

NORIT ACTIVATED CARBON AS ACID CATALYST FOR THE RING OPENING OF EPOXIDES

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Introduction

Products formed by rearrangement of epoxide compounds provide useful intermediates in organic syntheses, and some of them are valuable as raw materials in the chemical industry. Many studies in catalytic rearrangement of epoxides have been made. The reactions which have been used most frequently are homogeneous with acid or base catalysts such as BF_3 , MgBr_2 , $t\text{BuOH}$, or lithium dialkylamides; the acid catalysts form mainly carbonyl compounds (ketone and aldehyde) and the base catalysts in most cases yield allylic alcohols.

Recently heterogeneous reaction over solid catalysts was also investigated, but the catalysts used were just alumina and silica gel, solid acid and base catalysts, and it is very recent that various kinds of the solid acids have been used as catalysts for epoxide isomerization [1].

In this work, the use of a Norit activated carbon which has been subjected to an acid treatment, has been studied during the styrene oxide ring opening.

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 $\text{pH}=6$. 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 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 $10^\circ\text{C}/\text{min}$ to 900°C . The gases evolved were analyzed by a mass spectrometer (Balzers Thermostar) in MID (multiple ion detection) mode.

Reaction procedure.

Styrene oxide (5 mmol) was placed in absence of any solvent, in a pyrex flask and heated up to the reaction temperature. Then, 0.3 g. of the nitrated norit carbon (NN) was added and, the reaction time started. The reaction was followed by GC.

Results and discussion

The well-known and frequently used BET method cannot be applied for micropore solids, due to the fact that in micropores the adsorption of nitrogen is much stronger than in the larger pores and cannot be described by the theory of capillary condensation. For these reason, the adsorption isotherms were obtained with CO_2 gas, and the specific surface areas was calculated by Dubinin-Radushkevich equation [5]:

$$a = a_0 \exp[-D \ln_2(p/p_s)] \quad (1)$$

where a is the amount of vapor adsorbed, a_0 is the maximum amount of vapor adsorbed, p is the pressure, p_s is the saturation vapor pressure, and D is a constant.

In Table 1 surface areas of N and NN carbons are given. Differences in surface areas have been not observed (the values are in the error range). It has been reported that the treatment of some kind of

carbons with HNO₃ does not affect their physical morphology but alters their surface chemical properties [6,7]. The oxidation with HNO₃ introduces, on carbon surface, groups (mainly carboxylic) with acid character.

Table 1. Specific Surface Areas

Sample	S _{co2} (m ² /g)
N	1657
NN	1715

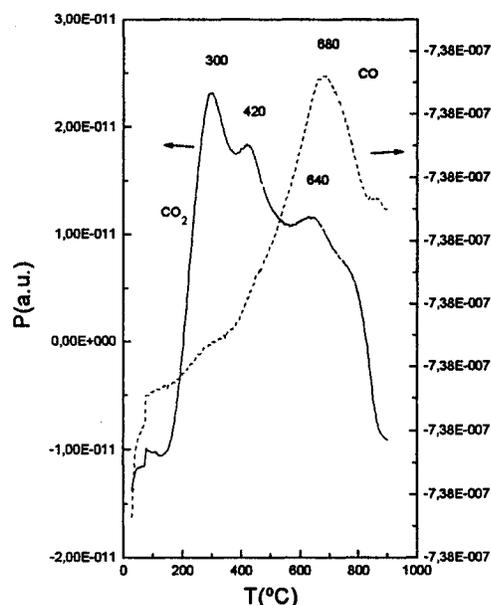


Figure 1. TPD profiles of nitrated carbon (NN)

From the Figure 1, the CO₂ peaks of NN carbon are tentatively assigned: 300°C to carboxyl groups, 420°C to anhydride groups and 640°C to lactones. The CO peak of NN is proposed to phenol groups [8].

The ring opening of styrene oxide was carried out at 150°C. Results are listed in Table 2.

Phenylacetaldehyde is the only product obtained during the acid isomerization of the styrene oxide by the NN sample.

Table 2. Reaction of styrene oxide (5mmol) at 150°C using nitrated carbon as catalysts (0.2 g.)

Catalysts	time(h)	Conversion (%)
N	1	3
	2	12
	3	21
NN	1	10
	2	36
	3	59

The highest activity observed in the NN carbon indicated that the reaction is favored by the acid sites of the carbon. Nevertheless isomerization reaction is also observed when the pristine carbon is used as catalysts. This can be explained considering the bifunctional mechanism of this type of rearrangements.

Conclusions

Nitrated norit carbon has been used as acid catalysts in the styrene oxide ring opening to afford the corresponding isomerization product (phenylacetaldehyde). The activity of the carbon increases with the acid treatment. We have found that the NN carbon is an active catalyst for the preparation of aldehydes with interest in the fine chemistry.

References

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