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Research Article

Catalytic Hydrogenation Reaction of Phenol to Cyclohexanol Using Supported Ruthenium Catalysts

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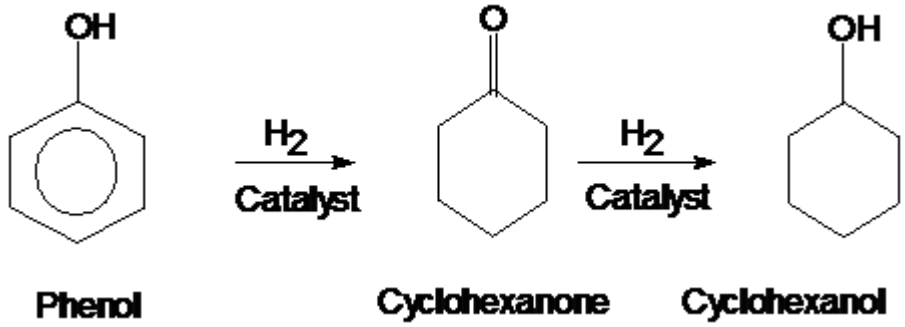
Abstract: Chlorinated organics released in aqueous effluent streams from various industries cause a major environmental concern. A systematic study of hydrogenation reaction of phenol to cyclohexanol over a Ruthenium supported catalyst was carried out. Different supports like alumina, silica, C and titania were used as Ruthenium support. Different kinetic parameters such as speed of agitation, temperature, pressure, catalyst concentration with respect to conversion of phenol were studied. The experimental conditions where maximum conversion of phenol obtained were determined and the conditions were used for phenol conversion from industrial waste water samples.



Keywords: Chlorinated organics , Ruthenium , phenol, cyclohexanol

INTRODUCTION

The hydrotreatment processes are used for reduction of pollutants from industrial effluents. These processes include catalytic hydrogenation reactions for protection of environment[1-4]. In the present investigations an attempt has been made to understand and demonstrate a bench scale catalytic process for the hydrotreatment of industrial effluents containing phenol under suitable conditions using ruthenium supported catalysts. Hydrogenation reaction of phenol to cyclohexanol was carried out at mild conditions. As LD_{50} value of cyclohexanol is much lower than phenol [5], cyclohexanol is more environmentally friendly product.

EXPERIMENTAL

Materials

All chemicals and solvents used in this study were A. R. grade from s. d. fine and Merck.

Experimental procedure

The precipitation reduction method was adapted for the catalyst preparation [6]. A stock solution of the phenol was prepared in deionised water. Absence of any chloride ions was confirmed by using $AgNO_3$ solution. A fixed quantity of the catalyst**,** 50 ml of the above stock solution and an additive, if required, were introduced in the 100 ml Parr High Pressure hastelloy HC-276 autoclave (Parr Instrumental Co. USA). The autoclave was then assembled. To remove the air present in the reactor, the autoclave was purged with hydrogen. Impeller speed was adjusted to 1200 rpm and heating was started. When the desired experimental temperature was reached, a sample was withdrawn (zero time sample). Then hydrogen was charged into the reactor so as to reach the desired partial pressure. Any drop in hydrogen pressure was made up periodically, so that the system could be deemed as isobaric.

Analysis

The intermediate samples taken were filtered to obtain clear solutions and they are analysed on Gas Chromatography. After the reaction is complete i.e. complete conversion of phenols the final reaction mixture is analysed for chloride contents.

RESULTS AND DISCUSSIONS

Following kinetic parameters were studied:

Effect of catalyst support

Various catalyst supports such as Al_2O_3, TiO_2, SiO_2 and carbon were used for the reaction. The hydrogenation reaction was carried out at the temperature of 373 K under hydrogen partial pressure of 2 MPa. The results of % Conversion of phenol after 60 mins are presented in Table 1. All ruthenium supported catalysts were found to be equally effective. However, TiO_2 was suitable support as it was stable catalyst during wet oxidation of oxygenated pollutants and phenol in an alkaline medium. Hence a catalyst consisting of 5 % Ru/TiO_2 was selected for further studies.

Table 1 Effect of catalyst support

Catalyst support	% Conversion of phenol
5 % Ru /Al_2O_3	95.2
5 % Ru / C	97.3
5 % Ru / SiO_2	100.0
5 % Ru / TiO_2	99.6

Effect of speed of agitation

The effect of agitation on the conversion of phenol was studied (Figure 1). The maximum conversion was observed at 1200 rpm. Hence 1200 rpm was used as speed of agitation for further study.

