CATALYTICALLY ACTIVATED SiC FOAM FOR REACTIVE DISTILLATION

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Abstract
The application of ceramic foam as a packing for distillation has been demonstrated in a previous work[1] but limited due to the low capacity. Nevertheless, the flow employed in reactive distillation are lower, it does not represent a major drawback. Moreover, the application of foam as a catalyst support has shown good activity[2] which let foresee an interesting application for reactive distillation. So, this paper describes the kinetic study of coating foam in a batch reactor on the target reaction application which is the esterification of acetic acid by methanol. Different catalyst coating methods have been tested to choose the most convenient.

Keywords: Ceramic foam, Reactive distillation, Structured packing, Catalyst coating, Pressure drop, Mass transfer efficiency

1. Introduction

Solid foams have been known for many years and have a wide range of applications due to their low density and attractive properties. In the last decade, interest in these foams has grown for applications such as heat exchangers, reformers, mixing improvement, and as catalysts or structured catalyst supports[2]. Although several hydrodynamics studies[3-4] have been realised with monophasic or biphasic countercurrent systems, a detailed investigation of ceramic foam as packing for distillation has been previously realised in term of hydrodynamics and mass transfer efficiency[1]. The solid foam studied in this work is an open celled SiC foam with a single PPI number (5 PPI) and porosity (91%) corresponding to a specific area of 640 m^2/m^3.

Pressure drop obtained are satisfactory with several millibar per meter whereas flooding behaviour is quite lower by report to classical distillation packing. On the other hand, liquid hold-up and mass transfer efficiency are found very good with values comprised between values of the classical distillation packing. So, an application of ceramic foam in reactive distillation seems to be possible.
Then, the objective of this work is to propose an alternative to classical catalytic packing with catalyst coating at the surface of the support study the application of ceramic foam as catalytic packing for reactive distillation.

This work describes the experimental steps necessary to determine the best possible catalyst coating method involving a satisfactory activity of the catalyst ceramic foam before experiments of reactive distillation.

2. Experimental setup and methods

2.1 Reaction kinetic procedure

The determination of activity of the foam coating has been realized in a batch reactor with the follow of kinetic of the esterification of acetic acid by methanol. The temperature inside the reactor (40°C) is maintained constant by using a thermostated bath; the kinetic reaction is followed by taking sample regularly during almost 24 hours of experiments. Sample was analyzed using Gas Chromatography. The volume of the reactants is almost of 400 ml for a mass of foam coating tested between 3 and 10 grams.
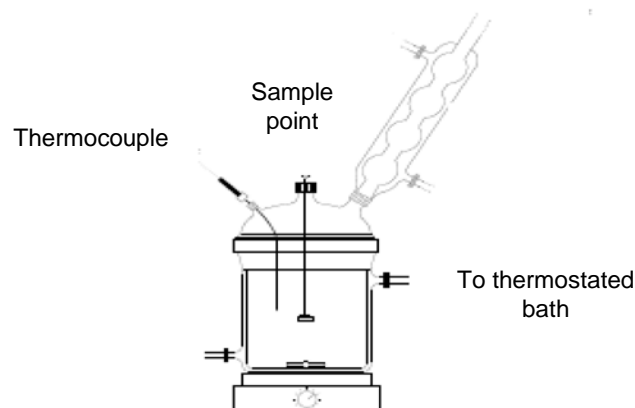
Figure 1. Batch reactor for kinetic experiments

Four different catalyst coating methods on ceramic foam have been tested with this material:

- Coating of acid function by immersion of the support (Impregnation)
- Coating of a porous layer follow-up of a coating by impregnation (Washcoating)
- Coating of Zeolithe ZSM-5
- Coating of Amberlyst 15[5] (ion exchange resin) by immersion of the support in a suspension of Amberlyst particles in water

