

DEVELOPMENT OF CARBON COATED MONOLITHS WITH SUITABLE FEATURES AS CATALYST SUPPORT

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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. However, in general, it can be concluded that monolithic reactors combine advantages of slurry reactors and trickle bed reactors, while eliminating the disadvantages [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-bed, 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 remarkable 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 catalyzed by the support surface hardly occur. Also 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 by 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 catalyzed reactions, mesopores in the range 5-15 nm are a desired compromise between surface area and accessibility [4].

Carbon coated monoliths have been prepared by dipcoating cordierite monoliths in a polymer mixture and subsequent curing and carbonization. Parameters of preparation that were varied were viscosity of the dipcoating mixture, carbon precursor and carbonization

temperature. Two different polymers have been used as carbon precursors, Novolac and Furan resins. Also monoliths have been coated with slurry of such resins and a commercial activated carbon.

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 make carbon coated monoliths very suitable for their use as catalyst support in three phase reactions.

Experimental

To coat the cordierite monoliths with a carbon layer the dipcoating method has been used. This consists in dipping the cordierite monolith into a liquid polymer. Subsequently the monolith is drained, flushed with pressurized N₂ to remove the excess of polymer mixture, cured and carbonized. To coat the monoliths two carbon precursors were used Novo lac resin (Dow Chemical) and Furan resin (Hüttenes-Albertus). Also monoliths were coated with slurry of a commercial activated carbon CP-97 (Engelhard) and a binder. As 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 cm³/g) but also to mesopores (0.45 cm³/g).

To determine the carbonization temperature thermogravimetric analysis (TGA) was performed on a Mettler-Toledo TGA/SDTA851 Thermobalance. Carbonization of the cured resins was carried out under a flowrate 30 ml/min of Argon during 2 hours. This experiment has been carried out in two steps. First is a dynamic experiment in which the sample is heated from 298 K up to the desired carbonization temperature at a heating rate of 10 K per min and the second step is an isothermal step in which the carbonization temperature is kept during 2 hours.

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 1:10 monolith/HCl 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 ICPOES 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.

Results

Figures 1 show the weight loss in the carbonization process in thermobalance at different carbonization temperatures for the pure Novolac and Furan resins. In the experiments carried out with pure Novolac resin it is observed that the final weight loss increases with carbonization temperature in carbonization temperatures below 973 K. Above 973 K the weight loss is around 78%, independent of the carbonization temperature. This indicates that above 973 K the carbonization can be considered complete and no further major changes in the composition take place, only structural changes can occur. For the pure Furan the carbonization can be considered complete at 873 K with a weight loss of ca. 52%. Therefore, all the following samples have been prepared by carbonizing at a temperature of 973 K for Novolac resin and 873 K for Furan resins.

Figure 2 shows the values of viscosity and carbon loading of the monoliths dipcoated with different mixtures of the two series in which the relative amount of each components have been varied. When the resin content in the dipcoating mixture increases the values 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.

Table 1 shows the values of pore volumes and areas in the ranges of micro- and mesoporosity of all the samples, measured by N_2 physisorption.

For the samples coated with slurry of CP-97 and binder, table 1 shows the theoretical parameters between parenthesis. These parameters have been calculated supposing additive properties and taking into account the contribution of CP-97 and the carbon derived from the resin. All experimental values are lower than the theoretical calculated ones. This indicates that the textural properties are not additive and some plugging of CP-97 pores occurs when is mixed with the polymer.

In table 1 it is observed that monoliths coated with pure Furan resin have around 50% less micropore volume and area than those coated with Novolac resin but the mesopore parameters are comparable.

In figure 3 the cumulative volume of the coated monoliths obtained by Hg intrusion is presented vs. the pore diameter. Cordierite only shows macropores larger than 1 μ m. In monoliths coated with pure resin the

diameter of macropores is around 0.1 μ m, while in monoliths coated with slurry of CP-97 and polymer also pores in the range 10-300 nm are present.

Figure 4 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 similar 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.

Figure 5a and b show the SEM pictures of monoliths coated with pure Furan from two points of view, perpendicular and along a channel, respectively and Figure 5c and d show similar SEM pictures for monoliths coated with slurry of CP-97 and Furan.

In both samples large macropores are visible. These macropores in cordierite wall are coated with carbon, especially for pure Furan (figure 5a).

It is observed that the corners have a thicker layer than the rest (figure 5a, c). In figure 5c and d 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 (figure 5b), especially in the corners of the channels. These cracks occasionally lead to flakes that are removed from the support.

Discussion

To avoid plugging of channels a viscosity of 0.1 Pas or lower is desired for both resins. Besides, 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 into account this 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 figure 2. Consequently, all the samples have been prepared using this viscosity.

The samples of carbons derived from slurry of CP-97 and binder exhibit higher mesopore volume than the corresponding samples of carbons derived from pure resin (figure 3 and table 1). It is this mesoporosity what 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 above 1 μ m in these samples is attributable to the macropores of cordierite without covering.

