

# CARBON MOLECULAR SIEVE FILMS AS CATALYSTS FOR FINE CHEMICAL PRODUCTION: AN EFFICIENT SYNTHESIS OF $\alpha$ - $\beta$ -UNSATURATED NITRILES.

*J.M. López-Pestaña<sup>1</sup>, H. Hatori<sup>2</sup>, S. Sihishiki<sup>2</sup>, R.M. Martín-Aranda<sup>1</sup>,  
A.J. López-Peinado<sup>1</sup> and Y. Yamada<sup>2</sup>.*

<sup>1</sup> *Dpto. Química Inorgánica. Universidad Nacional de Educación a Distancia.  
c/ Senda del Rey s/n, 28034-Madrid, Spain.*

<sup>2</sup> *National Institute for Resources and Environmet. 16-3 Onagawa. Tsukuba-shi. Ibaraki, 305  
Japan*

## Introduction

Alkaline carbon molecular sieve films from polyimide (PIC) have recently been employed as catalysts for fine chemical production [1, 2].

It is well known that when a commercially available polyimide film from "Kapton" is carbonyzed, it keeps the film form giving a highly crystalline graphite film further heat treatment [3, 4]. The characterization of the carbon surface basicity has also been studied with a series of Li, Na, and K carbon molecular sieve films from polyimide following the method described by López-González et al [5].

Base solids and base catalyzed reactions constitute a field which offers possibilities for selectively catalyzed reactions to produce fine chemicals [6].

Among these interesting reactions, which could be catalyzed by solids, it is the preparation of prepolymers which can be used in processes of polymerization.

The anionic polymerizations have been extended to prepare living polymers. These have wide industrial applications as plastics, synthetic fibers, and in the production of liquid crystals and ultratenaceous polymers [7]. In all the types of polymers, a decisive point is to produce the monomer (prepolymer) which leads to a desired polymer with specificity and selectivity.

The most desired prepolymers for preparing polymers to be used in these applications are alkenes with electron withdrawing groups such as

nitriles, which facilitate the addition to the double bound.

In this work we study the synthesis of a series of polymers by condensation of benzaldehyde with malononitrile using PIC and K-PIC under ultrasound activation.

## Experimental

The catalysts were prepared and characterized following the method describes by Hatori et al [3, 4].

### Reaction Procedure

The reactions were carried out in a Pyrex flask. Equimolar mixtures of the two reactants (benzaldehyde and malononitrile) in absence of any solvent were heated up to 308K. Then, 1 wt% of the carbon catalyst was added and the reaction time started in a ultrasonic bath. The reaction was followed by GC.

## Results and discussion

The condensation of benzaldehyde with malononitrile involves as a first reaction step the abstraction, by the solid base PIC, one of the activated hydrogens from the malononitrile molecule.

In the second step, the carbanion attacks the carbonyl group of the benzaldehyde with elimination of the hydroxyl group with the formation of water and released of the  $\alpha$ ,  $\beta$ -unsaturated nitrile into the reaction media.

Taking into account that the  $pK_a$  of malononitrile is 11, an alkali PIC with basic sites enough to abstract such protons should be used. In previous work [1]. We found that most of basic sites of alkali-PIC's have basicities which are able to abstract protons with  $pK_a$  within  $10.7 \leq pK_a \leq 13.3$ , increasing the order of basicity with the radius of the alkaline cations  $PIC < Li-PIC < Na-PIC < K-PIC$ . So, these alkaline PIC's are appropriate catalysts for the synthesis of  $\alpha, \beta$ -unsaturated nitriles.

The influence of the alkali cation was studied during the condensation of benzaldehyde with malononitrile using 2wt% of the corresponding catalysts (Table 1) using ultrasound activation.

Table 1.

Condensation of benzaldehyde (7mmol) and malononitrile (7mmol) using 1wt% of carbon molecular sieve film (PIC) under ultrasound activation.

T (°C)	t(min)	PIC	K-PIC
30	15	10	40
	30	18	57
	60	29	63
45	15	19	51
	30	26	82
	60	32	90

It is observed that for a determined amount of catalysts, the of the  $\alpha, \beta$ -unsaturated nitriles of the is higher in the case of ultrasound activation, being more active the K-PIC which is the catalyst which presents a high basicity, in contrast with the pristine PIC which does not present alkaline cations in its structure.

Table 2  
Conventional method of reaction.

T(°C)	t(min)	PIC	K-PIC
30	15	3	18
	30	10	39
	60	15	51
45	15	7	32
	30	13	56
	60	24	72

The  $\alpha, \beta$ -unsaturated nitriles is the only one product obtained in all cases, with conversion values comprised between 29 and 90 %, (Table 1) depending on the type of activation (conventional (Table 2) or sonication) and on the time of reactions. The combination of a basic PIC, ultrasound activation and dry media are presented as optimum conditions to obtain monomers of benzaldehyde with active methylenic compounds as malononitrile.

## Conclusions

$\alpha, \beta$ -unsaturated nitriles which are interesting prepolymer in anionic polymerization are obtained under mild ultrasound irradiation using carbon molecular sieve films from polyimide as base catalysts.

Values of 90% and 100% for conversion and selectivity respectively, which are higher than the results of other conventional reaction procedures, can be obtained in only 60 min. of reaction under ultrasound activation.

## References

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