Beforehand, first experiments performed with Amberlyst 15 have been used to benchmark the procedure and the experimental setup by making comparison with kinetic model developed by Popken et al.[6] for homogeneous and heterogeneous catalysis. So, the experimental results are compared with models of Pöpken et al. and especially the pseudohomogeneous model in Figure 2.
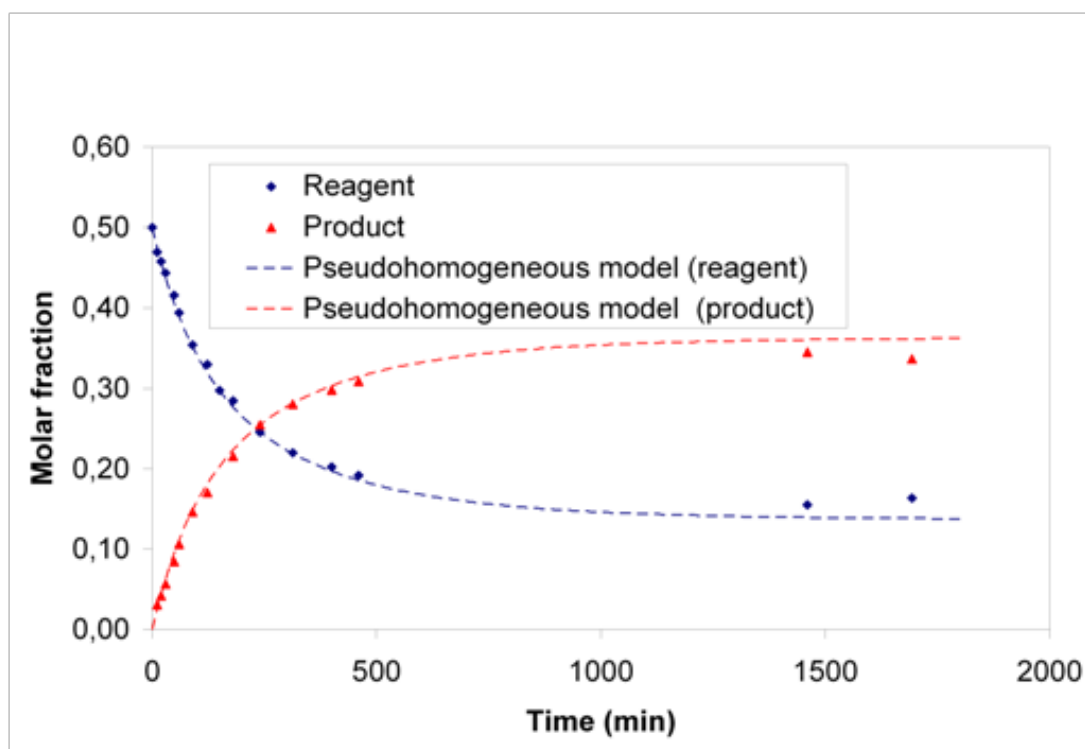
Figure 2. Comparison of experimental results in batch reactor with the pseudohomogeneous model of Pöpken et al.

We can see that the model corresponds well to the results except for the last points from 24 h; our procedure can so be considered as validated. This model will be used after to determine the equivalent weight of Amberlyst 15 for each method of catalyst coating to determine the most efficiency in term of activity. The kinetic model used is the following:

$$r = m_{cat}\left(k_1 . a_{AcAc} . a_{MetOH} - k_{-1} . a_{MetAc} . a_{H2O}\right)$$

with

$$k_i = k_{0,i} . \exp\left(-\frac{Ea,i}{R.T}\right)$$

$k_{o,1} = 2.961.10^4$ mol/s/g
$E_{a,1} = 49190$ J/mol
$k_{o,-1} = 1.348.10^6$ mol/s/g
$E_{a,-1} = 69230$ J/mol

Once the coating method has been determined, the equivalent weight of Amberlyst 15 is determined by fitting the kinetic model to our experimental points by modification of the mass of catalyst.

