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Alternative solution for strongly exothermal catalytic reactions: a new metal-structured catalyst carrier

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Abstract

In many processes of selective catalytic oxidation of hydrocarbons, e.g. benzene or *n*-butane to maleic anhydride, large amounts of heat are evolved and the catalytic bed has to be intensely cooled by the mixture of molten salts. At higher temperatures, the reaction rate and thus the amount of released heat increase causing local superheatings of the catalyst (hot spots) and hence its deactivation. In these studies, we report on a new metal-structured catalyst carrier with better heat and hydraulic characteristics.

The pressure drop and heat transfer characteristics of over 30 novel-structured metal carriers as well as the standard ceramic ones have been experimentally investigated and correlated in terms of the Fanning friction factor and Nusselt number vs. Reynolds number.

The best-structured carrier gave 16–18% larger heat transfer coefficients and 10–40% lower pressure drops in the operation range of the industrial reactors in comparison with the classic random ceramic supports. The utility of this structured carrier has been confirmed by reaction experiment of *n*-butane oxidation to maleic anhydride. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Selective catalytic oxidation; Maleic anhydride; Pressure drop; Heat transfer

1. Introduction

In many processes of selective catalytic oxidation of organic compounds large amounts of heat, of the order of 1400 kJ/kg of feed, are evolved and the catalytic bed has to be intensely cooled. The processes of oxidation of benzene or *n*-butane to maleic anhydride, *o*-xylene or naphthalene to phthalic anhydride or ethylene to ethylene oxide, are good examples. These processes are carried out in reactors containing thousands of tubes of approximately 1 in. ID, packed with supported catalysts. Nowadays, the active mass of the catalyst is usually deposited on the surface of ceramic carriers of half-ring shape and the size $\phi 10\times 6\times 2$ mm or on rings with rounded edges and the size $\phi 7\times 7\times 1.5$ mm [1].

The typical reactor is supplied from the top with feed — air mixture and cooled by the mixture of molten salts circulating in the intertubular space. This keeps the temperature of the reactive zone in a strictly predetermined narrow range. At lower temperatures, the extinction of the reactor takes place. On the other hand, at higher temperatures the reaction rate, and hence the amount of the released heat, increases causing local superheatings of the catalyst (so-called hot spots) and as a result its deactivation. Both the catalyst activity and selectivity decline, badly affecting the production and overall process economy.

The problem of catalyst superheating is caused by internal heat transfer coefficient which is too low in comparison with the amount of heat evolved inside

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Nomenclature

a	specific surface (m^2/m^3)
d	inner tube diameter (mm)
$f = \Delta P d / 2\rho w^2 h$	Fanning friction factor (Darcy–Weisbach equation)
h	height of the carrier's layer (mm)
$Nu = \alpha d/\lambda$	Nusselt number
ΔP	pressure drop of the whole packing layer (Pa)
$Re = \rho w d/\eta$	Reynolds number
w	superficial gas (air) velocity (m/s)

Greek symbols

α	heat transfer coefficient (W/m^2 K)
ε	void volume of the carrier (m^3/m^3)
η	dynamic viscosity of the gas (Pa s)
λ	thermal conductivity of the gas (W/m K)
ρ	density of the gas (kg/m^3)

the reactor's tube. Many attempts were made to tackle this problem. Most of them proposed the use of catalyst of different activity in different zones of the reactor. This leads to a decrease in the reaction rate and hence the amount of heat evolved in critical regions of the reactor. The shape and dimensions of the catalyst supports are unchanged as well as the heat transfer coefficients. In the present study, an attempt has been made at increasing the heat transfer coefficient and to use it — besides the catalyst activity — as one more steering parameter of the process.

