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Hydrodechlorination of 1,2-dichloroethane on active carbon supported palladium–nickel catalysts

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Abstract

Two series of 2 wt.% Pd–Ni/active carbon catalysts prepared from chloride and nitrate salts were characterized by hydrogen chemisorption, temperature programmed palladium hydride decomposition and X-ray diffraction, and investigated in the hydrodechlorination of 1,2-dichloroethane in the gas phase at a relatively low reaction temperature (210–230 °C). All catalysts showed very high stability with time on stream. Ni-rich bimetallic samples exhibited the highest selectivities towards ethene (desired reaction product). Addition of palladium, the metal which is known for its high hydrogenation activity, resulted in a massive production of ethane, at the expense of ethene. The correlation between the turnover frequency towards ethene and Pd–Ni phase composition resembles very much an expected relationship between surface and bulk composition of Pd–Ni alloys. This suggests that surface nickel atoms are the active sites for hydrogen-assisted dechlorination of 1,2-dichloroethane. The overall results indicate that, in agreement with the literature, palladium segregates to the surface of Pd–Ni (even during hydrodechlorination), shaping the overall catalytic behavior of bimetallic Pd–Ni catalysts. The monometallic, 2 wt.% Ni/C prepared from the chloride precursor, was the only catalyst which showed a noticeable selectivity for vinyl chloride which gradually increased with time on stream. The temperature programmed hydrogenation of deposits left after the reaction showed the presence of surface carbon and rather negligible amounts of chlorine.

Keywords: 1,2-Dichloroethane; Hydrodechlorination; Selectivity for ethene; Pd–Ni/Sibunit carbon; XRD

1. Introduction

Since the early 1990s [1,2] catalytic hydrodechlorination (HdCl) of organic wastes containing a variety of harmful and ozone-depleting compounds is a subject of growing interest. The motivation for studying this class of reactions, which constitute an alternative to catalytic combustion, as well as fundamental findings in this research area have been recently analyzed in the review article by Kovalchuk and d'Itri [3]. Hydrodechlorination is known to be effectively catalyzed by such noble metals like platinum and palladium [3], but the high cost of these metals hinders their practical application. Nickel is another good candidate to promote hydrodechlorination, and, indeed, catalytic properties of this metal have been investigated, especially in the transformation of chlorinated aromatic compounds [4–8]. On the other hand, in several cases successful transformation of vicinal chloroalkanes (such as 1,2-dichloropropane), application of Ni catalysts involved more severe reaction conditions, i.e. higher reaction temperatures and hydrogen pressures than those used for Pt and Pd catalysts (Refs. [9,10] reviewed in [3]). Our expectations with the use of bimetallic Pd–Ni/carbon catalysts in the hydrodechlorination of 1,2-dichloroethane related to a possible profit associated with a combination of high activity of palladium with high selectivity, exhibited by nickel catalysts. Therefore, the motivation was similar to that of Simagina et al. [11], who investigated hydrodechlorination of hexachlorobenzene on carbon supported Pd–Ni catalysts in hope that their effective catalysts containing small amounts of palladium had a strongly Pd-enriched surface, because a serious surface segregation of Pd in Pd–Ni alloys had been established [12,13]. Such an approach led to preparation of a cheaper but selective catalyst to convert hexachlorobenzene into useful products, i.e. mono and dichlorobenzene [11]. In the present work, because of a strong surface segregation of palladium in Pd–Ni alloys, the efforts were chiefly directed towards studying nickel-rich bimetallic catalysts.

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2. Experimental

2.1. Catalyst preparation and characterization

The 2 wt.% metal-loaded palladium–nickel catalysts were prepared by an incipient wetness co-impregnation of active carbon. The support was Sibunit carbon, washed with a boiling mixture of concentrated HCl and HF. After subsequent rinses with large amounts of redistilled water and drying in an air oven, the support was stored in a glass-stoppered bottle and kept in a desiccator. Its nitrogen BET surface area was 387 m^2/g, BJH pore volume (from desorption branch) 0.75 cm^3/g and average pore diameter ∼7 nm. Cumulative micropore volume (Horvath–Kawazoe) was 0.11 cm^3/g as estimated at relative pressure 0.012, and median micropore diameter was 0.59 nm [14].

