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Hydrodeoxygenation of lignin-derived compounds using Ru catalysts.

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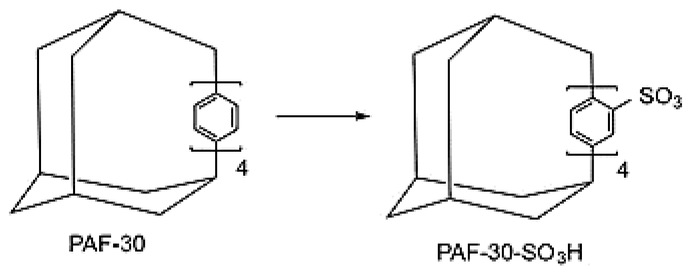
Lignin is one of the most widespread biopolymers and renewable energy source. The phenolic compounds with hydroxy-, carbonyl- or carboxylic groups are formed by the decomposition of lignin and contribute to 25-30% of bio-oil. These components give bio-oil acidic properties and low stability therefore it should be upgraded to obtain valuable chemicals or fuel grade hydrocarbons.

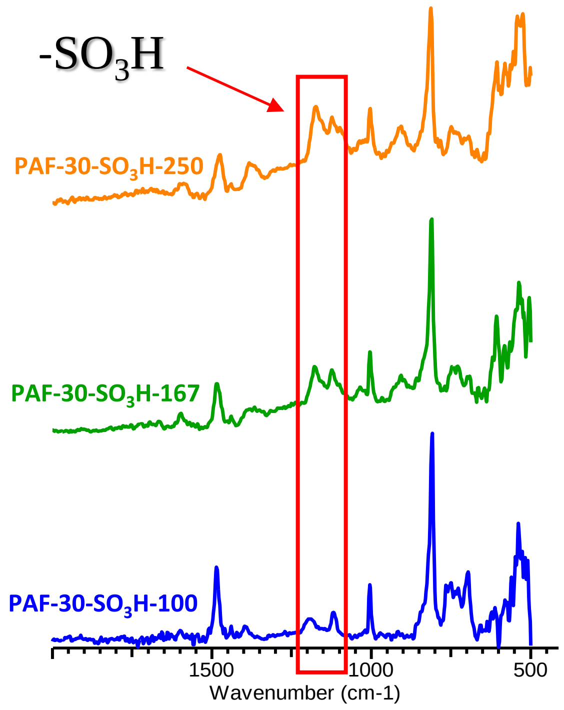
Heterogeneous catalysts play a central role in the efficient conversion of bio-oil to fuel and chemicals. Commercial sulfide catalysts can be used for the hydrodeoxygenation process. They are low cost, sulfur-resistant, but can be oxidize to oxides and demonstrate low activity. Catalysts based on noble metals are more expensive, but more active and can be used in the presence of a significant amount of water. The support also plays an important role in the properties of the catalyst. The main requirements for carriers are good stabilization of active sites, the availability of these for substrates, the possibility of surface modification and stability under reaction conditions.

Some of new carbon materials possess distinctive physicochemical properties such as high specific surface area, superior stability, tunable surface functional groups and variable porosity. For example, porous aromatic frameworks (PAFs) - polymer with a rigid structure consisting of aromatic rings connected to each other. These materials are attracting more and more attention of researchers due to their large surface area, the possibility of varying the pore size, and high thermal and mechanical stability. The aromatic structure of such carriers opens up the possibility of their modification with functional groups and effectively stabilizes nanoparticles.

The aim of current work was to study the activity of Ru catalysts based on PAFs, which were prepared by impregnation of PAFs with ruthenium chloride and subsequent reduction by sodium borohydride. In order to study the effect of the support and its acidity, different materials were studied: non-modified porous aromatic framework - PAF-30 and ones modified with sulfo-groups - PAF-30-SO_3H. The properties of the obtained catalysts were studied in the hydrogenation of guaiacol, catechol and veratrole at temperature of 250 °C and hydrogen pressure of 3.0 MPa in the presence of isopropyl alcohol. It was found that the presence of acid sites leds to a significant increase of yield deoxygenation products - cyclohexane and cyclohexanol.

