View Article Online View Journal

# **NJC** Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: A. Pandurangan and S. Pichaikaran, *New J. Chem.*, 2017, DOI: 10.1039/C7NJ00367F.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



# rsc.li/njc

View Article Online DOI: 10.1039/C7NJ00367F

# Rh/Ni wet-impregnated Ia3d mesostructured aluminosilicate and r-GO catalyst for hydrodeoxygenation of phenoxy benzene

## Pichaikaran Sudhakar, Arumugam Pandurangan\*

Department of Chemistry, Anna University, Chennai 600 025, India

\*Corresponding author at: Tel.: +91 44 22358653; fax: +91 44 22200660.

E-mail address: pandurangan\_a@yahoo.com (A. Pandurangan)

# **Graphical abstract:**



#### Abstract

Rh/Ni bimetal supported bifunctional 3D porous aluminosilicate and Rh/Ni supported reduced graphene oxide (r-GO) catalyst was synthesised and evaluated their structural behaviour by XRD, BET-Surface area, FT-IR, NH<sub>3</sub>-TPD, H<sub>2</sub>-TPR, ICP-OES, HRTEM-EDAX and XPS analysis. The catalytic activity of Rh/Ni/Al-KIT-6 and Rh/Ni-rGO catalyst was investigated by vapour phase hydrodeoxygenation of diphenyl ether and guaiacol. The Rh/Ni/Al-KIT-6 catalyst exhibited best catalytic performance on vapour phase HDO of diphenyl ether at 420 °C with WHSV 3.6 h<sup>-1</sup>. In addition, another lignin derived guaiacol was also probed and the desired product of benzene from guaiacol was not achieved on Rh/Ni/Al-KIT-6 and Rh/Ni/r-GO catalyst. Besides, Rh/Ni/Al-KIT-6 catalyst showed excellent stability due to the acidic Al-KIT-6 support, which stabilizes the Rh/Ni particles on the surface. However, the higher dispersion of Rh/Ni specious maximum observed on Rh/Ni/Al-KIT-6 catalyst as evidenced by HR-TEM image and it mainly due to their large surface area of Al-KIT-6 support, while Rh/Ni/r-GO catalyst shows larger metal aggregates due to weak Rh/Ni interaction with reduced graphene oxide (r-GO) support and furthers a narrow surface area in this catalyst could restricted the higher distribution of Rh/Ni particles. The superior catalytic activity in the C-O bond cleavage of diphenyl ether and guaiacol has been observed in Rh/Ni/Al-KIT-6 catalyst. The superior catalytic activity of this catalyst mainly due to the highly dispersed small Rh/Ni bimetallic species and further Rh/Ni interaction with mesoporous cubic acidic support via hydrogen spill over effect, which was favour the earlier NiO reduction, and it was confirmed by H<sub>2</sub>-TPR and HR-TEM. The Rh/Ni/Al-KIT-6 catalyst displayed excellent catalytic properties with 60 % benzene selectivity. Further, the bifunctional behaviour in this Rh/Ni/Al-KIT-6 catalyst with unique cubic morphology support, in addition to uniform dispersion of Rh/Ni species could enhance the diphenyl ether conversion and benzene selectivity.

Keywords: Diphenyl ether, guaiacol, benzene, Al-KIT-6, r-GO, Rh/Ni bimetal

#### Introduction

The modern civilization was highly suffered against decay of petroleum reservoir due to their limited resources and another horrible crisis is CO<sub>2</sub> emission. Since, the potential usage of alternative sources such as lignocellulosic biomass is find an great opening for replacing fossil fuel and regulating CO<sub>2</sub> emission. Moreover, the lignin feedstock from lignocellulosic biomass containing aryl ethers and phenolic compounds are significant for producing gasoline range hydrocarbon through C-O bond cleavage<sup>1</sup>. Lignin is a three dimensional network bio-polymer containing C<sub>9</sub>-propyl unit attached with C-C, and C-O chains and it treated with mild condition to produce phenolic monomers and dimers such as phenol, alkylguaiacols, alkyl-syringols and dimers like β-O-4, 4-O-5 ether linkage and 5-5, β-1 C-C linkage<sup>2</sup>. The 4-O-5 linkage is the strongest linkage in the lignin molecule and diphenyl ether is considered as model 4-O-5 linkage compound and further the diphenyl ether C-O bond cleavage need severe conditions<sup>3</sup>. However, the current utilization of liquid transportation fuel from lignin monomer and dimer is critical due to their higher oxygen ratio and this circumstances will decreases the fuel quality<sup>1,4</sup>. Furthermore, for understanding the conversion process of real bio-oil into liquid fuel or chemical is still difficult due to the presence of complex mixtures with higher oxygen functionalities in the bio-oil. Hence, more attention has been paid on study of individual lignin model compound for understanding reaction chemistry before upgrading of real lignin bio-oil<sup>5</sup>. In these aspects, the less reactive phenolic compound like guaiacol and diphenyl ether have significantly attracted for studying HDO model reaction<sup>2,6</sup>. Hence, hydrodeoxygenation is an efficient process for oxygen removal and further upgrading of better quality of fuel from their lignin monomer. The high degree of hydrodeoxygenation catalyst with minimum hydrogen consumption is still a major challenge in the area of catalysis. As reported earlier, the high selectivity and conversion of lignin-derived phenolic monomer and dimer was catalysed by transition metal<sup>7,8</sup>, transition metal sulphide<sup>9</sup>, and transition metal phosphides catalysts<sup>1,10,11</sup>. However, these catalysts were severely affected by deactivation and drastic experimental conditions; additionally, the sulphur contamination in sulphided catalyst also created a serious disadvantage. In these aspects, the advantages of mesoporous metal oxide supported bimetallic catalysts has significantly attracted because of its high structure regularity, controlling the metal oxide particle size, limiting the growth of metal cluster size and offered better dispersion over the external surface<sup>12-14</sup>.

Also, the type of support has significantly enhanced the rate of chemical reaction in the mono and bimetal supported catalysts. The various catalytic supports such as clay, zeolite, mixed oxides, carbon materials and mesoporous materials have been developed and tested by others with substantial progress<sup>15,16</sup>. Although the use of these support was paid less attention due to their limited surface area for available active sites, limited pore size and restricted hydrothermal stability. Consequently, the dilemma was conquer by using the invention of new class of mesoporous Ia3d cubic silica (KIT-6) support possessing higher surface area, large meso and micropores, thicker pore walls, higher hydrothermal stability, tunable 3D interconnected mesopores, which allows better dispersion of active species with faster diffusion of reactants and products, reproducibility, etc., <sup>12,15</sup>

In this contribution with the aim of increasing the HDO activity, we choosing Rh/Ni supported mesoporous aluminosilicate bimetallic catalysts. The catalyst was synthesised by wet-impregnation method and further their catalytic activity was investigated over vapour phase C-O bond cleavage of diphenyl ether and guaiacol under different experimental condition. Moreover, the activity pattern of mesoporous catalyst was compared with reduced graphene oxide supported Rh/Ni bimetal catalyst under the specific reaction condition. Further, the reaction pathway of diphenyl ether and guaiacol were investigated with respect to Rh/Ni bimetal catalyst. However, the catalytic reaction so far carried out using diphenyl ether and bimetallic system by the authors in the literature, using higher hydrogen pressure<sup>17-25</sup>. Therefore, in the present work was carried out under atmospheric hydrogen pressure and it showed highest diphenyl ether conversion. Further, Rh/Ni/Al-KIT-6 has been characterized by different physicochemical techniques for found the relationship between the catalytic properties and their HDO activity of diphenyl ether. Eventually, the deactivation and regeneration behaviour of bimetallic catalyst was studied briefly and further evaluated their regeneration activity with respect to diphenyl ether conversion. Therefore, their study could afford significant information about Rh/Ni bimetal system for improving the upgrading process of lignin bio oil via diphenyl ether model substrate, under the present atmospheric pressure condition.

