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Chemical Engineering Journal 101 (2004) 11–16

Chemical Engineering Journal

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Carbon-coated microstructured reactors for heterogeneously catalyzed gas phase reactions: influence of coating procedure on catalytic activity and selectivity

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Abstract

Carbon-coated microstructures have been prepared via carbonization of polymers, which have been deposited onto microstructured wafers. The amount of carbon deposited depends on the composition of the precursor monomer solution and on the presence of a template. The activity of the wafers after impregnation with ruthenium in the hydrogenation of acrolein is, among others, affected by the composition of the polymers and the time of the calcination step. Most likely, the number of functional groups at the carbon surface as well as the porosity are responsible for this behavior. The selectivity pattern in the hydrogenation of acrolein is similar to that of the acrolein hydrogenation using conventional Ru/C catalysts in a fixed-bed reactor.

Keywords: Carbon coating; Microstructured reactor; Hydrogenation of acrolein; Carbonization of polymers

1. Introduction

The availability of coatings as support for metal catalysts is an indispensable prerequisite for the use of microstructured reactors in heterogeneously catalyzed reactions. Commonly used coating techniques are anodic oxidation of Al wafers [1], sol–gel techniques [2], chemical vapor deposition (CVD) [3], and deposition of nanoparticles [4]. These techniques lead to inorganic coatings. On the other hand, techniques to produce carbon-based coatings on microstructures are much less investigated, which is surprising since carbon is a common and widespread support material in catalysis with a broad variety of applications [5].

We therefore are currently exploring the potential of carbon-coated microstructures for heterogeneously catalyzed gas (and liquid) phase hydrogenations. For the carbon-coated wafers a preparation method was chosen, which was developed by Hücke [6] for carbon-based coatings and modified by Kapteijn and coworkers for coating of monoliths [7,8].

The aim of our studies is to investigate the influence of the coating composition, the coating conditions and the resulting physico-chemical properties of the coating on the catalytic behavior of deposited metal nanoparticles. The focus of this presentation will be laid on carbon-coated microstructures with deposited ruthenium for heterogeneously catalyzed gas phase hydrogenation reactions.

The hydrogenation of acrolein was chosen as test reaction because of its sensitivity regarding electronic and structural effects of the catalysts [9,10] and because of much experience regarding this reaction exists in our laboratories [9,11]. For this α,β-unsaturated aldehyde the monometallic ruthenium catalysts are known to form propanal as main product instead of the more valuable unsaturated alcohol (allyl alcohol). A reaction scheme of the acrolein hydrogenation is given in Fig. 1.

2. Experimental

2.1. Preparation of the catalytic coatings of the wafers

The dimensions of the wafers were 50 mm in length and 10 mm in width. The microchannels were 700 μm in depth and 300 μm in width. One wafer contains 14 microchannels. The microchannels have been prepared by wire-cut electrical discharge machining (EDM) with a copper wire at the Faculty of Mechanical Engineering and Process Technology at the Department of Manufacturing Technology of the Chemnitz University of Technology. Before use all wafers

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doi:10.1016/j.cej.2003.11.009

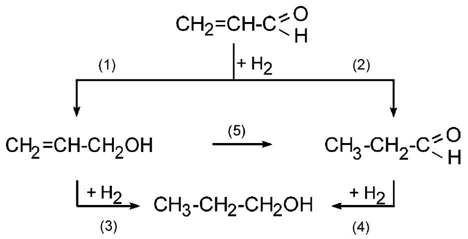

Fig. 1. Reaction scheme of the hydrogenation of acrolein.

