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Monolithic catalysts for selective hydrogenation of benzaldehyde

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Abstract

Nickel on alumina-washcoated cordierite or α-alumina monolithic catalysts for selective hydrogenation of benzaldehyde were prepared and characterised. Deposition precipitation method leads to a homogeneous distribution of nickel, whereas conventional adsorption method does not. Nickel in the catalysts was not completely reduced and the Ni loading per gram of washcoated alumina is very high. The catalysts can be reduced at a high temperature and passivated ex situ, followed by an in situ reduction before reaction commences. Despite the low Ni dispersions in the Ni monolithic catalysts, they showed high selectivity and activity towards the favourable product, benzyl alcohol, as compared to conventional catalysts.

Keywords: Monolithic catalysts; Selective hydrogenation; Benzaldehyde

1. Introduction

Monolithic catalysts have been widely used in the cleaning of exhaust gases, especially those from cars and power stations [1,2]. They have been recently reviewed by Cybulski and Moulijn [2]. Compared to conventional catalysts, e.g. pellets, spheres, granules, monolithic catalysts have several advantages, such as low pressure drop, possibility of using high flow rate, easiness in scale-up, and, in some cases, selectivity enhancement. However, they have not been extensively applied in chemical processes, e.g. in the production of fine chemicals. As part of a program to study the possibility of using monolithic catalysts in fine chemicals production, we have studied the preparation and characterisation of monolithic catalysts. Ni catalysts are widely used in industrial hydrogenation processes. Therefore, Ni monolithic catalysts have been studied in this work. For the performance tests, hydrogenation of an aromatic aldehyde, benzaldehyde, was chosen. Our work on washcoating has been reported earlier elsewhere [3]. Here, we report on metal loading and the characterisation of the monolithic catalysts.

2. Experimental

A cordierite monolith from Degussa (code name: C-D) and α-alumina (code: A-E) monoliths from ECN (both 62 cells/cm^2) were used for washcoating. The alumina-washcoated monoliths using C-D and A-E are coded as AC-D and AA-E, respectively. Those alumina-washcoated at TU Delft using monolith C-D are

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coded as AC-T. The preparation of Al-sols used and the procedures of washcoating were described earlier [3]. For the washcoating of the ECN alumina monoliths (AA-E), an Al-sol prepared from Disperial Spezial 10/2, 20/2 and 30/2 powders (CONDEA Chemie) was used. Ni was loaded onto alumina-washcoated monoliths using the following methods: adsorption using an aqueous solution of $Ni(NO_3)_2$ (Merck, pro Analyse, 0.617 or 8.2 M), or Ni acetate (Aldrich Chemie, 98%, 0.617 M), or so-called deposition precipitation using an aqueous solution containing both nickel nitrate (0.88 M) and urea (0.95 M). After drying the monolith was dipped in the salt solution for 1 h for adsorption. Afterwards it was drained of the salt solution and dried in a microwave oven. Subsequently, it was calcined in air up to 723 K and kept at that temperature for 2 h. In deposition precipitation, predried monolith was dipped in the nickel nitrate and urea solution and heated for at least 5 h above 363 K. After deposition precipitation, the catalysts were drained, dried and calcined as described above (see Fig. 1).

The amount of washcoated alumina was obtained by weighing. The Ni loading was calculated from the weight difference between the weight of catalyst after Ni loading and calcination, and before Ni loading.

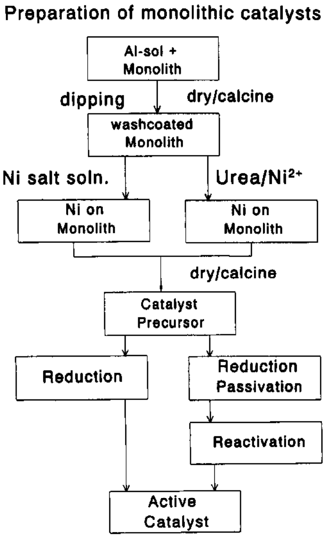


Fig. 1. Block scheme showing the preparation of Ni monolithic catalysts.