#### Experimental

#### Materials

Pluronic P123 [Poly (ethylene glycol)-block-poly (propylene glycol)-block-poly EO<sub>20</sub>; (ethylene glycol), (EO<sub>20</sub> PO<sub>70</sub> Aldrich: M.W.5800, >98%pure)], tetraethylorthosilicate (TEOS; Aldrich, >98% pure), n-Butanol (SRL Biochem, 99.5 % pure), hydrochloric acid (HCL; SRL Biochem, 35 %), deionised water (Evergreen India Ltd), aluminiumisopropoxide (Alfa-Aesar) were used for the synthesis of Al-KIT-6 support. Graphite powder (99 % pure, Sigma-Aldrich), concentrated sulphuric acid (H<sub>2</sub>SO<sub>4</sub>; SRL, 98 %), potassium permanganate (KMnO<sub>4</sub>; SRL, 99.5 %), sodium nitrate (NaNO<sub>3</sub>; SRL, 99.5 %), hydrazine hydrate (99 % pure, Fischer Scientific) were used for synthesis of graphene oxide (GO) and reduced graphene oxide (r-GO). Rhodium (III) chloride (Alfa-Aesar), nickel (II) nitrate hexahydrate (Aldrich) was used for preparation of metal supported catalyst. Diphenyl ether (SRL Biochem, 98 % pure) and Guaiacol (SRL Biochem, 99 % pure) were used in catalytic reaction. The entire chemicals used in the synthesis and reactions are AR grade and used without any further purification.

#### **Preparation of Catalysts**

Al-KIT-6 support was synthesised using triblockcopolymer surfactant as a structure directing agent and used with mild acidic conditions. A classic procedure for the synthesis of Al-KIT-6 (25) support with Si/Al ratio 25 was follows by reported in the literature<sup>26</sup>. 4 g of Pluronic P123 was added to 144 mL of deionised water in a polypropylene bottle with 7.9 g of 35 % HCL and stirred for 4 h under atmospheric condition. Followed by stirring for 4 h, an apparent homogeneous solution was formed then 4 g of n-butanol was added and further stirring was continued for 1 h. Then, 8.4 g of TEOS added slowly and followed by calculated weight of aluminiumisopropoxide was added. The obtained mixture was stirred for 24 h at 35 °C and hence the mixture was hydrothermally treated under closed condition at 100 °C for 24 h. After hydrothermal treatment, the obtained solid material was filtered hot without washing and further dried the material at 100 °C for 12 h. Finally the material was crushed and grained by mortar and the obtained fine powder was calcined at 540 °C in air atmosphere for 24 h to expel the surfactant. The recovered final material was denoted as Al-KIT-6 (25) support.

Graphene oxide (GO) was synthesised using graphite powder by the modified Hummer's method<sup>27-31</sup>. The complete synthesis procedures are as follows: 3 g graphite

powder and 1.5 g sodium nitrate were mixed properly in a 1000 mL round bottom flask then 69 mL of con.sulphuric acid was added in ice-bath with continuous stirring. After 20 min, 9 g of KMnO<sub>4</sub> was added slowly to the above mixture under the temperature below 20 °C to avoided explosion. The mixture was stirred at 35 °C in an oil-bath for 2 h after it was diluted by adding 138 mL of deionised water and further stirring continued for 12 h. Then, the reaction mixture was heated to 80 °C for 1 h and reaction temperature was maintained to ambient condition. Further, the oxidation of graphite with KMnO<sub>4</sub> was completed by the treatment of 30 % H<sub>2</sub>O<sub>2</sub> solution (10 mL) and then diluted with 400 mL of deionised water. The pH of the suspension was around 1 and kept for 12 h to separate the water and GO. Furthermore, the suspension was repeatedly washed with 10 % aq.HCl and deionised water until neutral pH was attained. Finally, the graphene oxide was filtered and dried overnight at 50 °C.

The obtained graphene oxide (GO) was reduced by chemical method<sup>32,33</sup>. Typically, 1 g of graphene oxide (GO) added with 10 mL of deionised water and ultrasonicated for 1 h, then 10 mL of hydrazine hydrate was added. Further, the mixture was heated at 100 °C in a refluxed condenser for 2 h. After reflux, the reduced graphene oxide was precipitated, filtered and washed thoroughly with deionised water and finally dried at 50 °C. The obtained black coloured solid material was r-GO and used as support for preparing bimetal catalyst.

Rhodium and nickel supported mesoporous Al-KIT-6 and reduced graphene oxide (r-GO) bimetallic catalysts were prepared by wet-impregnation method<sup>34–36</sup>. About 1g of each support separately transferred into a 50 mL round bottom flask and added 30 mL of deionised water and stirred for 15 minutes. The precursor salt of rhodium (1.0 Wt %) and nickel (7.0 Wt %) were added and stirring was continued for 6 h. After stirring the water from the mixture was evaporated at 100 °C for 12 h. Finally the material was crushed and grained by mortar. The obtained fine powder was calcined at 450 °C for 6 h under atmospheric air. The obtained solid material was individually represented as 1.0 % Rh/7.0 % Ni/Al-KIT-6 & 1.0 % Rh/7.0 % Ni-rGO .

#### **Materials characterization**

Published on 12 June 2017. Downloaded by University of California - San Diego on 13/06/2017 03:17:46.

The crystallographic features of bimetallic catalysts were investigated by powder XRD analysis, which was obtained from Bruker D8 Advanced X-ray diffractometer with a CuKα radiation source. The specific surface area, pore volume and pore size distribution of bimetallic catalysts were performed by nitrogen adsorption techniques at liquid nitrogen temperature (-195.657 °C). N<sub>2</sub> physisorption analysis were performed on micromeritics asap

#### New Journal of Chemistry

2020 porosimeter, Prior to nitrogen physisorption the sample was outgassed at 200 °C for 12 h. The specific surface area was measured by BET method and the pore volume, pore size distribution were measured by BJH method. Attenuated total reflection-infrared (ATR-IR) Perkin Elmer-Spectrum-two spectrophotometer was used for finger region of support and catalysts. The shape and metal oxide crystallite size of bimetallic catalysts were obtained from HR-TEM images using JEOL 3010 instrument with a UHR polepiece which gives lattice resolution around 0.14 nm, before analysing HR-TEM, the sample was well dispersed in acetone using sonication for 30 min. The dispersed sample was placed in a copper grid and the volatile solvent was evaporated before sample was evaluated for HR-TEM imaging. The elemental compositions present in the catalysts were performed with a Perkins-Elmer Optima 5300Dv inductively coupled plasma optical emission spectrometry (ICP-OES). The reduction behaviour of metal oxide was performed in Chemisorb 2750 TPD/TPR micrometrics equipment with a thermal conductivity detector (TCD). The sample was pretreated at 500 °C under air flow for 1 h to clean the surface of the catalyst. After cleaning the surface of the catalyst about 100 mg of the solid sample was treated with helium gas (25 mL min<sup>-1</sup>) for 1 h at 115 °C, after that the reducing gas mixture (5 vol. % H<sub>2</sub>/Ar, 25 mL min<sup>-1</sup>) was transferred into the sample port at room temperature until the base line was obtained and further the temperature was increased to 1000 °C at a heating rate of 10 °C min<sup>-1</sup>. The acidic properties of Al-KIT-6 support and bimetallic catalyst was investigated by temperature programmed desorption of ammonia (NH<sub>3</sub>-TPD). The NH<sub>3</sub>-TPD experiment were carried out in a similar Chemisorb 2750 TPD/TPR flow reactor, initially the sample was pre-treated at 500 °C for 1 h with helium flow and further ammonia was introduced at 50 °C for removing the physically adsorbed ammonia with purging of helium flow until the base line was started. Further, ammonia desorption started up to 600 °C with a heating rate of 10 °C min<sup>-1</sup>.