which consist of an AlMg alloy (3% Mg) were cleaned and degreased with acetone. Carbon coatings on microstructured wafers have been prepared via polymers in the following way [7,8]. First, the monomer mixture was prepared consisting of furfuryl alcohol (Merck, z.S., labeled "FA" in the following) and in some cases pyrrole (Merck, z.S., labeled "PY" in the following) and a pore former. In this work a block polymer consisting of polyethylene glycol and polypropylene glycol (PEG–PPG–PEG 4400, Aldrich) was used. In the following this pore-forming liquid is abbreviated as "PEG". The mixture was externally cooled (293 K) and well-stirred, when the catalyst (nitric acid) was added to start polymerization. The deposition onto the wafer was performed by dipping the wafer into the polymerization mixture as soon as the solution became dark, indicating ongoing oligomerization. Excess solution was removed with compressed air. After drying at 353 K, the polymer has been carbonized at 823 K in flowing nitrogen and then calcined in air at 623 K in order to develop a pore structure and to introduce functional groups into the carbon. Additional functionalization has been carried out via aqueous HNO_3. However, since it turned out that this additional functionalization has no beneficial effect on the behavior of the wafers in the gas phase hydrogenation of acrolein, this step has been skipped after a few experiments. The deposition of ruthenium onto the carbon coating has been carried out by ion exchange of a Ru complex compound using $[Ru(NH_3)_5Cl]Cl_2$ with functional groups such as carbonyl groups, carboxyl groups or hydroxy groups. The subsequent reduction was performed in 10% H_2 in N_2 (5 l/h) at 573 K. The so prepared microstructured wafers have been tested in the heterogeneously catalyzed gas phase hydrogenation of acrolein.

2.2. Characterization

Characterization of the catalyst wafers has been carried out via atomic emission spectroscopy (ICP-OES) and X-ray photoelectron spectroscopy (XPS). The metal contents of the catalysts were determined by atomic emission spectroscopy with inductively coupled plasma (ICP-OES, Perkin-Elmer Optima 3000XL) after dissolving the materials in a mixture of HF/HNO_3 by means of a MDS-2000 microwave unit (CEM). The X-ray photoelectron spectra were obtained on a Leybold LHS 12 MCD instrument.

2.3. Hydrogenation reaction

The hydrogenation of acrolein (AC) was carried out in the gas phase in an automated microchannel reactor system [12]. One single wafer was tested at a time. The hydrogenation of acrolein was carried out at temperatures ranging from 473 to 573 K at a pressure of 1 MPa and a H_2 to acrolein molar ratio of 20:1. A flow of 6754 ml H_2 and 1 ml AC (liquid) per hour has been used, corresponding to a modified residence time ("W/F", weight of the catalytic layer in gram per flow of acrolein in mol h^{-1}) of 0.069–0.796 g h mol^{-1}. The conventional supported Ru catalysts were tested in the same apparatus replacing the microstructured reactor by a conventional fixed-bed reactor. Here the same flow rate of the educts was used, resulting in a modified residence time W/F of 3.376 g h mol^{-1}. Product analyses were conducted by on-line gas chromatography.

3. Results and discussion

In preliminary experiments it was checked, whether a stronger adhesion of the coating on the wafer could be achieved, if the roughness of the wafers was increased for example by treating the wafer with nitric acid. But no difference was observed concerning the adhesion strength. Therefore, this additional step was omitted in the presented examinations. A photograph of carbon-coated wafers after different steps during preparation is shown in Fig. 2. The first one was treated with nitric acid to increase the roughness of the wafer surface to achieve stronger adhesion of the coating on the wafer. The second wafer is untreated as supplied. Wafer 3 was dipped into the polymerization mixture and dried afterwards at 353 K for 2 h. The final coatings after carbonization could be seen on wafers 4 and 5. Note that wafer 4 was prepared without pore former and shows a graphite like appearance, whereas wafer 5 was prepared with pore former and revealed a carbon black like appearance. The thickness of the carbon-based layers were estimated by weighting the wafers after each preparation step and assuming a layer density of 1. The results are given in Table 1.

