

Guaiacol hydrodeoxygenation over Ni-Fe supported on Nb₂O₅ and SiO₂ catalysts

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Significance and Relevance

Bio-oil upgrading is one of the key processes for enabling drop-in biofuel production by co-processing or BTL technologies. This contribution will help with the development of active, stable, and selective catalysts for bio-oil upgrading and/or *ex-situ* catalytic fast pyrolysis. The Nb₂O₅-supported catalysts developed in this work demonstrate to be efficient in the HDO reaction in both gas and liquid phases.

Preferred and 2nd choice for the topic: Green chemistry and biomass transformation, renewable resources conversion Preferred presentation: Oral preferred

Introduction and Motivations

The conversion of biomass in fuel is being considered a potential process for generation of sustainable energy. Fast pyrolysis of biomass produces bio-oil, which has to upgrade due to its high viscosity, corrosiveness, low heating value, high water content, and thermal instability of components [1]. Hydrodeoxygenation (HDO) is one of the available upgrading routes, which occurs in the presence of a solid catalyst and hydrogen as reactant at moderate temperature (300-600°C) [2]. Previous studies revealed the optimum thermodynamic condition [3] and the high stability and selectivity towards phenol in the HDO of guaiacol, a model compound representative of bio-oils derived from lignin, over Pt/Nb_2O_5 catalyst. This study reports the reaction over Ni-Fe/Nb₂O₅. Data were also collected for reactions over a traditional support, SiO2, for comparison

Materials and Methods

Niobium acid (HY-340/CBMM) and SiO₂ (AEROSIL-50, Degussa) were calcined at 773 K during 4 h to produce the supports Nb₂O₅ and SiO₂. Monometallic (5 wt. % Ni or 2 wt.% Fe) and bimetallic (5 wt. % Ni and 2 wt.% Fe) catalysts were prepared by incipient wetness impregnation of the supports with an aqueous solution of Ni(NO₃)₂.6H₂O and/or Fe(NO₃)₂. The samples were characterized by TPR, UV-Vis, X-ray diffraction (XRD), N₂ physisorption, and H₂-TPD. HDO of guaiacol catalytic tests were carried out in a fix-bed glass reactor at atmospheric pressure and vapor phase at conditions without mass transfer restrictions.

Results and Discussion

All the catalysts exhibited good stability after 50 hours on-stream, figure 1. The monometallic catalysts supported on Nb₂O₅ had their activities higher than the SiO₂-supported ones. The synergism between Ni or Fe and NbOx species probably enables oxophilic sites formation which enhances direct deoxygenation (DDO) reactions, since the main products observed in Table 1 are formed by them [3]. Moreover, over iron the DDO reaction towards phenol was higher with the Nb₂O₅ than SiO₂, while over nickel the formation of veratrole was enhanced. On the other hand, the selectivity has not changed when over the bimetallic catalysts. However, it was remarkable that the bimetallic catalysts activities were higher than the monometallic ones, which denotes a synergism between the metal



phases over both supports. This result is due to the new sites formation as indicated by the TPR, UV-Vis and H_2 -TPD results.



Figure 1. Gas-phase guaiacol HDO (H_2 /Guaiacol = 8) at 300 °C and atmospheric pressure over the Ni-Fe supported catalysts.

Catalyst	Guaiacol Conv.(%)	Selectivity (%)				
		Phenol	Catechol	o-Cresol	Veratrol	
Ni5%/SiO ₂	10.1	53.5	14.1	22.9	9.5	
Ni5%/Nb ₂ O ₅	23.5	49.9	6.2	25.2	19.0	
Fe5%/SiO ₂	22.4	49.3	13.5	20.6	16.6	
Fe5%/Nb ₂ O ₅	49.6	55.8	10.8	18.2	15.4	
Ni5%-Fe2%/SiO ₂	79.6	66.3	7.1	14.8	11.8	
Ni5%-Fe2%/Nb ₂ O ₅	50.3	60.1	9.3	15.5	15.1	

Table 1.	Guaiacol	conversion	and selectivity	after 50 hs.	TOS –	HDO (300 °C	, 1 k	oar)
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Acknowledgements

This work was supported by CNPq, CAPES, PETROBRAS, EMBRAER, SUZANO, KLABIN and FAPEMIG,

References

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