The specific surface areas of the samples were measured using nitrogen physisorption at liquid nitrogen temperature with either ASAP 2000 or Digisorb 2600 apparatus from Micromeritics.

Free metal surface area of nickel catalysts were measured in ASAP 2000 by hydrogen chemisorption at 323 K. The catalysts were reduced at 648 K for 1 h, followed by evacuation at 623 K for 2 h to expel the hydrogen adsorbed before the chemisorption measurement. After the first chemisorption, the catalyst was evacuated at 323 K and measured again. The difference in the amounts of hydrogen adsorbed between the two successive measurements was used to calculate the free metallic surface area, assuming a metal to hydrogen atom ratio of 1:1.

Temperature programmed reduction was performed in a H_2/Ar mixture ($H_2:Ar = 2:1$, 20 ml/min) at a heating rate of 10 K/min [4] for powder samples, using a quartz tube reactor (i.d. 7 mm). For monolithic catalyst blocks, a specially-designed quartz tube reactor was used, in which a cylindric monolithic catalyst block (diameter: 4 cm and length: 4 cm) can be reduced without prior crushing. The heating rate for monolithic blocks was 5 K/min and the flow of H_2/Ar mixture was 50 ml/min. The TPR set-up was able to measure the temperature of the sample inside the tube reactor. Hydrogen consumption was measured by a thermal conductivity detector (TCD). TPR signals (TCD signal, time and temperature) were acquired and integrated using home-written programs.

The performance of monolithic catalysts was tested in a gradientless Berty reactor [5]. Selective hydrogenation of benzaldehyde to benzylalcohol was chosen as model reaction. Prereduced and passivated Ni monolithic catalyst was reduced in situ in the Berty reactor in hydrogen up to 423 K. After reduction, the temperature was adjusted to the desired one (420 K), then, the reactant (benzaldehyde > 99.5%) was introduced. The reaction was performed batch-wise at 1250 rpm and 1.6 MPa. Samples were withdrawn at intervals and analysed by GC [5].

3. Results

The surface area of the cordierite monolith (C-D) without alumina-washcoating was 0.2 m^2/g. The Degussa alumina-washcoated monolith (AC-D) has a surface area of 34.0 m^2/g. Their alumina content in the ECN monoliths (AA-E) was between 12–27 wt%.

Chemisorption results of some Ni catalysts are presented in Table 1. It appears that the Ni dispersion on AA-E or AC-D monolithic catalysts is higher than that on AC-T. The reduction degree was calculated from the corresponding TPR patterns. The D_{mean} values are estimated volume-surface averaged diameter of nickel particles.

The TPR patterns of crushed Ni monolithic catalysts (A, Ni on AA-E and B, Ni on AC-T) are shown in Fig. 2, and those of the corre-

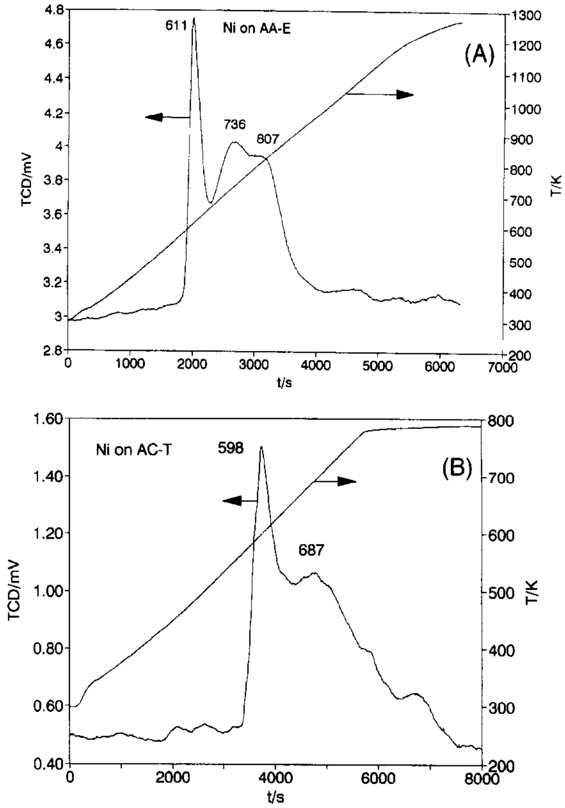


Fig. 2. TPR patterns of a Ni monolithic catalysts (crushed powder): A, Ni on AA-E and B, Ni on AC-T.