The amounts of the deposited layers after drying were in the range between 4.7 and 29.5 mg. A range of the deposited mass is given for every composition, since five or three wafers were coated. The range given for the untreated and the carbonized layer therefore corresponds to the reproducibility, which is reasonably good. Higher amounts of deposited carbon were found if pore former was used and for coatings of mixed monomers. Carbonization involves a loss of mass. A very high loss was found for the wafers prepared with furfuryl alcohol and pore former (FA–PEG), which show low stability during carbonization, leading to lower reproducibility. After this preparation step different calcination times of wafers, prepared by the same polymerization mixture followed. After this step, therefore, the range of weights no longer corresponds with reproducibility. After

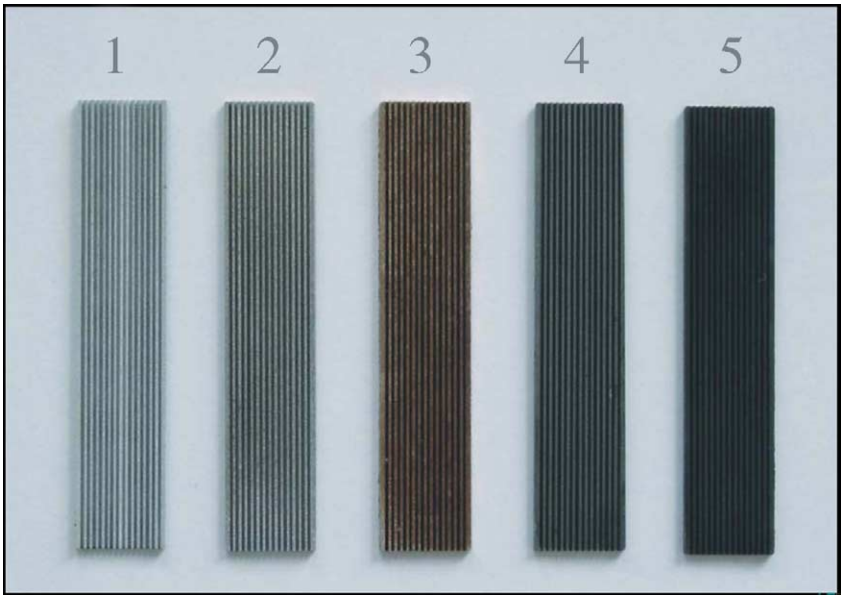

Fig. 2. A photograph of microstructured wafers after different steps during preparation of carbon coatings (see text for details).

Table 1
Mass and estimated thickness of the carbon layers after several preparation steps for four chosen compositions

Composition of carbon layer	Untreated layer (mg)	Carbonized layer (mg)	After immobilization of Ru and red (mg)	Thickness of layer (assumption: $\rho = 1$) (μm)
FA	4.7–6.8	1.2–2.2	0.4–1.5	0.27–1.01
FA–PEG	7.9–10.4	0.3–1.2	0.5–1.6	0.38–1.08
FA–PY	7.6–8.2	3.6–4.1	2.4–3.2	1.62–2.16
FA–PY–PEG	25.2–29.5	9.4–10.2	5.2–9.2	3.51–6.22

immobilization of ruthenium and reduction a loss of mass was found except for FA–PEG, probably due to a slight oxidation of the carbon layer by the ruthenium salt, which could be seen by the evolving gas bubbles during the immobilization step. The estimation of the thickness, assuming a density of 1 g/ml revealed thicknesses in the range of 0.27–6.22 μm. The highest thickness was achieved for the FA–PY–PEG system. In conclusion, higher thickness can be achieved if mixed monomers are used, especially when using pore former. These results imply, that the thickness of the layers depends mainly on the viscosity of the polymerization mixtures and the stability of the layer during carbonization.

