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Catalysis Today 79–80 (2003) 29–33

CATALYSIS TODAY

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Development of monolith with a carbon-nanofiber-washcoat as a structured catalyst support in liquid phase

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Abstract

Washcoats with improved mass transfer properties are necessary to circumvent concentration gradients in case of fast reactions in liquid phase, e.g. nitrate hydrogenation. A highly porous, high surface area (180 m^2/g) and thin washcoat of carbon fibers, was produced on a monolith support by methane decomposition over small nickel particles. Carbon fibers form a homogeneous layer less then 1 μm thin, covering the surface of the channels in the monolith. The fibers penetrated into the cordierite, which is suggested to cause a remarkable stability of the fibers against ultrasound maltreatment. The texture of the fibers is independent of both the thickness of the γ-alumina washcoat as well as the time to grow carbon fibers.

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Keywords: Carbon-nanofiber; Monolith; Structured catalyst; Ni; Mass transfer; Liquid phase

1. Introduction

Fast chemical reactions can easily cause concentration gradients in reactors and catalysts, when these gradients are necessary to give sufficiently rapid mass transfer rates to keep up with the chemical reaction rates. Gradients occur most easily in liquid phase because of relatively slow diffusion as well as the frequent occurrence of very low concentrations when gasses have to dissolve in the liquid phase before they can reach the catalyst. The consequence is that the local concentrations at the active sites vary, influencing reaction rates as well as selectivity.

Conventional technologies for heterogeneous catalytic reactions involving both liquid phase as well as gas phase comprise slurry reactors and trickle bed reactors. Trickle bed reactors end up easily in diffusion limitations because of the relatively large catalyst particle size that is necessary because of hydrodynamic reasons. Slurry reactors are more suitable for fast reactions because of much smaller catalyst particles sizes, at the expense of additional costs for separation of the catalyst from the products. Also, the lack of robustness of separation technologies, e.g. filtration, is an important concern. Quite some research has been performed and is still being performed to develop structured catalyst to combine the advantages of slurry reactors and trickle bed reactors, i.e. create a large liquid-solid surface area as well as short diffusion distances inside the catalysts without needing a separation step. Especially the group of Moulijn and Kapteijn have pioneered the use monoliths [1–5], whereas others used fibers, cloths and gauzes [6–9].

All structured materials used so far have a relatively small external surface area. Additional surface area needs to be generated to host a sufficiently extended catalytic surface area. This is usually achieved

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doi:10.1016/S0920-5861(03)00039-7

by preparing a porous washcoat on the surface of the structured material, e.g. on monoliths, or by generating pores in the structured material itself, e.g. in carbon fibers. In the rest of this contribution we will use the term washcoat, and the practical work in this contribution is limited to monoliths.

1.1. Demands for washcoats in liquid phase operation

The thickness of washcoats on monoliths as prepared for exhaust application is in the order of tens of microns. This is apparently the optimum for gas phase conditions in the exhaust; however, the optimum might be different for liquid phase operation.

In literature there are many examples that slurry catalysts need extreme small particles to arrive at high effectiveness. A typical example is the selective hydrogenation of nitrate to either hydroxylamine [10,11] or to N_2 [12,13]. In both cases high intrinsic activity is combined with a strong influence of the concentration of reactants on the selectivity obtained. Therefore, concentration gradients in the catalyst particles need to be avoided, which can be achieved only by limiting diffusion distances to the sub-micron range.

Therefore we will demonstrate in this contribution how to arrive at washcoats with superior properties, i.e. higher porosity and smaller thickness, preserving a significant surface area to support the active phase. New promising supports have been prepared based on carbon-nanofibers [14–18]. These fibers can be grown catalytically by decomposition of a carbon containing gas over small metal particles like nickel, iron and cobalt. The primary structure and dimensions of the fibers are determined by the temperature, gas composition, active metal, the metal particles size distribution and the support material [19,20]. The secondary structure of the support is determined by the extent of entanglement of the fibers and the extent of orientation of the individual fibers. It has been shown that e.g. nickel particles on oxide supports form an aggregate of carbon fibers shaped identically to the original support, except for an increase in size of typically a factor three [21]. The porosity of these aggregates is very high, e.g. 1 cm^3/g. Therefore, in this study we prepared stable washcoats that consist of carbon-nanofibers.