#### **Catalytic experiment**

All the catalytic reactions were carried out in a vapour phase fixed bed reactor under atmospheric pressure conditions. The reaction parameter viz, temperature, weight hourly space velocity WHSV, and time-on-stream was studied. Hydrodeoxygenation of diphenyl ether and guaiacol were studied as biomass representative compound. Before starting the catalytic reaction, the bimetallic catalyst was activated at 500 °C under hydrogen flow rate of 50 mL min<sup>-1</sup> then the reactor was cooled to room temperature. Further, the reaction was carried out at 370 °C and 420 °C with three different WHSV and at time-on-stream of 15 h.

During the catalytic run, the reaction products were sampled at every one hour intervals and further the sample was analysed using off-line gas chromatography equipped with flame ionisation detector (FID) and an Rtx-5 column. The conversion of diphenyl ether or guaiacol (X) was defined as the percentage of diphenyl ether or guaiacol converted to all the different products. The selectivity to benzene (S) is defined as the amount of benzene obtained was dived by the amount of diphenyl ether or guaiacol converted to all the products.

#### **Results and Discussion**

Published on 12 June 2017. Downloaded by University of California - San Diego on 13/06/2017 03:17:46

Physicochemical properties of catalysts





Figure 1(A) Low angle XRD patterns of Al-KIT-6 support and Rh/Ni/Al-KIT-6 catalyst

Figure 1(A) represented small-angle XRD pattern of mesoporous Al-KIT-6 support and the bimetal impregnated material. The diffraction signals of support shows at  $2\theta$ = 0.9, corresponds to (211) reflection and a very tiny hump observed at  $2\theta$ = 1.2 corresponds to (220) reflection. The main reflection pattern of (211) plane with unit cell parameter  $a_0 = 20.9$ nm was calculated from the expression  $a_0 = \sqrt{6} \times d_{(211)}$ , which was confirmed that the support possessing bicontinuous ordered mesostructured with Ia3d cubic space group symmetry<sup>26</sup>. The unit cell parameter  $a_0$  for Al-KIT-6 support and Rh/Ni/Al-KIT-6 catalyst was represented in Table 1. The  $a_0$  value for Al-KIT-6 support showed 20.9 nm, while Rh/Ni/Al-KIT-6 showed 20.4 nm. However, the  $a_0$  value of Rh/Ni/Al-KIT-6 was slightly less than the Al-KIT-6 support and it represented the presence of small metal oxide particles occupied on the

#### **New Journal of Chemistry**

pores. Further a small peak shifted towards higher angle and diminished peak intensity was observed in Rh/Ni/Al-KIT-6 with respect to Al-KIT-6 support and this behaviour was not alter the textural properties of Rh/Ni/Al-KIT-6 bimetallic catalyst as evidenced by the HR-TEM and N<sub>2</sub>-sorption analysis.

Figure 1(B) represented high angle XRD pattern of Rh/Ni/Al-KIT-6 and Rh/Ni/r-GO catalysts. The diffraction peak exhibited at 2 $\theta$  angle of 37.1°, 43.1°, 62.7°, and 75.5° designate cubic NiO of Rh/Ni/Al-KIT-6 and Rh/Ni/r-GO catalysts<sup>37</sup>. However, the diffraction signal of Rh<sub>2</sub>O<sub>3</sub> phase was not identified in both catalysts because of the fine dispersion of these nano-particles on the support. Though, a small hump was observed at 2 $\theta$  angle of 41° in the Rh/Ni/Al-KIT-6 catalyst indicated metallic rhodium.



Figure 1 (B) High angle XRD patterns of calcined Rh/Ni/Al-KIT-6 and Rh/Ni/r-GO catalysts

Table 1	Textural	Properties,	surface	acidity	and	coke	content	of	Rh/Ni/Al-KIT-6	and
Rh/Ni/r-GO catalysts										

Sample	Metal content <sup>a</sup> [%]		ao <sup>b</sup> [nm]	S <sub>BET</sub> <sup>c</sup> [m <sup>2</sup> /g]	V <sub>total</sub> <sup>d</sup> [cm <sup>3</sup> /g]	P <sub>D</sub> <sup>e</sup> [nm]	Pw <sup>f</sup> [nm]	Total acidity <sup>g</sup> [mmol/g]	Coke <sup>h</sup> [wt %]	
	Rh	Ni							Diphenyl ether	Guaiacol
Al-KIT-6(25) <sup>56*</sup>	-	-	20.9	684	1.10	6.8	3.6	0.34	-	
Rh/Ni /Al-KIT-6	0.95	6.75	20.4	582	0.90	6.4	3.8	0.31	5.1	8.5
Rh/Ni /r-GO	0.93	6.67	-	124	0.32	18.1	-	-	4.4	9.3

\* value obtained by ICPOES techniques

<sup>a</sup>Metal concentration obtained by ICPOES techniques

<sup>b</sup>Values calculated from low angle XRD

<sup>c</sup>Surface area obtained from BET-Surface area analysis

<sup>d</sup>Total pore volume obtained from adsorption isotherm

<sup>e</sup> Pore size distribution acquired by BJH method

<sup>f</sup> Wall thickness of Al-KIT-6 and Rh/Ni/Al-KIT-6 calculated from the expression  $P_w = a_0/2$ -

 $P_{\rm D}$ 

Published on 12 June 2017. Downloaded by University of California - San Diego on 13/06/2017 03:17:46.

where  $a_0 = \sqrt{6} \times d_{(211)}$ 

<sup>g</sup> Total acidity obtained by NH<sub>3</sub>-TPD technique

<sup>h</sup> Coke content of spent catalyst determined by TGA-technique

### N<sub>2</sub> Physisorption



**Figure 2 (A & B)** Nitrogen-adsorption desorption isotherms for Al-KIT-6 support and Rh/Ni/Al-KIT-6, Rh/Ni/r-GO catalyst with inset BJH pore size distribution

Figure 2(A & B) represents nitrogen adsorption-desorption isotherms of support and Rh/Ni supported bimetallic catalysts with inset BJH pore size distribution. The Al-KIT-6 support and Rh/Ni/Al-KIT-6 showed narrow pore size distribution with average pore size distribution of Al-KIT-6 showed 6.8 nm. Ia3d cubic mesoporous Al-KIT-6 support and Rh/Ni supported catalysts shows type IV isotherms with  $H_1$  hysteresis loop obtained at higher relative pressure indicating large pore size in a narrow type. The initial nitrogen adsorption in lower relative pressure at 0.5 for Al-KIT-6 attributed monolayer adsorption of micropores and mesoporous, whereas the Rh/Ni/Al-KIT-6 catalyst extend the relative pressure P/Po at higher order in the range of 0.6-0.8 attributing capillary condensation inside the mesopores<sup>15</sup>. The surface area, pore volume and pore diameter for Al-KIT-15 support and Rh/Ni/Al-KIT-6 catalyst was shown in Table 1. Generally the surface area, pore volume and pore diameter decreases as in the case of Rh/Ni/Al-KIT-6 catalysts than the Al-KIT-6 support, this may be due to the presence of Rh/Ni oxide particles occupied over the surface as well as pores. Figure 2 (B) and inset shows the nitrogen sorption isotherm and pore size distribution of Rh/Ni supported r-GO catalyst, according to the IUPAC classification the catalyst shows type IV isotherm with H<sub>3</sub> hysteresis loop<sup>39</sup> and specific surface area was found 124 m<sup>2</sup> g<sup>-1</sup>. The surface area, pore volume and pore diameter were presented in Table 1. On comparing the textural properties of Rh/Ni/KIT-6 and Rh/Ni/r-GO catalysts, the mesoporous catalyst seems to have superior textural characteristics than reduced graphene oxide supported catalyst.

