

ACID ACTIVATED CARBON FOR THE ACETALIZATION OF CARBOXYLIC COMPOUNDS.

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Introduction

Acetals and ketals are very versatile intermediates which can be used in the synthesis of a wide variety of organic compounds. A number of acetals are formed by treatment of aldehydes and ketones respectively, with alcohols in the presence of an acid catalyst [1]. This reaction is a useful method of protection of carbonylic compounds. This is a reversible reaction, and acetals and ketals can be hydrolyzed by treatment with acid. With small unbranched aldehydes the equilibrium lies to the right. If it is desired to prepare ketals or acetals of larger molecules, the equilibrium must be shifted, usually by removal of water.

The conventional acid catalysts have been shown to be effective for this class of reactions. However, they are required to be employed in molar or more proportions with reactants and are consumed during the reaction or in the subsequent recovery of the product.

The use of solid catalysts for this reaction can be advantageous, since they can be readily separated from the product, and the reaction medium remains non corrosive. The present work reports a detailed investigation on the suitability of acid norit carbon as a catalyst for this class of reaction.

Experimental

Surface treatment.

A commercial microporous activated carbon RX-1 Extra Norit (Norit N.V.) denoted as N, was treated with HNO₃. The mixture (carbon and acid) was stirred and heated at 80 °C until almost all the acid was evaporated. The ratio carbon/ 10% HNO₃ 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 known as very efficient for introducing oxygen surface groups over activated carbons [2-4].

Specific surface area.

The specific surface areas were determined by CO₂ adsorption at 273 K, taking 0.170 nm² for the cross-sectional area of the CO₂-adsorbed molecule. An automatic Micromeritics ASAP 2000 volumetric system was used to obtain the corresponding gas adsorption isotherms. The accuracy of these 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 Thermostat) in MID (multiple ion detection) mode.

Reaction procedure

Benzaldehyde (5mmol) and the corresponding alcohol (ethanol or t-butanol) (3ml) was mixed, without any solvent and kept in a batch reactor in silicone bath under magnetic stirring, while heating up to the reaction temperature. Then, 0.2g of catalyst was added and the reaction time started. Samples were taken periodically and the evolution of the reaction between 1 and 6 hours was followed by Gas-Liquid chromatography.

Results and discussion

The specific surface areas determined from CO₂ adsorption isotherms by Dubinin-Radushkevich method [5] are given in Table 1. Also, adsorption isotherms with N₂ gas were made. However N₂ adsorbed strongly in micropore region and the measurements were erroneous. As it can be observed the areas of N and NN carbons are very

Table 1. Specific Surface Areas

Sample	S _{CO2} (m ² /g)
N	1657
NN	1715

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It is known from literature [6] that surface groups, derived from carboxylic acids, such as anhydrides, lactones, yield predominantly CO₂ upon decomposition, whereas CO is formed during the decomposition of functional groups containing one oxygen atom. From the Figure 1, the CO₂ 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].

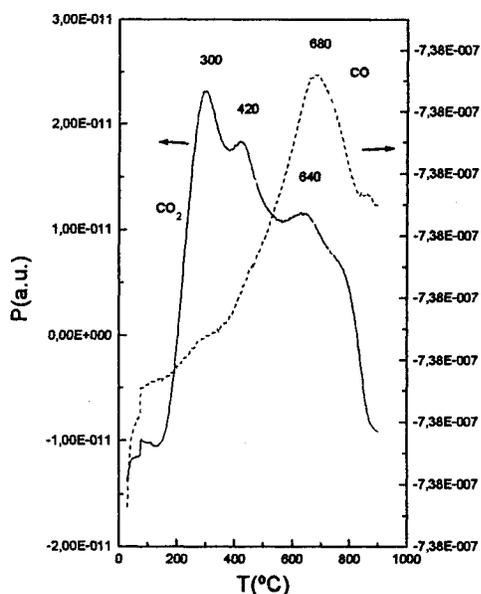


Figure 1. TPD profiles of nitrated carbon (NN)

Benzaldehyde was selected as carbonylic compound and, as alcohols, ethanol and t-butanol were chosen.

Acetalization reactions were carried out as shown in experimental section and the results are given in Table 2. From these results we can say that the nitrated carbon (NN) is an appropriate acid solid catalyst to carry out the selected reaction. Good conversion values around 40-50% can be achieved in six hours. Both alcohols, ethanol and t-butanol are convenient alcohols to be used in the protection of carbonylic groups of benzaldehyde.

In order to compare the activity of the pristine Norit carbon (N) with the nitrated sample, the

same reactions were carried out in the first one, observing that the reaction can be neglected. So, we can state that the acid treatment of the sample generates acid sites in the carbon catalyst with enough strength for the acetalization reaction selected as model acid reaction. The reaction is clean and no other products were detected.

The NN catalyst is presented as a convenient acid heterogeneous catalyst.

Table 1. Acetal formation from benzaldehyde on nitrated Norit carbon

ALCOHOL	TIME (h)	CONVERSION (%)
EtOH (75°C)*	0.5	4
	1	10
	2	18
	4	26
	6	38
t-Bu-OH (110°C)*	0.5	10
	1	13
	2	28
	4	46
	6	52

*Reaction temperature.

Conclusions

Application of solid acid carbon (NN) has been studied in the acetalization of benzaldehyde with different alcohols in a batch reactor. NN carbon is active catalyst in the preparation of acetals from aldehydes. The method is clean and avoid the generation of environmentally hazardous residues.

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