A new approach presented in this study makes use of the structured metal carriers instead of random ceramic supports. The new carrier should achieve higher heat transfer coefficients at lower pressure drops in comparison with the random ceramic carriers. Apparently, due to the clear analogy between heat and momentum transfer this task had to be reformulated into the equivalent one; to determine the novel shapes of structured carrier, matching the contradictory trends (of heat transfer and pressure drop) in an acceptable (possibly optimal) way. In addition, the surface areas of suitable metal carriers should not be less than those of the ceramic supports and the metal itself should exhibit good adhesive properties for the active compounds.

2. Experimental investigations

The present studies focussed on the investigation of pressure drop and heat transfer characteristics exhibited by novel-structured metal carriers as compared with the conventional random ceramic supports. They covered over 30 carriers of different construction, including many modifications, as well as two standard randomly packed ceramic supports used nowadays in the industrial reactors. All the structured carriers have been manufactured within the framework of this study by our institute; the ceramic supports are standard industrial products. Several most promising carriers are characterised in Table 1; the values of the specific surface area and void fraction are also presented.

The experimental setup is presented in Fig. 1. Air was used as the working medium under normal pressure and in the range 150–200°C. The range of temperatures was slightly lower than in the real industrial processes, due to the equipment limitations. The test tube (26 mm ID, about 600 mm long) filled with the investigated carrier was heated by an electric heater to provide for the constant heat flux density over the whole surface. Air throughput and its temperatures at the tube inlet and outlet were monitored. Nine thermocouples were used to measure the temperature at the inner surface of the tube. The heat transfer coefficients were calculated dividing the heat flux (verified by energy balance of the test tube) by the mean temperature difference between the flowing air and the tube surface. All the measurement devices were connected to the computer assuring collecting and calculating the data in real time.

For each carrier, the results were correlated in terms of the Fanning friction factor and the Nusselt number vs. the Reynolds number, as shown in Table 1. The constructions of the carriers investigated were different, and in consequence their hydraulic diameters differed from each other. In contrast, the inner diameter of the test tube remained constant and the same as used in the industrial installation of phthalic anhydride production, which has been selected as the model process. This tube diameter has been selected arbitrarily as the transversal dimension (unique for all the carriers) in definitions of all the parameters describing flow and heat transfer (Reynolds and Nusselt numbers, friction factor). This approach (less theoretical and more connected with industrial practice) leads

Table 1
Description of selected carriers and correlations for Fanning friction factor and Nusselt number[a]

No.	Carrier's nick name	Description of carrier	ε (m^3/m^3)	a (m^2/m^3)	Correlation, f	Correlation, Nu
1	Ceramic half-rings	Ceramic half-rings: $d_e = 10$ mm, $h = 6$ mm, $t = 2$ mm; randomly packed	0.546	690	$155.47\ Re^{-0.262}$	$0.0217\ Re^{1.048}$
2	Ceramic rings	Ceramic Raschig rings with rounded edges: $d_e = 7$ mm, $h = 7$ mm, $t = 1.5$ mm; randomly packed	0.537	750	$56.44\ Re^{-0.190}$	$0.0933\ Re^{0.884}$
4	Two rosettes and ring	Two rosettes (of 20 leafs, $d_e = 26$ mm, $h = 10$ mm) and after them one flat ring ($d_e/d_i = 25.3/16$ mm)	0.967	963	$44.13\ Re^{-0.171}$	$0.0295\ Re^{1.004}$
5B	Rosette, ring and disk type B	One rosette (as No. 4), one ring (as No. 4), one rosette, one disk type B (flat, $d_e = 23$ mm)	0.974	1040	$109.65\ Re^{-0.150}$	$0.0231\ Re^{1.063}$
6	Two rosettes and U-shaped ring A	Two rosettes (as No. 4) and one U-shaped ring type A (drawed, $d_e/d_i = 24.3/14.1$ mm, $h = 2$ mm)	0.971	896	$14.45\ Re^{-0.118}$	$0.0755\ Re^{0.873}$
7A	Rosette and U-shaped ring A	Rosette (as No. 4) and U-shaped ring A (as No. 6)	0.959	903	$49.50\ Re^{-0.222}$	$0.0338\ Re^{0.986}$
7B	Rosette and U-shaped ring B	Rosette (as No. 4) and U-shaped ring type B ($d_e/d_i = 24.4/12$ mm, $h = 2.2$ mm)	0.956	918	$62.34\ Re^{-0.216}$	$0.156\ Re^{0.820}$
8	Rosette, U-shaped ring A and U-shaped disk	One rosette (as No. 4), U-shaped ring A (as No. 6), one rosette and U-shaped disk ($d_e = 20$ mm, $h = 3.3$ mm)	0.967	840	$33.25\ Re^{-0.192}$	$0.0555\ Re^{0.913}$
14	Rosette with "drop" built-in and ring	One rosette (of 20 leafs, $d_e = 26$ mm, $h = 22$ mm) with built-in metal "drop" ($d_z = 11.8$ mm, $h = 19.1$ mm) in the center and one ring (as No. 4)	0.858	857	$17.80\ Re^{-0.102}$	$0.0442\ Re^{0.940}$