2. Experimental

2.1. Materials

Monolith support samples (600 cells per square inch, obtained from Degussa, Germany) were used with four different average thicknesses of the γ-alumina washcoat; bare cordierite, 9, 13, and 17 μm thick, respectively. Nickel (II) nitrate [$Ni(NO_3)_2 \cdot 6H_2O$] and ammonium nitrate [NH_4NO_3] (pure, Merck, Darmstadt, Germany) were used to prepare the nickel solution. Hydrogen and nitrogen gases with purity 99.999% (INDUGAS, The Netherlands) and methane with purity 99.995% (Hoek Loos, The Netherlands) were used for growing carbon fibers.

2.2. Catalyst preparation

Nickel was deposited on the washcoated monolith by adsorption from a pH-neutral nickel solution (0.1 M) as described else where [22]. The solution contained 29 g of $Ni(NO_3)_2 \cdot 6H_2O$, 80 g NH_4NO_3 and 4 ml of ammonia solution (25 wt.%) per liter.

The monolith samples were dipped (20 times/min) in the solution for 3 h. Free liquid was removed and the samples were dried over-night at room temperature and were then heated (1 K/min) to 393 K for 2 h, followed by calcination in static air (5 K/min) at 873 K for 2 h.

2.3. Experimental set-up for carbon fiber growth

Carbon fiber growth was carried out in a quartz reactor with a porous quartz plate at the bottom to support the sample [20,21]. The sample was heated to 973 K (5.5 K/min) in 20% H_2 in N_2 for 2 h. After cooling to 843 K carbon fibers were grown in 50% CH_4, 10% H_2 in N_2 (total flow rate 200 ml/min).

Methane conversion was determined with on-line chromatographic analysis (Varian GC model 3700 equipped with a 15 m Q-Plot column). Finally, the sample was cooled down in N_2 to room temperature. The amount of carbon formed on the monolith was determined by weight.

2.4. Characterization

The BET surface area, pore volume and pore size distribution were measured by N_2 adsorption–

desorption at 77 K using ASAP 2400 (Micromeritics) instrument.

Nickel loading on ceramic monolith was measured with Philips X-ray fluorescence spectrometer (PW 1480).

Nickel particle sizes were determined on powdered catalysts with transmission electron microscopy (TEM) (Philips CM30). The morphology of the carbon fibers was studied non-destructively with scanning electron microscopy (SEM) (LEO 1550 FEG SEM) equipped with EDX analysis. The monoliths were broken to allow direct observation of the carbon fibers on the surface of the wall of one of the inner channels in the monolith.

3. Results and discussion

3.1. Characterization of the ceramic supports

Table 1 shows the texture of the monolith supports. It is obvious that surface area as well as pore volume is determined almost completely by the γ-alumina phase. The large pores in the cordierite cannot be measured with N_2 adsorption and pore volume of cordierite has been estimated to be 0.5 cm^3/g based on the bulk density of cordierite (2.51 g/ml) and the apparent density of the monolith [23]. The surface area of all washcoats is 100 m^2/g. The washcoats contain mesopores only with a total pore volume of 0.33 cm^3/g.

3.2. Characterization of NiO on monolith

Table 1 shows the NiO concentrations in the samples. The relatively low nickel oxide concentration on cordierite is in agreement with introduction of NiO via pore-volume-impregnation exclusively. The NiO concentration on the samples with γ-alumina is significantly higher, indicating adsorption of $Ni(NO_3)_2$ in the washcoat. The coverage is well below one monolayer in all cases, assuming NiO to cover 8 $Å^2$/NiO (based on the bulk structure of NiO [24]). The surface coverage decreases with the thickness of the washcoat.

