



Short communication

## Crude bio-glycerol as a hydrogen source for the selective hydrogenation of aromatic nitro compounds over Ru/MgLaO catalyst



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### ABSTRACT

Crude glycerol has been utilized as a hydrogen source for the selective hydrogenation of aromatic nitro compounds over MgLaO, MgO and La<sub>2</sub>O<sub>3</sub> supported Ru catalysts. Ru dispersion and basicity of the catalysts had strongly influenced the turnover rates of aromatic amines. The catalyst was recovered and reused for 5 recycles without significant loss of activity. The physicochemical properties of the catalysts were rationalized by temperature programmed desorption (TPD) of CO<sub>2</sub> and CO pulse chemisorption in conjunction with rates of aromatic amines.

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### 1. Introduction

Selective hydrogenation of aromatic nitro compounds to the corresponding aromatic amines as a common functional group transformation in synthetic industrial chemistry is a topic of interest [1–3]. Although various methods have been explored, environmental friendly procedures are required in order to avoid the use of expensive and hazardous stoichiometric reducing agents [4]. Transfer hydrogenation is an attractive method than the conventional route as it can be done by utilization of various hydrogen sources such as hydrocarbons, alcohols, hydrazine, organic acids and their salts [5]. One of the better options to be considered is to explore biomass derived by-products as hydrogen source for the transfer hydrogenation reactions.

Recent advancements in the development of bio-diesel production by transesterification of edible or non-edible oils inevitably generate glycerol as a by-product. On the one hand production of alternate fuels is a prime objective; on the other hand utilization or safe disposal of the by-products obtained in the process is equally important. Apart from the bio-diesel industry bio-glycerol is also formed from the large scale processes based on the conversion of cellulose and lignocelluloses [6–8].

It has been reported that Ru, Rh and Ir complexes are found to be better than the other noble metal complexes for transfer hydrogen

reactions [9–10]. Selective hydrogenation of *ortho*-chloronitrobenzene over noble metal supported on Al<sub>2</sub>O<sub>3</sub> and MgF<sub>2</sub> catalysts was reported by Pietrowski at 2 MPa using ethanol as hydrogen source [11]. Hydrogen transfer reactions are also reported for carbonyl compounds, alkenes and nitro benzene using pure glycerol in the presence of a base [12]. The catalysts with basic nature are required for the in-situ generation of hydrogen by dehydrogenation of alcohols rather than dehydration which leads to potential coking (due to alkene formation by dehydration of alcohols) consequently rapid deactivation of catalyst. Bio-glycerol as a source of hydrogen for transfer hydrogenation reactions makes the process attractive due to ease of handling, non-toxic nature and the use of such renewable source is beneficial from economical and environmental perspectives. The present study explores Ru based catalysts and the highlights of this study are the following: (1) the transfer hydrogenation of *ortho*-chloronitrobenzene carried out in the absence of a base; as the support materials (MgLaO, MgO, La<sub>2</sub>O<sub>3</sub>) examined in this study, itself behaves as a base. (2) The catalyst is quite stable and can be recycled for 5 times. (3) The Ru/MgLaO is highly selective towards chloroaniline with no by-products formed due to hydrogenolysis reaction. (4) Using a simulated bio-glycerol mixture (expected from a bio-diesel industry) that contained impurities such as KOH, CH<sub>3</sub>OH, the Ru/MgLaO catalyst exhibited excellent yields. (5) Explored the influence of basicity of the supports such as MgO and La<sub>2</sub>O<sub>3</sub> for Ru in the transfer hydrogenation, while these systems can avoid the use of alkaline hydroxides. (6) Finally the carbon mass balance is remarkably good with minute amount of carbon deposition on the used catalysts.

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## 2. Experimental

### 2.1. Preparation of catalysts

All chemicals were purchased from Aldrich AR grade and were used in as-received form. The magnesium–lanthanum mixed oxide was prepared by a co-precipitation method as described earlier [13]. All the details pertaining to MgLaO, MgO, La<sub>2</sub>O<sub>3</sub> and Ru supported on these support materials are explained in ESI.

