NORIT CARBON AS CATALYST: ESTERIFICATION OF BENZOIC ACID WITH ALCOHOLS.

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Introduction

Solid and liquid acid catalysts are used extensively in the petroleum and chemical processing industries, and there is a significant opportunity to improve many of these processes by replacing the current liquid-phase systems with solid acid catalysts. The liquid acid systems, such as H_2SO_4, $AlCl_3$, and BF_3, for example, are very corrosive and present critical waste disposal problems. Many acid solids have been used in this type of reactions (zeolites, clays, among others).

This study presents the application of and acid activated carbon as catalyst in a model acid catalyzed reaction as the esterification of organic acids with alcohols [1, 2].

Experimental

Surface treatment.

A commercial microporous activated carbon RX-1 Extra Norit (Norit N.V.) denoted as N, was treated with HNO_3. The mixture (carbon and acid) was stirred and heated at 80 °C until almost all the acid was evaporated. The ratio carbon/ 10% HNO_3 was 1g/ 10 ml. The procedure was repeated three times. The resulting carbon (NN) was washed with bidistilled water using a soxhlet apparatus until reach pH=6. This treatment is well know as very efficient for introducing oxygen surface groups over activated carbons [3-5].

Specific surface area.

The specific surface areas were determined by CO_2 adsorption at 273 K, taking 0.170 nm_2 for the cross-sectional area of the CO_2-adsorbed molecule. An automatic Micromeritics ASAP 2000 volumetric system was used to obtain the corresponding gas adsorption isotherms. The accuracy of this measurements is at least of 5%.

Temperature programmed desorption (TPD).

The TPD experiment was performed in an oven under a flow (100ml/min) of helium. The heating rate was 10°C/min to 900°C. The gases evolved were analyzed by a mass spectrometer (Balzers Thermostar) in MID (multiple ion detection) mode.

Catalytic system.

A mixture of benzoic acid (5 mmol) and ethanol (4ml) was mixtured and heated up to 75°C in a Pyrex flask. then, o.0 g of nitrated carbon was added and the reaction time started, following the reaction by GC.

Results and discussion

The specific surface areas determined from CO_2 adsorption isotherms by Dubinin-Radushkevich method [6] are given in Table 1. No significant differences are observed so, the surface oxidation with HNO_3 do not affect the porosity of the carbon.

Table 1. Specific Surface Areas

Sample	S_{co2} (m^2/g)
N	1657
NN	1715

The oxygen surface groups introduced by HNO_3 treatment were detected by temperature programmed desorption of CO_2 and CO gases. From the Figure 1, the CO_2 peaks of NN carbon are proposed: 300°C to carboxyl groups, 420°C to anhydride groups and 640°C to lactones. The CO peak of NN is assigned to phenol groups [7].

The esterification of benzoic acid with ethanol involved and acid mechanism.

The esterification has been carried out between 1 and 11 hours. Table 2 lists the results obtained with the NN catalysts.

From these results it can be observed that the acid treatment enhances the activity of the norit carbon in the studied reaction.

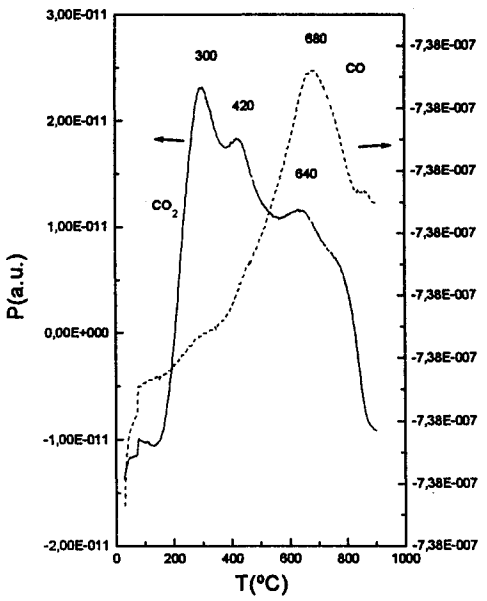

Figure 1. TPD profiles of nitrated carbon (NN)

Table 2. Esterification of benzoic acid (5mmol) with ethanol (3ml) at 75°C using nitrated norit as catalyst (0.3g)

TIME (h)	CONVERSION (%)
3	10
5	24
7	37
9	40
11	43

When the reaction was carried out using the Norit sample which was not subjected to acid treatment, no product was observed, indicating that the acidity of the NN sample is enough to promote the reaction, avoiding the generation of waste products.

Conclusions

In conclusion, it can be said that by using an nitrated norit carbon as solid acid catalyst, it is possible to prepare esters from carboxylic acids which are of interest to prepare fine chemicals.

References

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