New Journal of Chemistry Accepted Manuscript

#### **FT-IR Spectroscopy**



Figure 3 FT-IR spectra of support and Rh/Ni supported bimetallic catalysts

Figure 3 represented FT-IR spectra of support and metal oxide supported bimetallic catalysts. Al-KIT-6 support shows framework band at 463 cm<sup>-1</sup>, 811 cm<sup>-1</sup>, 961 cm<sup>-1</sup>, 1100 cm<sup>-1</sup> and the shoulder peak at 1210 cm<sup>-1</sup> corresponds to mesoporous Al-KIT-6 support<sup>39</sup>. The band at 1100 and the shoulder band at 1210 cm<sup>-1</sup> represented asymetric stretching mode of siloxane (Si-O-Si) while the band at 811 cm<sup>-1</sup> corresponded to symmetric stretching mode of Si-O-Si linkage of framework Al-KIT-6. Further, the band at 463 cm<sup>-1</sup> confirmed Si-O-Si and Si-O-Al bending vibration in the mesoporous framework<sup>39–41</sup>. Additionally, the band at 970 cm<sup>-1</sup> attributed silanol group (Si-OH) in the mesoporous solid or a stretching mode of SiO<sub>4</sub> unit bonded to Al atom<sup>39</sup>. The FT-IR spectrum of Rh/Ni/Al-KIT-6 mesoporous bimetallic catalysts showed absorption band similar to Al-KIT-6 support which indicated structural stability of Al-KIT-6 support<sup>42</sup>. Moreover, the intensity of the transmittance band sharply increased below the framework region as compared with Al-KIT-6 support after Rh/Ni

deposition<sup>43,44</sup>. FT-IR spectrum of graphene oxide shows the vibration mode of C-O-C epoxide linkage at 1230 cm<sup>-1</sup> and the sp<sup>2</sup> hybridized C=C plane vibration shows at 1630 cm<sup>-1</sup>. However, the keto group C=O appeared at 1850 cm<sup>-1</sup> and the OH stretching vibration due to water molecule appeared at 3380 cm<sup>-1</sup> and C-OH, C-O vibration appeared at 1386, 1051 cm<sup>-1</sup> respectively, which confirmed the formation of graphene oxide<sup>46-49</sup>. The FT-IR spectrum of reduced graphene oxide (r-GO) was shown in Figure 3 which on compared to graphene oxide (GO) was entirely different. This confirmed the reduction of various C-OH and C-O bond from the keto and carboxylic acid groups and further sp<sup>2</sup> hybridised C=C vibration appeared at 1640 cm<sup>-1 47,48</sup>. The FT-IR spectrum of Rh/Ni/r-GO catalyst was represented in Figure 3, here the sharp C=C band at 1640 cm<sup>-1</sup> similar to r-GO support confirmed the absence of any structural deformation in the catalyst.

#### Temperature programme desorption of ammonia (TPD-NH<sub>3</sub>)



Figure 4 Ammonia-TPD spectra of Al-KIT-6 support and Rh/Ni/Al-KIT-6 catalyst

The surface acidic characteristics of mesoporous Al-KIT-6 support and Rh/Ni/Al-KIT-6 bimetallic catalyst were probed through NH<sub>3</sub>-TPD analysis. Acid sites are classified based on the strength of desorbed ammonia with respect to temperature, usually weak (<200 °C), medium (200 °C-350 °C) and strong acid sites (>350 °C)<sup>49</sup>. Figure 4 represents ammonia desorption peaks of Al-KIT-6 support and Rh/Ni/Al-KIT-6 bimetallic catalyst. The broad peak with the area under the maximum ammonia desorption in Al-KIT-6 support implies that the support mostly gave medium and strong acid sites. However, Rh/Ni/Al-KIT-6 bimetallic catalyst shows weak, medium, and strong acid sites and the measured total acidity of the support and catalyst was represented in Table 1. The area under the TPD curve for Rh/Ni/Al-KIT-6 shows mainly weak and medium acid sites. Further, the hydrogenolysis of diphenyl ether and guaiacol required medium acid sites for cleavage of C-O bond and it was confirmed by the higher conversion of diphenyl ether and guaiacol obtained on Rh/Ni/Al-KIT6 bimetallic catalyst than non-acidic Rh/Ni/r-GO bimetallic catalyst. However, the total acid sites in bimetallic catalyst was relatively lower than the support, this may be due to the acid sites being occupied by the metallic sites.

#### Temperature programme reduction of hydrogen (TPR-H<sub>2</sub>)



Figure 5 H<sub>2</sub>-TPR spectra of Rh/Ni/Al-KIT-6 and Rh/Ni/r-GO catalysts

#### **New Journal of Chemistry**

The temperature programmed reduction of rhodium and nickel supported bimetallic catalysts were depicted in Figure 5. As reported from the previous work the mono metallic nickel supported catalysts showed the reduction maxima of NiO at 375 °C and 524 °C, which implied the hard reduction of nickel oxide particles <sup>50</sup>. However, the individual reduction peak of Rh<sub>2</sub>O<sub>3</sub> was not observed on bimetallic catalyst<sup>51</sup>. Besides, the Rh/Ni/Al-KIT-6 bimetallic catalysts showed three reduction maxima at 288 °C, 575 °C, and 785 °C, which indicated simultaneous reduction of both Rh and Ni particles and the reduction maxima of NiO shifted to lower temperature via hydrogen spillover effect<sup>51</sup>. Though, the lower reduction shift of NiO was considerably observed at 288 °C and the maximum hydrogen consumption was observed at 575 °C attributing higher surface nickel-rhodium atoms and furthers a sharp reduction peak at 785 °C indicating small amount of large metal oxide crystallites strongly interact with acidic support. The reduction properties of rhodium-nickel oxidic species observed in the case of Rh/Ni/r-GO catalyst at 257 °C and 615 °C. The reduction peak at 615 °C indicate maximum reduction point of Rh-Ni species, and the broader peak in the range between 411 °C-711 °C specified variable reduction size of Rh-Ni species. While, the peak at 257 °C illustrated well dispersed Rh-Ni species, on comparing the reduction behaviour of Al-KIT-6 and r-GO supported Rh/Ni bimetallic catalysts, Al-KIT-6 acidic support significantly improved the reduction properties of Rh/Ni bimetallic species towards lower reduction sites.

#### **HR-TEM** analysis

The HR-TEM images with statistical analysis of Rh/Ni/Al/KIT-6 and Rh/Ni/r-GO was represented in Figure 6 (A). Figure 6 (A) for Rh/Ni/Al-KIT-6 bimetallic catalyst showed metal particles with meso structure and indeed, no particles larger than 24 nm could be viewed as confirmed by the statistical analysis. Furthermore, the particle was highly distributed in the range over 6-14 nm and most of the particles located on the surface of the catalyst and further the existence of Rh/Ni species on the catalyst confirmed with EDAX analysis which was represented in Figure 6 (B). Moreover, Figure 6(A) showed HR-TEM images with statics analysis of Rh/Ni/r-GO catalyst and corresponding EDAX spectrum was represented in Figure 6 (B). Here the appearance of bimetallic species was entirely different with mesoporous supported catalyst, and in these catalysts the metal particles was slightly aggregated from the support surface. It may be due to the weak interaction between the metal and carbon support. Though, the particle size estimated by statics analysis was not exceeds 16 nm and all the particles was present on the external surface of the catalyst.



