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Preparation and characterisation of nickel-modified ceramic filters

Hongbin Zhao, Dirk J. Draelants, Gino V. Baron *

Department of Chemical Engineering, Vrije Universiteit Brussel, Pleinlaan 2, B-1050 Brussel, Belgium

Abstract

A nickel-activated alumina candle filter shows potential for the combined removal of particles, tars and ammonia from biomass gasification gas at high temperature. To deposit the nickel catalyst in the filter, only methods applicable to a preformed support can be considered. In this paper, we investigated the incorporation of a nickel precursor into small-scale α-Al_2O_3 filter substrates with a mean pore radius of 26 μm. Two preparation routes were used and compared: deposition–precipitation with urea and nickel nitrate and conventional impregnation with nickel nitrate. The substrates were characterised by X-ray mapping (SEM/EDX), mercury porosimetry and krypton adsorption. Preliminary experiments with the urea method have shown that an appropriate selection of the reaction time and the urea/nickel molar ratio is necessary to obtain a high controlled fixation of precursor during the slow decomposition of urea. The urea method gave a fairly uniform distribution of the nickel precursor throughout the support bodies. On the contrary, with the conventional impregnation method, most of the precursor was found in the outer pores of the substrate. Both methods can be repeated to increase the catalyst loading. Performing twofold deposition cycles, it was found that the urea method was more reliable and still gave a good distribution of the precursor. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Nickel; α-Al_2O_3; Preformed support; Urea; Hot gas cleaning; Catalytic filter

1. Introduction

The Integrated Gasification Combined Cycle (IGCC) is one of the most attractive options for electricity generation from biomass at the power scale of 50–150 MWe [1]. Most of the concepts are based on pressurised air gasification, followed by combustion of the product gas in a gas turbine. A steam turbine recovers the energy of the exhaust gases. At smaller scale, an atmospheric updraft or fluidised bed air gasifier followed by an engine is economically more viable. Apart from the main gas components (N_2, H_2, CO, CO_2, H_2O and CH_4), the biomass-derived product gas from the gasifier contains several impurities like particles (char, ash, gasifier additives), tars (polyaromatics), alkalis (Na, K), nitrogen compounds (mainly NH_3) and sulphur compounds (mainly H_2S). Particles can result in plugging and abrasion of downstream equipment, while tars can cause blinding of ceramic filters, pipe plugging and soot formation during combustion in gas turbines or engines. Alkali metals can cause severe corrosion of the gas turbine and heat exchanger. The nitrogen and sulphur compounds are converted during the combustion of the product gas to NO_x and SO_2, respectively, which are harmful for the environment.

Thorough gas cleaning of the high temperature gasification gas is therefore essential for reliable and environmentally sound operation. Apparently, performing the gas cleaning at high temperature may lead to a higher energy efficiency but more importantly to simplified processes and lower cost. The hot gas cleaning techniques mainly involve catalytic decomposi-

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* Corresponding author. +32-2-629-3246; fax: +32-2-629-3248.
E-mail address: gvbaron@vub.ac.be (G.V. Baron).

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tion of tar and ammonia followed by hot gas filtration for particle removal. From the work done by the Technical Research Centre of Finland (VTT), it appeared that commercial nickel-based steam reforming catalysts were very efficient at 900°C for the decomposition of tars and ammonia in biomass gasification gas [2]. The tar reactivity of nickel catalysts in gasification gas was confirmed by other research groups [3–5]. In most cases, the nickel-based catalysts are applied in a packed bed configuration, in which the catalysts have a low effectiveness factor mainly due to internal mass transfer limitations. On the other side, it has been demonstrated that ceramic candle filters can be applied to remove particles with sizes down to micrometer at high temperature. The filters consist of a coarse support body with on top of it a thin surface membrane with narrow pores [1]. The latter acts as a barrier for the particles and prevents plugging of the support body.

