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Synthesis and purification of anthraquinone in a multifunctional reactor

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Abstract

In the present paper the reaction of 2-benzoylbenzoic acid dehydration has been studied in the presence of different catalysts by using a batch reactor for screening the best catalysts and a pseudo-continuous multifunctional reactor for determining catalysts productivity, reaction yields, catalysts deactivation and regeneration on the previously selected catalysts that are acid bentonite, Y- and β-zeolites. This last reactor works also as evaporator and condenser for separating and collecting produced anthraquinone at a high level of purity, while water continuously formed evaporates in the atmosphere.

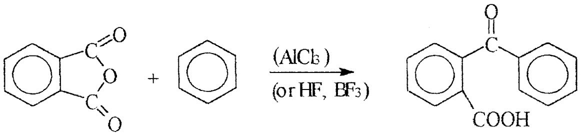
A kinetic model with vapour–liquid partition and catalyst deactivation has been used to interpret the experimental runs. The liquid reacting mixture showed strong non-ideality favouring the evaporation and collection of pure anthraquinone.

Keywords: Synthesis; Purification; Multifunctional reactor

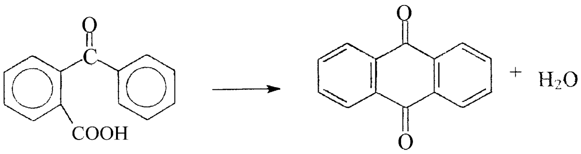
1. Introduction

Different routes have been suggested in the literature for the manufacture of anthraquinone (AQ), a key substance for the production of colorants. In the past, the most common method for the manufacture of AQ was the oxidation of anthracene by using different kinds of oxidants acting in gas phase or in liquid phase [1]. As, the availability of anthracene is declining, alternative processes have been developed starting, for example, from benzene and phthalic anhydride [1].

In the last case the synthesis occurs through the following two steps:



(1)



(2)

The first step has been studied by strongly improving yields and selectivities either in the presence of $AlCl_3$ [2] or in the presence of HBF_4 [3]. The second step of cyclization via dehydration of 2-benzoylbenzoic acid (BBA), is commonly promoted by using concentrated H_2SO_4, that is used also as a solvent [4,5]. The use of many other catalysts has been

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Nomenclature

J	total molar flow rate
J_{AQ}	anthraquinone molar flow rate
J_{H_2O}	water molar flow rate
k_c	kinetic constant
k_d	deactivation constant
k_0	initial kinetic constant
m	catalyst mass
n_{AQ}	moles of anthraquinone
$n_{AQ}{}^{L}$	moles of anthraquinone in the liquid phase
$n_{AQ}{}^{S}$	moles of anthraquinone collected as solid
n_{BBA}	moles of benzoylbenzoic acid
$n_{BBA}{}^{0}$	initial moles of benzoylbenzoic acid
n_{H_2O}	moles of water
P	total pressure
$P_{AQ}{}^{0}$	anthraquinone vapour pressure
r	reaction rate
t	time
x_{AQ}	anthraquinone liquid mole fraction
y_{AQ}	anthraquinone vapour mole fraction

Greek letter

γ_{AQ}	anthraquinone liquid activity coefficient

proposed in the literature such as: phosphoric acid [6], silica–alumina [7], acid clays [8,9], zeolites [10,11] and perfluoro acid resins [12]. The reaction is normally performed by contacting the solid catalyst with the melted reagent or with a solution of the reagent in an appropriate solvent at temperatures favouring the vaporization of the water formed in the reaction.

In the present paper the reaction of 2-BBA dehydration has been studied in the presence of different catalysts by using both a batch and a pseudo-continuous reactor. Batch runs have been made for screening the catalysts, while, continuous reactor was used on the best catalysts to gain more information such as: kinetics, catalyst productivity, reaction yields, catalyst deactivation and regenerability. The continuous reactor realized by us is a multifunctional reactor, because, it works also as a separation unit for collecting, by evaporation, produced AQ at a high level of purity. In the meantime water formed continuously evaporates in the atmosphere. We have found three catalysts giving good performances that are: bentonite, Y- and β-zeolites.

