Membrane reactors in gas phase oxidations

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Abstract

This research was aimed at developing new catalytic membrane reactors to be used for :

i)   partial oxidation of toluene (to benzaldehyde and benzoic acid)

ii)   oxidative dehydrogenation of propane

iii)   complete oxidation of propane and toluene.

The reactor is particularly useful for the optimisation and the industrial development of heterogeneous catalytic processes, particularly for those processes where it is necessary to control the reactants stoichiometry in the reaction zone. This control limits consecutive reactions, thus obtaining high selectivity with industrially interesting conversions. This presentation will concentrate on the partial oxidation of toluene.

Introduction

Benzoic acid and benzaldehyde are chemical intermediates of great relevance in the chemical industry. Benzoic acid can be used to prepare ε-caprolactam. Benzaldehyde is used as intermediate in the dye and perfume industry and as a solvent for resins and oils. The main production rout of these compounds (liquid phase oxidation) is negatively affected by some drawbacks, such as the corrosion problem associated to the type of solvent utilised (acetic acid) and the difficulties related to the separation of the products.

An alternative way to obtain benzoic acid and benzaldehyde is through the gas phase oxidation of toluene and this was the aim of this research work. Both traditional support (TiO_2) and a new mixed Al_2O_3-TiO_2 support for the active catalysts element, vanadium, were used. The oxidation process was carried out by using a packed bed reactor and an inorganic membrane reactor. Work is still in progress and in this presentation we will concentrate on the first results we have obtained, specifically

a)   study of the reaction pathway and estimation of the kinetic parameters

b)   study of a possible use of a membrane reactor to carry out the reaction in alternative to more traditional reactors

c)   catalysts preparation, its deposition on the porous wall of the membrane reactor, and first reaction runs

Reaction pathway and kinetic parameter estimation

When toluene is contacted with oxygen either form carbon dioxide directly or benzaldehyde which, in turn, can form benzoic acid or carbon dioxide again. The scheme of the reaction is that depicted in Figure 1. It is generally assumed that, when oxygen is present in large quantity, the reactions are first order with respect to the other reactants. Miki et al. (1996) have presented experimental data on product selectivity at 350 C, when vanadium was the active catalysts element and for slightly different support, for a wide range of toluene conversion. These data have been expressed in terms of product concentration to reactant concentration ratio; a minimisation routine applied to a simple material balance can give a first quantification of the relative values of the kinetic constants appearing in the reaction scheme of Figure 1.
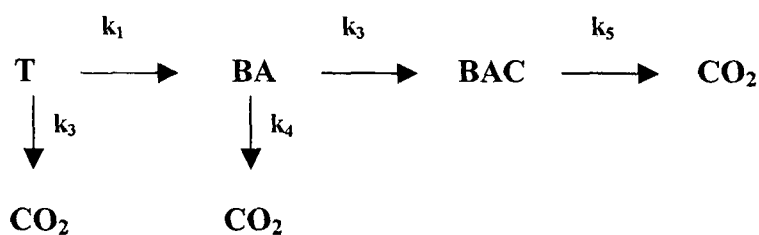
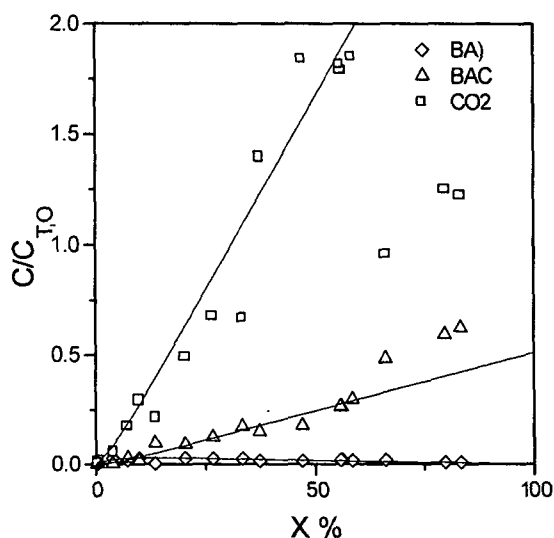Figure 1. Proposed reaction pathway

Figure 2. Product concentrations function of toluene conversion

Figure 2 reports the original experimental data and the fitting curves, whereas the following Table reports the estimated relative values of the kinetic constant. Also in the Table the same ratios, as independently estimated by Bulushev et al. (2001) are reported for comparison

Table 1. Estimated relative values of the kinetic coefficients for the reaction scheme of Figure 1.

	k_2/k_1	k_3/k_1	k_4/k_1	k_5/k_1
This work	20	0.30	10	1
Bulushev et al. (2001)	13	0.25	NA	NA

The use of a membrane reactor.