### 2.2. Procedure for transfer hydrogenation of *ortho*-chloronitrobenzene

Transfer hydrogenation was carried out in a 50 mL mechanically stirred Parr autoclave equipped with a PID controller 4848. In a typical experiment about 3 mmol (0.470 g) of *ortho*-chloronitrobenzene, 10 wt.% aqueous glycerol (20 ml) was used. In some case a crude bioglycerol mixture (that contained impurities such as KOH and CH<sub>3</sub>OH) was used under similar experimental conditions. The operating reaction conditions were maintained as follows; stirring speed 1000 rpm, reaction temperature (100–170 °C) and inert gas pressure (N<sub>2</sub> gas) 1 MPa. After 5 h, the sample was collected and analyzed by GC–MS (Varian GC-2010 FID) equipped with ZB5 wax capillary column.

## 3. Results and discussion

The XRD pattern (Fig. S1a) of pure MgO showed diffraction lines (ICDD # 4-829,  $2\theta = 42.8^\circ, 62.2^\circ, 78.3^\circ$  and their corresponding 'd' values are 0.211, 0.149 and 0.122 nm) are due to MgO phase [14]. The lanthanum oxide (Fig. S1b) showed characteristic diffraction lines of La<sub>2</sub>O<sub>3</sub> (ICDD # 24-0554; at  $2\theta = 30.6^\circ, 44.2^\circ, 57.2^\circ, 52.8^\circ$ ) [15]. In the case of MgLaO the diffraction pattern (Fig. S1c) showed both lanthanum oxide carbonates (La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>) and magnesium oxide (MgO) [16]. Diffraction lines appeared at  $2\theta = 29.5^\circ, 22.8^\circ, 13.1^\circ, 30.8^\circ, 31.3^\circ$  [ICDD # 23-0435] and their respective 'd' values of 0.302, 0.389, 0.675, 0.289, 0.285 nm are attributed to lanthanum oxide carbonate phase. In comparison with individual bulk oxides (MgO, La<sub>2</sub>O<sub>3</sub>) the diffraction pattern of Mg–LaO is more intense with well resolved peaks. Although the composition of Mg–La is 3:1 (mole ratio) the XRD peaks of La-oxides are more intense than MgO. This is probably due to biphasic solid consisting of a layer of lanthanum oxide deposited on magnesia or it may also be possibly due to some portion of MgO may be in amorphous nature. XRD patterns of 5 wt.% Ru supported on MgO, MgLaO and La<sub>2</sub>O<sub>3</sub> of reduced samples are shown in Fig. S2. The reduced ruthenium diffraction lines [ICDD # 06-0663] appeared at  $2\theta = 44.0^\circ, 38.4^\circ$  and  $42.1^\circ$ . The XPS analysis of fresh 5 wt.% Ru/MgLaO sample (Fig. S3) showed signal at a binding energy (BE) of 283.6 eV due to Ru 3d<sub>3/2</sub> (RuO<sub>2</sub>) species which is in agreement with reported literature [17]. The reduced 5 wt.% Ru/MgLaO sample exhibited (Fig. 1) characteristic peak at a BE of 280 eV (Ru 3d<sub>5/2</sub>) that is attributed to Ru in metallic form [18].

Fig. 2 represents TPR patterns of 5 wt.% Ru/MgO, 5 wt.% Ru/La<sub>2</sub>O<sub>3</sub> and 5 wt.% Ru/MgLaO samples and the H<sub>2</sub> uptakes are reported in Table 1. It shows that all the samples have undergone a three stage reduction. The low temperature reduction peak is due to dispersed RuO<sub>2</sub> and the peak around 460–500 °C is attributed RuOCl<sub>2</sub> [16]. The low temperature peak at 300 °C on Ru/Mg–LaO sample can be assigned to dispersed ruthenium oxide species. TEM images of reduced samples are shown in Fig. S4. Ru particles are uniformly distributed on the MgLaO support (Fig. S4c). The average Ru particle size measured from TEM images are found to be 26.9, 28.5, 23.5 nm over Ru/MgO, Ru/La<sub>2</sub>O<sub>3</sub> and Ru/MgLaO respectively.