Two series of Pd–Ni/C catalysts were prepared. The first one was obtained from metal chloride salts ($PdCl_2$, $NiCl_2\cdot 6H_2O$, both of analytical purity from POCh, Gliwice, Poland), the other from the nitrate precursors (Pd salt from a specpure Pd wire, Johnson Matthey, dissolved in nitric acid of analar purity, and $Ni(NO_3)_2\cdot 6H_2O$ from Johnson Matthey, Grade 1). Type of precursor is marked in notation of obtained series of catalysts. For example, 2 wt.% Pd5Ni95(Cl)/C stands for the chloride-derived catalyst with the composition of the metal phase: 5 at.% Pd and 95 at.% Ni. Similarly, 2 wt.% Pd25Ni75(N)/C stands for the nitrate-derived sample with the metallic composition: 25 at.% Pd and 75 at.% Ni. Apart from the monometallic Pd and Ni catalysts, only nickel-rich bimetallic catalysts were prepared. During impregnation and preliminary drying with infrared lamps, a good mixing was assured by the rotary motion of a beaker containing the catalyst precursor. Then, the solids were further dried overnight at an air oven at 90 °C and stored in a desiccator.

Before H_2 chemisorption the prepared catalysts were reduced in flowing 10% H_2/Ar (25 cm^3/min), ramping the temperature from 20 to 400 °C (at 8 °C/min) and kept at 400 °C for 3 h. After a subsequent purge in argon flow at 350 °C for 1 h, the catalyst was saturated with flowing H_2 at 150 °C. All the gases (H_2, Ar and 10% H_2/Ar mixture, all 99.999%) were further purified by passing through drying and MnO/SiO_2 traps. After a gradual cooling in hydrogen to room temperature and a short (10 min) purge with argon, the gas uptake was determined from the amount of desorbed hydrogen in an Ar flow at 350 °C (thermal conductivity detector, Gow-Mac), giving the dispersion of nickel on assumption of $H_{ad}/Ni_{surf} = 1$ chemisorption stoichiometry. This procedure adopted after Znak et al. [15], was preferred here over other chemisorption techniques because of a relatively long equilibration periods accompanying activated adsorption at room temperature. Hydrogen pulse chemisorption [16] and a static, double isotherm [17] methods performed at room temperature led in the case of carbon-supported Ni catalysts to a more or less serious underestimation of metal surface area.

After chemisorption, the samples were cooled down to room temperature and subjected to subsequent temperature programmed study in 10% H_2/Ar flow, ramping the temperature from 20 to 150 °C, at 8 °C/min. Since the samples had already been reduced, the aim of such experiments was to monitor hydrogen evolution in the decomposition of β-hydride, in the temperature programmed hydride decomposition (TPHD).

XRD experiments were performed on a standard Siemens D5000 diffractometer using Ni-filtered Cu Kα radiation. All samples of Pd–Ni/C catalysts, prior to and after reaction, were scanned by a step-by-step technique, at 2θ intervals of 0.02°.

2.2. Catalytic tests

The reaction of hydrodechlorination of 1,2-dichloroethane (1,2-DCE, HPLC grade, 99.8% pure from Sigma–Aldrich, Germany) was carried out at atmospheric pressure, in a glass flow reactor equipped with fritted disk to place a catalyst charge. Prior to reaction, the catalyst sample was reduced in flowing 10% H_2/Ar (25 cm^3/min), ramping the temperature from 20 to 400 °C (at 8 °C/min) and kept at 400 °C for 3 h. After reduction, the catalysts were cooled to 230 °C, then contacted with the reaction mixture (H_2 + Ar + 1,2-DCE) at 41.2 cm^3/min. 1,2-DCE was provided from a saturator kept at 0 °C, to give the partial pressure of 1,2-DCE of 2.9 kPa. The partial pressure ratio $P_{H_2}/P_{1,2\text{-DCE}}$ was 1:1. The flows of all gases, except 1,2-DCE, were fixed by using Bronkhorst Hi-Tec mass flow controllers. After screening at 230 °C for overnight and reaching a steady-state, the temperature of reaction was gradually decreased to 220 and 210 °C, and new experimental points collected. Finally, the reactor was heated to 230 °C, and, in nearly all cases, the previous results collected at 230 °C were restored. The reaction was followed by gas chromatography, using a HP 5890 series II gas chromatograph with FID, a 5% Fluorcol/Carbopack B column (10 ft) from Supelco. The results of GC analysis were elaborated using HP Chemstation.