Figure 6 (A) HR-TEM images with statics analysis of Rh/Ni/Al-KIT-6 and Rh/Ni/r-GO bimetallic catalyst



Figure 6 (B) EDAX analysis of Rh/Ni/Al-KIT-6 and Rh/Ni/r-GO bimetallic catalyst

#### **XPS** analysis



**Figure 7 (A & B)** XPS analysis of Rh/Ni/Al-KIT-6 and Rh/Ni/r-GO bimetallic catalyst: (A) Rh3d, (B) Ni2p

The oxidation state of Rh/Ni bimetallic catalysts were investigated by XPS analysis. The XPS spectrum of rhodium oxide in Rh/Ni/Al/KIT-6 and Rh/Ni/r-GO were presented in Figure 7 (A). The presence of Rh  $3d_{5/2}$  spins state corresponding to the binding energy 309.9 eV on both catalysts confirmed Rh exist in +3 oxidation state in the form of Rh<sub>2</sub>O<sub>3</sub><sup>52-54</sup>. However, the position of metallic Rh at binding energy 307.2 eV was not observed in reduced graphene oxide supported catalyst, whereas in the silica supported Rh/Ni catalyst shows very trace amount of metallic Rh in the region of 307.1 eV, this factor may be enhanced the additional diphenyl ether conversion. The XPS spectrum of nickel oxides on both Rh/Ni/Al-KIT-6 and Rh/Ni/r-GO catalysts were shown in Figure 7 (B). Here, Rh/Ni/Al-KIT-6 shows two spin states Ni2p<sub>3/2</sub> and Ni2p<sub>1/2</sub> with binding energy 855.5eV and 871.1eV respectively<sup>55</sup>. However, Rh/Ni/r-GO catalyst shows Ni2p<sub>3/2</sub> signal at 854.4 eV and Ni2p<sub>1/2</sub> signal at 873.2 eV respectively<sup>56-59</sup>, the binding energy value 854.4 eV with respect to Ni2p<sub>3/2</sub> signal illustrated pure Ni<sup>2+</sup> in Rh/Ni/r-GO catalyst in the form of NiO. With respect to this pure NiO, additional NiO phase shift highly observed in Rh/Ni/r-GO catalyst towards higher

binding energy around 2.1 eV. Mostly, the NiO reduction was simple towards lower binding energy region<sup>55,58</sup>. In these aspects on compared with Rh/Ni/r-GO catalyst, Rh/Ni/Al-KIT-6 catalyst shows this shift around 1.1 eV, this lower shift may enhance the reduction of NiO by the addition of Rh<sub>2</sub>O<sub>3</sub> in the silica support than in the carbon support.

#### 3.2 Catalytic process of diphenyl ether and guaiacol

Published on 12 June 2017. Downloaded by University of California - San Diego on 13/06/2017 03:17:46

The catalytic conversion of diphenyl ether and guaiacol were investigated in the vapour phase using Rh/Ni/Al-KIT-6 and Rh/Ni/r-GO bimetallic catalysts under the disparate experimental conditions (Temperature 370 °C & 420 °C, atmospheric hydrogen pressure 50 mL min<sup>-1</sup>, WHSV ( $h^{-1}$ ) = 1.8, 3.6, & 5.4). Figure 8 (A-C) elucidated conversion and selectivity of diphenyl ether for Rh/Ni/Al-KIT-6 catalyst under 370 °C with three different WHSV.





**Conditions:** WHSV ( $h^{-1}$ ) =1.8, 3.6, 5.4, atmosphere pressure, temperature=370 °C, H<sub>2</sub>=50 mL min<sup>-1</sup>.

Figure 8 (A) showed maximum diphenyl ether conversion of 38 % and the selectivity of benzene shows 17 % at the lower WHSV of  $1.8 \text{ h}^{-1}$ , initially the conversion was maximum

obtained and further increasing the time the trend was decreased. Similarly, Figure 8 (B) at WHSV 3.6 h<sup>-1</sup> displayed conversion and selectivity of diphenyl ether with the supreme conversion 28 % was obtained initially, and further the conversion was decreased at higher time-on-stream. Besides, the selective product of benzene maximum 31 % was obtained at WHSV of 3.6 h<sup>-1</sup>. Likewise Figure 8 (C) at WHSV 5.4 h<sup>-1</sup> showed highest diphenyl ether conversion of 31 % with the benzene selectivity of 37 % and further the conversion trend was decreased insignificantly as increasing the time-on-stream. We observed that the above experiment from Figure 8 (A-C) under the three different WHSV at 370 °C for Rh/Ni/Al-KIT-6 catalyst shows maximum diphenyl ether conversion below 40 % and it represented that the effect of WHSV did not significantly enhance the conversion of diphenyl ether and the temperature of 370 °C was not sufficient for obtaining higher conversion and selectivity. Consequently, the reaction temperature was increased to 420 °C





**Conditions:** WHSV ( $h^{-1}$ ) =1.8, 3.6, 5.4, atmosphere pressure, temperature=420 °C, H<sub>2</sub>=50mL min<sup>-1</sup>.

The conversion and selectivity of diphenyl ether at 420 °C with three different WHSV for Rh/Ni/Al-KIT-6 catalyst was shown in Figure 8 (D-F). Diphenyl ether conversion at 420

<sup>o</sup>C with WHSV 1.8 h<sup>-1</sup> [Figure 8 (D)] shows the highest conversion of 28 % and selectivity of benzene 39 %, on increasing the time-on-stream, a slight decrease in conversion trend was observed. However, on comparing the conversion trend with respect to temperature at 370 °C under lower WHSV 1.8 h<sup>-1</sup>, the conversion about 10 % was decreased this may be due to the higher temperature and lower WHSV conditions may not be suitable for obtaining higher conversion and further decreased the conversion by strong adsorption of reactant molecule leads to form faster coke deposition. However, Figure 8(E) showed conversion and selectivity of diphenyl ether at WHSV 3.6 h<sup>-1</sup>, the utmost conversion of diphenyl ether 63 % and the highest selectivity of benzene 60 % with cyclohexanol 8 % was observed. Figure 8 (F) represented conversion and selectivity of diphenyl ether at WHSV 5.4 h<sup>-1</sup> and this condition the conversion was maximum 37 % and selectivity was identified at 420 °C under moderate WHSV 3.6 h<sup>-1</sup>.



Published on 12 June 2017. Downloaded by University of California - San Diego on 13/06/2017 03:17:46.

**Figure 9(A-C)** Guaiacol conversion and selectivity with respect to time-on-stream for Rh/Ni/Al-KIT-6 catalyst

**Conditions:** WHSV ( $h^{-1}$ ) =1.8, 3.7, 5.5, atmosphere pressure, temperature=420 °C, H<sub>2</sub>=50mL min<sup>-1</sup>.

The conversion and selectivity of guaiacol on Rh/Ni/Al-KIT-6 catalyst was illustrated in Figure 9 (A-C) under the condition of 420 °C with three different WHSV (h<sup>-1</sup>) 1.8, 3.7 &

#### **New Journal of Chemistry**

5.5. The conversion and selectivity tendency of guaiacol under the lower WHSV 1.8  $h^{-1}$ represented in Figure 9 (A), and it shows that the conversion of guaiacol maximum 39 % with selectivity of mono oxygenated product of anisole maximum 44 %, phenol 32 %, 2methyl phenol 40 % and catechol selectivity 38 % was observed. Initially the conversion was increased with increasing the time-on-stream and it reaches maximum conversion still 9 h and beyond the limit, conversion tends to decrease. Figure 9 (B) shows guaiacol conversion and selectivity at WHSV 3.7 h<sup>-1</sup> the maximum conversion and selectivity observed at 12 h and it shows conversion of 36 % with maximum selectivity of phenol 56 %, 2-methyl phenol 49 %, 4-methyl phenol 37 %, anisole 12 % and catechol 43 % was observed. Similarly, Figure 9 (C) shows the conversion and selectivity of guaiacol for Rh/Ni/Al-KIT-6 catalyst under the higher WHSV 5.5 h<sup>-1</sup>, here the conversion of guaiacol 15 % with the selectivity of phenol maximum 34 %, 2-methyl phenol 47 %, 4-methyl phenol 59 %, anisole 17 % and catechol 30 % was observed. The present experimental condition of 420 °C with three different WHSV, the conversion of guaiacol was obtained maximum at lower WHSV and further on increasing the WHSV, the conversion decrease. Moreover, the product selectivity of guaiacol for Rh/Ni/Al-KIT-6 catalyst significantly produce methylated product than complete deoxygenated product of benzene. However, on comparing the guaiacol conversion with respect to diphenyl ether, the guaiacol conversion was less than that of diphenyl ether. It revealed that the conversion and selectivity mainly depend on nature of reactant; guaiacol has two types of reactive sites, methoxyl and hydroxyl groups<sup>60</sup>. However, guaiacol has been converted via methoxyl C-O bond cleavage to produce catechol as the major intermediate and further catechol deoxygenated through direct deoxygenation of hydroxyl group to produce phenol. Furthermore, phenol directly obtained from guaiacol via demethoxylation, which was insignificant path than catechol intermediate because the C-OCH<sub>3</sub> bond energy was higher than that of O-CH<sub>3</sub> and further it was confirmed by the equal distribution of catechol obtained with respect to phenol<sup>61-65</sup>. Phenol was identified as the secondary product or intermediate and further conversion of phenol into benzene was restricted, while methyl phenol formation via methyl transfer was significantly observed<sup>66–68</sup>.

