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Characteristics of metallic structured catalysts with high thermal conductivity

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Abstract

The heat transfer properties of home-made plate-type structured catalysts with coated metallic supports are investigated, using the oxidation of carbon monoxide over Pd–Al_2O_3 as a model reaction. It is shown that heat conduction in the supports can be exploited to curb effectively the temperature gradients. Hot spot temperatures are lower when using supports made of materials with higher intrinsic thermal conductivity and with thicker plates. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Structured catalysts; Monoliths; Fixed-bed reactors; Effective thermal conductivity; CO oxidation

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1. Introduction

The use of structured monolith catalysts is well established in environmental catalysis [1]. On the other hand, only sparse attempts have been reported in the literature concerning their applications to gas/solid processes for the production of chemicals [2,3]. However, such applications involve at least one great potential advantage over conventional packed-bed reactors, namely, strongly reduced pressure drops (roughly by two orders of magnitude). A second potential benefit, i.e. more favorable heat transfer properties due to heat conduction in the connected monolith structure, is more controversial. In fact, published theoretical and experimental studies of heat transfer in monoliths, addressing either Sulzer-type structured metallic supports [4] or FeCr Alloy honeycomb monoliths [5], have demonstrated only modest improvements of the effective heat transfer characteristics in comparison to packed beds of pellets. Such results refer however to existing commercial supports, not originally designed in view of optimal heat conduction. On the contrary, some of their features conflict with this goal, including, e.g. the very thin walls associated with high void fractions, as well as the support materials, which are typically selected for their resistance to high temperatures but exhibit a relatively poor thermal conductivity. The question of whether structured catalysts with optimized specific design can effect significant reductions of the temperature gradients in fixed-bed catalytic reactors has not been experimentally addressed so far.

In previous papers [6–8] some of us have shown by analysis and simulation that: (i) novel metallic honeycomb supports designed with suitable geometric properties and materials can afford much higher effective radial and axial thermal conductivities than conventional packed beds of catalyst pellets; (ii) externally cooled multitubular fixed-bed reactors loaded with such structured catalysts would operate in principle with markedly reduced hot spot temperatures even in the case of very exothermic gas/solid reactions as, e.g. in industrial partial oxidation processes.

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Herein we present an experimental study of the thermal behavior of structured (plate-type) catalysts with coated metallic catalysts supports, using CO oxidation as a model reaction. The catalyst samples have been constructed expressly for this investigation. The influence of the intrinsic heat conductivity of the support material, as well as the effect of changing the thickness of its slabs, are investigated in order to obtain guidelines for future catalyst design work.

2. Experimental

2.1. Structured catalysts and reactor

Three plate-type catalyst samples were prepared, with structured metallic supports made of aluminum (99.5% commercial purity, sample A) and of stainless steel (AISI 304, samples B and C). In all cases, as shown in Fig. 1, the supports consisted of four slabs (width=46 mm, length=200 mm), with half-thickness of the two central slabs=0.5 mm (samples A and B) or 0.2 mm (sample C). For all samples, the thickness of the two outer slabs was equal to the half-thickness of the central ones, since they were coated with catalyst on one side only. The slabs were assembled with spacers 3 mm apart in order to form three parallel rectangular channels.

The catalytic washcoat was obtained starting from a commercial γ-Al_2O_3 powder impregnated with Pd (3% w/w) and dissolved in a solution of sodium silicate. The resulting slurry was then deposited onto the metal slabs pretreated with HNO_3. Calcination up to 500°C followed, yielding adherent uniform coatings with bulk composition 40.3% w/w SiO_2, 18.4% w/w Al_2O_3, 9.3% w/w Na evaluated by atomic adsorption. A uniform washcoat thickness of about 150 μm was observed in SEM micrographs. BET and Hg porosimetry revealed very low porosity and specific surface area. Further details on the coating are given elsewhere [9].