Membrane reactors are an interesting alternative to traditional reactors. The catalysts is fixed to the wall of the membrane so that losses are negligible, and the possibility to have a product or a reagent entering the reactor through the wall give rise to a number of interesting arrangements. Obviously, we want to be sure first that the reactor performance is not mass transfer limited and a mathematical model was utilised for this purpose. For low fluid velocity in the tube, such as the case considered in this work, the component concentration in the reactor changes both with in the radial and the axial direction. However it has been shown (Tronconi and Forzatti, 1992) that the system can be described by mono-dimensional equations as long as the correct mass transfer coefficient is utilised. We have followed here that approach and, in order to find

out if mass transfer of reaction kinetics is the limiting factor, we have defined a parameter Φ which represent the ratio of the maximum mass transfer rate to the maximum kinetic rate. The value of the concentration at the wall of the reactor relative to that in the bulk can be estimated function of Φ for any kinetic law, and for few representative cases is reported in Figure 3. From the Figure we can see that wall concentration is practically equal to bulk concentration, i.e. we are in kinetic limiting regime, when $\Phi<0.01$.
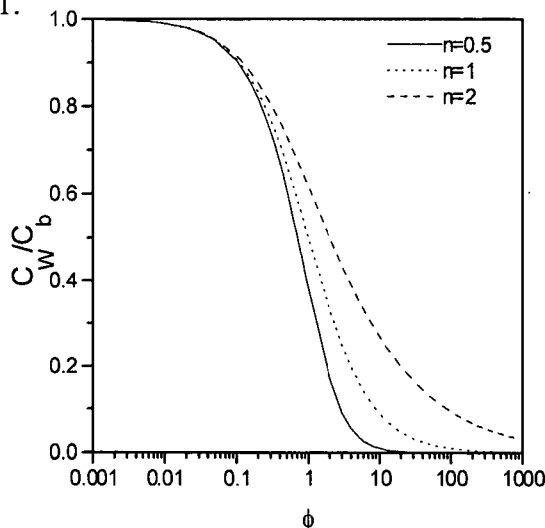

Figure 3. Calculated reactant concentration at the wall

Catalysts preparation and characterisation

Two types of ceramic membranes were utilised. These membranes were ceramic tubes with an inner diameter of 6.7 mm and an outer diameter of 10 mm. These tubes were cut for a total length of about 15 mm and both the end were enamelled to assure the gas tight in a stainless reactor. Both the ceramic tubes (supplied by Atech and Schumacher, Germany) were formed of α-Al_2O_3 and the pore dimension decrease from the outer to the inner side. The Schumacher tube had an inner layer of TiO_2 (anatase) with a nominal pore diameter of 5 nm. Vanadium was deposited on the Schumacher membrane by five impregnation cycles of the dried tube from an ammonium metavanadate solution (9 g/100ml) and it was called T-V membrane. The inner side of the Atech tubes was coated with a thin layer of Al_2O_3-TiO_2 by the dip coating technique starting from a sol prepared as described above. Vanadium was deposited on this last membranes by the adsorption technique as done for the catalytic powders. The membranes were characterised in terms of permeance to helium at room temperature, by SEM photograph and EDX analysis.

Catalytic test results

The sample catalytic test presented here were made with two membrane differing in the total amount of vanadium deposited on them. In the first membrane the amount of active catalysts was such that very low conversion of toluene were achieved for any gas residence time investigated. At such low residence time only benzaldehyde and carbon dioxide were detected as products. Their exit concentrations are reported in Figure 4 function of total toluene conversion. It is interesting to stress, however, that for this very low conversion the kinetic model derived before was fully satisfactory, as the continuous lines in Figure 4 demonstrated.
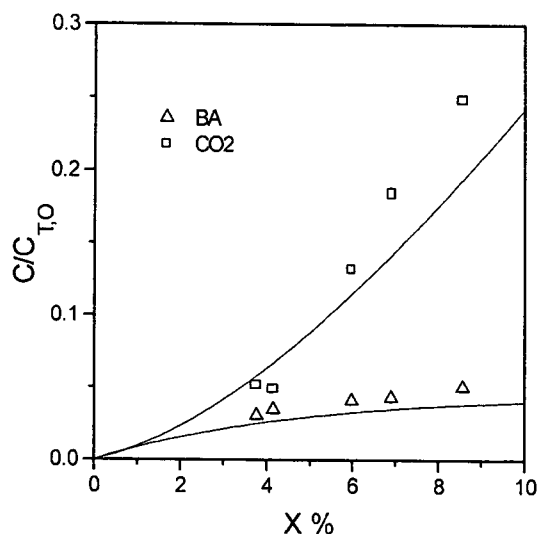
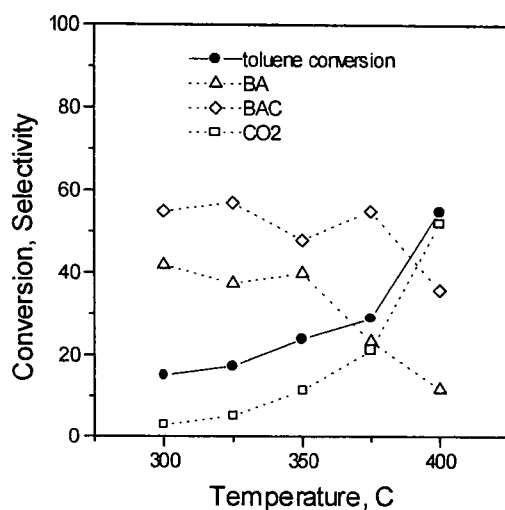Figure 4. Product exit concentration in the membrane reactor.

Figure 5. Toluene conversion and product selectivity at various temperatures.

The second membrane reactor utilised had a much greater vanadium content, therefore the toluene conversion was also greater. Figure 5 reports experimental toluene conversions and product selectivity at the various temperature investigated. The trends are in agreement with similar results presented in literature. A full interpretation and discussion of these results will be given in the workshop.

References

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