplus of glycerol. Glycerol is the main byproduct (10 wt.%) in the manufacture of biodiesel fuel through the transesterification of seed oils with methanol [5]. Glycerol can be selectively converted into many derivatives, which can be used as fuels, chemicals, pharmaceuticals, detergents, etc. [6–9]. Numerous methods for the catalytic conversion of glycerol have been reported, including selective oxidation [10,11], hydrogenolysis to propylene glycol [12,13], dehydration to acrolein [14,15], reformation to syngas [16,17],

fermentation to 1,3-propanediol [18,19], the synthesis of glycerol carbonate [20], and the formation of fuel oxygenate additives [21,22].

In this work, glycerol was converted to liquid fuels through a one-pot process catalyzed by mesostructured Ir–Re–W/SiO₂. The reactant mixtures were solid–liquid slurries. The fine particles of the catalyst were well dispersed in the aqueous solution of glycerol. After the conversion in an autoclave under hydrogen, the mixture of glycerol, the fine catalyst particles, and water was transformed into a three-phase mixture. The three phases—the oil layer, the aqueous solution, and the used catalyst—were clearly discriminated. The carbon of the oil layer was derived from glycerol in the incipient aqueous solution.

2. Experimental

2.1. Materials and chemicals

Tetrabutyl ammonium bromide (TBABr), H₃PW₁₂O₄₀, dodecyl amine (DDA), tetraethylorthosilicate (TEOS), [(NH₄)₆H₂W₁₂O₄₀], glycerol, acetonitrile, DMSO, and sulfuric acid were purchased from Sinopharm Chemical Reagent. H₂IrCl₅ and NH₄ReO₄ were purchased from Strem. Commercial silica aerosol (500 m²/g) and H-ZSM-5 (Si/Al: 30) were purchased from Alfa-Aesar. All the reagents were used as received.

* Corresponding authors. Tel.: +86 10 62634920; fax: +86 10 62559373.

E-mail addresses: lifb@iccas.ac.cn (F. Li), yuangq@iccas.ac.cn (G. Yuan).