[a] Designation of the dimensions of carrier's element: d_e/d_i — external/internal diameter; h — height; t — thickness (for ceramic supports). Carriers No. 4–14 are made from metal leaf of 0.05 mm (rosettes) and 0.3 mm (rings and disks) of thickness.

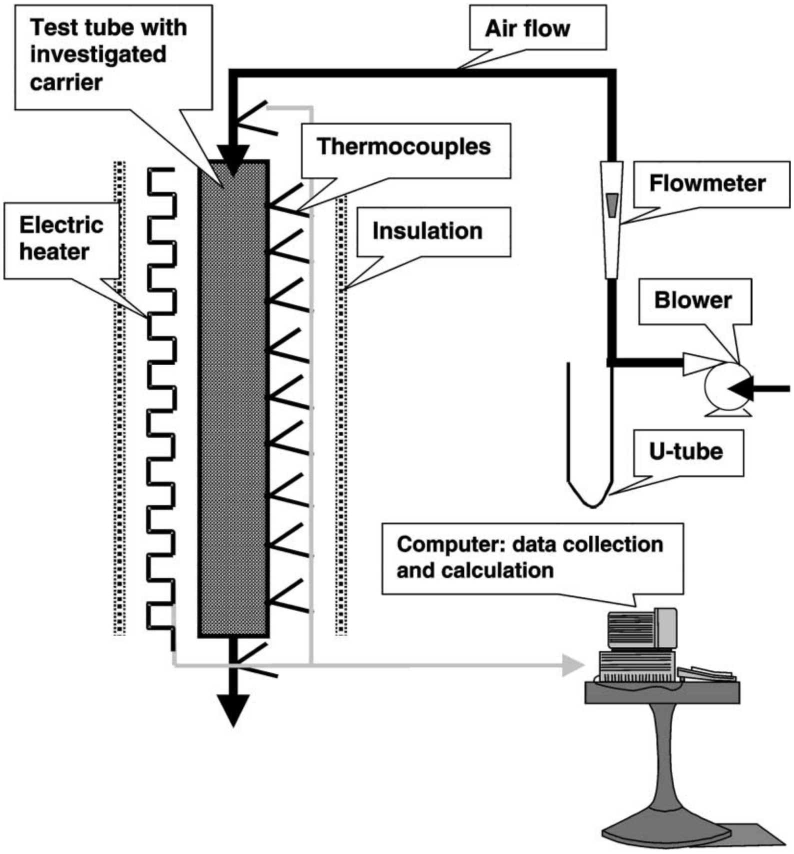

Fig. 1. Experimental setup.

to a comfortable comparison of carriers investigated from the standpoint of the reactor performance.