Figure 10 (A) represented conversion and selectivity of diphenyl ether for Rh/Ni/r-GO catalyst at 420 °C with WHSV 3.6 h<sup>-1</sup>, the maximum conversion of diphenyl ether 55 % with selectivity of benzene 39 %, phenol 80 %, and cyclohexanol 5 % was observed. Figure 10 (B) illustrate conversion and selectivity of guaiacol for Rh/Ni/r-GO catalyst under 420 °C with WHSV 3.7 h<sup>-1</sup>, the maximum conversion of guaiacol 40 % with selectivity of phenol 56 %, 2-methyl phenol 25 %, 4-methyl phenol 40 %, anisole 2 % and trace amount of benzene

1% was observed. The superior catalytic performance was observed over Rh/Ni/Al-KIT-6 acidic bimetallic catalyst than Rh/Ni/r-GO catalyst, apparently due to the interaction between rhodium and nickel with acidic mesoporous support enhancing the adsorption properties of reactant molecule and further enhanced the C-O bond cleavage of reactant molecule. Moreover, the diffusion of product from mesoporous catalyst was accelerated more than that of reduced graphene oxide supported catalyst as evidenced by the higher conversion of diphenyl ether.



**Figure 10** Conversion and selectivity of (A) diphenyl ether, (B) guaiacol with respect to time-on-stream for Rh/Ni/r-GO

**Conditions:** WHSV ( $h^{-1}$ ) =3.6 & 3.7, atmosphere pressure, temperature=420 °C, H<sub>2</sub>=50 mL min<sup>-1</sup>, diphenyl ether/guaiacol flow rate (mL  $h^{-1}$ ) =1.0

Table 2 represents comparison between Rh/Ni/Al/KIT-6 activities with other reported work in the literature under the different experimental condition. In Table 2, Rh/Ni/Al-KIT-6 shows highest diphenyl ether conversion of 63 % under atmospheric pressure. However, the work reported by the others showed complete conversion, but they are all done the experiment at higher hydrogen pressure and using high pressure reactor. Therefore, minimizing hydrogen consumption in the HDO process has been considered as significant factor for achieving higher diphenyl ether conversion.

Catalyst	Reactant	Reactor	Temp. (°C)	Pres. (atm)	Con. (%)	Ref.
Rh/Ni/Al-KIT-6	Diphenyl ether	Fixed bed reactor	420	1	63	This Work
Rh/H-Beta	Diphenyl ether	High pressure autoclave	140	39	98	2
Rh/C	Diphenyl ether	Batch reactor	80	5	100	18
Ni/SiO <sub>2</sub>	Diphenyl ether	Parr reactor	120	6	100	19
Pd/C	Diphenyl ether	High pressure autoclave	190	39	92	20
Rh/C	Diphenyl ether	Batch reactor	80	5	100	21
Ni/ZrPO <sub>4</sub>	Diphenyl ether	High pressure autoclave	180	5	84	23
Ni/SiO <sub>2</sub>	Diphenyl ether	Autoclave reactor	120	6	100	24
Raney Ni	Diphenyl ether	Batch reactor	200	49	100	25

 Table 2 Comparison of Rh/Ni/Al-KIT-6 activity with other literature

Diphenyl ether conversion for Rh/Ni bimetal supported catalyst and its possible reaction pathway was represented in Figure 11.



Figure 11 Possible reaction routes for diphenyl ether deoxygenation over Rh/Ni bimetal supported catalysts

The target product of benzene maximum 60 % was obtained and the direct ring saturated product of cyclohexyl phenyl ether and dicyclohexyl phenyl ether was not identified

under the present atmospheric pressure condition. Since the direct hydrogenation of diphenyl ether was limited than hydrogenolysis pathway and the major hydrodeoxygenation route was diphenyl ether hydrogenolysis into benzene and phenol. And further, hydrogenation of benzene and phenol into cyclohexane and cyclohexanol was not highly observed due to the obstruction of Rh/Ni sites by aromatic ring or hydroxyl group, this indicated that hydrogenolysis was a significant class of reaction<sup>2,69–71</sup>. At earlier stage the hydrodeoxygenation of diphenyl ether conversion increases and further increasing the time, conversion decreased and it revealed that hydrogenolysis of diphenyl ether was much faster than subsequent benzene hydrogenation. Moreover, the percentage of phenol and benzene was not regular for all the experimental conditions and the phenol percentage was highly observed than that of benzene percentage and even though the highest benzene selectivity 60 % was observed.

Published on 12 June 2017. Downloaded by University of California - San Diego on 13/06/2017 03:17:46

In continuation with Rh/Ni/Al-KIT-6 for diphenyl ether conversion, Rh/Ni/r-GO catalyst follows the similar reaction sequence for diphenyl ether conversion (Figure 10 A). However, the conversion maximum 55 % with benzene selectivity 39 % was observed, which was less than that of Rh/Ni/Al-KIT-6 catalyst, it reveals that the acidic support play a crucial role for diphenyl ether conversion by the strong interaction with Rh/Ni bimetallic species<sup>25,72,73</sup>. In general, the HDO of lignin model compound converted via hydrogenationdeoxygenation or direct deoxygenation pathway<sup>74</sup>. However, some reports recommended that the bimetal catalysts could enhance the direct deoxygenation pathway than deoxygenationhydrogenation pathway<sup>75</sup>, more over the addition of Rh to Ni offers the possibility of direct deoxygenation of diphenyl ether via hydrogenolysis of C-O bond to produce benzene and phenol, although it could not produce significantly hydrogenated product of cyclohexanol and cyclohexane under the atmospheric pressure condition. Obviously the acidic Al-KIT-6 support had great improvement for enhancing the benzene selectivity of 60 %. However, in contrast to r-GO support had only metal component, which catalyse the hydrogenolysis bond breaking slower than the bifunctional Rh/Ni/Al-KIT-6 catalyst. Despite, the hydrogenolysis of C-O bond required bifunctional reactive sites i.e., acid and metal sites and further the presence of higher acid sites on the catalyst may increases the HDO efficiency<sup>50,67,70</sup>. The advantages of using bimetallic catalysts for diphenyl ether and guaiacol conversion was apparently high and still the complete deoxygenation and hydrogenation in the case of guaiacol conversion was restricted under the present experimental condition due to the loss of active sites by condensation of secondary oxygenated product to form carbon deposition over

the catalyst surface<sup>76</sup>. The coke deposition on the catalyst surface was studied by thermal gravimetric analysis.



Figure 12 Thermal gravimetric analysis of coke deposited bimetallic catalysts for diphenyl ether and guaiacol conversion after 15h on-stream

Figure 12 (A-D) shows thermogramme of Rh/Ni/Al-KIT-6 and Rh/Ni/r-GO spent bimetallic catalyst for diphenyl ether and guaiacol conversion. The coke deposition was highly observed in guaiacol converted spent catalyst than diphenyl ether converted catalyst. The amount of coke deposition for diphenyl ether converted spent Rh/Ni/Al-KIT-6 catalyst was shows 5.1 %, while guaiacol converted spent Rh/Ni/Al/KIT-6 catalyst was shows 8.5 %. However, the coke deposition for diphenyl ether converted spent Rh/Ni/r-GO catalyst was shows 4.4 % and for guaiacol converted spent Rh/Ni/r-GO catalyst was shows 9.3 %. Also, it represented that the nature of oxygen model substrate were crucial to catalyst deactivation under the present experimental condition<sup>76</sup>.