A kinetic model with vapour–liquid partition, also considering catalysts deactivation has been developed for simulating the pseudo-continuous runs and related parameters have been collected.

A discussion on the obtained kinetic parameters and a comparison of the different catalysts performances obtained will conclude the paper.

2. Experimental

2.1. Methods, apparatus and reagents

Catalytic screening has been made in a 250 cm^3 bottom flask of glass, 4 g of 2-BBA were put in the flask together with about 2 g of the solid catalyst. Then, the flask was dipped for 2 h in a thermostatted oil bath, kept at 200°C, stirring the reaction mixture with a magnetic stirrer. After 2 h of reaction the flask was cooled and the reaction mixture was treated with dichloromethane, dissolving both AQ and 2-BBA separating them from the catalyst. The solution obtained is then separated by filtration and the solvent is evaporated in rotavapour leaving the residual reagent and the product in the rotating flask. This mixture was then submitted to chemical analysis. A weighed amount of the mixture was dissolved in 20 cm^3 of methanol and titrated with NaOH 0.1 N. In this way the mass residual of 2-BBA in the mixture was determined. AQ formed was determined by difference. The conversion to AQ is, therefore, the ratio of the mole of formed AQ with respect to the total. The list of the used catalysts is reported in Table 1, together with the adopted operative conditions.

All the catalysts are solids with high acid character. β- and Y-zeolites have been decationated from the ammonia form by heating them, at 550°C, for 4 h. Aluminium sulphate supported on silica has been obtained by grafting on a silica support the aluminium alkoxide previously treated with an equimolecular amount of pure sulphuric acid. The obtained catalyst was then calcinated, at 500°C, for 2 h. AW 500 zeolite and bentonite F-21, available in the sodium form, were both exchanged with HCl solutions. In particular bentonite F21-a has been obtained by treating the sodium form

Table 1
Type of catalysts proven, ratio reagent/catalyst adopted and obtained conversion to AQ at 200°C for 2 h

Catalysts	BBA/catalyst	$(n_{\mathrm{AQ}}/n_{\mathrm{TOT}}) \times 100$
β-zeolite	2	43.7
Aluminium sulphate on silica	2	12.9
Silica–alumina	2	23.3
Nafion NR	2	33.0
AW 500 zeolite	2	18.9
Bentonite F21-a	2	43.8
Bentonite F21-b	2	87.9
Alumina	2	3.0
Y-zeolite	2	40.7

twofolds with HCl 2 M for half-an-hour, at room temperature. The solid was then filtered, washed with distilled water and calcinated at 400°C for 2 h. Bentonite F21-b has been obtained in the same way but using HCl 6 M.

AW 500 was treated for half-an-hour with HCl 6 M and then washed with distilled water until the neutral pH is obtained. All mentioned zeolites were calcinated at 400°C.

Continuous runs have been made in the reactor/evaporator schematized in Fig. 1. We can recognize three zones in this reactor working at different temperatures: (i) the reacting zone in which the reagent and catalyst are initially loaded and are kept at about 290°C with a furnace; (ii) the neck heated at temperatures of about 340°C to favour the diffusion of the vapours of AQ and water; (iii) the product recovering zone that is frozen with a cold air stream in which the sublimated AQ crystallizes.

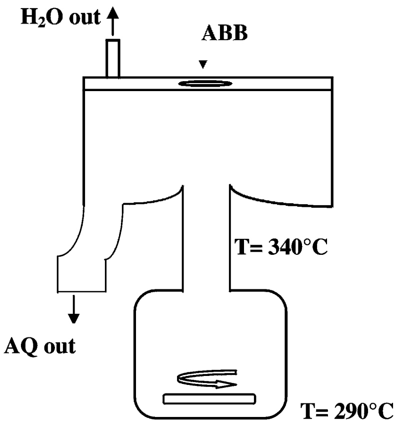

Fig. 1. A scheme of the reactor/evaporator used in the pseudo-continuous kinetic runs.