The assembled packet of coated slabs was equipped with five $\frac{1}{16}$ in. stainless steel tubes at different transverse locations, acting as thermowells for sliding J-type thermocouples, and eventually loaded into a stainless steel reactor tube (46 mm×26 mm internal cross section) placed inside an oven with air recirculation (Mazzali Thermotest) driven by a proportional-integral-derivative controller. A uniform temperature distribution (within 1°C) on the external reactor walls was achieved under all the investigated conditions.

2.2. CO oxidation runs

The structured catalysts were tested in CO oxidation. The reactor feed stream consisted of 2–9% v/v CO in air or air/N_2, with feed flow rates in the range 700–2000 cm^3/min (STP). Analysis of reactants and products was performed by an online GC (HP 6890 Series) equipped with a Porapak Q packed column and

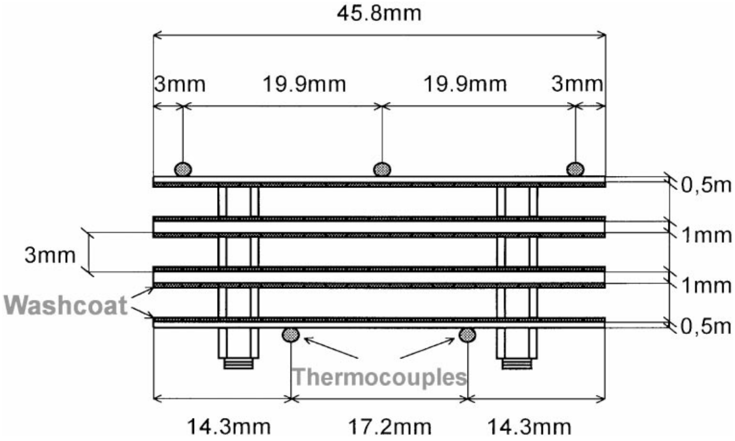

Fig. 1. Schematic diagram of the tested plate-type catalysts with metallic supports (front view).

Table 1
Light-off behavior of catalyst samples A, B and C in CO oxidation. Reaction conditions: $Y^{\circ}_{CO} = 0.05$, feed flow=1000 cm^3/min (STP)

Structured catalyst	T_{20} (°C)[a]	T_{50} (°C)[b]
Sample A: Al, s=0.5 mm	189	205
Sample B: steel, s=0.5 mm	192	216
Sample C: steel, s=0.2 mm	176	202

[a] T_{20}: maximum catalyst temperature at 20% CO conversion.
[b] T_{50}: maximum catalyst temperature at 50% CO conversion.

a 5 Å molecular sieve packed column in series with TCD detectors.

3. Results and discussion

3.1. Catalytic activity

For samples A, B and C, Table 1 presents the maximum catalyst temperatures corresponding to 20 and 50% conversions of CO under standard conditions. The three tested catalysts exhibited similar activities, with oxidation of CO starting around 180°C and approaching complete conversion of the reactant above 220–230°C.

Notably, the measured temperature distributions over the structured catalysts remained virtually isothermal up to significant CO conversions, particularly in the case of the Aluminium support (sample A), as discussed in more details in the following section. This greatly simplified the kinetic analysis of the data, and allowed extension of the investigation to large values of the CO feed concentration and of the feed flow rate, both conditions being associated with large thermal loads. A similar investigation of CO oxidation over the same Pd–Al_2O_3 catalyst in the form of powder, loaded in a conventional micro-flow reactor, was limited to a much more narrow range of conditions due to the onset of strong temperature gradients already at $Y^{\circ}_{CO} = 0.03$.

A preliminary kinetic study in the range $Y^{\circ}_{CO} = 0.02$–0.09 yielded a varying negative reaction order for CO and a positive fractional order (=0.5) for O_2. A more detailed kinetic analysis, based on a Langmuir-type rate expression, is reported in [10].