The diameter of macropores (figure 3) for monoliths coated with pure resin (>100 nm) decrease one order of magnitude compared to that of pure cordierite (>1 μ m). This indicates that the carbon coating covers the walls of the macropores of cordierite, decreasing their size as can be observed in SEM pictures (figure 5a).

From comparison of the leaching tests (figure 4) of monolith coated with pure Furan and with 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 drastically with respect to those coated with pure Furan.

The removal of flakes (figure 5b and d) could be attributed to the process of cutting the sample for SEM characterization. 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, they were present before the preparation of the sample for characterization. These cracks in the monoliths coated with pure resin are attributed to the shrinking of the coating during carbonization [4]. On the other hand, in the monoliths coated with slurry of CP-97 and Furan the cracks are hardly formed because the amount of pure polymer is lower than in monoliths coated with only Furan resin and, therefore, the effect of shrinking is not appreciable. The crack formation may also explain the stronger leaching of monoliths coated with pure Furan than with slurry of CP-97 and Furan.

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 resin and Furan resin 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 resins the

mesoporosity of CP-97 is transferred to the resulting carbon coating that makes this carbon 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 carbonization. On the other hand, in monoliths coated with slurry of CP-97 and Furan, crack formation do not take place because the effect of shrinking is less pronounced than in monoliths coated with only Furan due to the lower amount of binder in the coating.

References

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Table 1 N₂ physisorption of CP-97 and carbon coated monoliths

	Carbon content (%)	S _{BET} (m ² /g carbon)	Total pore volume (cm ³ /g carbon)	t-method micropore Analysis		Mesopore Area (m ² /g carbon)	Mesopore Volume (cm ³ /g carbon)
				Micropore Area (m ² /g carbon)	Micropore Volume (cm ³ /g carbon)		
CP-97	100	1140	0.80	837	0.35	303	0.450
Coated with Novolac	18.0	600	0.28	577	0.23	23	0.044
Coated with Furan	15.4	351	0.18	330	0.14	21	0.038
Coated with CP-97 +Novolac	5.5	698 (864)	0.43 (0.53)	605 (704)	0.25 (0.29)	93 (160)	0.18 (0.24)
Coated with C97+Furan	11.3	424 (642)	0.31 (0.41)	344 (517)	0.15 (0.22)	80 (125)	0.16 (0.19)

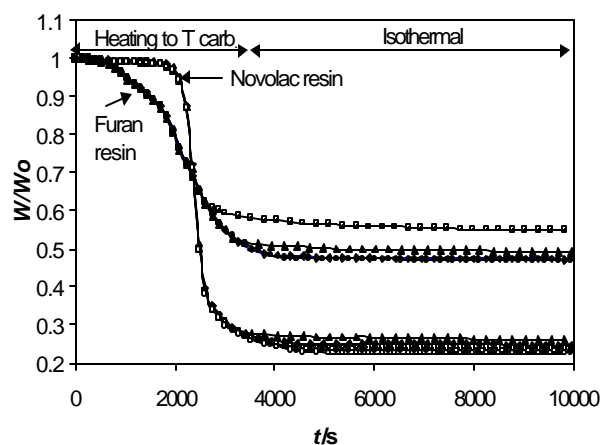


Figure 1. Carbonization at different temperatures in thermobalance for both Novolac and Furan resins performed in two steps: dynamic step, heating up to the carbonization temperature and isotherm step, remaining 2 hours at the carbonization temperature. † 673 K, † 773 K, ⚡ 873 K, ⚡ 923 K, † 973 K, ⚡ 1023 K

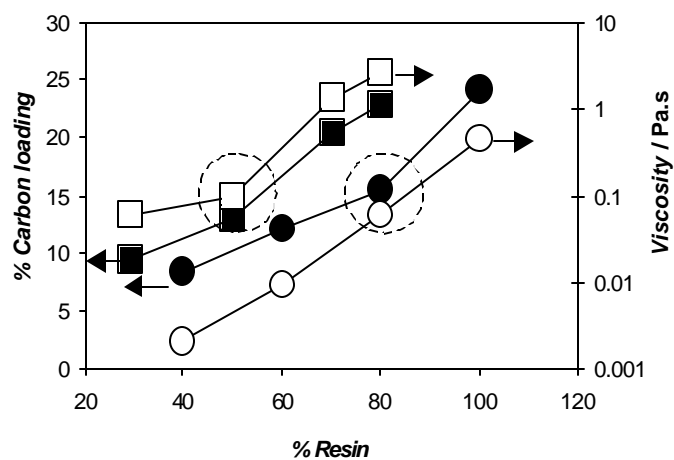


Figure 2. Viscosity of mixtures of Furan resin+acetone and Novolac resin+butanone in different ratios and corresponding carbon loadings. Mixtures of Novolac/2-Butanone: ⚡ viscosity, † % carbon loading. Mixtures of Furan/acetone: ⚡ viscosity, † % carbon loading

