

ALKALINE CARBON AS BASE CATALYSTS: CONVENIENT ROUTE TO α , β -UNSATURATED KETONES.

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Introduction

Developing new solid catalysts to produce fine chemicals is one of the most promising lines of research in Catalysis [1]. Whereas solid acids are widely used in esterifications, alkylations etc., the use of basic catalysts have been much less studied. However, organic molecules react on basic catalysts through carbanions formed by abstraction of a proton from the hydrogen carbon by the base. The reactivity of these carbanions, in contrast to the carbocations formed on acid sites, can be better controlled and, therefore, the selectivity with respect to a given product can be improved [2].

In basic catalysis, as has been done in acid catalysis, it would be interesting to generate the basic sites on activated carbons in order to combine activity due to the active sites of the superficial properties of the carbon material. Moreover, in bimolecular reactions, the ability of the carbon to concentrate reactants inside the pores can be of great utility.

In this work, we have studied the catalytic activity and selectivity of a series of alkaline Norit carbon for the Knoevenagel type reaction between cyclohexanone and malononitrile under mild conditions.

Experimental

An activated carbon RX-1 Extra Norit has been used as carbon substrate. A series of alkaline carbons was prepared by ionic exchange using the corresponding K and Cs carbonates over about 60 h at 353K. In all cases the liquid to solid ratio was 10 by weight, and metal content was 30%. Samples were filtered and washed to give carbonate-free material. After drying for 16h at 383K, the carbons were crushed and sieved to different particle sizes (0.074, 0.140 and 0.250mm).

Norit is a well characterized, steam-activated peat-char, which has a wide range of pores

[3]. The basicity of the samples have been measured by the method described in the literature [4].

Reaction procedure.

The reactions were carried out in a Pyrex glass reactor. Equimolar mixtures of the two reactants (cyclohexanone and malononitrile) without any solvent were heated up to the reaction temperatures with stirring. Then, 1wt% of the carbon was added and the reaction time started in a ultrasonic bath. The reactions were followed by GC.

Results and Discussion

By using different catalyst particle sizes and different stirring rates (1000 and 3500 rpm) it was confirmed before a kinetic study that, under our experimental conditions, the reactions were controlled by neither external nor internal diffusion.

In Table 1 the conversion at different reaction times for the condensation of cyclohexanone (10mmol) with malononitrile (10mmol) using 1wt% of the K-Norit at 303, 318 and 333K is given (particle size within 0.074 and 0.140mm).

The assumed mechanism for this reaction is the following:

step 1.- the proton of malononitrile is abstracted by the basic carbon forming a stabilized carbanion.

step 2.- the carbonyl group of the cyclohexanone is attacked by the carbanion, forming a new C-C bond and the corresponding enol.

step 3.- the adduct so formed, affords the corresponding condensation product by elimination of the hydroxyl group as hydroxide ion.

step 4.- water is generated and the active sites of the carbon are restored.

Table 1

Influence of the temperature in the condensation of cyclohexanone (10mmol) and malononitrile (10 mmol) on K-Norit Carbon 1wt%.

Temp. (K)	time (min)	K-Norit
303	5	2.44
	15	6.95
	30	11.01
	45	13.14
	60	14.70
	120	18.50
318	5	9.72
	15	22.77
	30	20.00
	45	21.42
	60	16.62
	120	20.00
333	5	8.30
	15	12.71
	30	14.75
	45	17.27
	60	16.27
	120	18.10

Table 2

Influence of the alkali cation in the condensation of cyclohexanone (10mmol) and malononitrile (10 mmol) on Norit Carbon catalysts (1wt%) at 303 K.

Time (min)	K-Norit	Cs-Norit
5	2.44	8.16
15	6.95	17.34
30	11.01	27.37
45	13.14	29.98
60	14.70	33.97
120	18.50	40.56

A second order kinetic expression has been considered [5], so the controlling step of the reaction is the attack on the carbonyl group of the cyclohexanone (step 2):

$$r = K_o [S_o] [\text{cyclohexanone malononitrile}]$$

where r is the reaction rate, K_o is the rate constant and S_o is the concentration of basic sites.

In order to study the influence of the cation size, the condensation between cyclohexanone and malononitrile ($pK_a=11$) was carried out on alkaline carbons at 303, 318 and 333 K. Table 2 shows the results obtained. From these results, it can be stated that the order of activity is $K < Cs$, and the same order was observed at all temperatures studied. Thus, it can be concluded that the activity, in general trends, increases with the radius of the cation, it is with the basicity of the alkali metal.

The condensation reaction was very clean. The Cs-Norit carbon is more active catalyzing the condensation.

Conclusions

In conclusion, it can be said that, by using alkaline Norit carbons as solid catalysts able to abstract the hydrogen in the malononitrile with a $pK_a=11$, it is possible to prepare efficiently α , β -unsaturated compounds which are of interest to prepare efficiently prepolymers of malononitrile ketone which are very useful for the formation of living polymers.

For this reactions and on the catalysts studied here, the controlling step of the reaction is the addition of the carbanion of the malononitrile to the carbonyl group of the ketone, and not the abstraction of the proton by the alkali activated carbons.

References

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