3. Experimental results

3.1 Comparison of the method
Firstly, the results obtained are reported in term of initial reaction rate for the different methods of catalyst coating are presented in Figure 3.
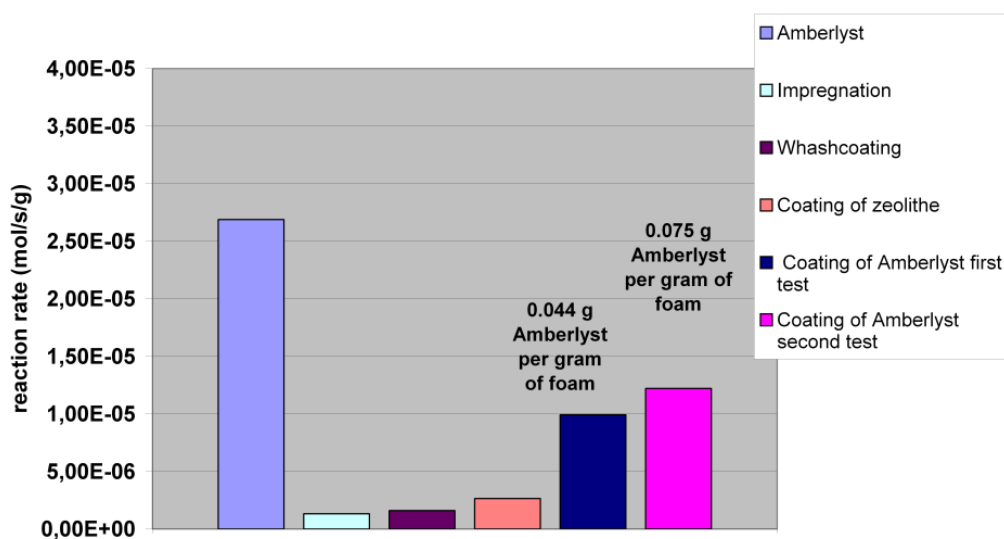
**Figure 3.** Comparison of the coating method in term of reaction rate

Thanks to this figure, it is obvious that the three first method tested present a very low activity characterized by a low reaction rate. First test with coating of Amberlyst has given the higher reaction rate so that is why a second test with the same procedure of coating has been realized to check the results. The second test with a higher mass of Amberlyst coated per gram of foam gave a higher reaction rate, these findings seems to be logical because reaction rate is higher when the quantity of Amberlyst coated is higher. Thus, we can consider that Amberlyst coating is the most interesting way to follow to develop an efficient catalytic packing from ceramic foam.

3.2 Optimization of the coating method
The method used to coating Amberlyst at the beginning was followed the procedure developed by Peters et al.[5]. This procedure consists in three phases:

- Pretreatment of the support by washing in ethanol under ultrasonic conditions following by a drying of 1h at 100°C
- Coating of the support by immersion in a suspension of Amberlyst 15 (particle size<56µm) and water with a rheology modifier (Aculyn 22). Concentration of the suspension is of 50 g/L of Amberlyst 15. This step is following by a drying of 2h at 90°C
- Regeneration of the catalytic coating by treated with sulfuric acid (10 wt.%) following by a drying of 2h at 90°C