More detailed description of the carriers investigated is given in Table 1 presenting the best group from among the studied carriers. These carriers have been composed of elements such as rosettes, rings and disks are shown in Fig. 2. This group of the best carriers has to exhibit simultaneously reasonable levels of heat transfer coefficient and pressure drop; some carriers, in spite of a good ratio of heat transfer to pressure drop, have not been included due to very low values of heat transfer coefficients. Other carriers, e.g. screw surfaces, wire screw surfaces or regularly stacked metal Raschig rings, showed distinctly inferior characteristics [2]. All the metal carriers have been prepared from a thin leaf (0.05–0.3 mm) of a chromium–aluminum steel 00H20J5.

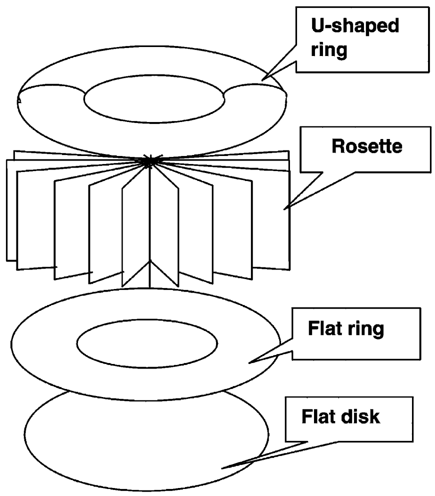

Fig. 2. Elements of the structured carriers.

3. Results and conclusions

The results for the selected structured carriers and for the random ceramic supports are presented in Fig. 3a–c, whereas the corresponding correlations are given in Table 1. In the correlation for Nusselt number, exponents of Reynolds number are relatively high due to the flow range which lies near the transition region. The experimental data fit to the correlations very well. The correlation coefficients are above 0.95 (usually 0.99) and maximal scatter of the experimental points referred to the correlation only incidentally exceeds 10%.

Several important conclusions could be derived from the results obtained:

- For all reasonably designed structured carriers and random ceramic supports, the flow and heat