In our work, we propose to study the concept of catalytic ceramic filters by which particle removal and tar and ammonia decomposition are integrated in a single nickel-activated alumina candle filter. It simplifies the entire gas cleaning process with a potential reduction in investment costs. In addition, due to the intrinsic pore structure of the filter, the gas now flows through the catalytic active pores and internal diffusion is no longer a limiting factor for the tar conversion, as in a packed or fluidised catalytic bed, which was one of our main motivations to study this system. The catalytic candle filter can be regarded as a catalytic membrane reactor, because it combines a chemical reaction with a separation through a filter membrane. The accumulation of particles at the outer surface of the catalytic filter will not affect its activity, since the catalytic material is situated in the interior of the support body. The nickel-modified discs discussed in this paper are used in the laboratory-scale evaluation of the catalytic processes of the filter. However, this paper focuses only on their preparation and characterisation. Preliminary tests with the materials described in this paper demonstrated the principle and high performance, and further, more detailed testing is under way.

Due to the high temperature preparation steps used in forming the alumina filter material, and in contrast to conventional catalysts, only techniques applicable to a preformed support can be considered. The objective in this paper is to deposit a nickel precursor on the external surface of the non-porous α-Al_2O_3 particles (100–350 μm diameter) and this as homogeneously as possible throughout the macroporous filter substrates. The most straightforward method to apply a nickel precursor into preformed support bodies is incipient wetness impregnation with a nickel salt solution, followed by drying to bring about the deposition of the salt inside the pores of the support. The drying step is critical since the solution migrates and the precursor is deposited mainly where the solvent evaporates. Even when performed carefully, some non-uniformity must always be expected [6]. An important improvement is realised by immobilising the precursor on the carrier before the drying step. This can be achieved by deposition–precipitation [7]. However, the use of preformed support bodies requires that the salt and the precipitant are distributed uniformly throughout the pore volume before the initiation of the precipitation. Urea can serve well as a precipitant, because it decomposes very slowly at 90°C in aqueous media [8] according to the following reaction, which is of first order with respect to urea:

$$CO(NH_2)_2 + 3H_2O \rightarrow 2OH^- + 2NH_4^+ + CO_2 \uparrow \quad (1)$$

Consequently, hydroxyl groups are slowly formed, uniformly throughout the pores and the precipitation takes place homogeneously [6].

In this work, the deposition–precipitation method with urea was explored to introduce a nickel precursor into the ceramic substrates and was compared with the conventional impregnation method using the nickel salt only. The resulting modified substrates were characterised by SEM/EDX, mercury intrusion and krypton adsorption. To gain better insight in the urea method, the influence of the reaction time and the urea/nickel molar ratio on the fixation of the precursor on the carrier prior to drying, was investigated in a system nickel nitrate/urea/α-Al_2O_3 powder.

2. Experimental

2.1. Preparation methods

Porous α-Al_2O_3-based filter substrates were used in this work and were supplied by an industrial partner (Schumacher, Crailsheim, Germany), which is an important candle filter manufacturer. They were disc-shaped with a diameter of 3 cm and a thickness of 1 cm and are representative for the candle filter support body on a small scale.

Incorporation of a nickel precursor into the porous α-Al_2O_3 ceramic substrates was performed by deposition–precipitation through the urea method. The discs were first evacuated to a few torr for 1 h to avoid that occlusion of air leads to a poor wetting of the support. Subsequently, 15–50 ml of the impregnation solution was sucked into the glass vessel containing 1–3 discs. This solution contained appropriate amounts of a nickel salt ($Ni(NO_3)_2 \cdot 6H_2O$, p.a. from Fluka) and urea (p.a. from Fluka) as precipitant. After 1 h, the glass vessel was opened to the atmosphere, which applied an additional force on the solution to penetrate the pores. After the excess solution was drained off, the disc was put in a closed glass vessel and placed in an oven at 90°C for a certain period, resulting in precipitation of the nickel precursor by the slow hydrolysis of urea in the pores of the disc. After reaction, the substrate was dried at 110°C for a few hours. To decompose the precipitated nickel precursor to nickel oxide, the disc was heated at 2°C/min till 450°C and calcined for 4 h in an air atmosphere. For the multiple impregnation experiments, all previous steps (including the calcination) were repeated. The final step, the reduction of the nickel oxide to the active nickel metal, was not performed.

To compare the distribution of the nickel precursor throughout the support body, some modified substrates were prepared by conventional impregnation with a nickel nitrate solution. Except for the absence of urea in the impregnation solution, other steps and experimental conditions were identical to the preparation procedure with the urea method.