Table 1
Ni monolithic catalysts

Sample code	Ni (wt%)	Al_2O_3 (wt%)	S_{metal} (m^2/g)	D (%)	D_{mean} (nm)	Red. degree (%)
AA-E/Ni (10.5)	10.5	12.5	4.28	6.1	16.5	63.7 [a]
						60.9 [b]
AA-E/Ni (0.7)	0.7	12.5	1.09	23.4	4.3	> 100 [a]
AA-E/Ni (7.1)	7.1	16.8	3.31	7.0	14.5	92.2 [a]
AA-E/Ni (7.7)	7.7	27.1	4.11	8.1	12.5	95.2 [a]
AC-T/Ni (6.0)	6.0	12.0	0.76	1.8	57.8	63.2 [a]
						72.4 [b]
AC-D/Ni (5.05)	5.05	n.d.	3.8	11.4	8.8	n.d.

[a] Crushed monolith sample.

[b] Block monolith samples.

The codes for the monolithic samples are as follows:

Degussa cordierite monolith:	C-D
Alumina-washcoated Degussa cordierite monolith:	AC-D
TU Delft alumina-washcoated Degussa cordierite monolith:	AC-T
ECN α-alumina monolith:	A-E
Alumina-washcoated ECN α-alumina monolith:	AA-E

For catalysts, the number in parenthesis denotes the nickel weight percentage in the catalyst. For example, AA-E/Ni(10.5) refers to a Ni monolithic catalyst supported on AA-E monolith with 10.5 wt% of Ni.

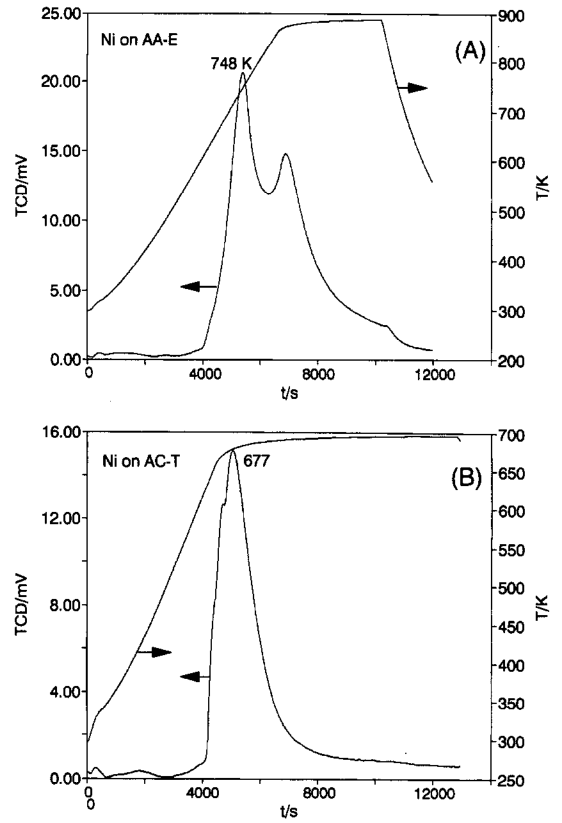


Fig. 3. TPR patterns of a Ni monolithic catalysts (block samples): A, Ni on AA-E and B, Ni on AC-T.

sponding block samples are given in Fig. 3. It appears that the TPR patterns of powdered Ni monolithic catalysts are different from those of block samples. Moreover, the peak maximum

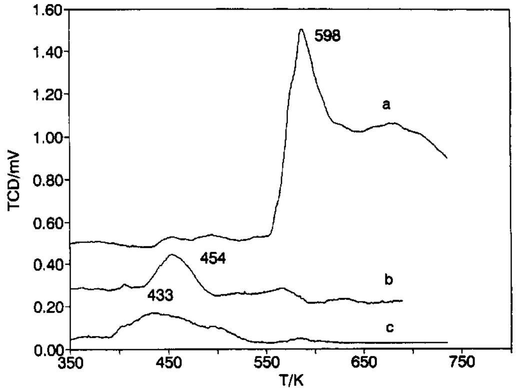


Fig. 4. TPR patterns of a crushed Ni on AC-T monolithic catalyst, AC-T/Ni (6.05): a, fresh, b, after passivation at 327 K and c, after passivation at 293 K.