The coated wafers have been tested in the gas phase hydrogenation of acrolein, as described in the experimental part. Fig. 3 summarizes the catalytic results for the different compositions. All wafers of Fig. 3 have been calcined for 30 min. Conversion degrees of acrolein were in the range of 3.6–11.2%. Blank experiments with uncoated wafers have shown, that the observed catalytic activity is completely due to the ruthenium/carbon layer and not due to the wafer itself. The selectivity pattern is similar for all four systems. The main product, as expected, is propanal (PA, $S = 85$–95%). The highest selectivity to allyl alcohol (AyOH) was 3%. If pore formers are used higher conversion degrees can be achieved. According to Vergunst et al. [7], the addition of PEG-based pore formers leads to the formation of macropores, whereas carbon layers formed of FA only mainly show micropores. The higher activity of the PEG-containing samples is therefore due to the higher amount of macropores. It is likely, that the deposition of catalytic active material is more hindered in the micropores, additionally, mass transport

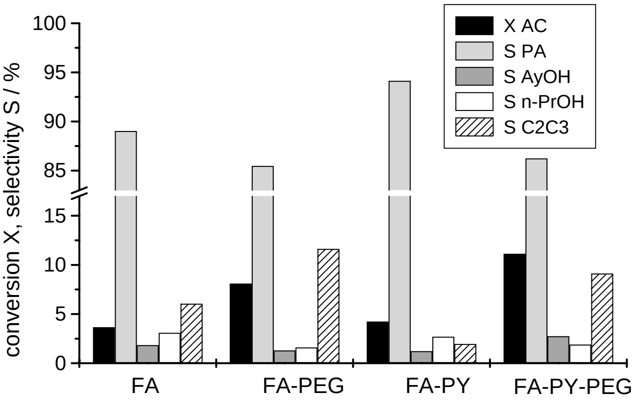

Fig. 3. Conversion and selectivities to the main products obtained in the gas phase hydrogenation of acrolein at various carbon-coated microstructured wafers impregnated with Ru.

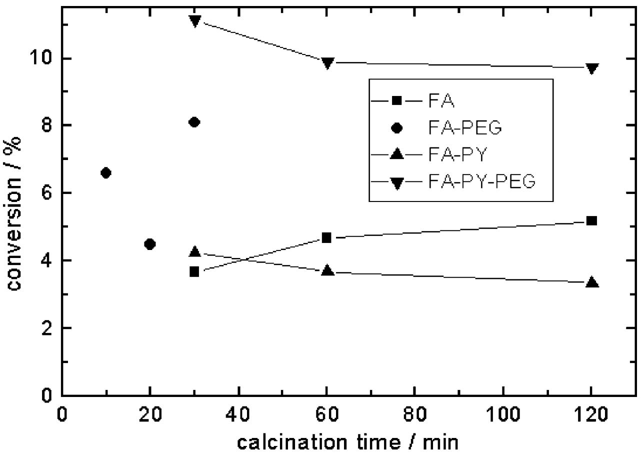

Fig. 4. Dependence of the conversion on the calcination time of the carbon layer for various carbon-coated microstructured wavers.

effects may also play a role during catalytic reaction. Also the selectivity to C_2 and C_3 hydrocarbons (C_2C_3, via decarbonylation, dehydration) is enhanced, when pore formers are used. This can be explained by the longer residence time of already hydrogenated molecules in the pores, allowing for the mentioned reactions leading to hydrocarbons.

The catalytic activity depends also slightly on the calcination time. This is shown in Fig. 4. Increasing the calcination time from 30 to 120 min reveals a small decrease in conversion regarding the mixed polymers and a small increase for FA. FA–PEG did not seem to be stable against air. Here distortion of the carbon coating was observed after 30 min. However, on the whole the influence of the parameters of the calzination process to the catalytic results seems to be low.

