ELSEVIER

Catalysis Today 69 (2001) 357–363

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Preparation and characterisation aspects of carbon-coated monoliths

E. García-Bordejé*, F. Kapteijn, J.A. Moulijn

Industrial Catalysis, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

Abstract

Carbon-coated monoliths have been prepared by dipcoating cordierite monoliths in a polymer solution and subsequent carbonisation. Parameters of preparation that were varied were viscosity of the dipcoating solution, carbon precursor and carbonisation temperature. Two different commercial polymers have been used as carbon precursors, Novolac and Furan resins. Also monoliths have been coated with slurry of such resins and a commercial mesoporous activated carbon (CP-97).

The features of the final carbon that have been optimised are carbon loading, carbon layer thickness, coverage and mesoporosity. Coverage has been tested by leaching test in acid media. Both coverage and mesoporosity are considerably enhanced when the dipcoating mixture was a slurry of Furan resin and a commercial activated carbon. These features makes carbon-coated monoliths very suitable for their use as catalyst support in three-phase reactions. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Carbon-coated monoliths; Polymer; Carbonisation

1. Introduction

In three-phase reactions, the choice for a type of reactor will primarily depend on the reaction under consideration, the experience with a type of reactor, and economics. In general, monolithic reactors combine advantages of slurry reactors and trickle-bed reactors, while disadvantages are eliminated [1]. As in slurry reactors, small catalyst particles are used resulting in high catalyst utilisation because of the short internal diffusion distances and the large geometrical surface. As in trickle-beds, the drawbacks of slurry reactors, e.g., catalyst separation and attrition are avoided. Main advantages over the trickle-bed are that the pressure drop is much lower for beds with the same external surface area. A trickle-bed is also sensitive to flow maldistributions that can lead to problems with hot-spot formation and runaway behaviour.

Carbon has some clear advantages over other (ceramic) support materials. The most-attractive advantage of carbon is its stability in acidic and alkaline media [2]. Moreover, the surface of carbon is relatively inert, so that undesired side reactions catalysed by the support surface hardly occur. Also a too strong interaction of the support with the active phase, which results, e.g., for alumina support in the formation of hardly reducible aluminates [3] is limited. Besides, recovery of noble metals is very easy by burn out of the carbon support. Another advantage of carbon is that both the physical and chemical surface properties of carbon, like surface area, pore-size distribution, oxygen surface groups, and isoelectric point are adjustable over a wide range of values, enabling the tailoring of a carbon support to desired support properties [2].

The advantage of the coated type monolithic support over integral type is that the former benefits

---

* Corresponding author. Tel.: +31-15-278-1186.
E-mail address: e.garcia@tnw.tudelft.nl (E. García-Bordejé).

PII: S0920-5861(01)00392-3

from the high mechanical strength of ceramic support while integral monoliths made out of activated carbon are known for their lower mechanical strength. It is, however, important that the coating adheres well to the monolithic structure so that flaking is prevented. Flaking can cause loss of active material and damage of the downstream equipment. For gas–liquid–solid catalysed reactions, mesopores in the range 5–15 nm are a desired compromise between surface area and accessibility [4].

This work focuses on the optimisation of the dipcoating method to prepare carbon-coated monoliths for application as catalyst support in three-phase reactions. The parameters that have been varied are the carbon precursor, viscosity of the dipcoating mixture and carbonisation temperature (773–1023 K). Two commercial carbon precursors have been used, Novolac and Furan resin. Moreover, an activated carbon has been used as filler. The features of the final carbon coating that have been optimised are the carbon loading, coverage and mesoporosity.