Effect of Temperature

Effect of temperature on conversion of phenol was investigated over the range of 323 – 373K under the hydrogen partial pressure of 2.07 MPa. The catalyst was effective even at lower temperature. The maximum conversion was observed at 373K.

Effect of pH

The reaction was carried out at different pH of 4, 7 and 12 (Figure 3). It was observed that the catalyst was more effective at basic pH than acidic.

Effect of Hydrogen partial pressure

The effect of hydrogen partial pressure on phenol hydrotreatment reaction was investigated over the hydrogen partial pressure range of 0.69 – 2.07 MPa at 423 K. From Figure 4, it can be seen that the rate of reaction was increasing with an increase in hydrogen partial pressure.

Effect of Catalyst quantity

Different catalyst quantity 1.0 - 2.5 g/L was used (Figure 5) for reaction it was observed that % conversion was increasing with the increase amount of catalyst.

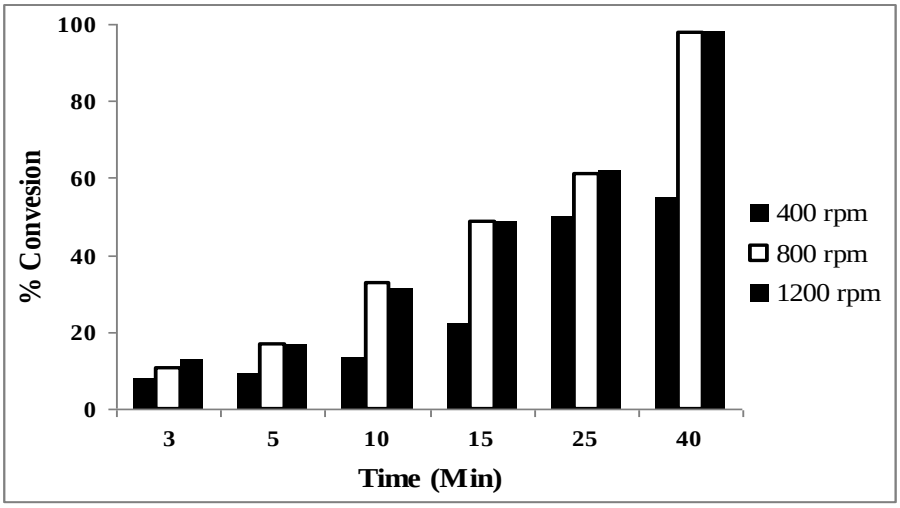


Figure 1. Effect of speed of agitation

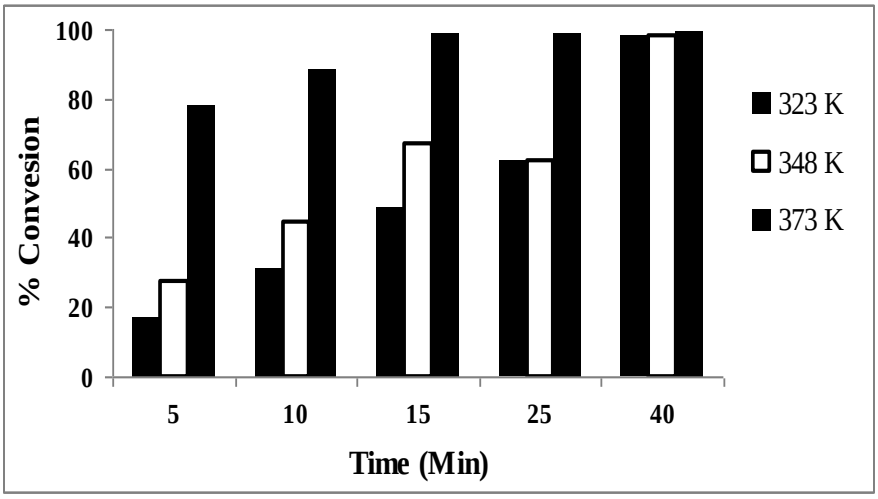


Figure 2. Effect of Temperature

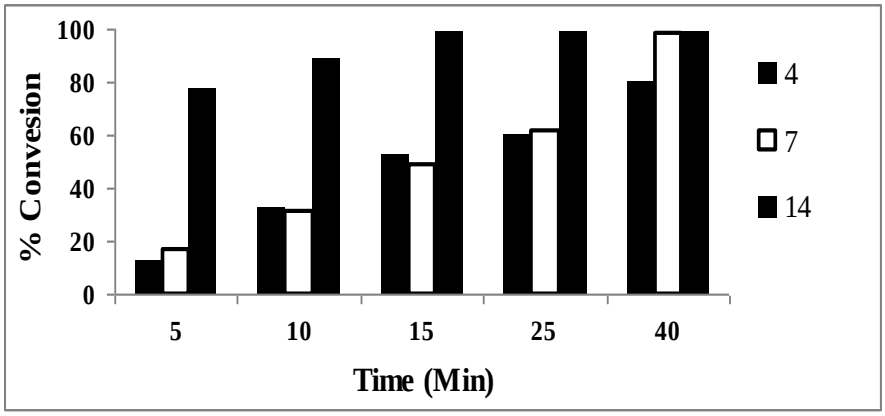


