**Zeolite-supported FeMoP catalysts for the hydrodeoxygenation of a raw black poplar bio-oil towards hydrocarbons**

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**Highlights**

* Zeolite supports enhance dehydration/condensation reactions
* The acidity features of the catalyst play a primary role in their performance
* The FeMoP/ZSM5 catalyst is the most selective towards aromatics

**1. Introduction**

In the recent years, bio-oil has been attracting great research attention given its potential as a sustainable source of fuels and platform chemicals [1]. When aiming for the production of chemicals (*i.e.*, aromatics, phenolics), hydrodeoxygenation (HDO) has proven to be a versatile approach for achieving an efficient conversion of the most refractory bio-oil components [2]. In this context, phosphided catalysts are known to provide high HDO activities [3]. However, no studies with raw bio-oil are reported to date.

**2. Methods**

The supported FeMoP catalysts (20 wt. %) were prepared by impregnation of three zeolites of different topology (*i.e.*, HZSM-5, H and HY) with an aqueous citric acid solution in which were previously added Fe, Mo and P. A “bulk” FeMoP catalyst was also prepared as a reference. The catalysts were characterized by means of ICP-MS, N2 adsorption-desorption, NH3-TPD, and XRD. The bio-oil hydrodeoxygenation runs were carried out in a downflow fixed bed reactor described elsewhere [2] at 450 °C, 65 bar, space time, 0.15 gcath g-1bio-oil; 90 ml min-1 H2; and time on stream, 0-8 h. Organic liquid products were assessed through two-dimensional Gas Chromatography coupled with Mass Spectrometry (GCxGC-MS).The water content in the aqueous product phase was quantified by Karl-Fischer titration.

**3. Results and discussion**

In contrast to the negligible specific surface of the bulk FeMoP, the FeMoP/ H and FeMoP/HZSM-5 catalysts showed a specific surface of 356-366 m2 g-1 (Table 1), with this value being significantly higher for the FeMoP/HY catalyst (750 m2 g-1) due to a much higher microporosity. The latter catalyst was also the most acidic (1.11 mmolNH3 g-1) and with a higher proportion of medium-strong acidic sites (66 %). The FeMoP/ H catalyst was the least acidic (0.27 mmolNH3 g-1) with a higher contribution of weak-medium acidic sites (35 %).

**Table 1**- Physico-chemical properties of the fresh catalysts

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | **FeMoP/H** | **FeMoP/HZSM-5** | **FeMoP/HY** | **Bulk FeMoP** |
| SBET (m2 g-1) | 365.9 | 355.9 | 750.3 | 6.0 |
| Vmicropore (cm3 g-1) | 0.084 | 0.082 | 0.207 | 0.002 |
| Total acidity (mmolNH3 g-1) | 0.27 | 0.57 | 1.11 | 0.24 |
| Weak-medium (%) | 65 | 47 | 34 | 48 |
| Medium-strong (%) | 35 | 53 | 66 | 52 |

In Figure 1a, an increase was observed in carbon products upon incorporating the zeolite support (22.8-27.0 wt%) in contrast to the bulk FeMoP phase (16.5 wt%), due to the enhancement of dehydration/condensation reactions performed by the zeolites. The highest total acidity and stronger nature of the acidic sites of the FeMoP/HY zeolite enhanced HDO reactions (higher amount of water being formed), leading to lower carbon product yields. On the other hand, the highest carbon product yields were attained with the FeMoP/HZSM-5 catalyst, likely due to a compromise between total acidity and a moderate content of stronger acidic sites. Moreover, FeMoP/HZSM-5 catalyst is also the most selective towards phenol and phenolic compounds (Figure 1b, 12.6 wt% total phenolics), as well as aromatics (13.5 wt% total aromatics).



**Figure 1.** a) Total product yields (in a wet basis) and b) carbon product lump yields (in a dry basis) obtained with the different zeolite-supported catalysts and bulk FeMoP at TOS = 8 h.

**4. Conclusions**

The total acidity of the catalyst and an equilibrium between weak-medium and medium-strong acidic sites are the dominant catalyst property on the HDO of a raw bio-oil towards hydrocarbons, with shape selectivity playing a secondary role. The FeMoP/HZSM-5 catalyst was the most suitable, providing the highest yield of total carbon products, and also the most selective towards the formation of aromatics, phenol and phenolic components.

**References**

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