The CO<sub>2</sub> TPD profiles of supported Ru samples reported in Fig. 3 and their corresponding CO<sub>2</sub> uptakes are reported in Table 1. Substantial changes can be seen in the distribution of basic sites upon impregnation of RuCl<sub>3</sub> on the support materials. The support materials demonstrated slightly higher basicity than their Ru loaded samples (SI). 5 wt.% Ru/MgO showed main desorption at 335 °C along with a small peak around 425 °C [19]. The 5 wt.% Ru/La<sub>2</sub>O<sub>3</sub> sample indicated

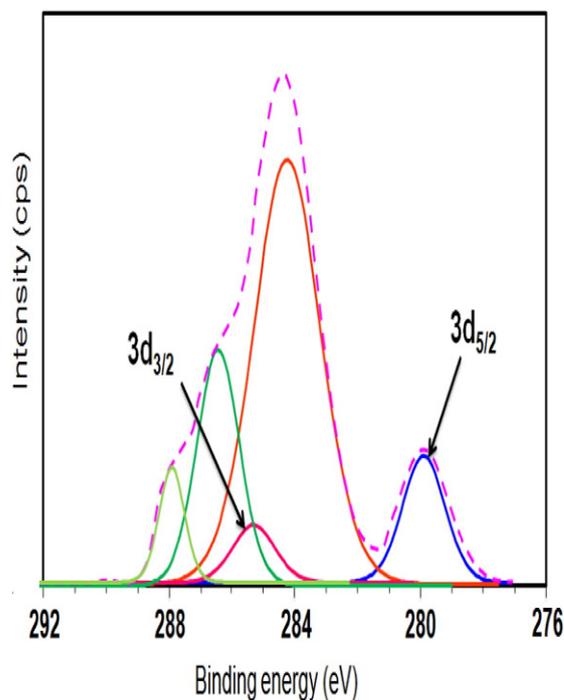


Fig. 1. X-ray photo electron spectra of reduced Ru/MgLaO catalyst.

weak ( $T_{\max} \sim 275^\circ\text{C}$ ) and very strong peak around 700 °C due to strong basic sites [20]. An intense and broad signal is found over 5 wt.% Ru/MgLaO around  $\sim 460^\circ\text{C}$  with a shoulder peak at 600 °C. These results illustrated that there are substantial changes that occurred upon doping of Ru. These changes are likely due to the presence of traces of chloride on the catalyst surface. The basic sites are redistributed upon RuCl<sub>3</sub> impregnation followed by calcination in air.

Raman spectra of MgO, La<sub>2</sub>O<sub>3</sub> and MgLaO samples are reported in Fig. 4. Bulk MgO indicated bands at 1090, 1260, 1500 and 1758 cm<sup>-1</sup> which are ascribed to Mg–O vibrational modes [21]. The bulk La<sub>2</sub>O<sub>3</sub>

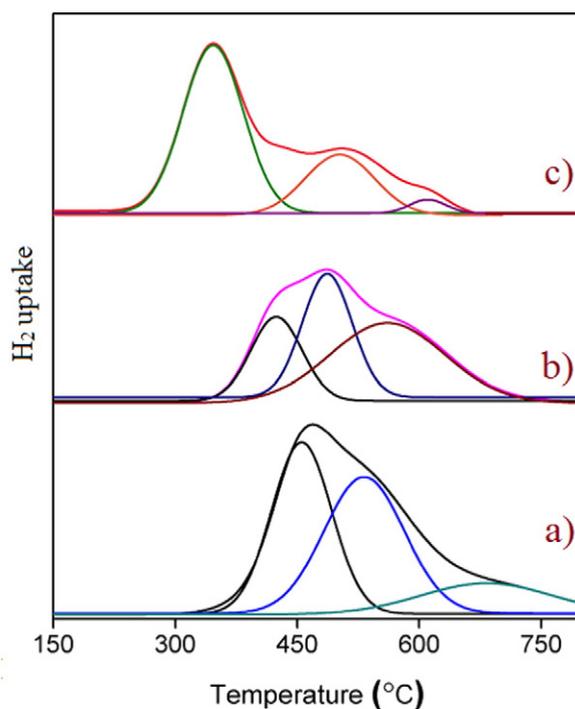


Fig. 2. TPR profiles of a) 5 wt.% Ru/MgO, b) 5 wt.% Ru/La<sub>2</sub>O<sub>3</sub>, and c) 5 wt.% Ru/MgLaO catalysts.

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