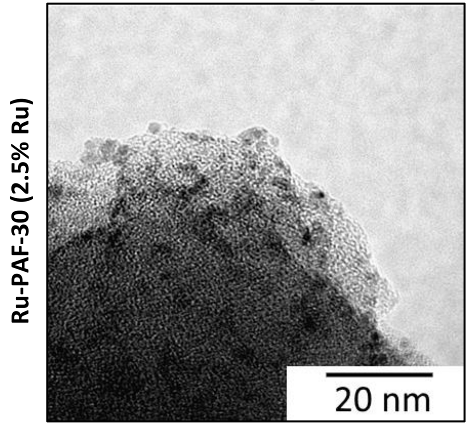
Materials modification and characterisation

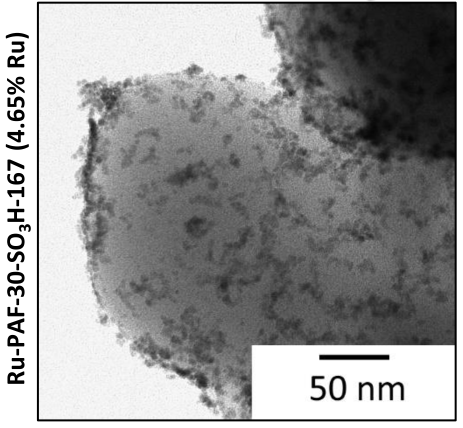




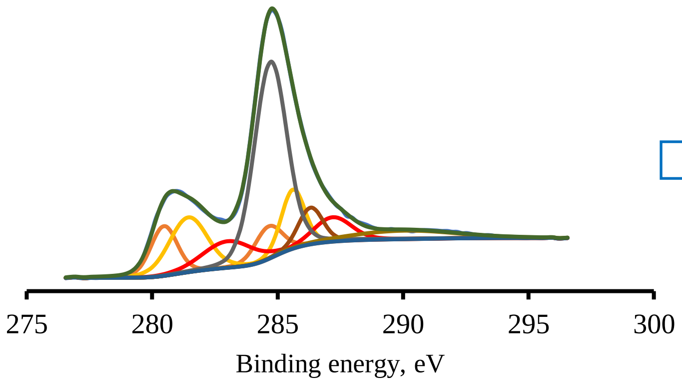
Materials	S_{BET}, м²/г	S, wt. %
PAF-30	489	-
PAF-30-SO_3H-100	442	2.4
PAF-30-SO_3H-167	198	4.9
PAF-30-SO_3H-250	121	7.8

Ruthenium catalysts based on PAF-30 and PAF-30-SO_3H-167





Ru-PAF-30-SO_3H-167 (4.6% Ru – 4.9% S)