2. Experimental

Two polymers were used as carbon precursors Novolac resin (Dow Chemical) and Furan resin (Hüttenes-Albertus). To coat the cordierite monoliths with a carbon layer the dipcoating method has been used. This consists in dipping the cordierite monolith into the liquid polymer that is subsequently cured and carbonised. The temperatures of carbonisation were 873 and 973 K for Furan and Novolac resins, respectively. At these temperatures the carbonisation was found to be complete since there is no further weight loss in thermobalance by increasing the temperature. Also monoliths were coated with slurry of a commercially activated carbon CP-97 (Engelhard) and a binder. As a binder, both Novolac and Furan resins were used giving rise to a weight composition of CP-97 in the final carbon of 49 and 37%, respectively. CP-97 has a high porosity that is not only due to a relatively high amount of micropores (0.35 cm^3/g) but also to mesopores (0.45 cm^3/g). The viscosity of the dipcoating mixture was measured with a Rheometric ARES apparatus.

Scanning electron microscopy (SEM) was performed using a Philips XL-20 scanning electron microscope and sputtering samples with gold to make them more conductive. Mercury porosimetry was performed on a CE instruments PASCAL 140/440 in the pressure range of 0.01–400 MPa, after outgassing the samples at 423 K in vacuum. In the leaching test a harsh acid treatment is carried out with the coated monoliths. These monoliths are introduced in 1 M HCl solution in a weight ratio of 1:10 monolith/HCl

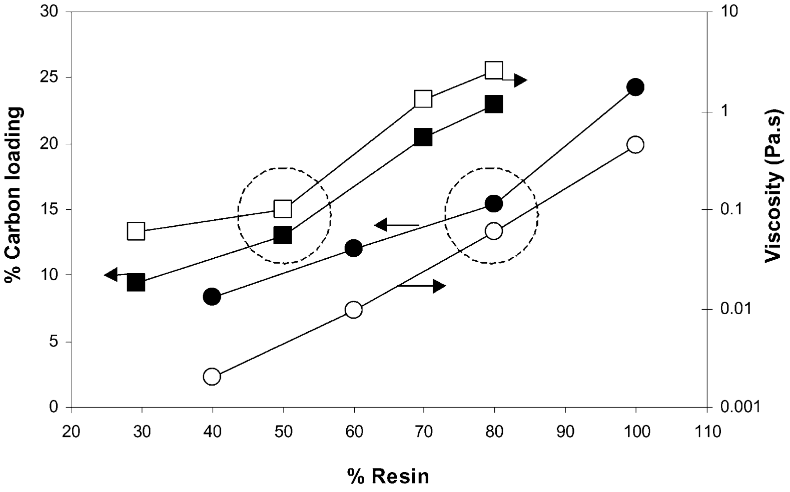

Fig. 1. Viscosity of mixtures of Furan resin + acetone and Novolac resin + butanone in different ratios and carbon loadings obtained thereof. Mixtures of Novolac/2-butanone: (□) viscosity; (■) % carbon loading. Mixtures of Furan/acetone: (○) viscosity; (●) % carbon loading.

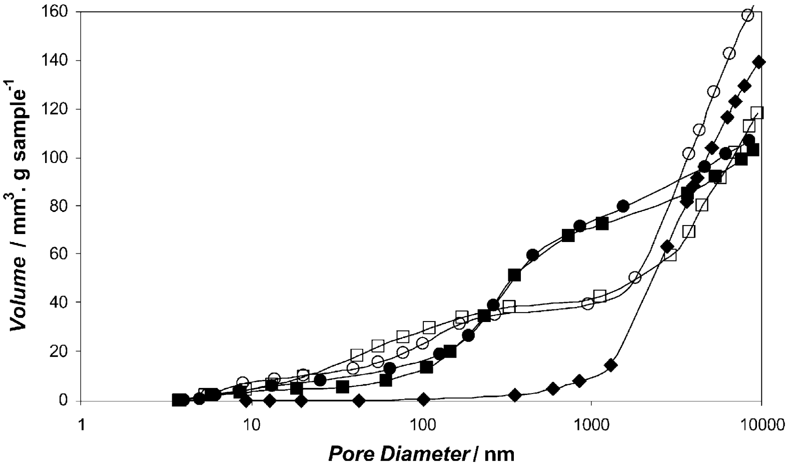

Fig. 2. Cumulative pore volume of carbon-coated monoliths derived from the following precursors: (◆) cordierite; (■) Novolac; (●) Furan; (☐) slurry of CP-97 and Novolac; (○) slurry of CP-97 and Furan.

for 18 h at room temperature shaking the monolith occasionally during this time. After 18 h the monolith is withdrawn from the solution. The latter is analysed by ICP-OES of the concentration of the cations Si, Mg and Al. A blank test was carried out with the vials used in the leaching test observing some Si leaching. The results presented here are corrected for this blank test.