The reuse experiment was carried out to check the stability of bimetallic Rh/Ni/Al-KIT-6 catalyst under the optimum reaction condition of 420 °C with WHSV 3.6 h<sup>-1</sup>. The spent catalyst was regenerated by calcination at 500 °C for 6 h in air and reused for another

catalytic experiment. The regenerated Rh/Ni/Al-KIT-6 catalyst was characterized by low and high angle XRD, which was represented in Figure 13.



Published on 12 June 2017. Downloaded by University of California - San Diego on 13/06/2017 03:17:46.

Figure 13 Low and high angle XRD patterns of regenerated Rh/Ni/Al-KIT-6 bimetallic catalyst

The low angle XRD confirmed the intact of mesoporous nature of Rh/Ni/Al-KIT-6 catalyst by retaining the (211) and (200) plane and further high angle XRD shows existence of crystalline metal oxide phases.



Figure 14 Conversion and selectivity of diphenyl ether for regenerated Rh/Ni/Al-KIT-6 bimetallic catalyst

**Conditions:** WHSV ( $h^{-1}$ ) = 3.6, atmosphere pressure, temperature=420 °C, H<sub>2</sub>=50mL min<sup>-1</sup>.

The result was shown in Figure14, for diphenyl ether conversion with respect to regenerated Rh/Ni/Al-KIT-6 bimetallic catalyst, the maximum conversion 63 % with benzene selectivity 57 % was observed and it revealed that the regenerated catalyst could not significantly altered the activity pattern with respect to fresh catalytic reaction. Though, a variation in the product distribution was observed, which may be due to the redistribution of Rh/Ni particles during the regeneration process.

#### Conclusions

In this study, Rh/Ni bimetal impregnated mesoporous Ia3d cubic and r-GO supported catalysts were synthesised and consistently characterized by XRD, FT-IR, HR-TEM,  $N_2$ sorption, NH<sub>3</sub>-TPD, H<sub>2</sub>-TPR, EDAX and ICP-OES techniques. The potential diphenyl ether and guaiacol conversion were identified on Rh/Ni/Al-KIT-6 catalyst than non acidic Rh/Ni/r-GO catalyst due to their bifunctional activity (metal and acid function). Diphenyl ether conversion maximum 63 % and benzene selectivity maximum 60 % was achieved on Rh/Ni/Al-KIT-6 catalyst at 420 °C with WHSV 3.6 h<sup>-1</sup>. However, for guaiacol conversion into benzene on Rh/Ni/Al-KIT-6 and Rh/Ni/r-GO catalyst was restricted due to the formation of secondary oxygenated product. The maximum coke tolerance was observed in diphenyl ether converted Rh/Ni bimetallic catalysts than guaiacol converted Rh/Ni bimetallic catalysts. The higher oxygen functionality in guaiacol was the major cause for coke deposition, which was not completely converted after secondary product formation. The Rh/Ni/Al-KIT-6 catalyst was regenerated and it was confirmed by low and high angle XRD. Further, their catalytic activity of diphenyl ether shows similar conversion and selectivity with respect to earlier catalytic reaction, which was demonstrating the stability of Rh/Ni/Al-KIT-6 catalyst. Moreover, the presence of hydrogen spill over effect, acidic behaviour with higher dispersion of Rh/Ni particles on this Rh/Ni/Al-KIT-6 catalyst could appear as auspicious applicant for the C-O bond cleavage of diphenyl ether and guaiacol.

#### Acknowledgements

This work is financially supported by UGC-BSR New Delhi, India. The instrumentation facility mainly contributed by department of Chemistry, IIT Madras, Chennai. The laboratory facility provided by department of Chemistry, Anna University, Chennai under DST-FIST and UGC-DRS are gratefully acknowledged.

#### References

- 1 D. J. Rensel, S. Rouvimov, M. E. Gin and J. C. Hicks, J. Catal., 2013, 305, 256–263.
- 2 G. Yao, G. Wu, W. Dai, N. Guan and L. Li, *Fuel*, 2015, **150**, 175–183.
- J. He, C. Zhao, D. Mei and J. A. Lercher, J. Catal., 2014, **309**, 280–290.
- 4 H. Fang, J. Zheng, X. Luo, J. Du, A. Roldan, S. Leoni and Y. Yuan, *Appl. Catal. A Gen.*, 2017, **529**, 20–31.
- 5 T. Huynh, U. Armbruster, C. Kreyenschulte, L. Nguyen, B. Phan, D. Nguyen and A. Martin, *Catalysts*, 2016, **6**, 176.
- 6 Y. K. Hong, D. W. Lee, H. J. Eom and K. Y. Lee, *Appl. Catal. B Environ.*, 2014, 150-151, 438–445.
- P. M. De Souza, R. C. Rabelo-Neto, L. E. P. Borges, G. Jacobs, B. H. Davis, U. M. Graham, D. E. Resasco and F. B. Noronha, *ACS Catal.*, 2015, 5, 7385–7398.
- B. Güvenatam, O. Kurşun, E. H. J. Heeres, E. A. Pidko and E. J. M. Hensen, *Catal. Today*, 2014, 233, 83–91.
- 9 A. L. Jongerius, R. Jastrzebski, P. C. A. Bruijnincx and B. M. Weckhuysen, J. Catal., 2012, 285, 315–323.
- 10 L. F. Feitosa, G. Berhault, D. Laurenti, T. E. Davies and V. Teixeira Da Silva, J. *Catal.*, 2016, 340, 154–165.
- S. Ted Oyama, T. Onkawa, A. Takagaki, R. Kikuchi, S. Hosokai, Y. Suzuki and K. K. Bando, *Top. Catal.*, 2015, 201–210.
- 12 K. Soni, B. S. Rana, A. K. Sinha, A. Bhaumik, M. Nandi, M. Kumar and G. M. Dhar, *Appl. Catal. B Environ.*, 2009, **90**, 55–63.
- D. M. Alonso, S. G. Wettstein and J. A. Dumesic, *Chem. Soc. Rev.*, 2012, 41, 8075– 8098.
- 14 C. Li, X. Zhao, A. Wang, G. W. Huber and T. Zhang, *Chem. Rev.*, 2015, **115**, 11559– 11624.

- 15 K. Soni, K. C. Mouli, A. K. Dalai and J. Adjaye, Catal. Letters, 2010, 136, 116–125.
- J. Chang, T. Danuthai, S. Dewiyanti, C. Wang and A. Borgna, *ChemCatChem*, 2013, 5, 3041–3049.
- 17 Y.Song, S. H. Chia, U. Sanyal, O.Y. Gutiérrez and J.A. Lercher, *Journal of Catalysis*, 2016, 344, 263-272.
- 18 M.Chatterjee, T. Ishizaka, and H. Kawanami, *Catalysis Today*, 2017, 281, 402-409.
- 19 J. He, C. Zhao, D. Mei and J. A. Lercher, Journal of Catalysis, 2014, 309, 280-290.
- 20 M.Wang, H. Shi, D. M. Camaioni, and J. A. Lercher, Angewandte Chemie International Edition, 2017, 56, 2110-2114.
- 21 M. Chatterjee, A. Chatterjee, T. Ishizaka, and H. Kawanami, *Catalysis Science & Technology*, 2015, *5*, 1532-1539.
- 22 M. Zaheer, and R. Kempe, ACS *Catalysis*, 2015, 5, 1675-1684.
- S. Jin, X. Chen, C. Li, C. W. Tsang, G. Lafaye, and C. Liang, *ChemistrySelect*, 2016, 1, 4949-4956.
- J. He, C. Zhao, and J. A. Lercher, *Journal of the American Chemical Society*, 2012, 134, 20768-20775.
- 25 X. Wang, and R. Rinaldi, *Catalysis Today*, 2016, 269, 48-55.
- A. Prabhu, L. Kumaresan, M. Palanichamy and V. Murugesan, *Appl. Catal. A Gen.*, 2009, 360, 59–65.
- 27 W. S. Hummers and R. E. Offeman, J. Am. Chem. Soc., 1958, 80, 1339–1339.
- L. Shahriary and A. A. Athawale, *Int. J. Renew. Energy Environ. Eng.*, 2014, 02, 58–63.
- 29 V. Thirumal, A. Pandurangan, R. Jayavel and R. Ilangovan, *Synth. Met.*, 2016, 220, 524–532.
- 30 G. Shao, Y. Lu, F. Wu, C. Yang, F. Zeng and Q. Wu, J. Mater. Sci., 2012, 47, 4400– 4409.