Both visual inspection (greenish color of NiO) as well as local determination of Ni concentration in the monolith proves homogenous distribution of NiO. Particles sized in the range of 6–10 nm are observed in all washcoats. Particle sizes in the cordierite without washcoat are obviously much larger because of the extreme low surface area.

3.3. Carbon fiber growth on the monolith supports

The effect of time on stream on the rate of formation of carbon fiber, calculated from the rate of methane conversion, is shown in Fig. 1. The initial rate per gram nickel is somewhat larger for the thinner washcoats whereas the activity decreases faster. No explanation can be given at this moment.

Table 1 shows the amount of carbon fiber grown on the samples in 3 h based on weight. The integral methane conversion calculated from Fig. 1 is in

Table 1
Properties of monolith support, NiO and carbon fiber on monolith.

Thickness of γ-alumina washcoat (μm)	No washcoat	9	13	17
Characterization of ceramic support				
BET surface area (m^2/g monolith)	<1	26	35	45
Pore volume (cm^3/g monolith)	–	0.085	0.116	0.149
Average pore size (Å)	–	130	128	130
Characterization of NiO on monolith				
NiO wt% (g NiO/100 g monolith)	0.33	1.18	1.44	1.51
NiO monolayers	–	0.31	0.28	0.23
Carbon fiber after 3 h growth				
Amount of carbon fiber (g/g monolith)	0.0085	0.107	0.154	0.157
Amount of carbon fiber (g/g Ni)	3.3	11.5	13.2	13.6
BET surface area (m^2/g monolith)	–	42	55	63
BET surface area (m^2/g carbon fiber)	–	181	179	190

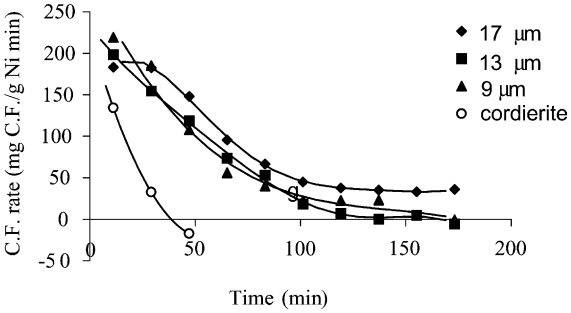

Fig. 1. Rate of formation of carbon fiber on nickel loaded monolith with different washcoat thickness.

agreement with these numbers within 20%. The integration of the methane consumption suffers from inaccuracy especially when methane conversion is low.

3.4. Characterization of carbon fiber washcoat

Formation of carbon fibers causes an increase in the total surface area of the samples. Assuming that the surface area of the washcoat remains unchanged and using the carbon concentrations achieved (Table 1), the surface area of the carbon fibers was calculated. Also, identical surface areas of the carbon fibers are found when the time of carbon growth was varied. In all cases the surface area is 180 m^2/g within 5%. Apparently, the primary structure of the carbon fibers is independent of both the thickness of the washcoat as well as the time of growth.

The secondary structure of the fibers was studied with SEM. Fig. 2a shows the typical morphology of carbon fibers grown out of metal particles; the fibers contain the metal particle in the top of the fiber and the diameter of the fibers varies between 10 and 30 nm. Fig. 2b shows that carbon fibers cover the surface of the monolith wall homogenously for all washcoated samples; the side-view in Fig. 2c indicates that this layer is about 0.5 µm thick. It is clear that the layer formed by the carbon fibers is extremely open and thin. However, in some places reminders of the alumina washcoat can be observed (Fig. 2d) suggesting that the alumina washcoat is fragmentized by carbon fiber growth. Finally it was observed that much more carbon fibers are present in the cordierite compared to the nickel impregnated bare cordierite. From this follows that carbon fibers penetrate from the washcoat into the

