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Mild-condition hydrodeoxygenation of lignin-derived phenolics to BTX aromatics

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Highlights

- BTX production by mild-condition HDO of lignin-derived phenolics
- Atmospheric HDO of phenolics to BTX at low temperature of 250 °C
- The enhanced dehydration efficiency caused by rhenium oxide addition
- The remarkable potential of zirconia as catalyst support for HDO of phenolics

1. Introduction

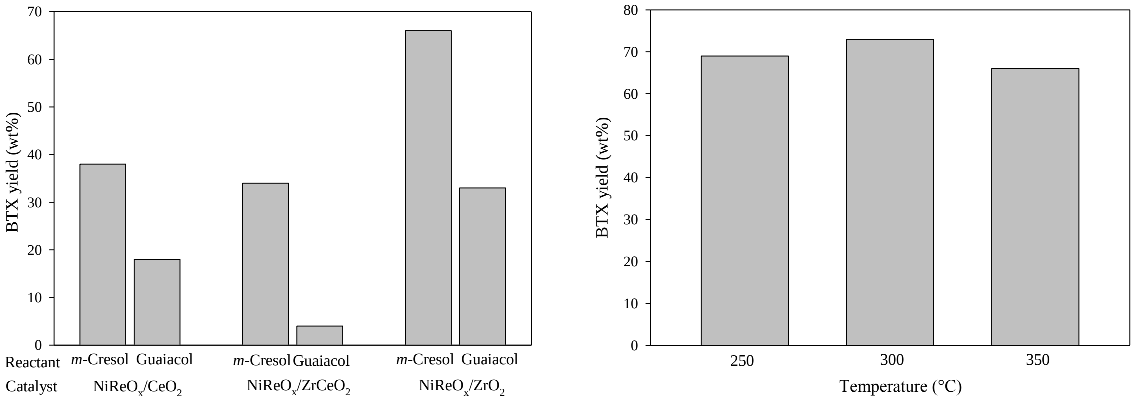
Monoaromatic hydrocarbons of benzene, toluene and xylenes (BTX), which are the building blocks for the petrochemical industry, are currently produced from fossil sources mostly through catalytic reforming of naphtha in petroleum refineries. The increasing demand for BTX products and the rapid depletion of fossil resources necessitate to find alternative sources for sustainable and renewable production of BTX. The lignin fraction of lignocellulosic biomass with its polyaromatic structure is considered as a potential renewable aromatic resource. Hydrodeoxygenation (HDO) including the reactions of hydrogenation and dehydration is a commonly used method for efficient deoxygenation of the lignin-derived phenols to aromatic hydrocarbons. So far, bifunctional catalysts of zeolite-supported transition metals have been largely used for HDO of phenolics (transition metals for hydrogenation and zeolites for dehydration). However, zeolites are not suitable catalyst supports for mild-condition HDO of phenolics due to the strong adsorption of phenolics on zeolite acid sites which results in catalyst deactivation and low deoxygenation degree. Therefore, the purpose of this study is to use acid sites other than zeolites to achieve high catalytic HDO efficiency under mild conditions of atmospheric pressure and low reaction temperatures.