To study the urea method, 2 g of the sieved fraction between 100–160 μm of α-Al_2O_3 powder, (>99% purity, Gouda, The Netherlands), was added to a glass vessel, containing 15 ml of a 5 M Ni^{2+} solution of $Ni(NO_3)_2 \cdot 6H_2O$ with varying urea concentration. The vessel was closed and placed in an oil bath at 90°C to perform the urea decomposition while the mixture was stirred. The reaction time varied between 1 and 24 h. After reaction, the final pH of the suspension was measured with a pH meter (WTW pH 537). Subsequently, the mixture was filtered to obtain the residue, using a 0.45 μm polymer membrane. To remove further the Ni^{2+} ions that did not precipitate during the urea decomposition, the residue was thoroughly washed with demineralised water. After drying at 90°C, the residue was weighed and the known weight of the added alumina powder was subtracted to obtain the amount of precipitated nickel precursor.

2.2. Characterisation methods

A static volumetric method was used to measure the krypton adsorption isotherm at 77 K (liquid nitrogen) of the α-Al_2O_3 and nickel-modified substrates. The measurements were performed on a Sorptomatic 1990 (Fisons). The BET method was applied to derive the surface area from the physisorption isotherm data.

Mercury intrusion, performed on the Pascal 140 and Porosimeter 2000 from Fisons, was used to determine the bulk density, the pore volume, the mean pore radius and the pore size distribution of the virgin and modified substrates. A contact angle of 141° and a cylindrical pore model were used in the Washburn equation. The apparent density of the discs was obtained by pycnometry (Accupyc 1330, Micromeretics) using helium.

For some selected calcined discs, the elemental distribution of nickel throughout the modified disc was examined by investigation of a polished radial cross section of the disc with SEM/EDX (Energy Dispersive X-ray). The analysis was performed on a JSM 6400 (JEOL), equipped with a NORAN X-ray analysis system with an energy dispersive detector. The Kα line of Ni was used as analytical energy line for the X-ray detector. The electron probe worked at an acceleration voltage of 15–25 kV and a current intensity of 3×10^9 A.

3. Results and discussion

3.1. Study of the urea method

The group of Geus [9] pioneered the investigation of the deposition–precipitation method with urea to deposit nickel on a suspended silica carrier. Later on, the urea method was applied successfully to incorporate nickel and other catalysts within the pores of preformed support bodies [7,10–13]. Experimental parameters which determine the fixation degree, that is, the amount of nickel precursor fixed by precipitation on the support before drying relative to the maximum amount that can be deposited, are the reaction temperature, the reaction time and the concentrations of urea and Ni^{2+} in the impregnation solution. This paper deals with the influence of the reaction time and the urea concentration. The latter is lumped into the urea/nickel molar ratio (defined here as the ratio of the initial molar concentration of urea and Ni^{2+} in the impregnation solution), since the initial Ni^{2+} concentration was kept constant. Mok and his co-workers [10], used a urea/nickel molar ratio of 3.0, but the reaction time at 90°C for the precipitation of the metal salts (Ni, La, Mg, Al) within the pores (0.5–2 μm diameter) of alumina Raschig rings, was not reported. In Knijff's work [7], a slight excess of urea was used (8%) and the impregnated supports were kept at 90°C for 3–20 h. In recent work on the urea method applied on a monolith, the precipitation was performed with a urea/nickel molar ratio of 1.1 at 90°C for 5 h [11].

It appears that there is no general agreement in literature about the choice of some experimental parameters and their values are rarely motivated. For that reason, we decided to investigate the urea method first, to determine adequate values of reaction time and urea/nickel molar ratio for the impregnation of the ceramic substrates. As the supply of ceramic discs was limited, these tests were performed on α-Al_2O_3 powder. The reaction temperature was 90°C, which is generally used. Every experiment was performed twice and the average result is displayed.

To investigate the role of the reaction time, the urea/nickel molar ratio was fixed at a value of 1.3. The result is shown in Fig. 1. The precipitation amount and suspension pH both increased with reaction time. The overall reaction appeared to be quite slow and approaches apparent chemical equilibrium after 24 h reaction. It should be noted that the amount of nickel precipitate exhibited a sharp increase during the first 6 h of the deposition reaction. Accordingly, at least 6 h reaction time was needed to fix a reasonable amount of precursor on the support during the wet stage of the urea method. Based on the above experimental results, using two fixed reaction times (6 and 24 h), the effect of the urea/nickel molar ratio on the nickel precipitation was investigated in a range of ratios from 1 up to 3.