3. Results

Fig. 1 shows the values of viscosity and carbon loading of the monoliths dipcoated with different mixtures of polymer and solvent of the two series in which the relative amounts of each component have been varied. When the resin content in the dipcoating mixture increases the values

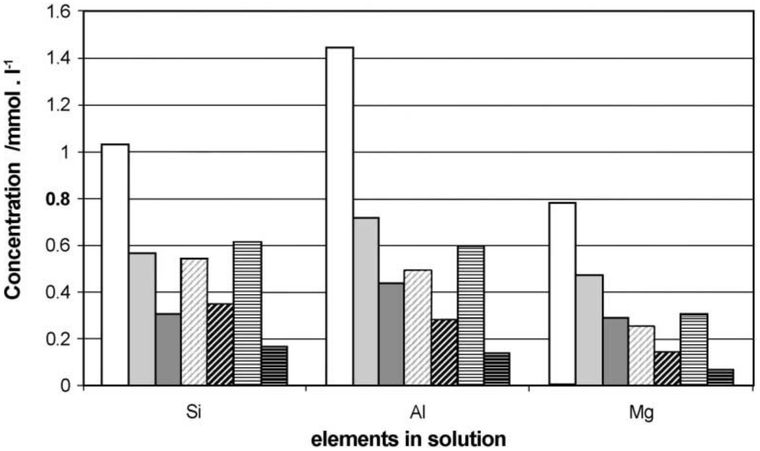

Fig. 3. Leaching of monoliths coated with different carbon precursors and different loadings after treatment with 1 M HCl: ☐ cordierite; ░ Novolac/one dipcoating (13.1% carbon); ▓ Novolac/two dipcoatings (17.9% carbon); ▨ Furan/one dipcoating (13.7% carbon); ▩ Furan/two dipcoatings (18.8% carbon); ▤ slurry of CP-97 + Furan/one dipcoating (9% carbon); ▦ slurry of CP-97 + Furan/two dipcoatings (16.4% carbon).

of viscosity and carbon yield also increase. The values of viscosities and carbon loadings are more reproducible in the monoliths dipcoated with Furan resin–acetone than with the Novolac resin–butanone because in the latter some evaporation of solvent can occur due to the higher dipcoating temperature, room temperature and 323 K, respectively.

In Fig. 2, the cumulative volume of the coated monoliths obtained by Hg intrusion is presented vs.