3.2. Thermal behavior of the structured catalysts

Upon increasing the thermal load, e.g. by incrementing the oven temperature and consequently the CO conversion, the average catalyst temperature progressively exceeded the oven temperature. Such an effect is shown in Fig. 2 for catalyst sample A, and is

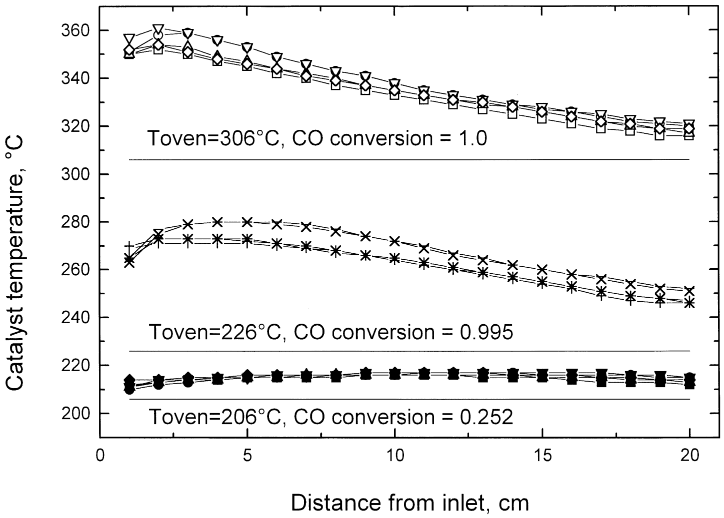

Fig. 2. Catalyst sample A (Al support): influence of the oven temperature on the temperature profiles measured in CO oxidation. Symbols represent the readings of the five thermocouples. Reaction conditions: $Y^{\circ}_{CO} = 0.07$, feed flow=2000 cm^3/min (STP).

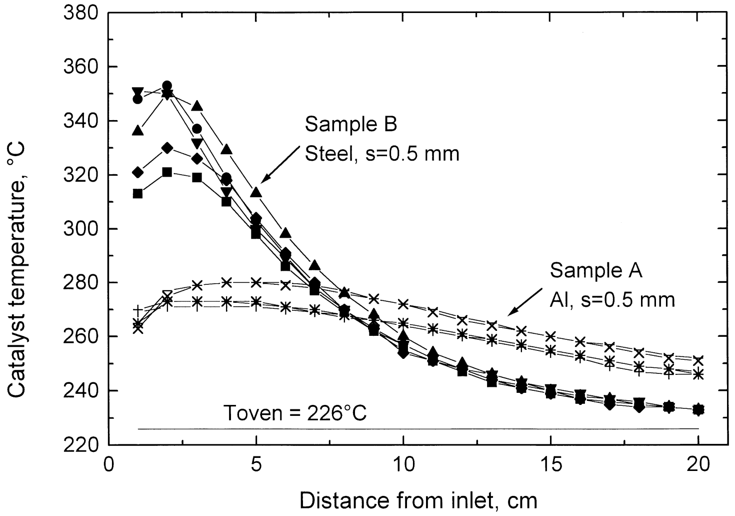

Fig. 3. Comparison of temperature profiles measured in CO oxidation over catalyst samples A (Al support, s=0.5 mm) and B (steel support, s=0.5 mm). Reaction conditions: $Y^{\circ}_{\mathrm{CO}} = 0.07$, feed flow=2000 cm^3/min (STP).

clearly due to the heat transfer resistances hindering removal of the growing heat of reaction from the catalyst structure.