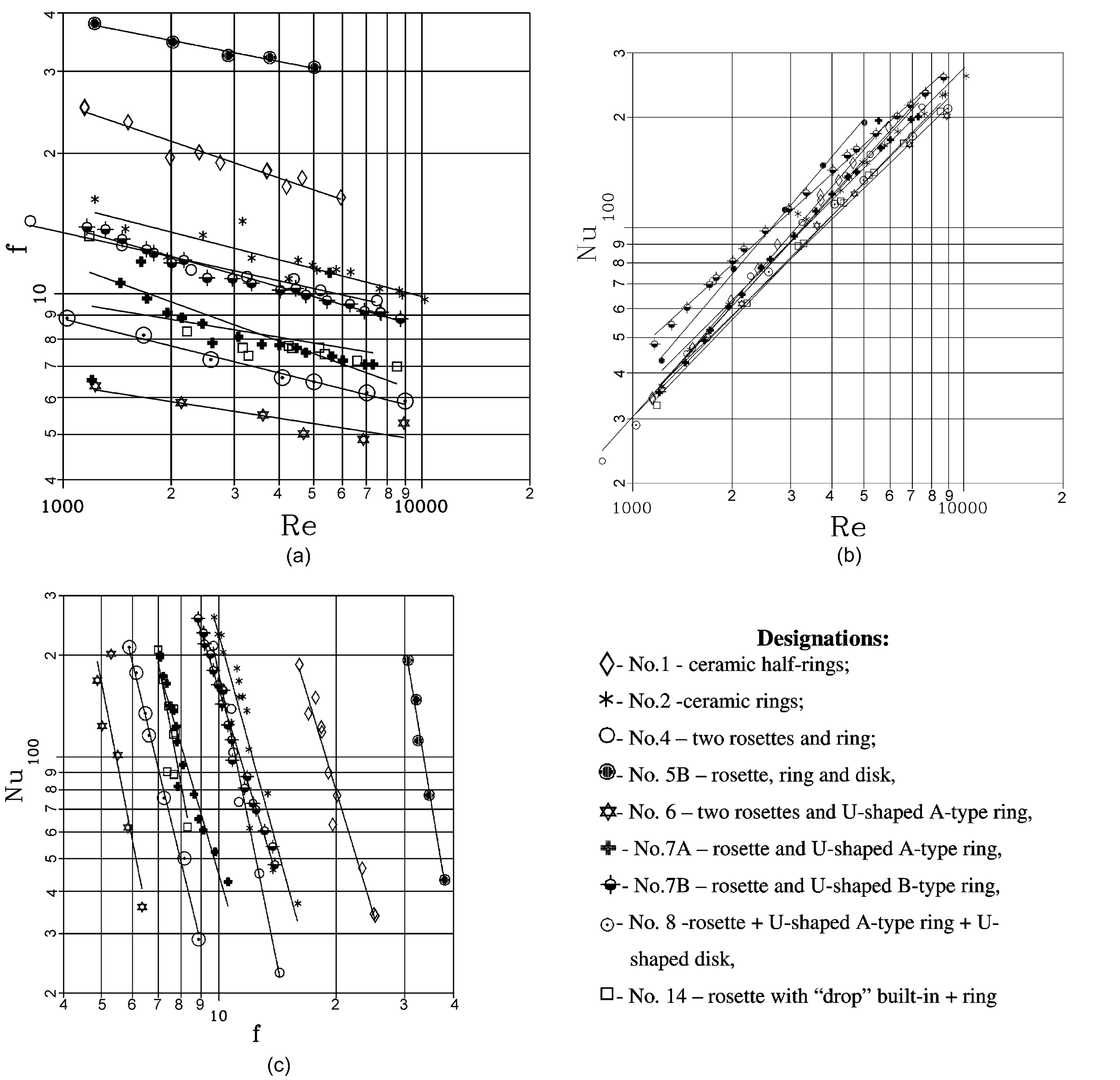

Fig. 3. Heat and flow characteristics of carriers: (a) friction factor vs. Reynolds number; (b) Nusselt vs. Reynolds numbers; (c) Nusselt number vs. friction factor.

transfer characteristics lie very close to each other. The better heat transfer, the higher the pressure drop.

- Some carriers can apparently give very promising results as judged from the Nusselt number vs. friction factor plots. However, to obtain reasonable intensities of heat transfer unrealistically high gas flow velocities have to be applied.
- The random carrier of the small ring shape with rounded edges gives very good results, especially very low pressure drops.
- The best-structured carrier (No. 7B) gives approximately 18 and 16% higher heat transfer coefficients (at $Re \cong 3000$, i.e. in the operation range of the industrial reactors) than ceramic rings and half-rings, respectively, and pressure drops lower by 10 and 40%. Moreover, its specific/volumetric surface area is larger than of the corresponding ceramic supports by 22 and 33%.
- The use of the suitable metal-structured carrier instead of the conventional ceramic support may notably improve reactor's performance.
- It is very difficult to find a simple and reliable criterion, easy to express in a mathematical form, which could indicate the best carrier. Our aim was to improve such parameters as pressure drop, specific surface area, heat transfer coefficient. The complex process modeling with respect to the reaction kinetics and heat and momentum transfer should give more precise information about how to select the best carrier avoiding overdimensioning. This task goes, however, beyond the scope of this study.

The ultimate verification of the carrier should be undoubtedly the reactive experiment. A vanadia–phosphoria catalyst has been deposited on a structured carrier 7B. In order to obtain this, the surface of chromium–aluminum steel has been chemically treated to form a thin layer of alumina. Further stages of the catalyst preparation were the same as for the ceramic supports. Then the reactive experiments of *n*-butane oxidation to maleic anhydride have been performed using a laboratory reactor of 23.9 mm in diameter and 165 mm in length. The conversion of *n*-butane attained 44.5%, the selectivity towards maleic anhydride was 31%. For such a small reactor the results proved to be very good. The mechanical properties of deposited catalyst were as good as for ceramic supports. These results confirmed the utility of the metal-structured carrier for such processes.

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