At the top of the reactor a hole in the cover allows the evacuation of the vaporized water. AQ is manually withdrawn from the lateral tube reported in the scheme having at the extremity a stopper. The amounts of AQ, withdrawn at regular intervals of time during the reaction, were replaced by fresh reagent introduced from another hole on the cover that is normally kept closed with a stopper. The reacting mixture is magnetically stirred. Small amounts of tars accumulate in the reactor reducing the catalyst performance. Catalyst exhaust, then, can be regenerated, by calcinating it, at 500°C. Regenerated catalysts have been reused in the same way.

3. Results and discussion

A preliminary screening of different acid solid catalysts has been performed in the already described batch reactor. The results of the screening are reported in Table 1. As it can be seen, zeolites β and Y and bentonite are the most active catalysts. As expected, AW 500 is less active than the other zeolites despite the higher acidity because the pores section is too small. A similar observation is reported in the literature for ZSM5 zeolite [10]. Therefore, the behaviour of the most active catalysts have been studied in the already described pseudo-continuous reactor. Preliminary runs performed with bentonite F21-b have been made to evaluate the optimal operative conditions for what concerns: the initial weight ratio between the reagent BBA and the catalyst and this resulted BBA/catalyst about 0.5; the temperature of the reaction zone that has been chosen 290°C; the temperature of the evaporator neck that has been taken 340°C. These conditions have been kept the same for all the runs performed. The runs have been performed by putting initially 3–5 g of the reagent and a double quantity of catalyst in the reactor kept at the reaction temperature. Reactor produces AQ that evaporates and is collected at regular intervals of time of about 60 min. Product resulted pure at more than 99%. Collected AQ is weighed and a correspondent amount of BBA is added to the reacting mixture. In Figs. 2–4 the overall productivity of AQ as a function of time for, respectively, Y- and β-zeolites and bentonite F21-b is reported.

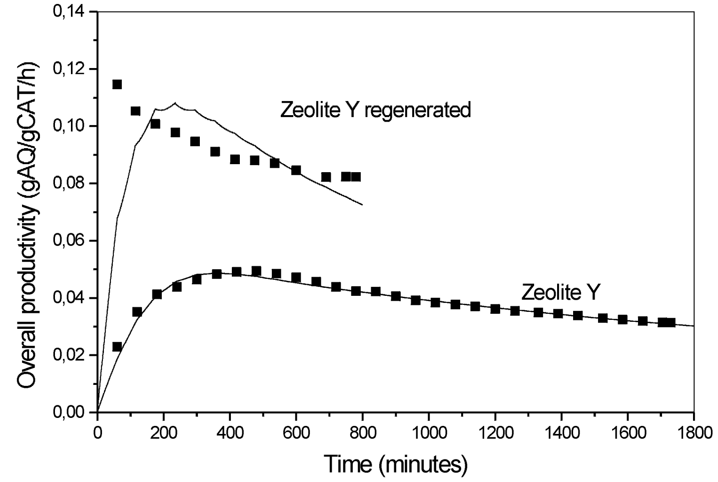

Fig. 2. Overall productivity with zeolite Y.

Overall productivity is the amount of pure AQ collected at the top of the reactor referred to the unit of time and of mass of catalyst. Scattering of data observed is probably due to the manual operation of withdrawing the product and loading the reagent. Nevertheless, we can see a behaviour that is roughly the same for all the examined catalysts, that is, an initial period in which productivity increases until to reach a maximum, then, a more or less steep decrease occurs. This behaviour can easily be interpreted by considering the accumulation of AQ in the liquid phase before to reach a composition favourable to an active evaporation. On the contrary, the decrease of the productivity can be attributed to the accumulation of tars in the reaction zone corresponding to 5–10% of the fed reagent as it resulted by the analysis at the end of the reaction.