In order to correlate the observed behavior in the gas phase hydrogenation of acrolein with the properties of the layer, the ruthenium content has been determined via ICP-OES. The ruthenium loadings and the corresponding catalytic results are given in Table 2. For comparison, also results of a conventional 2% Ru/C catalyst are included (see below). All layers listed in Table 2 have been calcined for 60 min, except where indicated. The amount of carbon was in the range 1–11.3 mg and the amount of ruthenium in the range 8–89 μg. The resulting ruthenium contents were in the range 0.36–2.65 wt.%, related to the amount of catalytic layer. If no pyrrole is used for the preparation of the carbon layer, higher ruthenium loadings could be achieved. This could be due to a higher carbon surface area. However, it is also possible, that different amounts or kinds of functional groups are formed when starting from different carbon precursors. As expected the conversions increase with increasing ruthenium content and increasing catalyst amount. However, it seems that the specific activity is higher, when the carbon layers are formed without pyrrole. It is therefore likely that a relatively higher amount of surface functional groups is formed when the carbon layer is formed with FA and PEG only, leading to a higher ruthenium dispersion and a higher specific activity. In order to correlate the higher specific activity with surface functionalities, an attempt has been made to characterize the carbon layers, especially at the O 1s edges, with XPS. This attempt failed, since it turned out that not only the carbon layer, but also the underlying wafer contributes to the XPS signal in the O 1s region. One reason for this is, that the carbon layer shows inhomogeneities, as seen with scanning electron microscope: even if the optical appearance of the wafers is that of a homogeneous layer, SEM indicates that this is not true and that there are holes and cracks in the layer, leaving small parts of the wafer uncoated, as displayed in Fig. 5 for two different wafers (FA and FA–PY–PEG). It can be seen, that the inhomogeneities are in the range of 5–10 μm in size and consist of holes and cracks. Also inhomogeneities on a larger scale can be found. By using EDX it was found that there are small parts with homogeneous carbon coatings (dark areas in the lower figures), where only carbon was detected, whereas the areas of the holes and cracks reveal high amounts of the wafer components in the EDX spectra. However, the wafer does not contribute to the catalytic activity as mentioned above. To gain information about the oxidation state of Ru in the catalytic layer as well as about possible shifts in signals due to Ru–C interaction, XPS has also been performed at the Ru 3p edge. The signals were consistent with the existence of metallic Ru but are to weak and noisy to identify possible small signal shifts and do not allow any further conclusion (see Fig. 6).

Table 2
Ruthenium content and specific activity of different carbon layers (all layers calcined for 60 min., except layer FA–PEG, which would have been destroyed after this calcination time)

Composition of carbon layer	mg C	mg Ru	Ru content (wt.%)	X_{acrolein} (%)	Specific activity (mmol $\mathrm{mg_{Ru}}^{-1}$ h^{-1})
FA	1.0	0.016	1.57	4.7	43.5/20.0[a]
FA–PEG (calcination: 20 min)	1.6	0.008	0.50	4.5	87.0
FA/FA–PEG	1.8	0.049	2.65	16.1	48.7
FA–PY	2.8	0.010	0.36	3.7	54.8
FA–PY–PEG	7.6	0.067	0.87	9.9	21.9
FA–PY/FA–PY–PEG	11.3	0.089	0.78	12.8	21.3
Conventional 2% Ru/C	49.0	1.0	2.0	52	7.7[b]

Wafers which have been coated twice are also included. Specific activity has been determined at 250 °C, 1 MPa and a molar ratio of H_2 to acrolein of 20.

[a] Reaction temperature = 200 °C.

[b] Reaction temperature = 160 °C.

