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Kinetics of phenol hydrodeoxygenation over a Cu/SBA catalyst

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Highlights

- Cyclohaxene and Cyclohaxene are the main products of phenol hydrodeoxygenation over Cu/SBA catalyst.
- Selectivity to cyclohaxene is greater than the selectivity to cyclohaxane.
- A satisfactory fitting of the kinetic model proposed to the experimental data was achieved.
- The phenol hydro-deoxygenation reaction scheme over Cu/SBA was investigated.

1. Introduction

Bio-oils produced by pyrolysis or liquefaction of the lignocellulosic biomass, is considered as an alternative to petroleum-based sources for a wide range of fuels and high value-added chemicals. Due to the high content in oxygenate compounds, bio-oil needs to be up-graded by removing oxygen. The most widely used process for the bio-oil upgrading is HDO. The phenolic compounds of bio-oil have received considerable attention because of their low reactivity in HDO process and they are used as bio-oil representative model compounds [1]. A range of heterogeneous materials have been tested as catalyst in phenol HDO process. The main objective of this work is the study of the phenol hydrodeoxygenation over a laboratory prepared catalyst Cu/SBA and the kinetic modeling with power law kinetics.

2. Methods

The experiments were carried out in a mini scale unit, and a spiral bed reactor 2.1 mm in internal diameter. The reactor was loaded with a laboratory prepared catalyst Cu/SBA in the form of small granules 0.160-0.315 mm. Two different compositions of Cu were tested 1.4% wt and 11 wt % in Cu. The catalyst mass loaded was 0.19 g and 0.25 g for the low and high content of copper respectively. The liquid feed consisted of 1% wt phenol diluted in n-hexane. Phenol hydrotreatment experiments have been conducted at pressure range 20-40 bar, weight hourly space velocities 11-32 h^{-1} and temperatures 150-230 ^{o}C. The experiments at high enough gas to liquid flow rate ratio to eliminate the external mass transfer effects. Standard experiments were repeated at regular time intervals for the determination of the catalyst activity level. The catalyst was reduced in situ hydrogen atmosphere and the thermo-program reached a maximum temperature of 350 ^{o}C.

For the investigation of phenol hydrodeoxygenation reaction scheme to products, the experimental study involves hydroprocessing of the possible intermidiate aromatic and cyclic unsaturated products from the phenol hydrogenation as benzene, cyclohexanol and cyclohexanone at the same conditions.

3. Results and discussion

The main products of the phenol hydrodeoxygenation over the supported Cu/SBA catalyst is cyclohexene and cyclohexane, appearing full selectivity to deoxygenated products. The selectivity to cyclohexene is greater in comparison to cyclohexane at the tested conditions.

The experiments with the possible intermidiate aromatic and cyclic unsaturated products as benzene, cyclohexanol and cyclohexanone have shown that the main path of the phenol deoxygenation is the direct deoxygenation of phenol to cyclohexene with dehydration and partial addition of H_2, followed by hydrogenation to cyclohexane.

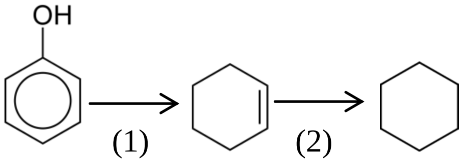

Figure 1. Hydrodeoxygenation scheme of phenol over Cu/SBA catalyst at the tested conditions.

The decrease of Cu content in the catalyst from 11 wt % to 1.4 wt %, have shown about 11 times lower activity to phenol conversion, higher selectivity to cyclohexene and lower selectivity to cyclohexane.

A power law technical of n-th order with respect to phenol or cyclohexexene and m-th order with respect to H_2 was assumed for the kinetic modeling of the phenol towards cyclohexene and cyclohexane. The fitting of the kinetic model to the experimental data is presented in Figure 2.

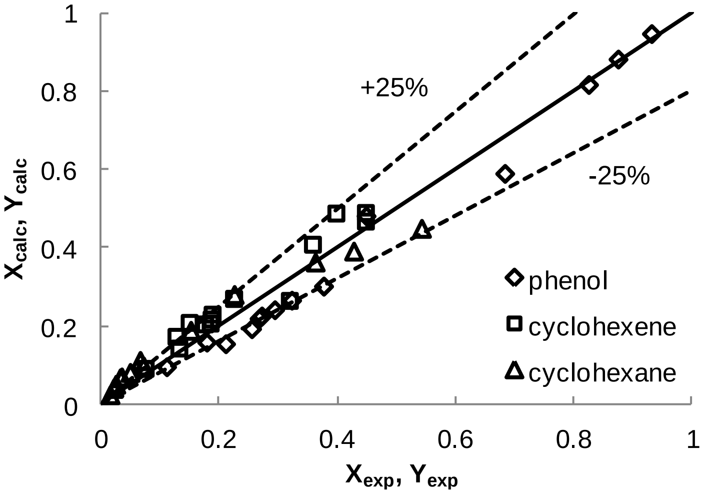

Figure 2. Fitting of the kinetic model to the experimental data.

The fitting of the kinetic model to the experimental data of phenol conversion and cyclohexene and cyclohexane yields is satisfactory.

4. Conclusions

The reaction scheme of the phenol hydro-deoxygenation over Cu/SBA catalyst at the tested conditions was investigated and a technical kinetic model of the phenol conversion to cyclohexene and cyclohexane is proposed with a satisfactory fitting to experimental data.

References

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Keywords
Phenol, hydrodeoxygenation, Cu/SBA catalyst, kinetic modeling