The exhaust catalysts have been regenerated by calcination, at 500°C, for 2 h and reused. It is very interesting to observe that regenerated catalysts show very high initial productivity that decrease with time, but remaining always higher than the ones observed in the first run. With the exception of the initial

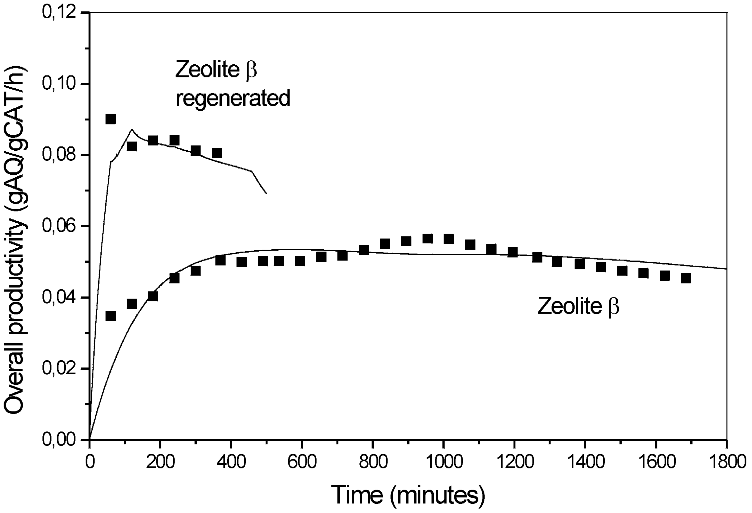

Fig. 3. Overall productivity with zeolite β.

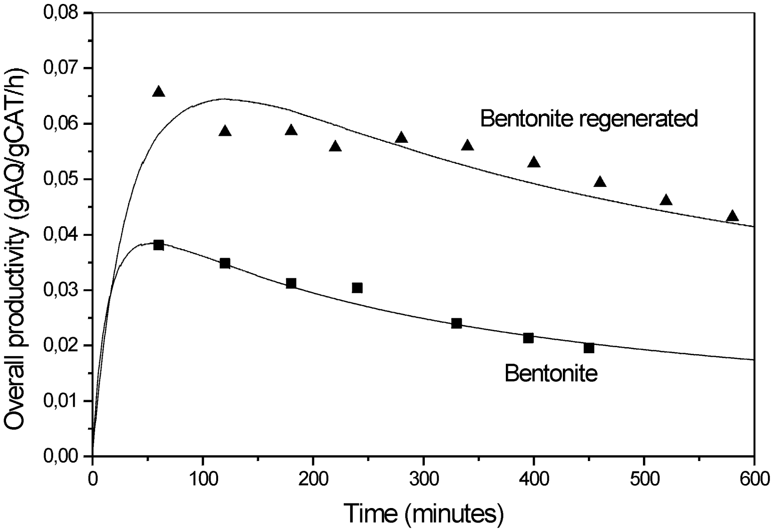

Fig. 4. Overall productivity with bentonite.

behaviour, reused catalysts have about the same trend of deactivation with time. The higher initial activity could be explained with a better accessibility of the reagent molecules to the active sites originated by the regeneration process. By comparing the behaviour shown by Y- and β-zeolites it can be noted that the two zeolites have similar behaviour, but Y-zeolite deactivates before. This behaviour is in agreement with the different structures of the two zeolites. Y-zeolite has supercages of 12 Å of diameter in which polyaromatic condensation products can be formed and trapped preventing the accessibility to the active sites in the normal cavities (7.4 Å of diameter), β-zeolite having a more uniform porosity is less incline to deactivation. This behaviour is also consistent with the observation that Y-zeolite produces more tars than β-zeolite accumulating in the mixture of reaction. The overall conversion, in fact, is 90% for Y-zeolite and 95% for β-zeolite for the same duration time of about 1750 min. On the basis of these observations β-zeolite is the best catalyst for the performances, but bentonite F21-b is a valid and cheaper alternative.

3.1. Kinetic model

The runs reported in Figs. 2–4 have been interpreted by using a kinetic model with vapour–liquid partition. Considering the reaction (2) rewritten in the form

$$\mathrm{BBA} \rightarrow \mathrm{AQ} + \mathrm{H_2O} \tag{3}$$

The reagents and products evolution with time can be calculated by solving the following ordinary differential equation

$$-\frac{\mathrm{d}n_{\mathrm{BBA}}}{\mathrm{d}t} = \frac{\mathrm{d}n_{\mathrm{AQ}}}{\mathrm{d}t} = \frac{\mathrm{d}n_{\mathrm{H_2O}}}{\mathrm{d}t} = r \tag{4}$$