As the reaction rate increase with the amount of Amberlyst coated, we can consider that a modification in the procedure could lead to an increase of the weight of Amberlyst coated per gram of foam which will be favorable to the reaction. So, different procedures for the coating of Amberlyst have been tested by modifying the concentration of the suspension and the number of coating phase (multiple successive impregnations) to determine the best conditions allowing to obtain a high quantity of Amberlyst. This quantity per gram of foam is presented in Figure 4 for different procedure of coating.
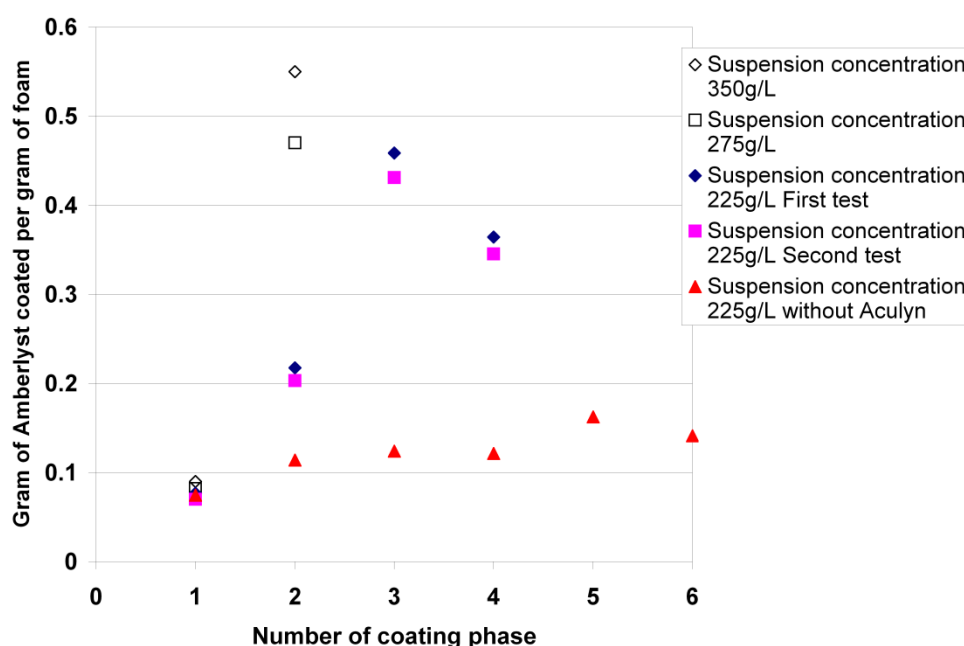

Figure 4. Mass of catalyst coating per gram of foam for different procedure

First, it is interesting to note that the amount of catalyst coating is the same for the first step of coating whatever the procedure used. Then, for high concentration (350 and 275 g/L), an important weight of Amberlyst per gram is obtained from the second step but it results in a total blockage of the pores of the foam. In the case of the concentration of 225 g/L, the fourth step of coating is corresponding to the regeneration with sulfuric acid carrying out to a weak loss of mass. Two different tests have been done to check the repeatability of the mass catalyst coated. With this procedure (225 g/L and three steps of coating), a coating of almost 0.35 g of Amberlyst 15 per gram of foam can be attained, it constitutes the maximum possible load of catalyst without blockage of the pores. A last trial without Aculyn in the suspension involving the not requirement of the regeneration phase is realized, it shows that the quantity of catalysis coated can not be increased in spite of the multiplication of the coating phase. So, the importance of the Aculyn in the starting suspension is demonstrated. The procedure with a concentration of 225 g/L and three successive coating is kept for the following tests.

Pieces of foam coated with this procedure are tested in kinetic experiment while an additional test with a concentration of 90 g/L and two successive coating is also done to have a comparison point and determine the low part of the range of equivalent activity of the ceramic foam. Results obtained for these two tests are presented in Figure 5 with also the comparison with the others coating method and the Amberlyst 15. This figure confirms that the equivalent activity of the first method of coating are