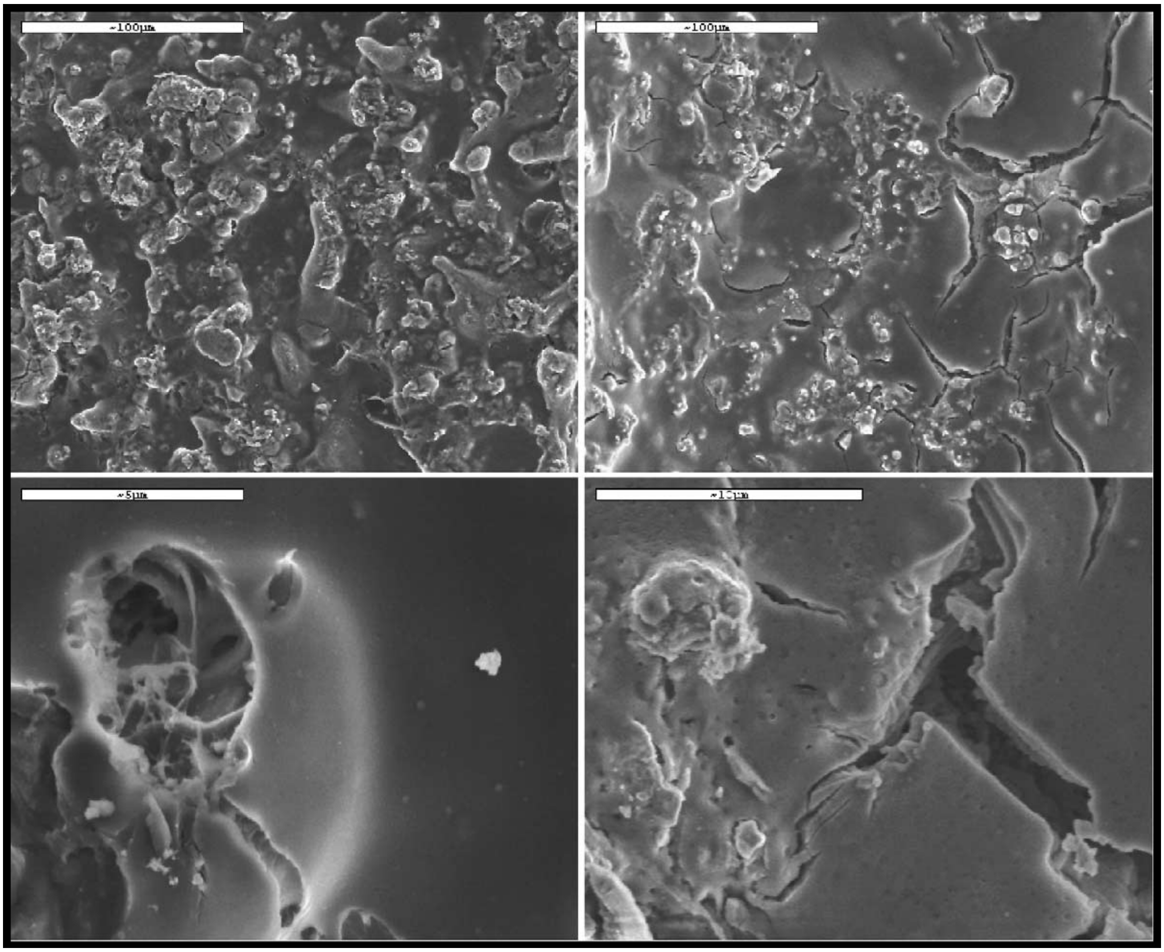

Fig. 5. Typical SEM pictures of carbon-coated microstructured wafers at the end of the preparation process. Left two pictures: layer prepared with furfuryl alcohol only (“FA”); right two pictures: layer prepared with pyrrole, furfuryl alcohol and pore former (“FA–PY–PEG”).

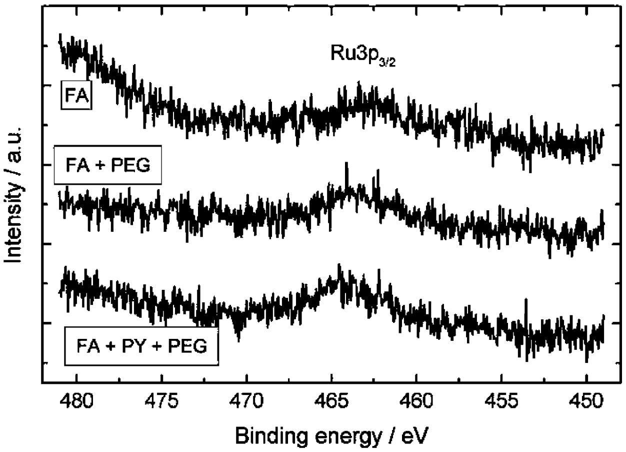

Fig. 6. XPS spectra of the Ru 3p edge of three different microstructured wafers after carbon and ruthenium deposition and reduction. The Ru 3p edge has been chosen, since the signals at the Ru 3p edge overlap with the ones for the carbon layer.