2. Methods

The catalysts used in this study were Ni/HBeta, $NiReO_x/ZrO_2$, $NiReO_x/CeO_2$ and $NiReO_x/ZrCeO_2$. HBeta was prepared by calcination of the ammonium form of Beta zeolite (Zeolyst, CP814C, SiO_2/Al_2O_3 molar ratio: 38) at 550 °C for 12 h. Zirconia was synthesized through a supercritical synthesis procedure. Ni/HBeta was prepared through incipient wetness impregnation of HBeta with an aqueous solution of $Ni(NO_3)_3.6H_2O$. $NiReO_x/ZrO_2$, $NiReO_x/CeO_2$ and $NiReO_x/ZrCeO_2$ were obtained by incipient wetness co-impregnation of the supports with an aqueous solution containing both $Ni(NO_3)_3.6H_2O$ and NH_4ReO_4. After impregnation, all catalysts were dried first at 60 °C for 12 h and then at 110 °C for further 12 h, with subsequent calcination at 550 °C for 12 h with a heating ramp of 3 °C min^{-1}. X-ray diffraction, nitrogen isothermal (-196 °C) adsorption-desorption, NH_3-TPD and TEM were used for characterization of catalysts. The catalytic reactions were conducted using a micro-scale analytical pyrolyzer (Rx-3050TR, Frontier Laboratories Ltd.) containing two heating zones in series: the first zone for vaporization and the second zone for catalytic HDO. In each experiment, 1 µl *m*-cresol or 0.9 µl guaiacol was injected to the first zone by a syringe. The temperature of first zone was set at 300 °C. The vapors from the first zone were conducted to the second zone where a fixed bed of catalyst (40 mg) was placed on a plug of quartz wool. The temperature of second zone was varied in the range of 250-350 °C. Hydrogen (100 ml min^{-1}) was used as carrier gas, and all runs were conducted at atmospheric pressure. Prior to the reaction, in-situ reduction of catalyst was carried out at 350 °C for 1 h. The upgraded vapors were passed through a heated interface (320 °C) to a gas chromatograph (7890A, Agilent Technologies), separated in a capillary column (UA-5, 30 m length × 0.25 mm i.d. × 0.25 µm film thickness), and detected by MSD and FID for qualitative and quantitative analysis.

3. Results and discussion

As shown in Fig. 1a, $NiReO_x/ZrO_2$ revealed a considerably higher HDO activity compared to $NiReO_x/CeO_2$ and $NiReO_x/ZrCeO_2$; $NiReO_x/ZrO_2$, $NiReO_x/CeO_2$ and $NiReO_x/ZrCeO_2$ gave BTX yields of 66, 38 and 34 wt% from HDO of *m*-cresol, and 33, 18 and 4 wt% from HDO of guaiacol, respectively. This is due to the better dispersion of nickel particles on the surface of zirconia support which facilitates the Ni catalyzed hydrogenation. Furthermore, Fig. 1b illustrates that the HDO activity of $NiReO_x/ZrO_2$ was not decreased by a temperature reduction from 350 to 250 ℃, indicating that this catalyst was remained active at the low reaction temperature of 250 ℃. However, Ni/HBeta as a zeolite supported catalyst showed almost no activity at 250 ℃. One reason for this is the high acid strength of zeolites which results in strong adsorption of phenolics on zeolite acid sites, and this adsorption is enhanced by a decrease of reaction temperature due to its exothermic nature. The other reason can be the microporous structure of HBeta which limits the diffusivity of phenolic molecules, and this diffusion limitation is intensified by a temperature reduction because of the increased energetic barrier for phenolics to diffuse into the narrow pores of Beta zeolite at lower temperatures. In contrast, zirconia with mild acidity and mesoporous channels causes much lower phenolic trapping. Besides, the strong interaction between the oxygen atoms of phenolics and the zirconia oxophilic sites facilitates the activation of phenolic compounds on the catalyst surface. Therefore, zirconia is an appropriate catalyst support to be used for mild-condition HDO of phenolics due to its mild acidity, mesoporousity and oxophilicity. Furthermore, the mild acidity induced by rhenium oxide (confirmed by NH_3-TPD) showed a remarkable dehydration activity, leading to high HDO efficiency (confirmed by the comparison of the HDO activities of Ni/ZrO_2 and $NiReO_x/ZrO_2$ (data are not shown)).



(a) (b)

Figure 1. BTX yield obtained by HDO of (a) *m*-cresol and guaiacol at 350 ℃, (b) *m*-cresol over $NiReO_x/ZrO_2$ at different temperatures (reduction temperature, 350 ℃; pressure, 1 atm; reactant, 1 µl; catalyst, 40 mg; H_2 flow, 100 ml/min).

4. Conclusions

$NiReO_x/ZrO_2$ is a highly potential catalyst for mild-condition HDO of lignin-derived phenolics. In contrast to a zeolite-supported catalyst like Ni/HBeta, $NiReO_x/ZrO_2$ remained active at temperatures as low as 250 ℃ as a result of its mild acidity, mesoporosity, oxophilicity and enhanced dispersion of Ni. Mild-condition HDO of lignin-derived phenolics using such catalyst is a potential method for cost-effective production of bio-based BTX.

Keywords
Hydrodeoxygenation; Lignin-derived phenolics; BTX aromatics; Mild acidity

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