By trying different reaction orders (zero and first) we observed that the kinetics can be better interpreted with a zero order. Probably, the real order of the reaction is intermediate between zero and one in agreement with the reasonable assumption of a Langmuir–Hinshelwood kinetic law. We assumed, therefore, for simplicity, a zero-order kinetics, as a consequence the reaction rate is expressed as it follows:

$$r = k_{\mathrm{c}} m \tag{5}$$

AQ is partitioned between liquid and vapour phase and an accumulation of this product occurs in the liquid phase that can be described by the following relation:

$$\frac{\mathrm{d}n_{\mathrm{AQ}}{}^{\mathrm{L}}}{\mathrm{d}t} = r - J y_{\mathrm{AQ}} \tag{6}$$

where J is a total vapour flow rate, that is,

$$J = J_{\mathrm{AQ}} + J_{\mathrm{H_2O}} \tag{7}$$

Considering that water is completely removed from the liquid phase, water flow rate corresponds to the reaction rate and hence

$$J = J_{\mathrm{AQ}} + r \qquad (8)$$

Then, by introducing the vapour–liquid relation

$$P y_{\mathrm{AQ}} = \gamma_{\mathrm{AQ}} x_{\mathrm{AQ}} P_{\mathrm{AQ}}{}^{0} \qquad (9)$$

and remembering that $P = 1$ atm, we have

$$y_{\mathrm{AQ}} = \gamma_{\mathrm{AQ}} x_{\mathrm{AQ}} P_{\mathrm{AQ}}{}^{0} = \frac{J_{\mathrm{AQ}}}{J_{\mathrm{AQ}} + r} \qquad (10)$$

By substituting y_{AQ} and J into the relation (6) we obtain the relation

$$\frac{\mathrm{d}n_{\mathrm{AQ}}{}^{\mathrm{L}}}{\mathrm{d}t} = r\left[1 - \left(1 + \frac{\gamma_{\mathrm{AQ}} x_{\mathrm{AQ}} P_{\mathrm{AQ}}{}^{0}}{1 - \gamma_{\mathrm{AQ}} x_{\mathrm{AQ}} P_{\mathrm{AQ}}{}^{0}}\right) \gamma_{\mathrm{AQ}} x_{\mathrm{AQ}} P_{\mathrm{AQ}}{}^{0}\right] \qquad (11)$$

that must be integrated together with relation (4) taking into account the following mass balance equation:

$$n_{\mathrm{AQ}}{}^{\mathrm{S}} = n_{\mathrm{BBA}}{}^{0} - n_{\mathrm{BBA}} - n_{\mathrm{AQ}}{}^{\mathrm{L}} \qquad (12)$$

At $t = 0$ we shall have $n_{\mathrm{BBA}} = n_{\mathrm{BBA}}{}^{0}$, $n_{\mathrm{AQ}}{}^{\mathrm{L}} = 0$, $n_{\mathrm{AQ}}{}^{\mathrm{S}} = 0$ and $n_{\mathrm{AQ}} = 0$.

Table 2
Kinetic parameters used in the model

Catalyst	k_0	k_{d}
Bentonite	0.3534×10^{-4}	0.8992×10^{-1}
Bentonite regenerated	0.2201×10^{-4}	0.2112×10^{-1}
Zeolite Y	0.9439×10^{-5}	0.3716×10^{-2}
Zeolite Y regenerated	0.1800×10^{-4}	0.5523×10^{-2}
Zeolite β	0.8010×10^{-5}	0.1490×10^{-2}
Zeolite β regenerated	0.2168×10^{-4}	0.1704×10^{-1}

As it has been seen the catalysts deactivate and we have assumed a deactivation law of the type

$$k_{\mathrm{c}} = \frac{k_0}{1 + k_{\mathrm{d}} t} \qquad (13)$$

All the runs performed have been simulated and the fitting can be appreciated in Figs. 2–4 for the overall productivity. In Fig. 5, an example of the amount of AQ collected during the time and related simulation is reported. In Table 2 the kinetic parameters used in the model are reported.