The mass of catalysts used for reaction was ∼0.1 g, in order to not exceed conversion levels beyond 10%, at steady state, at 230 °C, i.e. at the highest temperature used in this study. Only in the case of Pd100(Cl)/C the conversion was higher than 10%. A typical run lasted ∼20 h. Blank experiments with Sibunit carbon showed very low activity at 230 °C.

After reaction, all samples of used Pd–Ni/C catalysts were subjected to temperature programmed hydrogenation (TPH, next subsection).

2.3. Temperature programmed experiments with Pd–Ni/C catalysts

Temperature programmed reduction (TPR-MS) of catalyst precursors and temperature programmed hydrogenation (TPH-MS) of used Pd–Ni/C catalysts were followed with an MA200 mass spectrometer from Dycor-Ametek, Pittsburgh, USA. After kinetic runs the catalysts were investigated by a temperature programmed hydrogenation (TPH) to detect species which can be removed by hydrogen from used catalysts. TPR (catalyst samples of ∼0.24 g) and TPH (∼0.085 g samples) runs were performed by flowing a 10% H_2/Ar mixture (25 cm^3/min) at a 10 °C/min ramp. In TPR experiments major attention was focused on monitoring *m/z* 2 (hydrogen consumption), *m/z* 18 (water evolution) and *m*/*z* 36 (HCl liberation from chloride precursors) or *m*/*z* 30 and 44 (nitric oxides evolution from nitrate precursors). In TPH runs of used catalysts attention was focused at *m*/*z* 15 and 16 (methane evolution), and *m*/*z* 36 and 38, which are suggestive of HCl liberation from used catalysts.

3. Results and discussion

3.1. Catalyst characterization: pre-reaction study

TPR spectra of Sibunit carbon supported Pd–Ni precursors, ex-nitrates and ex-chlorides, showed that the incipient wetness impregnation leads to deposition of both metal salts which do not interact with each other (TPR profiles not shown). Reduction of $PdCl_2$/C occurs at a relatively low temperature (TPR peak at <200 °C) while reduction of $NiCl_2$/C proceeds at much higher temperature (TPR peak at 400 °C). For mixed Pd–Ni chloride precursors, the Pd chloride reduced at <200 °C, while reduction of the remaining, Ni-based material occurred at ~350 °C. A ~50 °C decrease of reduction temperature was attributable to the availability of dissociated hydrogen formed on a prereduced palladium. Besides, the results of TPR experiments indicated that the conditions of catalyst reduction prior to reaction studies were sufficient to obtain fully reduced metals. Hydrogen consumption during TPR shows that reduction of Pd–Ni salts is a two-electron process. In addition, TPR experiments additionally performed on selected samples of both precursors pretreated in H_2/Ar at 400 °C for 3 h, i.e. after our standard reduction procedure prior to kinetic studies, showed no further reduction. On the other hand, such a durable catalyst pretreatment had a beneficial influence on alloy homogeneity of finished catalysts.

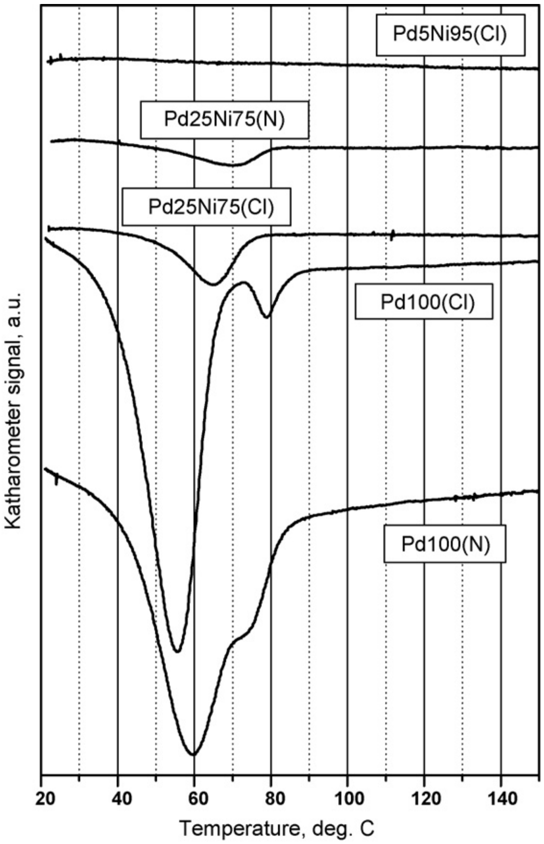

Fig. 1. Temperature programmed hydride decomposition (TPHD) profiles of Sibunit-supported Pd–Ni catalysts.