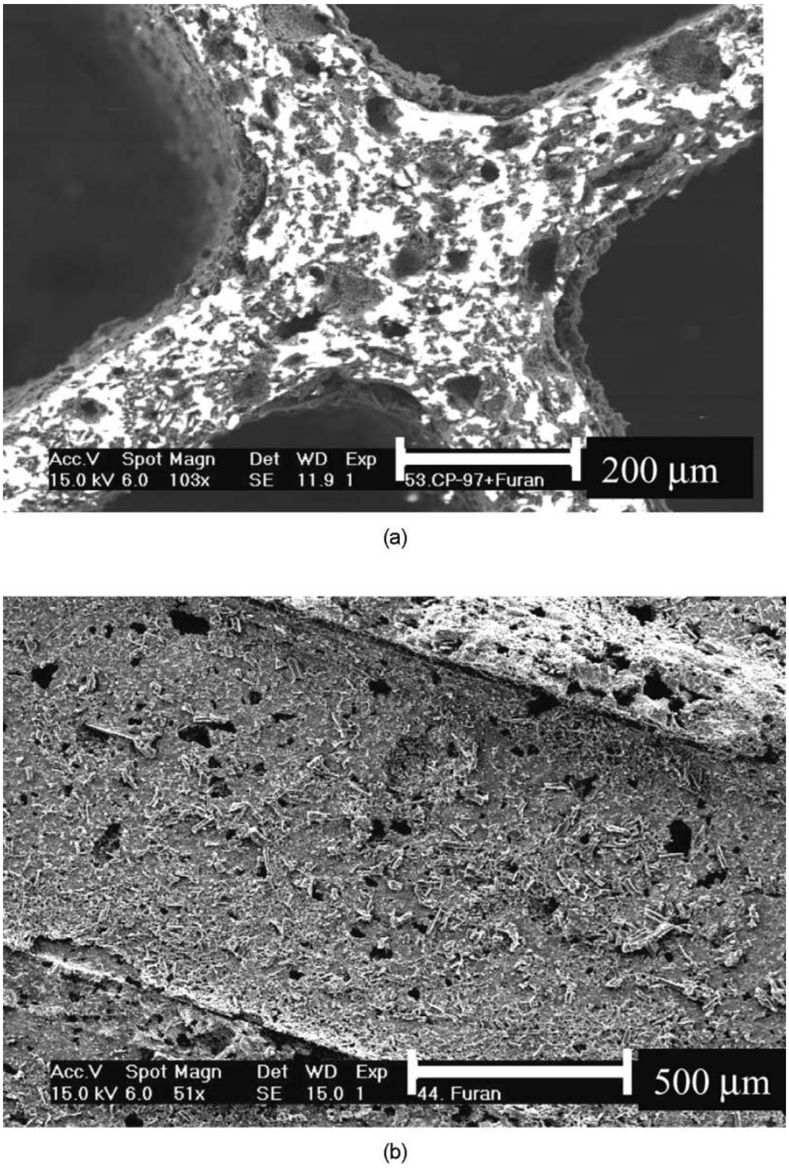

Fig. 4. SEM micrographs of monoliths: (a) cross-section of monoliths coated twice with slurry of CP-97 + Furan resin; (b) coverage along the channel wall of monoliths coated twice with slurry of CP-97 + Furan resin; (c) cross-section of monoliths coated twice with pure Furan resin; (d) coverage along the channel wall of monoliths coated twice with pure Furan resin.