- 31 P. Lian, X. Zhu, S. Liang, Z. Li, W. Yang and H. Wang, *Electrochim. Acta*, 2010, 55, 3909–3914.
- 32 L. Stobinski, B. Lesiak, A. Malolepszy, M. Mazurkiewicz, B. Mierzwa, J. Zemek, P. Jiricek and I. Bieloshapka, J. Electron Spectros. Relat. Phenomena, 2014, 195, 145–154.
- 33 S. Pei and H. M. Cheng, *Carbon N. Y.*, 2012, **50**, 3210–3228.

- J. Panpranot, J. G. Goodwin and A. Sayari, Catal. Today, 2002, 77, 269–284.
- 35 H. Liu, H. Wang, J. Shen, Y. Sun and Z. Liu, *Catal. Today*, 2008, **131**, 444–449.
- M. Santhosh Kumar, D. Chen, J. C. Walmsley and A. Holmen, *Catal. Commun.*, 2008, 9, 747–750.
- 37 A. E. Barrón Cruz, J. A. Melo Banda, H. Mendoza, C. E. Ramos-Galvan, M. A. Meraz Melo and D. Esquivel, *Catal. Today*, 2011, 166, 111–115.
- 38 G. J. Liu, L. Q. Fan, F. Da Yu, J. H. Wu, L. Liu, Z. Y. Qiu and Q. Liu, J. Mater. Sci., 2013, 48, 8463–8470.
- 39 R. Merkache, I. Fechete, M. Maamache, M. Bernard, P. Turek, K. Al-Dalama and F. Garin, *Appl. Catal. A Gen.*, 2015, **504**, 672–681.
- 40 N. S. Sanjini and S. Velmathi, J. Porous Mater., 2016, 23, 1527–1535.
- Q. Liu, J. Li, Z. Zhao, M. Gao, L. Kong, J. Liu and Y. Wei, *J. Catal.*, 2016, 344, 38–52.
- L. Li, W. Han, J. Zhang, G. Lu and Z. Tang, *Microporous Mesoporous Mater.*, 2016, 231, 9–20.
- 43 M. Pudukudy, Z. Yaakob and Z. S. Akmal, *Appl. Surf. Sci.*, 2015, **353**, 127–136.
- 44 D. Zhang, A. Duan, Z. Zhao and C. Xu, J. Catal., 2010, 274, 273–286.
- 45 N. Kumar, S. Das, C. Bernhard and G. D. Varma, *Supercond. Sci. Technol.*, 2013, 26, 095008.
- 46 S. Kellici, J. Acord, J. Ball, H. S. Reehal, D. Morgan and B. Saha, RSC Adv., 2014, 4,

New Journal of Chemistry Accepted Manuscript

14858–14861.

- 47 Z. Ji, G. Zhu, X. Shen, H. Zhou, C. Wu and M. Wang, New J. Chem., 2012, 36, 1774.
- 48 S. Gurunathan, J. W. Han, E. S. Kim, J. H. Park and J. H. Kim, *Int. J. Nanomedicine*, 2015, **10**, 2951–2969.
- 49 G. Karthikeyan and A. Pandurangan, J. Mol. Catal. A Chem., 2012, 361-362, 58-67.
- 50 S. Pichaikaran and P. Arumugam, Green Chem., 2016, 18, 2888–2899.
- 51 W. K. Jóźwiak, M. Nowosielska and J. Rynkowski, *Appl. Catal. A Gen.*, 2005, 280, 233–244.
- 52 J. Kugai, V. Subramani, C. Song, M. H. Engelhard, and Y. H. Chin, *Journal of Catalysis*, 2006, 238, 430-440.
- 53 A. Bueno-Lopez, I. Such-Basanez, and C. S. M. de Lecea, *Journal of Catalysis*, 2006, 244, 1, 102-112.
- 54 C. Lin, G. Wu, H. Li, Y. Geng, G. Xie, J. Yang, and J. Jin, *Nanoscale*, 2017, 9, 1834-1839.
- J. Liu, J. He, L. Wang, R. Li, P. Chen, X. Rao, and J. Lei, Scientific reports, 2016, 6.
- 56 L.Wang, X. Lu, C. Wen, Y. Xie, L. Miao, S.Chen, H. Li, P. Li and Y.Song, J. Mater. Chem. A, 2015, 3, 608
- 57 A. J. Akhtar, A. Gupta, and S. K. Saha, *RSC Advances*, 2015, *5*, 9594-9599.
- 58 R. V. Malyala, C. V. Rode, M. Arai, S. G. Hegde, and R. V. Chaudhari, *Applied Catalysis A: General*, 2000, 193, 71-86.
- 59 G. D. Park, J. S.Cho and Y. C. Kang, Nanoscale, 2015 7, 16781-16788.
- 60 Q. Lai, C. Zhang and J. H. Holles, Appl. Catal. A Gen., 2016, 528, 1–13.
- 61 M. V. Bykova, D. Y. Ermakov, S. A. Khromova, A. A. Smirnov, M. Y. Lebedev and V. A. Yakovlev, *Catal. Today*, 2014, **220-222**, 21–31.
- 62 D. Gao, C. Schweitzer, H. T. Hwang and A. Varma, *Ind. Eng. Chem. Res.*, 2014, 53, 18658–18667.

- A. Gutierrez, R. K. Kaila, M. L. Honkela, R. Slioor and A. O. I. Krause, *Catal. Today*, 2009, 147, 239–246.
- 64 A. Aqsha, L. Katta and N. Mahinpey, *Catal. Letters*, 2015, **145**, 1351–1363.
- K. Leiva, N. Martinez, C. Sepulveda, R. García, C. A. Jiménez, D. Laurenti, M. Vrinat, C. Geantet, J. L. G. Fierro, I. T. Ghampson and N. Escalona, *Appl. Catal. A Gen.*, 2015, 490, 71–79.
- 66 J. Sun, A. M. Karim, H. Zhang, L. Kovarik, X. S. Li, A. J. Hensley, J. S. McEwen and Y. Wang, J. Catal., 2013, 306, 47–57.
- N. T. T. Tran, Y. Uemura, S. Chowdhury and A. Ramli, *Appl. Catal. A Gen.*, 2016, 512, 93–100.
- 68 C. Sepúlveda, R. García, P. Reyes, I. T. Ghampson, J. L. G. Fierro, D. Laurenti, M. Vrinat and N. Escalona, *Appl. Catal. A Gen.*, 2014, 475, 427–437.
- 69 S. Jin, Z. Xiao, X. Chen, L. Wang, J. Guo, M. Zhang and C. Liang, *Ind. Eng. Chem. Res.*, 2015, 54, 2302–2310.
- 70 X. Wang and R. Rinaldi, Catal. Today, 2016, 269, 48–55.

- 71 J. K. Kim, J. K. Lee, K. H. Kang, J. C. Song and I. K. Song, *Appl. Catal. A Gen.*, 2015, 498, 142–149.
- 72 S. J. Tauster, Accounts of Chemical Research, 1987, 20, 389-394.
- 73 C. Linsmeier, and E. Taglauer, Applied Catalysis A: General, 2011, 391, 175-186.
- H. Lee, Y.-M. Kim, I.-G. Lee, J.-K. Jeon, S.-C. Jung, J. Do Chung, W. G. Choi and Y. K. Park, *Korean J. Chem. Eng.*, 2016, **32**, 1–17.
- Y. Romero, F. Richard and S. Brunet, Appl. Catal. B Environ., 2010, 98, 213–223.
- 76 G. S. Foo, A. K. Rogers, M. M. Yung and C. Sievers, ACS Catal., 2016, 6, 1292–1307.