very low, lower to 0.1 g equivalent of Amberlyst per gram of foam. Concerning coating of Amberlyst 15, the equivalent weight Amberlyst per gram of foam is almost 0.6 g for the first test (Concentration of 90 g/L and two step of coating). Moreover, the second test (Concentration of 225 g/L and three step of coating) shows an activity approaching the activity of Amberlyst 15 with a gram of foam giving an equivalent activity of 1 gram of Amberlyst 15; this allows to foresee the application in reactive distillation.
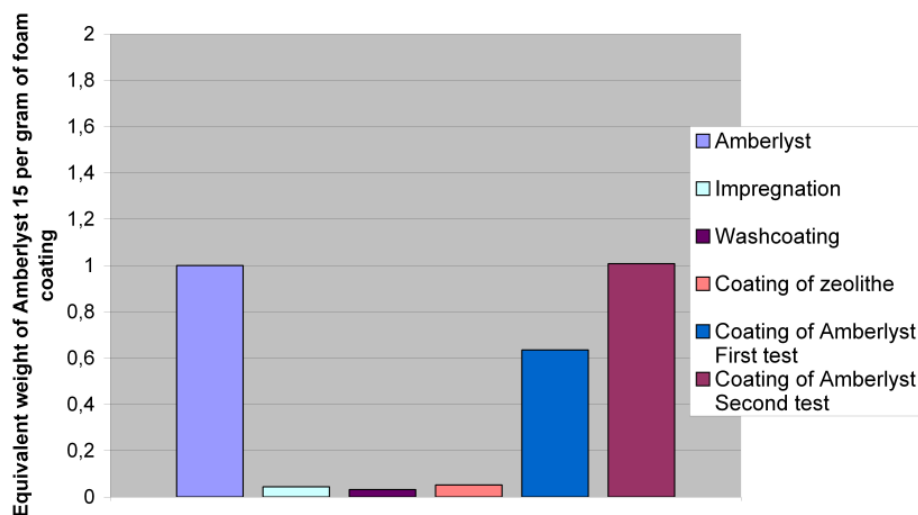
Figure 5. Equivalent weight of Amberlyst 15 per gram of foam coating

To have a point of comparison with Sulzer KATAPAK for example, it is important to define another criterion. That is why we decided to estimate the possible activity of ceramic foam in term of mass of Amberlyst per cubic meter of packing. From the studies available in literature concerning different type of KATAPAK, a range of values can be released; the quantity of Amberlyst 15 per cubic meter of KATAPAK is comprised between 100 and 200 kg/m^3.

While considering that the ceramic foam used in this work has an apparent density of 140 kg/m^3, it is possible to calculate the equivalent mass of Amberlyst installed per cubic meter of foam by using the results of kinetic experiments.A summary of these values is presented in Table 1 for each method.

Table 1. Comparison of the mass equivalent of Amberlyst 15 for each method of catalyst coating

Type of catalyst	Mass equivalent of Amberlyst 15 per m^3 of foam (kg/m^3)
KATAPAK	100-200
Impregnation	4.6
Washcoating	4.5
Coating of Zeolithe	7.2
Coating of Amberlyst first test	80
Coating of Amberlyst second test	141

This table shows that our range of possible mass equivalent of Amberlyst installed per cubic meter of packing is almost 80-140 kg/m^3 which is in agreement with the range of values of KATAPAK. Thus,

theoretically, we can consider that ceramic foam coating with Amberlyst 15 will exhibit a similar activity than KATAPAK for reactive distillation experiments.

4. Conclusions

After having shown that application of ceramic foam as a packing for distillation is possible[1], this work deals with the second part of the development of a catalytic internal which is the determination of the efficiency of catalyst coating by kinetic experiments. The kinetic study is realized in a batch reactor on the esterification of acetic acid by methanol.

Different method of catalysts coating have been tested showing that the most efficiency in term of activity is the coating of Amberlyst 15 following the procedure of Peters et al.[5].This procedure has been modified to determine the maximal weight of Amberlyst being able to be coated per gram of ceramic foam. A mass of almost 0.35 g of Amberlyst per gram of foam has been coated for a starting suspension with a concentration of 225g/L and three successive step of coating.

The activity obtained with this foam is very good with an activity approaching the activity of Amberlyst 15 itself. To have a point of comparison with existing catalytic packing like KATAPAK, we decide to talk in term of Amberlyst weight per cubic meter of packing installed. While considering a range of values comprised between 100 and 200 kg/m^3 for KATAPAK, our results give a corresponding range of 80-140kg/m^3 which is in agreement with KATAPAK.

So, the activity obtained of foams coating with Amberlyst 15 is satisfactory for test in reactive distillation. Currently, tests of reactive distillation with KATAPAK and foam coating for the esterification of acetic acid are in progress to compare the efficiency of our packing with a classical catalytic packing used in industry.

Acknowledgements

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