Over sample A, temperature differences between the catalyst and the oven up to 50°C were measured at 100% CO conversion with $Y^{\circ}_{\mathrm{CO}} = 0.07$ and feed flow=2000 cm^3/min (STP). It is worth emphasizing that such conditions correspond to an adiabatic temperature rise of nearly 700°C: nevertheless, as shown in Fig. 2, the measured temperature profiles under such conditions were almost flat in the case of the aluminum (intrinsic thermal conductivity k_{m}=200 W/(m K)) support (sample A), with limited axial gradients and no significant transverse gradients. However, Fig. 3 points out that, under the same reaction conditions, much more marked axial temperature gradients were observed in the case of sample B, with a support having exactly the same geometry as sample A but made of less conductive stainless steel ($k_{\mathrm{m}} \approx 20$ W/(m K)). Furthermore, over such a steel support significant gradients (up to 30°C) were detected also in the direction transverse to flow, as indicated in Fig. 3 by the different readings provided by the five thermocouples at the same axial locations. Even greater hot spot temperatures, associated with more marked gradients, were measured in the case of the structured catalyst based on the steel support with the thinnest slabs (sample C).

For the three tested structured catalysts, Fig. 4 summarizes the influence of material and geometry of the support on the maximum observed catalyst temperature, plotted as a function of the oven temperature. In the low-temperature region, corresponding to low CO conversions, only small positive deviations from the oven temperature (represented by the dashed line in Fig. 4) were observed. Upon light-off of the reaction, greater temperature differences became apparent, which exhibited an asymptotic behavior as the oven temperature was raised and total CO conversion was approached. In such an asymptotic region, the different behaviors exhibited by the three catalyst samples are directly related to their heat transfer characteristics, with sample A being remarkably more effective than the catalysts with steel supports (B and C) in removing the heat of reaction. Likewise, the advantage associated with using thicker slabs is also apparent when comparing catalysts B and C.

A global analysis of the thermal behavior of the tested structured catalysts is presented in Fig. 5, where the maximum difference between the catalyst and the oven temperatures observed in each CO oxidation run is plotted versus the thermal load HL associated with the run. HL represents the total heat of reaction evolved per unit time during the run; it is computed according to the following equation, with symbols

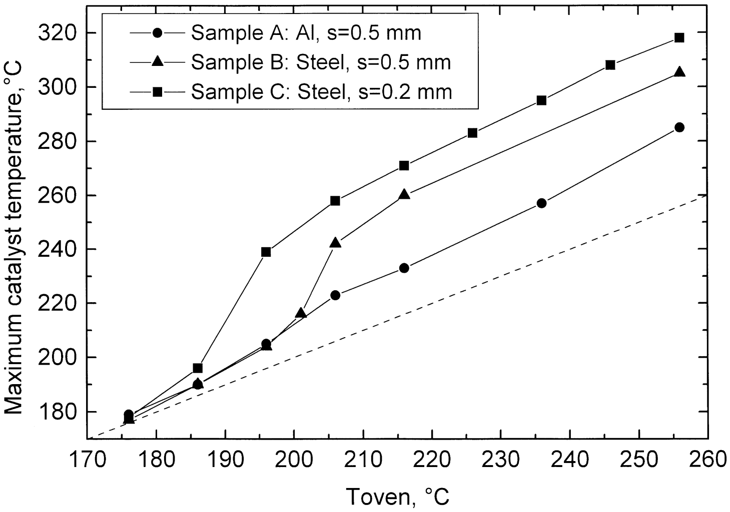

Fig. 4. Comparison of the thermal behaviors of the three tested catalyst samples: maximum catalyst temperature versus oven temperature. Reaction conditions: $Y^{\circ}_{CO} = 0.05$, feed flow=1000 cm^3/min (STP).

explained in Section 5:

$$\mathrm{HL} = FY^{\circ}_{\mathrm{CO}}\eta_{\mathrm{CO}}\Delta H_{\mathrm{R}} \tag{1}$$

Inspection of Fig. 5 shows that, for each structured catalyst, the data points roughly fall on a straight line through the origin, whose slope can be regarded as representative of the overall heat transfer resistance associated with the catalyst sample. The estimates of such a slope, obtained by simple linear regression on the temperature data of the three catalysts, are given in Table 2.

