# Vapor phase hydrodeoxygenation and hydrogenation of *m*-cresol on silica supported Ni, Pd and Pt catalysts

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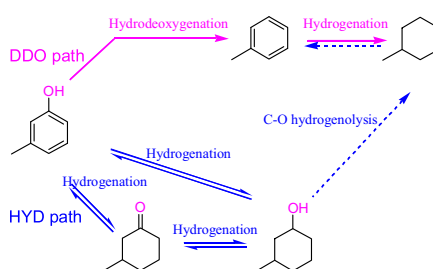[b] Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, IL 62901, United States
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## HIGHLIGHTS

- Hydrogenation and hydrodeoxygenation are the primary reactions for cresol conversion.
- Intrinsic activity of hydrogenation follows $Ni < Pd < Pt$, deoxygenation follows $Ni \ll Pd \approx Pt$.
- Oxygen removal is mainly through the direct deoxygenation path.
- Toluene is the major final product at full conversion of cresol.
- Increase of temperature improves hydrodeoxygenation and C–C hydrogenolysis.

## GRAPHICAL ABSTRACT

## ABSTRACT

Hydrodeoxygenation of *m*-cresol (a model compound of lignin derived phenolics in bio-oil) has been studied on silica supported Ni, Pd and Pt catalysts at 250 °C and atmospheric pressure. Hydrogenation (to 3-methylcyclohexanone and 3-methylcyclohexanol) and hydrodeoxygenation (to toluene) are the primary reactions over all catalysts. The intrinsic hydrogenation activity follows the order of $Ni < Pd < Pt$, and the deoxygenation activity follows the order of $Ni \ll Pd \approx Pt$. The oxygen removal is mainly through a direct deoxygenation (DDO) route. The hydrogenation–deoxygenation (HYD) route is not important due to the lack of acidic sites to catalyze dehydration and a rather low hydrogenolysis activity of the C–OH bond of 3-methylcyclohexanol. At high conversions, the initial hydrogenation products are reversely dehydrogenated to *m*-cresol, making the deoxygenation to toluene and its subsequent hydrogenation to methylcyclohexane the major pathway. In general, increasing reaction temperature suppresses the hydrogenation reaction but promotes the hydrodeoxygenation as well as C–C bond hydrogenolysis. On Pd and Pt, increasing temperature improves deoxygenation to toluene over the C–C bond hydrogenolysis. In contrast, higher temperature favors the successive C–C hydrogenolysis to produce the low value methane on Ni.

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# 1. Introduction

Hydrodeoxygenation of phenolic compounds has received increasing attention recently, since it represents an important route to produce chemicals and fuels from biomass derived bio-oils (Saidi et al., 2014; Wang et al., 2013). Phenolics, such as phenol, cresol, anisole, guaiacol, and syringol (Zhu et al., 2011), are produced from depolymerization of the lignin fraction of biomass. Those molecules have a phenyl ring connecting the functional groups such as the hydroxyl (–OH), methoxyl (–OCH$_3$) and alkyl (–R) groups (Zhu et al., 2011). Oxygen removal from phenolics can directly produce fuel components. However, the oxygen removal is very challenging due to the strong C$_{aromatic}$–OH bond, which is refractory to hydrodeoxygenation (Furimsky, 2000).