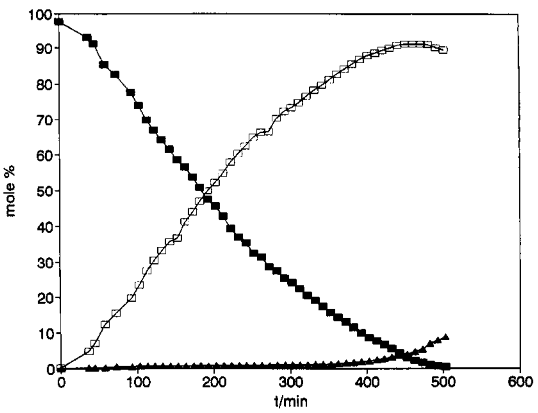


Fig. 5. Concentrations of benzaldehyde, benzyl alcohol and toluene changes as a function of reaction time over a Ni on alumina washcoated monolithic catalyst at 420 K, 1250 rpm and 1.6 MPa using 1.37 mol of benzaldehyde.

temperature depends on the type of the monolithic support used and the type and amount of washcoated alumina.

TPR pattern of a Ni monolithic catalyst (crushed, on monolith AC-T) and its TPR patterns after passivation at two different temperatures, viz. 293 or 327 K, are shown in Fig. 4. It appears that the temperature maxima of the reduction peaks for the passivated catalysts (454 or 433 K, respectively) are much lower than that of the fresh catalyst (598 K). Moreover, the peak area becomes much smaller, as compared to that of fresh sample.

Fig. 5 shows the concentration changes of benzaldehyde, benzyl alcohol and toluene as a function of reaction time over a Ni on AC-T (alumina-washcoated cordierite) monolithic catalyst. Similar patterns were obtained for other Ni monolithic catalysts.

4. Discussion

It appears that adsorption methods, in general, lead to a poor nickel distribution in the monolithic catalysts [4]. Microwave drying was introduced to improve the homogeneity of the nickel dispersion [6,7]. Though microwave heating, in general, is fast and favourable in improving the homogeneity of the dispersed phase, calcined samples prepared by the adsorption method, were not homogeneous. This was attributed to the low melting points of the nickel salts used which causes redistribution in calcination [3].

Deposition precipitation method [8,9], in principle, may lead to a more homogeneous distribution of the active phase. Decomposition of urea leads to an increased pH [Eq. (1)], leading to the deposition of metal as hydroxide. In the case of nickel, it is deposited as nickel hydroxide [Eq. (2)].

$$NH_2CONH_2 + 3\,H_2O = 2\,NH_4^+ + CO_2 + 2OH^- \quad (1)$$

$$Ni^{2+} + 2\,OH^- \rightarrow Ni(OH)_2 \quad (2)$$

Due to the relatively high melting points of the oxide and hydroxide, redistribution of the Ni species is suppressed and a more homogeneous Ni distribution is the result. Usually, the metal loading using deposition precipitation method is lower than those by impregnation or coprecipitation method. The metal loading can be enhanced by using a higher concentration of the nickel salt solution and/or a longer period of time. The explanation for the favorable effect of a longer time probably is a more extended urea decomposition which was suggested to be the rate-determining step [9].

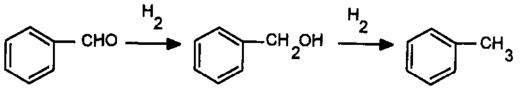
As can be seen from Table 1 the reduction of the Ni catalysts is not complete under the reduction conditions applied. Too high a reduction temperature might lead to sintering of the nickel, hence a lower temperature (723 K) was used in this work.

