

## Pt-Fe<sub>2</sub>O<sub>3</sub> based catalysts for anisole hydrodeoxygenation

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The depletion of fossil fuels along with massive emissions of greenhouse gases (GHG) emissions are serious issues facing society nowadays. Considering that almost a quarter of fossil fuel consumption is associated with the transport sector, the scientific community has focused a great deal of its research to the quest of alternative environmentally friendly technologies and products with minimum GHG emissions derived from renewable energy sources. In this context, lignocellulosic biomass has demonstrated a great potential, since from its fast pyrolysis a bio-oil with interesting properties can be obtained to be used as liquid fuel for internal combustion engines. However, this bio-oil contains a considerable percentage of water and oxygenated compounds that impoverishes its quality making it unstable, acid, corrosive and with low calorific value. Thus, hydrotreating technologies like hydrodeoxygenation reaction are essential to upgrade bio-oil by means of removing oxygen from oxygenated compounds.

The hydrodeoxygenation reaction usually takes places at high temperature and moderate hydrogen pressure, in the presence of a bifunctional catalyst that, on the one hand, promotes the oxygen removal with acid sites and, on the other hand, activates the hydrogen molecule in metallic hydrogenating sites. Regarding the latter function, noble metals like Pt, Ru or Pd have demonstrated outstanding hydrogenation capability even with low metal loading. To maximise metal dispersion, these noble metals are supported on mesoporous solids that in turn provide the moderate acidity necessary to remove oxygen heteroatom.

In this work, supported Pt on Fe<sub>2</sub>O<sub>3</sub>-containing SBA-15 were tested in the HDO reaction of anisole at 275 °C and 30 bar in a fixed-bed reactor in continuous down flow. Pt was added in 1 wt. % as the hydrogenating metal and different Fe<sub>2</sub>O<sub>3</sub> loadings (5 wt. %, 15 wt. % and 30 wt. %) as the oxyphilic and acid counterpart.

The catalytic tests in Figure 1 showed that the catalysts activity followed the trend: Pt-15Fe<sub>2</sub>O<sub>3</sub>/SBA > Pt-30Fe<sub>2</sub>O<sub>3</sub>/SBA > 30Fe<sub>2</sub>O<sub>3</sub>/SBA > Pt/SBA > Fe<sub>2</sub>O<sub>3</sub>/SBA > 15Fe<sub>2</sub>O<sub>3</sub>/SBA, which suggests a synergistic effect between Pt and Fe<sub>2</sub>O<sub>3</sub>.

The catalyst showing the best HDO conversion, Pt-15Fe<sub>2</sub>O<sub>3</sub>/SBA, was also in-situ reduced before reaction in order to study the influence of hydrogen pre-treatment, resulting in an improvement in total conversion of 80%. Moreover, reaction products were exclusively deoxygenated ones, with cyclohexane and benzene selectivity of 60% and 10%, respectively.

In order to study pressure influence, HDO reaction of anisole was performed at 275 °C at 15 bar and 30 bar, with HDO conversions of 29% and 49%, respectively.

Likewise, temperature contribution was also studied carrying out HDO reaction of anisole at 30 bar at 275 °C and 300 °C, showing the latter an increase of 16% in HDO conversion and 13% and 25% increase in cyclohexane and benzene selectivities, respectively.

**Figure 1:** HDO conversion for Pt-Fe<sub>2</sub>O<sub>3</sub> supported catalysts

To fully understand the catalytic behaviour, the catalysts were characterized by nitrogen adsorption-desorption isotherms (N<sub>2</sub> ads-des, S<sub>BET</sub>), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), X-ray powder diffraction (XRPD), thermoprogrammed hydrogen reduction (TPR-H<sub>2</sub>) and elemental analysis (CNH).

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