The combination of results from hydrogen chemisorption, X-ray diffraction and temperature programmed hydride decomposition allows estimation of alloy homogeneity, metal particle size of the Pd–Ni nanoparticles in carbon supported catalysts. In our previous work [14] a clear correlation between TPHD spectra and X-ray diffraction data for Pd-Au/Sibunit catalysts led to proposition of using the former technique for diagnosing the quality of Pd–Au alloying. In the present case, when our interest was focused on Ni-rich Pd–Ni/Sibunit catalysts the usefulness of this technique is less significant. This is because under hydrogen pressures used in this study, the β-hydride phases of Pd–Ni alloys can be formed only for Ni concentration ≤10 at.% [18,19]. However, even with such a limitation, this method still yields useful information. Fig. 1 shows TPHD traces from selected Pd and Pd–Ni catalysts which showed the presence of β-hydrides. For the remaining catalysts no evidence for hydride presence was found (Table 1) and an exemplary result for Pd5Ni95(Cl) sample is also included in Fig. 1. The TPHD trace of 2 wt.% Pd100(Cl) catalyst showed two minima: one, very intense, at 56 °C and a smaller at 78 °C. In the light of a previous analysis of TPHD spectra of supported Pd catalysts [14,20] the present trace implies the presence of two palladium phases: a more dispersed (minimum at 56 °C) and the other (less plentiful) characteristic of larger Pd particles (minimum at 78 °C). The bimodal distribution with a minor fraction of lesser dispersion is

Table 1
Characteristics of Pd–Ni/Sibunit carbon catalysts

Catalysts	Metal dispersion (H/M)[a]	H/Pd from TPHD	Results of XRD study of reduced catalysts (phases[b] + crystallite sizes[c])
Ex-nitrate series			
Ni100	0.073	0	3 nm
Pd5Ni95	0.083	0	*97 at.% Ni (4 nm)* + 53 at.% Ni (3.5 nm)
Pd10Ni90	0.079	0	67 at.% Ni (3 nm) + Ni (3.7 nm)
Pd25Ni75	0.074	0.06	*62 at.% Ni (2.5 nm)* + small amount of Pd (12 nm)
Pd100	0.147	0.23	4 nm[d]
Ex-chloride series			
Ni100	0.033	0	20 nm
Pd2.5Ni97.5	0.053	0	*Ni (5.5 nm)* + 62 at.% Ni (4 nm)
Pd5Ni95	0.075	0	91 at.% Ni (3.1 nm)
Pd25Ni75	0.082	0.09	~60 at.% Ni[e] + ~100 at.% Ni[e] + Pd (25 nm)
Pd100	0.177	0.23	*4 nm* + small amount of >20 nm[f]

[a] M = Pd + Ni.

[b] Predominant phases are italicised.

[c] Average metal diameter based on (1 1 1) XRD line broadening.

[d] TPHD suggests a relatively wide range of particle size (Fig. 1).

[e] Estimation of metal crystallite difficult because of a large gradient of alloy composition.

[f] Bimodal distribution from TPHD (Fig. 1). The ratio of low-to-high dispersed phase <1:10.