The smallest thermal resistance is clearly associated with sample A: in fact, because of the excellent intrinsic conductivity of the support material, the only significant heat transfer resistances in this case were located at the boundary of the monolith structure, i.e. at the interface between the catalyst slabs

Table 2
Estimated overall thermal resistances of catalyst samples A, B and C, with 95% confidence limits

Structured catalyst	Thermal resistance (K/W)
Sample A: Al, *s*=0.5 mm	1.55±0.01
Sample B: steel, *s*=0.5 mm	4.25±0.06
Sample C: steel, *s*=0.2 mm	5.62±0.34

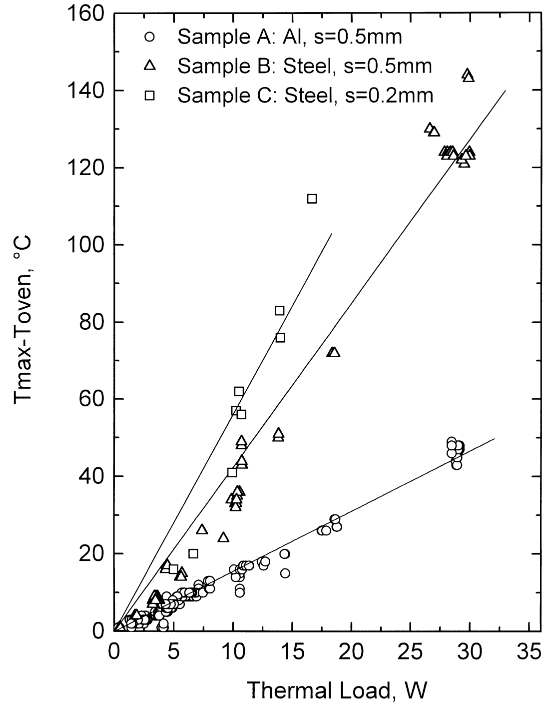

Fig. 5. Correlation between the thermal load of CO oxidation runs, Eq. (1), and the maximum temperature increment observed over the three tested catalyst samples.

and the inner reactor wall, and between the external reactor wall and the oven. Accordingly, the reciprocal of the value given for sample A in Table 2 is essentially an estimate of the wall heat transfer coefficient for the structured reactor. On the other hand, the significantly greater estimates corresponding to samples B and C include additional heat transfer resistances due to the lower effective conductivity of their supports, resulting both from the lower intrinsic thermal conductivity of the construction material and from the reduced thickness of the catalyst slabs.

4. Conclusions

A number of industrial catalytic processes are carried out in gas–solid fixed-bed reactors whose operation is limited by the convective heat transfer rates prevailing in the packed beds of catalyst pellets. Our experiments show that heat conduction in the metallic supports of structured catalysts can provide an effective alternative mechanism to remove the heat generated by strongly exothermic reactions. In view of this purpose, however, a rational design of the support requires that its construction material and its geometry are selected appropriately, since they both play a significant role in determining the effective thermal conductivity of the catalyst matrix.

In line with previous theoretical evaluations, the data herein presented confirm that structured catalyst supports made of highly conductive materials (e.g. Al) and with reasonably thick walls (several hundred microns) are able to limit drastically the temperature gradients even in the presence of large heats of reaction. Notably, such supports differ considerably from those of commercially available structured catalysts for environmental applications.

The present results may suggest new opportunities for the improvement of industrial gas/solid catalytic processes with strongly exothermic reactions, where the operation of packed-bed reactors is limited by the onset of hot spots. Further work is currently in progress in order to better control and eventually reduce the residual heat transfer resistance located at the interface between the structured catalyst and the inner reactor wall.

5. Nomenclature

F	feed molar flow rate (mol/s)
HL	heat load in CO oxidation runs (W)
k_m	intrinsic thermal conductivity of support material (W/(m K))
s	half-thickness of slabs in plate-type catalyst (m)
T	catalyst temperature (K)
Y°_CO	feed CO concentration (mol/m^3)
ΔH_R	heat of reaction (J/mol)
η_CO	fractional CO conversion

Acknowledgements

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