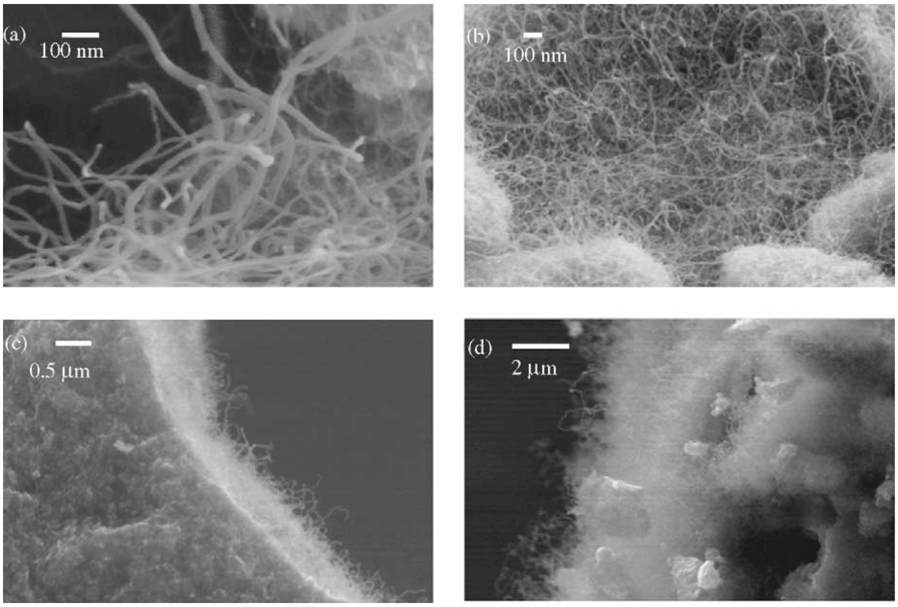

Fig. 2. SEM images of carbon-nanofibers produced by CH_4 decomposition over nickel particles supported on γ-alumina monolith washcoats: (a) high resolution SEM of carbon fiber; (b) top-view on monolith wall covered with fibers; (c) side-view on monolith wall; (d) fragments of γ-alumina occluded by fibers.

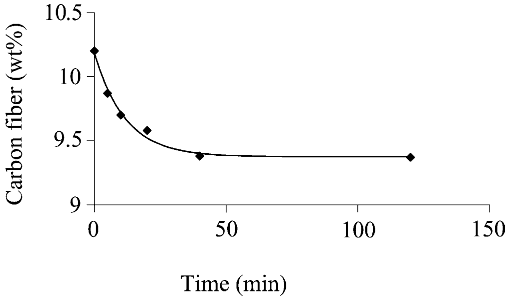

Fig. 3. Stability of carbon attachment against ultrasound (40 kHz) treatment; fibers grown during 1 h on 17 μm washcoat.

cordierite. This phenomenon is probably the reason for the strong attachment of the fibers to the monolith.

Extended maltreatment of the sample with 40 kHz ultrasound resulted in limited loss of carbon fibers as shown in Fig. 3. About 10% of the fibers can be removed and no losses are observed anymore after 40 min. Nevertheless, stability under flow conditions applying shear force remains to be demonstrated.

Work is in progress to determine the performance of this type of washcoat for fast reactions in liquid phase.

4. Conclusions

A highly porous, high surface area (180 m^2/g) and thin washcoat, based on carbon fiber, was produced on a monolith support by methane decomposition over small nickel particles. Carbon fibers form a homogeneous layer less then 1 μm thin, covering the surface of the channels in the monolith, provided care is taken to distribute the Ni homogeneously. The fibers penetrated into the cordierite, which is suggested to cause a remarkable mechanical stability of the attachment of fibers against ultrasound maltreatment.

The structure of the fibers is independent of both the thickness of the γ-alumina washcoat as well as the time used to grow carbon fibers.

Acknowledgements

This work was performed under the auspices of NIOK, the Netherlands Institute of Catalysis Research, and the Process-Technology Institute Twente.

The authors are gratefully acknowledging Degussa for supplying monoliths, we are grateful to Ing. J.A.M. Vrielink, Ing. V. Skolnik, Dr. M. Smithers and Dr. R. Keim for XRF, BET, SEM, and TEM measurements, respectively. We acknowledge Ing. B. Geerdink for technical support, as well as Prof. K.P de Jong and Drs. Thoebes for an introduction in carbon fiber chemistry.

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