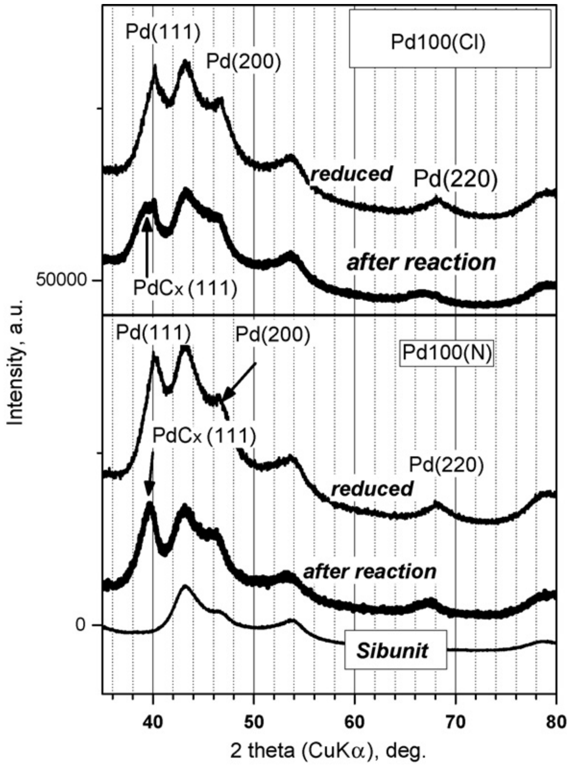

Fig. 2. XRD profiles of Sibunit-supported Pd catalysts (ex-chloride and ex-nitrate) after reduction and subjected to 1,2-dichloroethane hydrodechlorination.

indicative of the preparation method used in this study and resembles very much the analogous data for 3 and 1.5 wt.% Pd/Sibunit catalysts prepared by impregnation in the previous study [14]. The XRD data of the 2 wt.% Pd100(Cl) catalyst (Fig. 2 and Table 1) are in line with the results of TPHD studies. The presence of a small fraction of large Pd crystallites in this catalyst can be deduced from a very sharp peak of the (1 1 1) reflection. In this respect, both TPHD and XRD data for the Pd(N)/C catalyst suggest a better metal homogeneity in terms of its crystallite size. However, one has to appreciate the diagnostic value of TPHD because a relatively low metal loading combined with a considerable background from Sibunit support leads to considerable difficulties in assessing the XRD spectra.

As mentioned before, in the case of bimetallic samples, the presence of hydride phases was detected only for both Pd25Ni75 catalysts. For Pd25Ni75(N) the amount of the β-hydride was somewhat smaller than for Pd25Ni75(Cl) (Fig. 1). Table 1 presents the ratio of H/Pd, based on integrated peak areas for Pd hydride decomposition. The values of this ratio (0.06 and 0.09), in combination with the H/Pd ratio for monometallic palladium catalyst of similar metal dispersion, suggests that ∼30% of palladium is not alloyed with nickel. In fact, the XRD spectra of these catalysts after reduction reveal some presence of unalloyed palladium, especially in Pd25Ni75(Cl) (Fig. 3), but again the TPHD spectra are found to be very useful, because of mentioned difficulties in assessing

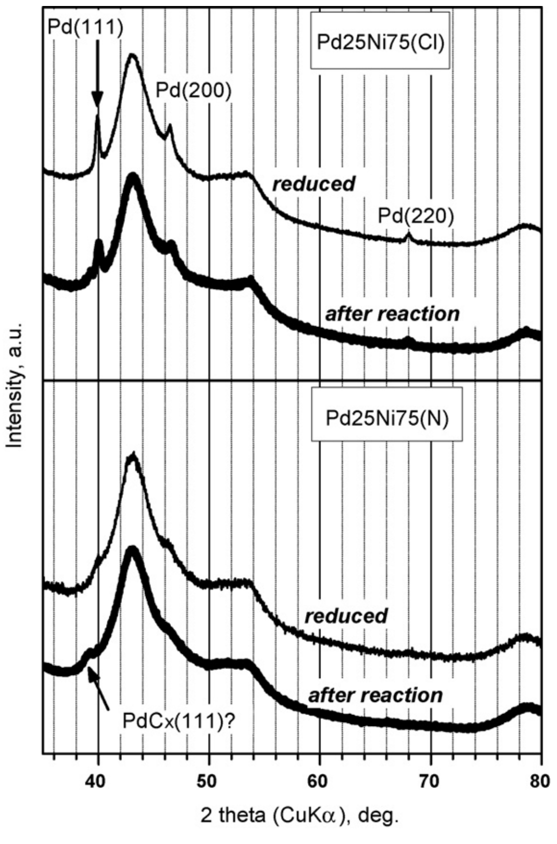

Fig. 3. XRD profiles of Sibunit-supported Pd25Ni75 catalysts (ex-chloride and ex-nitrate) after reduction and subjected to 1,2-dichloroethane hydrodechlorination.