Figure 3. Effect of pH

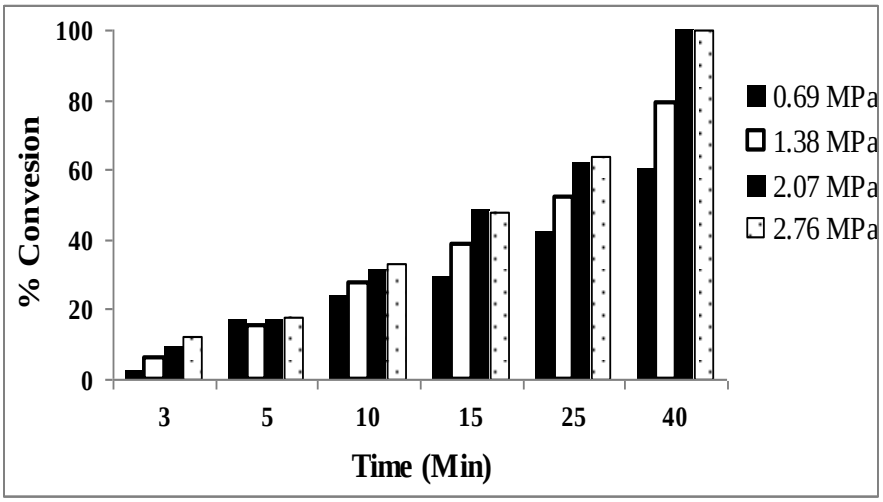


Figure 4. Effect of Hydrogen partial pressure

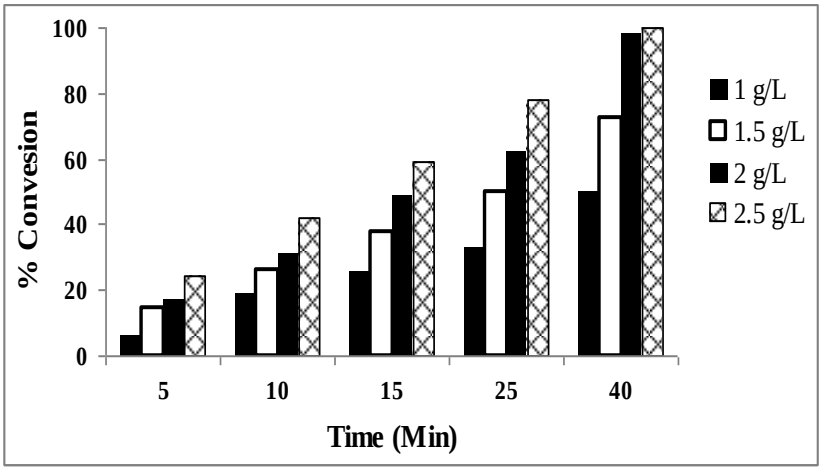


Figure 5. Effect of Catalyst quantity

Application of the method to Industrial Waste water sample

Samples of industrial waste water were used for hydrogenation reaction of phenol. The results are as follows:

Table 2 Application of the method to Waste water sample

Waste water sample	% Conversion of phenol
Sample 01	99.9
Sample 02	99.9

Temperature : 323 K

Hydrogen partial pressure : 2.07 MPa

Speed of agitation : 1200 rpm

Catalyst : 5% Ru/ TiO_2

Reusability of catalyst

The catalyst activity for hydrodechlorination reaction remained constant even after three recycles.

CONCLUSIONS

An activated 5% Ru/ TiO_2 catalyst can be successfully used for hydotreatement of industrial waste water to remove phenol at 323 K and 2.07 MPa hydrogen pressure. Hydrogenation reaction of phenol can be successfully carried out using supported ruthenium catalyst to make the stream more ecofriendly.

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