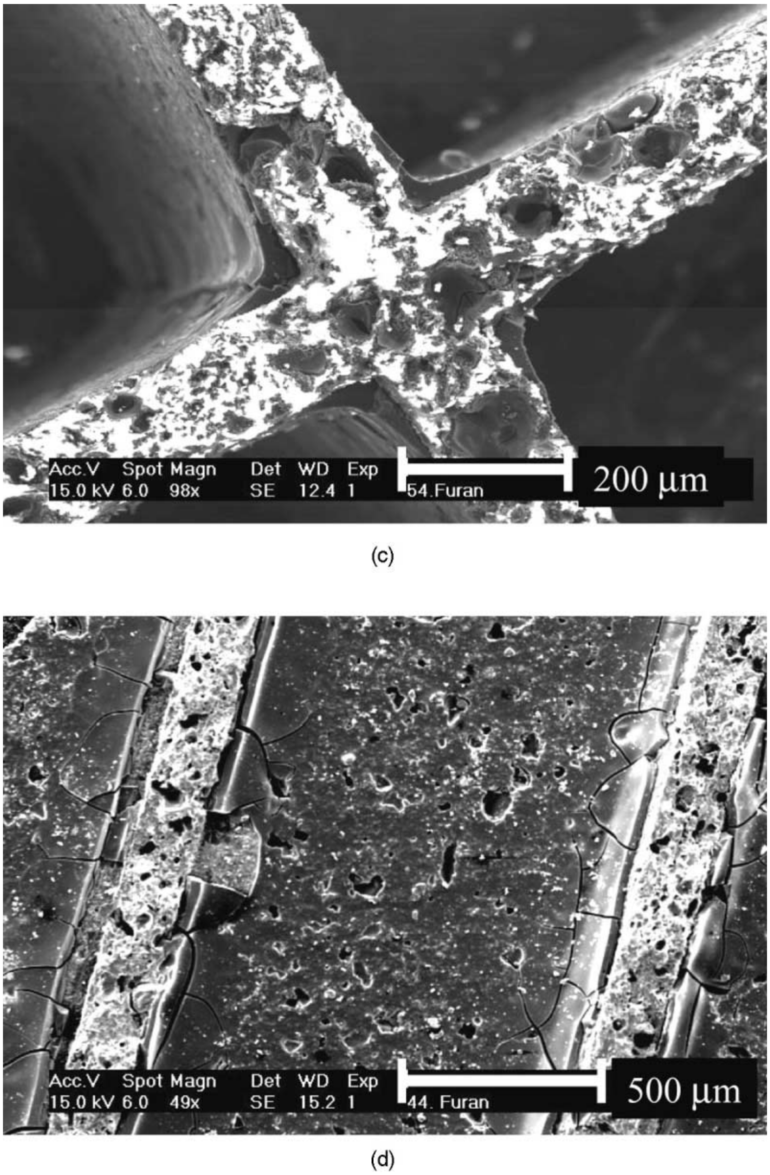

Fig. 4. (*Continued*)

the pore diameter. Cordierite shows only macropores larger than 1 μm. In monoliths coated with pure resin the diameter of macropores is around 0.2 μm, while in monoliths coated with slurry of CP-97 and polymer also pores in the range 10–300 nm are present.

Fig. 3 displays the comparison of the leaching test at pH = 0 for bare cordierite, the different types of carbon precursors used and the different loadings. Comparing the leaching of Novolac and Furan-coated monoliths with the same carbon loading, Si ions are leached to the same extent in both resins but Al and Mg are leached to a higher degree in samples coated with Novolac than with Furan. Consequently, Furan resin exhibits better coverage than Novolac. The leaching of the samples coated twice is always lower than that of the samples coated once. This is because the second layer covers the parts of cordierite that remained uncovered after the first dipcoating.

Fig. 4a and b shows the SEM pictures of monoliths coated with a slurry of CP-97 and Furan from two points of view, perpendicular and along a channel, respectively, and Fig. 4c and d shows similar SEM pictures for monoliths coated with pure Furan. In both samples large macropores are visible. These macropores in the cordierite wall are coated with carbon, especially for pure Furan (Fig. 4c).

It is observed that the corners have a thicker layer than the rest (Fig. 4a and c). In Fig. 4a and b, CP-97 particles can be clearly seen, while there are no cracks in the coating. On the contrary, in monolith coated with Furan the surface is smooth and cracks can be clearly observed (Fig. 4d), especially in the corners of the channels. These cracks occasionally lead to flakes that are removed from the support.

4. Discussion

To avoid plugging of channels a viscosity of 0.1 Pa s or lower of the dipcoating solution is desired for both resins. At carbon loadings higher than 20%, flakes are observed for both resins. This potential source of carbon loss should be avoided in order to increase the useful life of the catalyst. Taking this into account and in order to get a carbon loading as high as possible, the regions to obtain an optimal coating are pointed out by a dashed circle in Fig. 1. Consequently, all the samples have been prepared using this viscosity.

The samples of carbons derived from a slurry of CP-97 and binder exhibit higher mesopore volumes than the corresponding samples of carbons derived from pure resin (Fig. 2). It is this mesoporosity that is desired for three-phase reactions. From this point of view monoliths coated with slurry will be more suitable than monoliths coated with pure resin. The macropore volume for pores larger than 1 μm in these samples is attributable either to the interparticle voids between CP-97 particles or to the macropores of cordierite itself. The diameter of macropores for monoliths coated with pure resin (>100 nm) decreases one order of magnitude compared to that of pure cordierite (>2 μm). This indicates that the carbon coating covers the walls of the macropores of cordierite, decreasing their size as can be observed in SEM pictures (Fig. 4c).