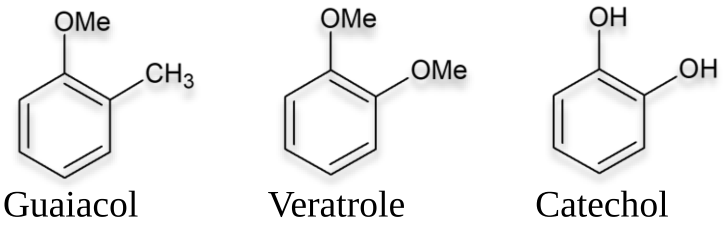


Ru^0 – 28%

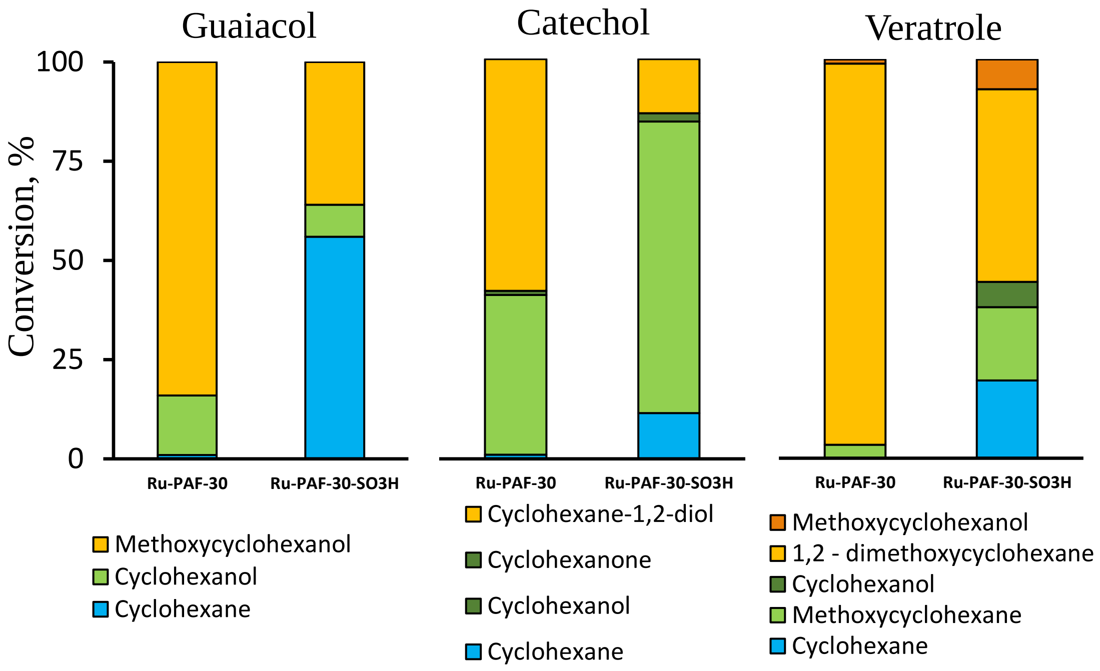
RuO_2 – 44%

RuO_3 – 28%

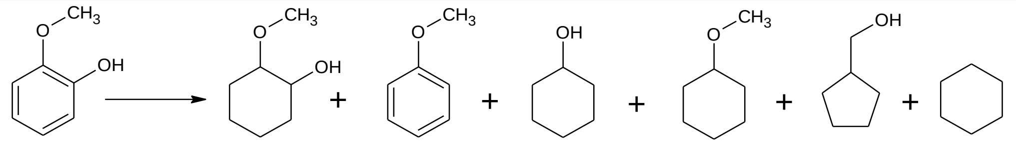
Model substrates



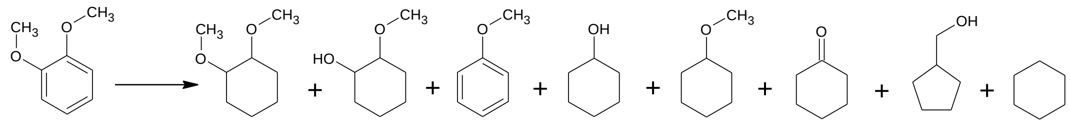
The influence of –SO_3H



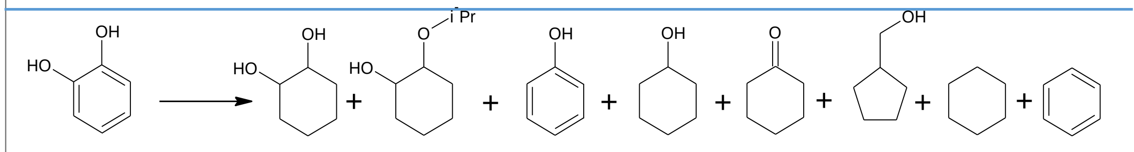
Catalysts with different contents of ruthenium and sulfo-groups



1% Ru – 2.4% S	53	-	22	1	2	13
4.8% Ru - 2.4% S	56	-	26	-	-	2
4.6% Ru – 4.9% S	35	2	8	-	-	55
4.7% Ru – 7.8% S	-	4	7	-	-	19



1% Ru – 2.4% S	53	21	-	7	8	-	-	5
4.8% Ru - 2.4% S	66	22	-	7	2	-	-	3
4.6% Ru – 4.9% S	46	7	-	6	18	-	2	18
4.7% Ru – 7.8% S	2	2	2	-	-	4	11	57



1% Ru – 2.4% S	37	3	12	15	-	1	15	-
4.8% Ru - 2.4% S	47	13	4	24	1	1	8	2
4.6% Ru – 4.9% S	13	-	-	73	1	1	12	-
4.7% Ru – 7.8% S	-	-	-	-	5	-	-	-

Reaction conditions: substrate (0.4 mmol); catalyst (5 mg),; isopropyl alcohol (0.5 ml); 250 °C, 2h, 30 atm H_2