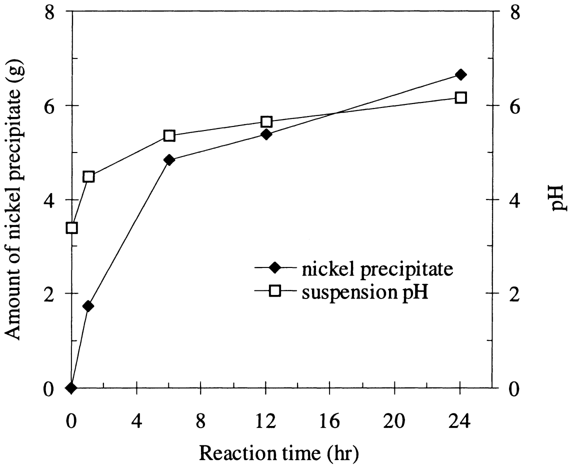

Fig. 1. Precipitation amount of the nickel precursor and the suspension pH as a function of reaction time (urea/nickel molar ratio: 1.3).

Fig. 2 shows the data obtained for a reaction time of 6 h. The amount of nickel precipitate increased markedly below a urea/nickel molar ratio of 2 and then flattened out. However, the pH increased quite linearly over the full range with the urea/nickel molar ratio.

Fig. 3 shows the effect of the urea/nickel ratio determined under the same conditions as in Fig. 2 but for a reaction time of 24 h. The behaviour is clearly

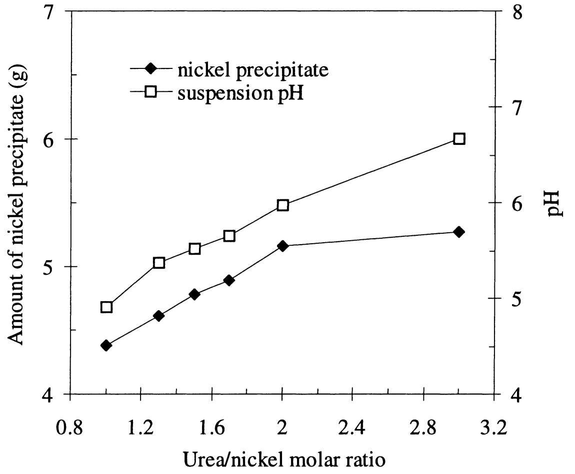

Fig. 2. Precipitation amount of the nickel precursor and the suspension pH as a function of urea/nickel molar ratio (6 h reaction time).

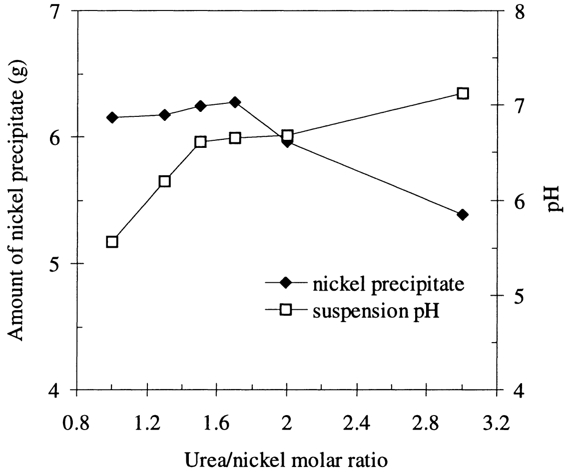

Fig. 3. Precipitation amount of the nickel precursor and the suspension pH as a function of urea/nickel molar ratio (24 h reaction time).

different from the 6 h reaction time experiments. The amount of the nickel precipitate hardly increased when the molar urea/nickel ratio was varied between 1 and 1.7. For higher ratios, the amount of nickel precipitate surprisingly decreased, although the pH continued to increase. It was also noticed that the final colour of the solution changed from green to green/blue with increasing urea/nickel ratio. Comparing the maximum amount of precipitate of Fig. 2 with that of Fig. 3, the latter is 19% higher, although the pH was comparable in both points.