From comparison of the leaching tests (Fig. 3) of monoliths coated with pure Furan and with a slurry of Furan and CP-97 some important conclusions can be drawn. After the first dipcoating with a slurry of CP-97 + Furan (9% carbon loading) leaching is comparable to sample coated once with pure Furan (carbon loading 13.7%). Monoliths coated with slurry of CP-97 and Furan twice (16.4% C loading) show a ca. 56% lower leaching than monolith coated twice with pure Furan resin (18.8% C loading). Therefore, the coverage of monoliths coated with slurry of CP-97 and Furan is enhanced dramatically with respect to those coated with pure Furan.

The removal of flakes (Fig. 4b and d) could be attributed to the process of cutting the sample. Both samples, however, have been cut in the same way and only the latter shows cracks in the coating. This suggests that the cracks are more easily produced in the monoliths coated with pure Furan resin or, what is more likely, that they were present before the preparation of the sample for characterisation. These cracks in the monoliths coated with pure resin are attributed to the shrinking of the coating during carbonisation [4]. On the other hand, in the monoliths coated with a slurry of CP-97 and Furan the cracks are hardly formed because the amount of pure polymer is lower and therefore, the effect of shrinking less appreciable than in monoliths coated with only Furan resin. The crack formation may also explain the stronger leaching of monoliths coated with pure Furan than with slurry of CP-97 and Furan.

5. Conclusions

In the preparation of carbon-coated monoliths by the dipcoating method the optimum viscosity of dipcoating mixture has to be used in order to achieve a maximum carbon loading without plugging channels, with a good coverage and without formation of flakes. This was investigated with two synthetic polymers of completely different composition, Novolac and Furan resins and in both cases the optimum viscosity for dipcoating is around 0.1 Pa s. In the monoliths coated with pure resin, a layer of coating covers the walls of macropores and reduces the diameter of macropores in the coated monoliths compared to pure cordierite.

By adding a highly mesoporous commercial activated carbon (CP-97) to Furan or Novolac resin the mesoporosity of the resulting carbon coating increases considerably that makes this carbon more suitable to be used as catalysts support in three-phase reactions. In addition, the coating efficiency of all prepared monoliths was tested by acid leaching. The resistance to leaching is enhanced by applying a second layer of carbon over the first layer, but what is more important is the fact that the resistance is more than 50% improved if we coat twice with a slurry of CP-97 and Furan than with only Furan.

SEM analysis of monoliths coated with pure Furan reveal cracks, but not in the monoliths coated with slurry of CP-97 and Furan. This makes carbon loss by flaking less likely in the latter case. The cracks in the carbon coating have been attributed to shrinking of the coating during carbonisation. On the other hand, in monoliths coated with slurry of CP-97 and Furan, crack formation does not take place because the effect of shrinking is less pronounced than in monoliths coated with only Furan due to the less amount of binder in the coating.

Acknowledgements

The authors wish to thank Engelhard (De Meern), Dow Chemical (Midland) and Hüttenes-Albertus (Hannover) for supplying the materials. E. García-Bordejé acknowledges the European Union for the M. Curie Fellowship (MCFI-1999-01110).

References

[1] F. Kapteijn, J.J. Heiszwolf, T.A. Nijhuis, J.A. Moulijn, Monoliths in multiphase catalytic processes — aspects and prospects, CATTECH 3 (1999) 24–41.

[2] L.R. Radovic, F. Rodriguez-Reinoso, Carbon materials in catalysis, Chem. Phys. Carbon 25 (1997) 243–358.

[3] F. Kapteijn, J.A. Moulijn, A. Tarfaoui, Temperature programmed reduction and sulphiding, Catalysis — An Integrated Approach to Homogeneous, Heterogeneous and Industrial Catalysis, Elsevier, Amsterdam, Stud. Surf. Sci. Catal. 79 (1993) 401–417.

[4] Th. Vergunst, F. Kapteijn, J.A. Moulijn, Carbon (2001), submitted for publication.