For comparison a conventional Ru/C catalysts, prepared with “Vulcan XC72” (a carbon black from Cabot) via incipient wetness, was tested in a fixed-bed reactor. The ruthenium content was 2 wt.%. Due to the much higher catalyst amount used in the fixed-bed reactor (50 mg), the tests have been performed at 433 K. With these conditions, still the conversion is much higher than with the microstructured wafers. Having a look at Table 2, it can be seen that the specific activities of the microstructured wafers are higher than the ones for the 2% Ru/C catalysts, however, at higher reaction temperatures. The lowest temperature, where a microstructured wafer has been investigated, was 473 K. At this temperature, a specific activity of 20 mmol mg^{-1} h^{-1} has been obtained for the “FA” layer calcined for 30 min compared to 7.7 mmol mg^{-1} h^{-1} for the conventional 2%Ru/C catalyst at 433 K. For this catalyst, 100% conversion has been obtained at 473 K, therefore it was not possible to compare the specific activities at identical temperatures. It can be concluded that the specific activity of both kinds of catalysts is in the same order of magnitude, however, the lower conversion of the microstructures is due to their much lower metal content.

At a conversion of 52%, selectivities to propanal of 89%, to allyl alcohol and propanal (*n*-PrOH) of less than 1% and to hydrocarbons of 10% have been obtained with the conventional catalyst. The selectivity pattern is similar to those of the wafers, especially when pore former is used. The same conclusions could be drawn examining the selective hydrogenation of 1,3-butadiene to butenes comparing gold catalysts in fixed-bed reactors and deposited on microstructured wafers. For this purpose, nanosized gold particles dispersed on different supports (SiO_2, Al_2O_3, TiO_2 and ZrO_2) were prepared by deposition–precipitation, precipitation, incipient wetness (fixed-bed experiments) on the one hand. On the other hand, the microstructured wafers were coated with alumina using Disperal (Sasol) as binder or were prepared via spin-coating (SiO_2, Al_2O_3, TiO_2 and ZrO_2) and then impregnated using $AuCl_3$ or $HAuCl_4$ solutions. In these experiments the same selectivity pattern was found for the supported gold catalysts and the microstructured wafers coated with gold/oxide. Conversion degrees were in the same range, slightly higher for the supported catalysts, whereas the specific activities were two orders of magnitude higher for the microstructured wafers due to much lower gold contents. These results are described in detail elsewhere [13].

It seems therefore, that the use of microstructures is not advantage when performing the gas phase hydrogenation of acrolein using Ru catalysts. However, on the other hand, it has been shown that it is possible to use carbon as support material for heterogeneous catalysis in microstructures. In order to gain more information about the reasons for the different behavior of differently prepared carbon layers, it would be necessary to perform a more throughout characterization of the catalyst layers, especially the surface functionalities and the pore texture.

4. Conclusions

The preparation method leads to carbon films on the wafer in the micrometer range. The amount of carbon deposited, however, depends on the composition of the monomer solution and on the presence of the pore-forming liquid. The activity of the wafers in the hydrogenation of acrolein is, among others, affected by the time of the calcination step. Most likely, the number of functional groups at the carbon surface as well as the porosity are responsible for this behavior. The selectivity pattern in the hydrogenation of acrolein (i.e. the amount of allyl alcohol, propanal or consecutive products formed) is similar to that of the acrolein hydrogenation using conventional Ru/C catalysts in a fixed-bed reactor.

Acknowledgements

This work has been supported by the Max-Buchner-Forschungsstiftung under Grant 2353 and Grant 2139. The authors are grateful to A. Hornik for experimental work and Dr. A. Knop-Gericke and U. Wild (FHI Berlin) for performing the XPS and SEM investigations.

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