An explanation for the behaviour in Figs. 2 and 3 can be found by looking at the balance of the interaction of the free Ni^{2+} ions with OH^- ions and NH_3 molecules, which both result from the decomposition of urea. Equilibrium calculations of the relative amount of soluble Ni(II) species, that is, free Ni^{2+}, $Ni(OH)^+$ and Ni(II)/NH_3-complexes (blue), as a function of pH have shown that above a pH of around 5, which is encountered in all experiments, the Ni(II)/NH_3-complexes exist as main species. Their dominance is more explicit for higher pH values and a higher total concentration of NH_4^+ and NH_3, consequently, for higher initial urea concentrations and a longer reaction time. But the overall reaction of the precipitation of the nickel precursor is not only determined by the balance at equilibrium between free Ni(II) precipitation and ammonia complex-formation. After all, from the standpoint of kinetics, the precipitation of Ni(II) could be faster than the complex-formation with NH_3 at a low total concentration of NH_4^+ and NH_3. This could result yet in an increase of the amount of nickel precipitate, as can be seen in Fig. 2. Nevertheless, the decrease in the amount of nickel precipitate at high urea/nickel molar ratios in Fig. 3 can be attributed to enhanced complex-formation with ammonia. In between, there is a region where neither the precipitation, nor the complex-formation dominates and the amount of precipitate will hardly increase, which is found in the last part of Fig. 2 and the first part of Fig. 3.

To know to what extent the total of the dissolved nickel salt was immobilised as precipitate during the urea decomposition, the washed precipitates from the experiments shown in Fig. 3 were calcined at 450°C for 4 h to bring about the decomposition to NiO. The calcined samples were weighed to obtain the amount of NiO present. Since those experiments were performed with 15 ml of a 5 M Ni^{2+} solution, a maximum amount of 5.6 g NiO can be obtained when all the nickel ions precipitate. From this, the fixation degree of the urea method was calculated, defined here as the measured amount of NiO relative to the maximum amount that can be deposited. A maximum fixation degree of 75% was obtained for a urea/nickel molar ratio of 1.7. This means that about 25% of the initial Ni^{2+} ions still remained in the solution after 24 h of reaction. One can remove those ions by washing, or one can choose to let them precipitate during the drying stage, where the already deposited nickel species probably act as germs. To obtain a higher loading of catalyst, the last option was chosen for the preparation of the modified discs. This could have an influence on the spatial distribution of the nickel precursor.

3.2. Porous alumina substrates

Table 1 shows some morphological parameters of the virgin filter substrates. The pore volume and bulk density obtained by mercury porosimetry confirms the value of the apparent density obtained by helium pycnometry, which means that all the pores could be measured by mercury intrusion as no micropores were present. Furthermore, it appeared that the discs exhibited a narrow pore size distribution. The measurements were reproducible within a few percent

Table 1
Characterisation of the filter substrates before and after a single or twofold deposition with the urea method or the conventional impregnation method

Parameter	Before impregnation	After 1 × urea method	After 1 × conv. impregnation	After 2 × urea method	After 2 × conv. impregnation
Pore volume (mm^3/g)	102	90	95	83	74
Mean pore radius (μm)	26	23	24	23	23
Bulk density (g/cm^3)	2.83	2.95	2.94	3.04	3.15
Apparent density (g/cm^3)	3.98	4.03	4.08	4.06	4.09
Specific surface area (m^2/g)	0.33	0.49	0.44	0.42	0.56
Porosity (%)	29	26.5	28	25	23
Amount of NiO (g)	–	0.41	0.51	0.87	1.02
NiO loading (wt.%)	–	2	2.5	4.3	5

for other discs of the same batch. The surface area is very low, because the constituent α-Al_2O_3 particles are non-porous. Consequently, the pores are only attributed to the space between the particles and the available surface for nickel deposition is limited to the total external surface of the α-Al_2O_3 particles. Scanning Electron Microscope (SEM) observations showed that the pore shape was irregular because of the irregular shape of the particles. Since the mean pore radius is determined with a cylindrical pore model, its value must be interpreted with caution.

3.3. Nickel-modified porous alumina substrates

As in the preliminary experiments, a urea/nickel molar ratio of 1.7 with a reaction time of 24 h at 90°C led to a maximum fixation of the precursor on the support during the wet stage of the urea method, these values were chosen for the impregnation of the discs.