In Fig. 6, it is possible to observe the evolution with time of the amount of AQ accumulated in the liquid phase. After an initial period in which accumulation increases, a pseudo-stationary conditions is obtained after about 3 h. The amount of accumulated AQ in the pseudo-stationary conditions has been experimentally

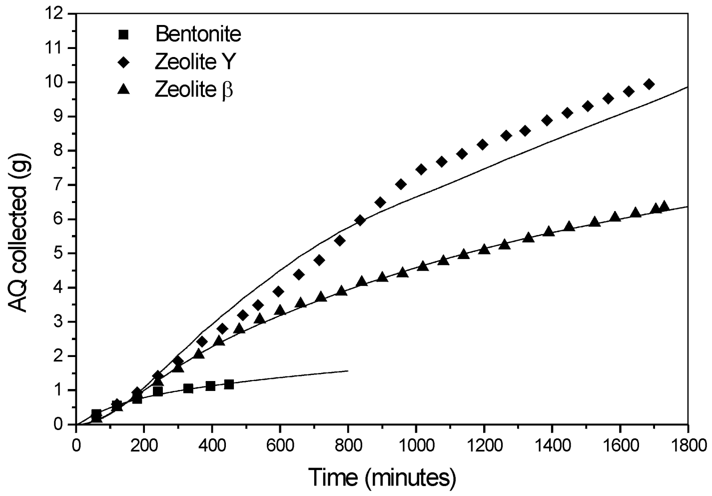

Fig. 5. Amount of AQ collected as a function of reaction time.

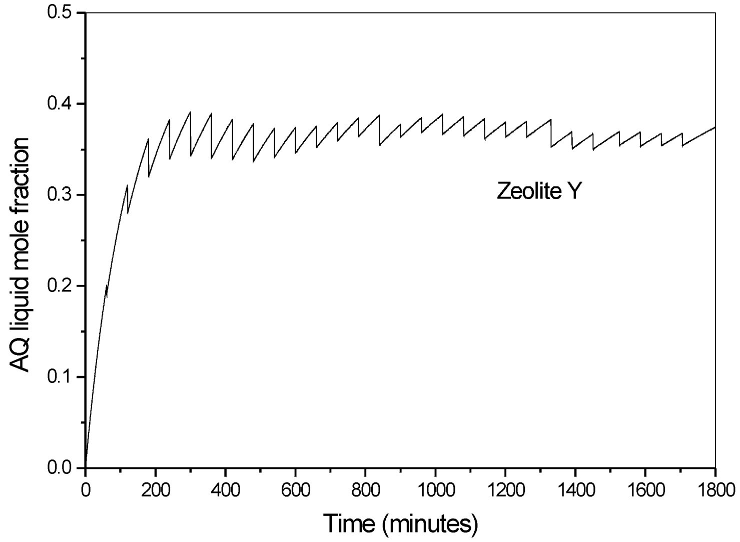

Fig. 6. Liquid mole fraction of AQ as a function of time (zeolite Y).

determined at the end of a run, corresponding to the mole fraction reported in Fig. 6 of about 0.35.

It is very interesting to observe that considering ideal the vapour–liquid equilibrium of this system, the vapour pressure of AQ [13], at 290°C, should be too low for obtaining the experimentally observed vaporization. To simulate the observed productivity with an accumulation of AQ such as the one reported in Fig. 6, we must introduce an activity coefficient of about 10.

4. Concluding remarks

It has been shown the possibility to promote the cyclization of 2-BBA by using solid acid catalysts instead of sulphuric acid in a reactor–evaporator, that is a unique continuous multifunctional device, that is able to:

1. convert the reagent BBA to the desired product AQ,
2. separate, purify and collect in solid form the reaction product AQ,
3. eliminate continuously water formed during the reaction, shifting in this way the equilibrium of the reaction to the right.

This device allowed us to collect and compare productivity data from three different catalysts that are largely available. The catalysts examined after deactivation, can easily be regenerated and tars are formed in a small acceptable amount. The operation could be optimized and scaled up in a continuous industrial plant by using the kinetic model with vapour–liquid partition, developed by us. At last, a strong non-ideality of the dissolved AQ has been observed largely favouring the process of separation by evaporation.

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