From the chemisorption results the volume-surface averaged diameter of Ni particles and the dispersion were calculated. It appears that on the Ni monolithic catalysts the nickel dispersion is low ranging from a few percent to ca. 23%, whereas the dispersion of conventional catalysts is much higher. This is partly caused by the relatively low specific surface areas of the monolithic catalysts which are typically 20–40 m^2/g, whereas those of conventional catalysts range between 100–400 m^2/g. Obviously, a low total surface area is unfavourable for a high metal dispersion. Moreover, in monolithic catalysts, the washcoat (alumina support) layer is less than 100 μm thick. Probably, nickel species are distributed mainly in this thin external layer of the monolith and, as a consequence, sintering is promoted. Note that the Ni loading per gram of alumina in the monolithic catalysts is much higher (up to 84 wt%) than the corresponding conventional catalysts (up to typically 33 wt%). Furthermore, nickel oxide is known to be able to react with alumina, forming Ni aluminate spinel-like species, which is only reduced at much higher temperatures (> 1100 K). A high probability of interaction between Ni species and alumina in monolithic catalysts also contributed to the low dispersion of monolithic catalysts. Relatively low metal dispersion, as compared to that of conventional catalysts, are generally observed on monolithic catalysts.

The TPR patterns of crushed monoliths and the corresponding monolith blocks are not identical, which can be ascribed to the different reduction conditions used. Moreover, one may ask how representative is the crushed sample of the monolithic catalysts. Improper sampling procedure may lead to inaccuracy in the results. This is the reason that a special TPR set-up, able to measure a block of monolithic catalysts, has been built.

From Fig. 4, it is clear that the passivated Ni catalyst can be reduced at much lower temperatures than the fresh catalyst, which is reduced typically above 673 K. Furthermore, the peak area of the passivated sample is relatively small compared with that of the fresh sample. The explanation is that only the external layer of the nickel metal particles was oxidized during the passivation. The lower reduction peak temperature is probably caused by an autocatalytic effect of the nickel metal in the passivated catalysts. The results show that it is possible to prereduce at a high temperature and passivate the Ni catalyst ex situ, followed by reduction at a moderate temperature in situ in the reactor. This is advantageous since often industrial reactors cannot tolerate the high temperatures necessary for the reduction of fresh nickel catalysts.

Selective hydrogenation of benzaldehyde was used as the model reaction [10,11]. The reactions can be presented by the following scheme:



The results in Fig. 5 show a high selectivity towards the alcohol. Although toluene is the sequential product of the consecutive hydrogenation of the alcohol, it appears only when essentially all aldehyde has disappeared. Note that no ring hydrogenation products were detected showing the high selectivity towards side-chain hydrogenation. This phenomenon is well known for this reaction system. The monolith catalyst shows a promising behavior. We compared our catalyst with a commercial Ni catalysts. It appeared that it shows slightly higher selectivities for benzyl alcohol under similar reaction conditions and the reaction rate per gram of nickel for Ni on alumina-washcoated catalysts is ca. twice higher than the commercial Ni catalyst tested. The reaction rates over our Ni monolithic catalysts observed (from $0.15 \cdot 10^{-2}$ to $5.7 \cdot 10^{-2}$ mol/g min) are comparable to those reported in the literature [12–15].

The enhanced rate, as compared to conventional catalysts, is obviously not due to a higher metal dispersion. It is attributed to a relatively short diffusion length and/or more efficient hydrogen diffusion in the monolithic catalysts during the three-phase hydrogenation, caused by the Taylor flow. Preliminary results show that this rate can be further enhanced when a carbon layer is coated on the alumina layer before Ni loading. Further study is needed to clarify the results.

5. Conclusions

Homogeneously distributed Ni monolithic catalysts were prepared using the deposition precipitation method. This method is preferred to the adsorption method for preparing nickel monolithic catalysts.

The Ni monolithic catalysts showed high selectivity and activity in the hydrogenation of aromatic aldehyde, though metal dispersion in the monolithic catalysts is, in general, low and the metal loading per unit weight of alumina washcoat is extremely high.

The enhanced activity is believed to be caused by a high rate of hydrogen diffusion in the reactor due to a short diffusion length.

Ni catalysts can be reduced ex situ at high temperatures and passivated at room temperature. They can, then, be reduced in situ in the reactor at much lower temperatures.

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