The maximum loading amount of precursor that can be deposited in one step is determined by the total pore volume of the disc and the Ni^{2+} concentration of the impregnation solution. If a single deposition–precipitation cycle does not give a sufficient amount of catalyst, the procedure can be repeated several times. Two consecutive deposition cycles with urea were carried out. It is advantageous to heat the support body between successive depositions to bring about the decomposition of the precipitate previously formed. This increases the capacity of the pores for subsequent impregnations [10]. However, the chance on pore plugging increases with increasing number of deposition cycles [13], which is detrimental to the filtration capacity.

The distribution of NiO throughout the above mentioned modified substrates was observed by SEM/EDX. In addition, to compare the nickel distribution obtained with the urea method, single and twofold impregnated substrates were prepared by conventional impregnation with a solution containing only the nickel salt.

3.3.1. Single deposition

The initial concentration of Ni^{2+} ions in the impregnation solution was 3.44 M for both methods. After calcination, the modified substrates were weighed and characterised. Table 1 shows some morphological parameters before and after a single deposition. It must be borne in mind that the parameters for a virgin substrate can vary a few percent from disc to disc.

After a single deposition cycle, it appears that the precipitation of nickel oxide inside the pores hasn't changed the morphological parameters of the substrates too much, and hence, the resistance for permeating gases will hardly change. The pore size distribution slightly shifted to smaller pore sizes. The specific surface area increased, but remained very low.

The amount of NiO deposited for the disc prepared by the urea method is clearly lower. Equilibrium calculations at 90°C of the relative amount of the carbonic acid species (H_2CO_3, $HCO_3{}^-$ and $CO_3{}^{2-}$) as a function of pH have shown that CO_2 can be produced in the system. The lower loading of NiO could be attributed to CO_2 release during the urea hydrolysis, which could expel some impregnation solution from the disc. Furthermore, it was noticed that after reaction some solution had drained off the substrate, and hence some nickel precursor was lost for precipitation

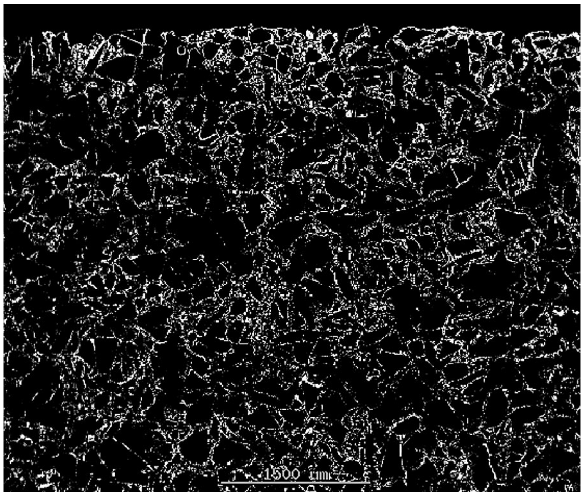

Fig. 4. SEM/EDX mapping for Ni of a cross section for a substrate after a single deposition cycle with the urea method.

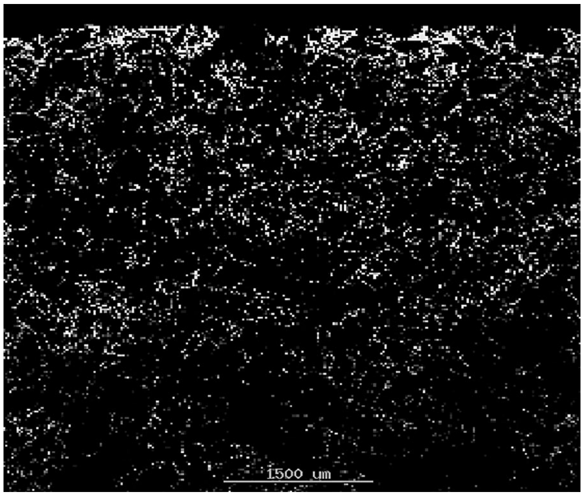

Fig. 5. SEM/EDX mapping for Ni of a cross section for a substrate after a single deposition cycle with the conventional impregnation method.

inside the disc. In spite of the fact that more nickel oxide is loaded on the conventionally impregnated disc, the remaining pore volume remains somewhat higher relative to the urea impregnated disc, because part of the NiO was deposited at the outer surface of the disc instead of inside the pores. However, for a lower catalyst loading (e.g. 1 wt.%), the CO_2 release will be less, and consequently, the tendency to expel impregnation solution will decrease.