Earlier studies on hydrodeoxygenation of phenolics used the industrial hydrodesulfurization catalysts (CoMoS and NiMoS) at 200–400 °C and high hydrogen pressures (Odebunmi and Ollis, 1983; Weigold, 1982; Laurent and Delmon, 1993; Massoth et al., 2006; Romero et al., 2010). Two reaction pathways were proposed based on the product distributions (Odebunmi and Ollis, 1983; Massoth et al., 2006). One is the direct deoxygenation (DDO) route, producing aromatics. The other is the hydrogenation–deoxygenation (HYD) pathway, i.e., hydrogenating the phenyl ring first, followed by dehydration/hydrogenolysis to cyclohexenes and finally hydrogenation to cyclohexanes. The catalyst is effective for oxygen removal but it deactivates due to the loss of sulfur, which ends up in a sulfur-containing stream. More recently, various types of catalysts were tested under different reaction conditions, among which group VIII metals such as Ni, Pd, Pt have attracted much attention (Zhao and Lercher, 2012; Zhao et al., 2012; Hong et al., 2010; Nimmanwudipong et al., 2011; Fisk et al., 2009; Mortensen et al., 2013; Wan et al., 2012). At low reaction temperature (200 °C) and high hydrogen pressures (5 MPa) and in the presence of acid sites, it was suggested that hydrogenation on metal sites (Pd, Pt, Ni) followed by dehydration on acid sites, and then hydrogenation to cyclohexanes on metal sites is the major pathway (Zhao and Lercher, 2012; Zhao et al., 2012; Hong et al., 2010). At high reaction temperature (400 °C) and atmospheric pressure, aromatics are the major products from hydrodeoxygenation of cresol and anisole on the Pt catalysts supported on inert SiO$_2$ or acidic zeolite (Zhu et al., 2011, 2014). At intermediate temperature of 275 °C and 10 MPa hydrogen, Ni, Pd and Pt supported on an inert support (carbon or silica) are active for phenol conversion, with major products being cyclohexanol and cyclohexane (Mortensen et al., 2013). When ZrO$_2$ was used as support, the yield of cyclohexane is significantly improved (Mortensen et al., 2013). At 2 MPa and 300 °C, propylbenzene was the major product during hydrodeoxygenation of 4-propylphenol on a Pt–Re/ZrO$_2$ catalyst. It has been suggested that the major reaction pathway is hydrogenation to 4-propylcyclohexanol first, and then dehydration to 4-propylcyclohexene, followed by dehydrogenation to propylbenzene (Ohta et al., 2014). For p-cresol hydrodeoxygenation on the supported Pd and Pt catalysts at 300 C and 8.3 MPa, toluene was the major product when water was used as solvent, but the major product was methylcyclohexane in a heptane solvent (Wan et al., 2012). Shin and Keane (1998, 2000) reported that benzene started to form when the temperature was higher than 250 °C for vapor phase conversion of the phenol/methanol mixture. While at 300 °C and atmospheric pressure, hydrodeoxygenation of cresol on the Ni and Pt catalysts produces mainly methylcyclohexanone, methylcyclohexanol, and toluene (Foster et al., 2012, Nie et al., 2014a, 2014b; Zanuttini et al., 2014). However, it is difficult to directly compare these results due to variation in reaction conditions. Thermodynamically, hydrogenation/dehydrogenation of aromatics/cyclohexanes are sensitive to the reaction temperature and pressure due to the complexity of the reaction mechanism. For example, the primarily formed aromatics may be hydrogenated to cyclohexanes at high hydrogen pressures whereas the cyclohexanes produced in the reaction may further be dehydrogenated to aromatics at high temperatures. Moreover, different supports and/or solvents may further complicate the reaction mechanism.

The purpose of the current work is to compare the hydrodeoxygenation properties of the Ni, Pd, and Pt catalysts without the influences of the solvent and support. m-Cresol was used as a model phenolic compound because it is in liquid form at room temperature and could be easily fed without a solvent. Silica was used as the support since it is inert. Reaction temperature of 250 °C and atmospheric hydrogen pressure were chosen for the vapor phase reaction. At this temperature, aromatics are not thermodynamically prevailing over cyclohexanes. In the meantime, this pressure does not drive the equilibrium from aromatics toward cyclohexanes, which would allow us to track the evolution of the primary products and to better understand the reaction mechanism.

# 2. Experimental

## 2.1. Catalyst preparation

The supported Ni, Pd, and Pt catalysts were prepared by incipient wetness impregnation of silica (Sigma-Aldrich, $S_{BET}=200$ m$^2$/g) with an aqueous solution of calculated amounts of NiNO$_3 \cdot$6H$_2$O (Strem Chemicals), PdCl$_2$, and H$_2$PtCl$_6 \cdot$6H$_2$O (Tianjin Kemiou Chemical), respectively, overnight. It was then dried at 110 °C for 12 h, followed by calcination at 400 °C for 4 h. The corresponding metal loadings of the as-prepared catalysts were 5 wt% for the Ni catalyst, and 1 wt% for the Pd and Pt catalysts, confirmed by the ICP measurements. The catalysts were then pressed, crushed and sieved to 40–60 mesh before characterization and test.

## 2.2. Catalyst characterization

The specific surface areas of the catalysts were measured using an ASAP 2020 (Mircomeritics) at liquid nitrogen temperature. Powder X-ray diffraction (XRD) patterns of the catalyst samples were recorded on a Rigaku D/max 2500 diffractometer. The transmission electron microscopy (TEM) observation was carried out on a JEM 2010F system. The metal dispersion was measured by CO pulse adsorption at room temperature, monitored by a Cirrus 200 mass spectrometer (MKS). A CO/Metal stoichiometry of 1/1 was used to estimate the dispersion.

## 2.3. Catalytic performance

The catalytic performances of the supported Ni, Pd, and Pt catalysts were studied in a tubular quartz reactor (6 mm o.d.) at atmospheric hydrogen pressure. The Ni catalyst was reduced at 450 °C for 1 h and the Pd and Pt catalysts were reduced at 300 °C for 1 h in flowing hydrogen before the reactivity test. After the reactor was adjusted to the reaction temperature, m-cresol was fed using a syringe pump (KDS100, KD scientific) and vaporized before entering the reactor. All lines were heated using heating tapes to prevent condensation of the reactants and products. The quantification of the products was achieved online using a 7890B GC (Agilent) equipped with a 60-m Innowax column and a FID detector. The qualitative analysis of products was done in a Shimadzu QP 2010 SE GC–MS. Space-time ($W/F$, g$_{cat}$/g$_{reactant}$ h) was adjusted in the range of 0–12 h through changing both the amount of catalyst used and the flow rate of the feed, and the product evolutions were followed. A H$_2$/reactant molar ratio of 60 was used in all activity tests. The conversion and yield were reported in terms of molar carbon percentage.