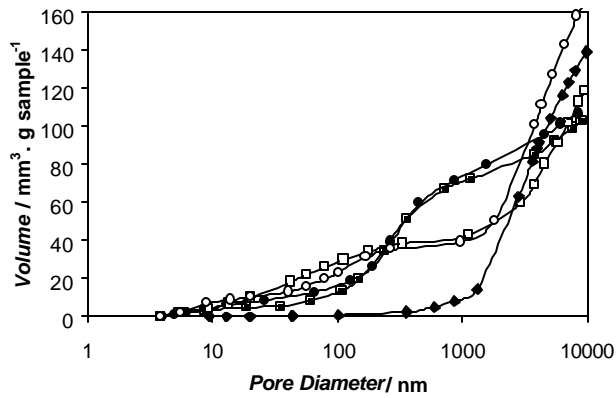


Figure 3. Cumulative pore volume of carbon coated monoliths derived from the following precursors, \blacktriangle cordierite, \dagger Novolac, \ddagger Furan, \lessdot slurry of CP-97 and Novolac, \lessdot slurry of CP-97 and Furan.

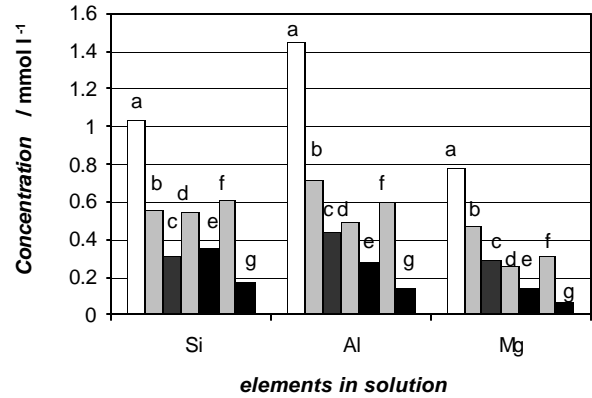


Figure 4. Leaching of monoliths coated with different carbon precursors and different loadings after treatment with 1 M HCl. a) Cordierite, b) Novolac/1 dipcoating (13.1%), c) Novolac/2 dipcoatings (17.9%), d) Furan/1 dipcoating (13.7%), e) Furan/2 dipcoating (18.8%), f) Slurry of CP-97+Furan/1dipcoating (9%), g) Slurry of CP-97+ Furan/2 dipcoatings (16.4%)

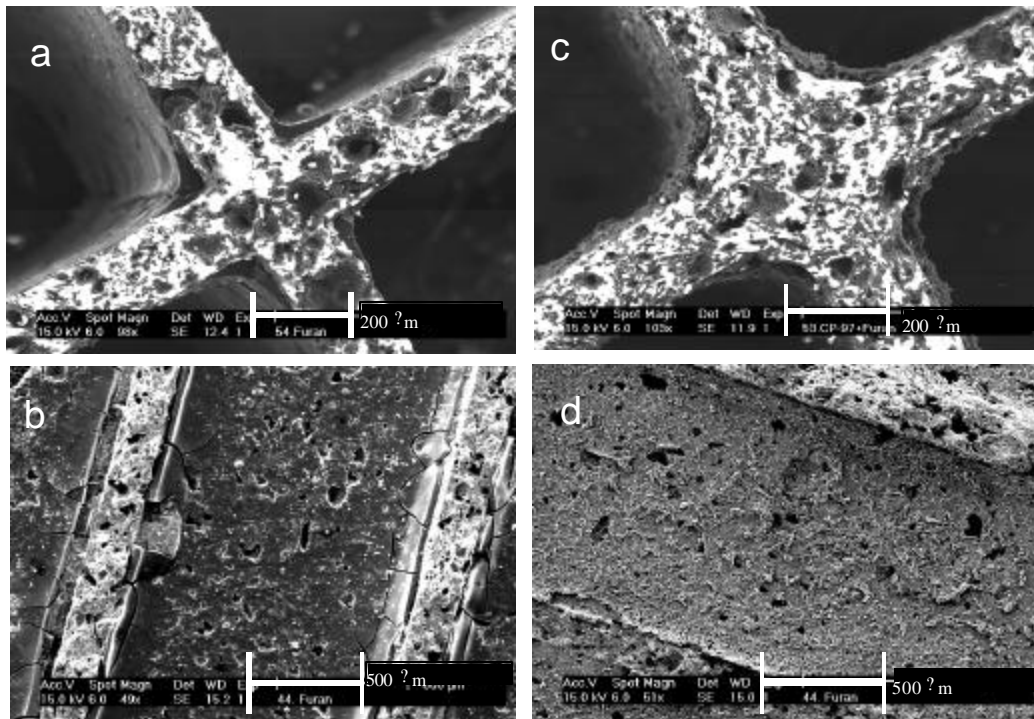


Figure 5. SEM micrographs of coated monoliths: a) cross section of monoliths coated twice with pure Furan resin; b) coverage along the channel wall of monoliths coated twice with pure Furan resin c) cross section of monolith coated twice with slurry of CP-97+furan resin; d) coverage along the channel wall of monoliths coated twice with slurry of CP-97+furan resin;