To compare the distribution of NiO throughout the substrates, an X-ray area scanning was made of part of a polished radial cross section of the discs. The results are shown in Fig. 4 (urea method) and Fig. 5 (conventional impregnation) for an analysis till a depth of about 3.5 mm (vertical direction) in the disc. The white dots represent the EDX-mapping for the element Ni. It appears that when using the urea method, a fairly uniform macroscopical distribution of the nickel oxide can be accomplished, in spite of the fact that some part of the precursor was deposited in a poorly controlled fashion during the drying stage. Also, the release of CO_2 did not really prevent the uniform distribution of precursor. However, with the conventional impregnation method, most of the NiO is situated in the pores close to the outer surface (top area of Fig. 5). Consequently, less NiO is detected near the middle of the disc (bottom area of Fig. 5), compared with Fig. 4.

3.3.2. Twofold deposition

To increase the NiO loading further, the deposition cycle was performed two successive times on other discs under the same conditions previously used. The right half of Table 1 shows the characterisation parameters after the second calcination for the two methods employed. The NiO loading for both cases doubled compared with a single deposition. The second deposition lowers the permeability further, especially for the conventionally impregnated disc. Moreover, the change in parameters of the twofold conventionally impregnated disc, relative to the virgin disc, is appreciable higher than what could be expected from the results of the one time conventionally impregnated disc from the previous paragraph. This points out that the conventional impregnation procedure was not so reproducible. Possibly, in this experiment more precursor was already deposited inside the disc after the first of a total of two conventional impregnations, compared with the one time conventionally impregnated disc of the previous paragraph. Hence, sometimes more catalyst is deposited inside the pores and sometimes less. With the urea method, the deposition is performed in a more controlled fashion, which enhances the reproducibility.

Again, SEM/EDX analysis was performed on a cross-section of the twofold impregnated substrates.

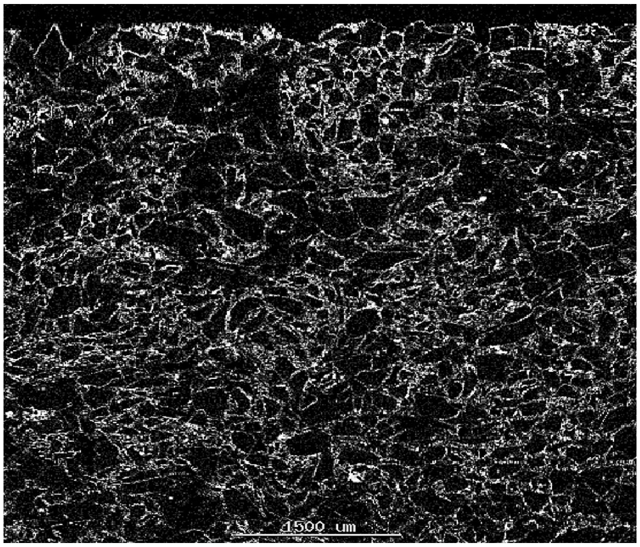

Fig. 6. SEM/EDX mapping for Ni of a cross section for a substrate after two deposition cycles with the urea method.

The Ni element mapping is displayed in Fig. 6 (urea method) and Fig. 7 (conventional impregnation). The mappings confirm the points already observed after one deposition. The urea method gives still a fairly homogeneous precipitation throughout the disc after two cycles. Depositing NiO in the middle of disc remains more problematic with the conventional impregnation, even after two times, since most precipitation occurs in the outer pores or at the outer surface of the substrate. Repeating the impregnation could have averaged out the inhomogeneity of each separate deposition cycle, but our observations confirm the opposite. It is doubtful that a second deposition cycle would enhance the catalytic activity, as the available surface is important and not the amount.

