PITCH-BASED ACTIVATED CARBON FIBERS CONTAINING K2CO3 AS CATALYSTS: AUTOCONDENSATION OF CYCLOHEXANONE

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Introduction

The literature on carbon as catalysts is growing rapidly, but it is not as voluminous as literature on carbon as a support (1). By other hand, the basic properties of alkaline carbon surfaces is now recognized not only for catalysts supports (as well as adsorbents applications (2), but also for catalytic applications as well. Even though the basic properties of many carbon surfaces in solution have been studied (3, 4) and several theories have been proposed to explain their basic character (5) the measure of this basic strength distribution and type of active sites present are still under study.

Recently, basic carbons able to catalyze reactions selectively have been studied in fine chemistry, specially in the field of anionic activation (6, 7). Catalysts can be prepared in a wide range of basic strengths. Therefore, depending on the basic strength required, the appropriate catalyst can be selected to catalyze the desired reaction more selectively. In this sense, the textural and chemical properties of alkaline carbon molecular sieve films from polyimide were tested in some anionic reactions showing excellent catalytic properties (8, 9).

In the present work, we demonstrate that, a pitch-based carbon fiber (ACF) containing K_2CO_3 in outer parts presents excellent basic properties. This type of carbon material is a suitable catalyst for use in organic synthesis.

Experimental

Catalysts

Isotopic coal picth supplied by Nippon Carbon Co. Ltd (Japan) was used as a raw material to prepare KACF. At first, the quinoline solution of pitch was mixed with KOH (1.8 wt%) dissolved in ethanol. After removing of solvents the obtained pitch was crushed, spun by the centrifugal method and then treated with air and CO_2 at elevated temperature for stabilization/carbonization/activation, of which temperature-time program is shown in Fig. 1. The stabilization was carried out under the air/CO_2 (1:1) mixture. The CO_2 gas was used to change KOH into K_2CO_3 according to the following reaction:

$$2\,KOH + CO_2 \rightarrow K_2CO_3 + H_2O$$

The diameter of KACF thus prepared was ca. 15~ 25μ m.

Catalytic reaction procedure

Cyclohexanone (10 mmol) without any solvent was stirred continuously while heating to the reaction temperature, then, 4 wt% of the potassium-activated carbon fiber (KACF) was added and the reaction time started. Samples were taken periodically and the evolution of the reaction between 1 and 360 min. was followed by GC.

Results and Discussion

Specific surface area:

KACF showed a relatively low N2-BET specific surface area, 508 m^2/g, resulted, mainly from the micropores.

Potassium content

The atomic absorption spectrophotometry technic showed that potassium contents were 1.3 wt% in the raw fiber and only 1.5 wt% after stabilization/carbonization/activation process, which means that potassium loss of ca. 42% occurred during KACF preparation

EPMA measurements

EPMA maps show that potassium is dispersed uniformly through the raw fiber containing KOH. In the stabilized and the activated fibers the highest concentration of potassium was observed in the outer parts of fiber.

Catalytic behavior

Autocondensation of cyclohexanone is an important aldolic-type reaction employed in many fine chemical processes for the manufacturing of pharmaceutical products.

In liquid-phase reactions catalyzed by solid catalysts, the diffusion of reactants through the film around the solid particles is the first step in the catalytic process, and one has to be certain that it is not the controlling step if the reactivity of the catalyst has to be studied.

In this work, the autocondensation of cyclohexanone was carried out on a KACF by stirring the solution at 1000 and 3500 rpm. No differences in conversion were observed, indicating that the reaction is not controlled by diffusion of reactants.

Table 1
Autocondensation of cyclohexanone (10 mmol) using 4wt% of KACF as catalysts.

Temp (°C)	Time (h)	Prod. (%)
100	1	12
	2	26
	3	37
	4	45
	5	47
	6	52
145	1	25
	2	51
	3	63
	4	70
	5	76
	6	82

The autocondensation of cyclohexanone was carried out at 100 and 145 °C. The results obtained are given in Table 1.

From these results it can be observed that KACF shows the appropriate basicity to abstract hydrogen from carbonylic compounds (cyclohexanone). Values of around 85% activity and good selectivity are achieved when the reaction is carried out at 145 °C.

Conclusions

Fine particles of K_2CO_3 supported on activated carbon fiber influences on the catalytic behavior of the fiber, when it is used as alkali catalyst of anionic reactions.

KACF are active and selective catalyst in the production of fine chemicals of commercial interest through aldolic reaction.

A maximum in activity was found at 145 °C for the aldolic autocondensation of cyclohexanone.

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