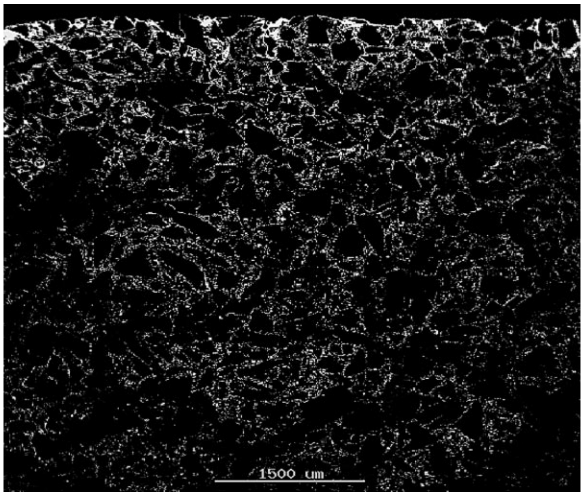

Fig. 7. SEM/EDX mapping for Ni of a cross section for a substrate after two deposition cycles with the conventional impregnation method.

4. Conclusions

1. The study of the urea method in a system nickel nitrate/urea/α-Al_2O_3 powder showed that a reaction time of at least 6 h was necessary. A higher initial urea concentration can lead to less fixation, depending on the reaction time used. This is due to enhanced complex-formation of the Ni^{2+} ions with NH_3. Finally, a maximum fixation of 75% of the precursor was found for a reaction time of 24 h and a urea/nickel molar ratio of 1.7.
2. It was demonstrated that the urea method could be applied to deposit a nickel precursor fairly homogeneously throughout the α-Al_2O_3 disc, in spite of that part of the precursor was fixed in a poorly controlled fashion during the drying stage and in spite of the release of CO_2. A single deposition

cycle gave rise to a NiO loading of about 2 wt.%. This did not change the flow-through capacity of the filter substrate too much. With the conventional impregnation method, more nickel oxide is deposited at the outer surface or in the pores close to the outer surface than in the middle pores of the disc. Hence, the catalyst distribution was less uniform.

3. If needed, consecutive deposition cycles can be performed to increase the nickel loading of the substrates. For a twofold deposition, the urea method again gave the best results concerning uniform distribution of the precursor. It seemed that the conventional impregnation method was less reliable and reproducible. Future work will include detailed reaction tests with discs prepared by the urea method to assess the amount of catalyst needed for a high and stable activity. The first results indicate already a high activity for a single deposited substrate with 2 wt.% NiO.

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References

[1] M. Nieminen, P. Simell, J. Leppälahti, P. Ståhlberg, E. Kurkela, in: Proc. 9th European Bioenergy Conference, Copenhagen, June 1996.
[2] P. Simell, Catalytic Hot Gas Cleaning of Gasification Gas, VTT Publications, Espoo 330 1997.
[3] E.G. Baker, L.K. Mudge, M.D. Brown, Ind. Eng. Chem. Res. 26 (1987) 1335.
[4] I. Narvaéz, J. Corella, A. Orio, Ind. Eng. Chem. Res. 36 (1997) 317.
[5] D.N. Bangala, N. Abatzoglou, J.-P. Martin, E. Chornet, Ind. Eng. Chem. Res. 36 (1997) 4184.
[6] J.T. Richardson, Principles of Catalyst Development, Plenum Press, New York, 1989.
[7] L.M. Knijff, P.H. Bolt, R. van Yperen, A.J. van Dillen, J.W. Geus, in: B. Delmon, P. Grange, P. Jacobs, G. Poncelet (Eds.), Preparation of Catalysts V, Elsevier, Amsterdam, 199l, p. 166.
[8] W.H.R. Shaw, J.J. Bordeaux, J. Am. Chem. Soc. 77 (1955) 4729.
[9] L.A.M. Hermans, J.W. Geus, in: B. Delmon, P. Grange, P. Jacobs, G. Poncelet (Eds.), Preparation of Catalysts II, Elsevier, Amsterdam, 1979, p. 113.
[10] K.B. Mok, J.R.H. Ross, R.M. Sambrook, in: G. Poncelet, P. Grange, P. Jacobs (Eds.), Preparation of Catalysts III, Elsevier, Amsterdam, 1983, p. 291.
[11] X. Xiaoding, H. Vonk, A. Cybulski, J.A. Moulijn, in: G. Poncelet, J. Martens, B. Delmon, P.A. Jacobs, P. Grange (Eds.), Preparation of Catalysts VI, Elsevier, Amsterdam, 1995, p. 1069.
[12] R.J.R. Uhlhorn, Ph.D. Thesis, University of Twente, The Netherlands, 1992, p. 33–65.
[13] G. Sarraco, L. Montanaro, Ind. Eng. Ind. Res. 34 (1995) 1471.