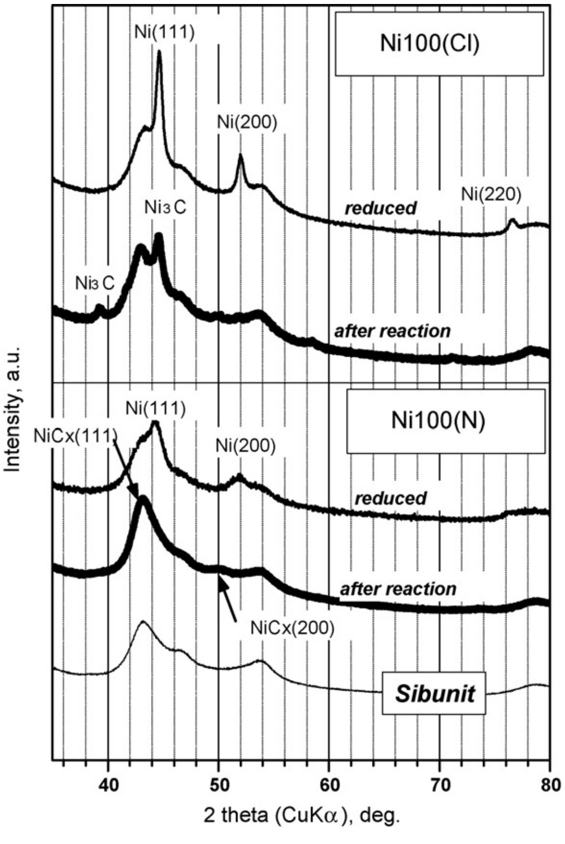

Fig. 4. XRD profiles of Sibunit-supported Ni catalysts (ex-chloride and ex-nitrate) after reduction and subjected to 1,2-dichloroethane hydrodechlorination.

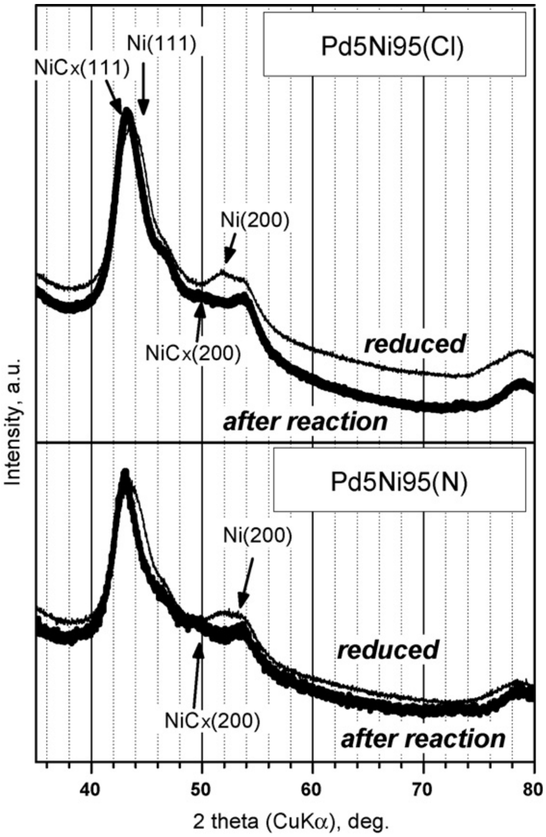

Fig. 5. XRD profiles of Sibunit-supported Pd5Ni95 catalysts (ex-chloride and ex-nitrate) after reduction and subjected to 1,2-dichloroethane hydrodechlorination.

the XRD spectra of low metal loaded catalysts with a rich background from the support.

Figs. 4 and 5 show XRD profiles of the 2 wt.% Ni/C and Pd5Ni95/C catalysts. Their usefulness is demonstrated in the next subsection, when comparing the spectra of the catalysts prior to and after reaction.

3.2. Hydrodechlorination of 1,2-dichloroethane on Pd–Ni/Sibunit carbon catalysts: post-reaction study of catalysts

Fig. 6 shows changes of conversions as a function of time on stream (TOS) in the 1,2-dichloroethane hydrodechlorination over Pd–Ni/Sibunit catalysts prepared from nitrates and chlorides. It is seen that during ∼20 h period of screening the overall conversion was very stable. Fig. 7 shows analogous changes in the selectivity towards ethene. Steady state data of turnover frequencies, product selectivities and activation energies are collected in Tables 2 and 3.

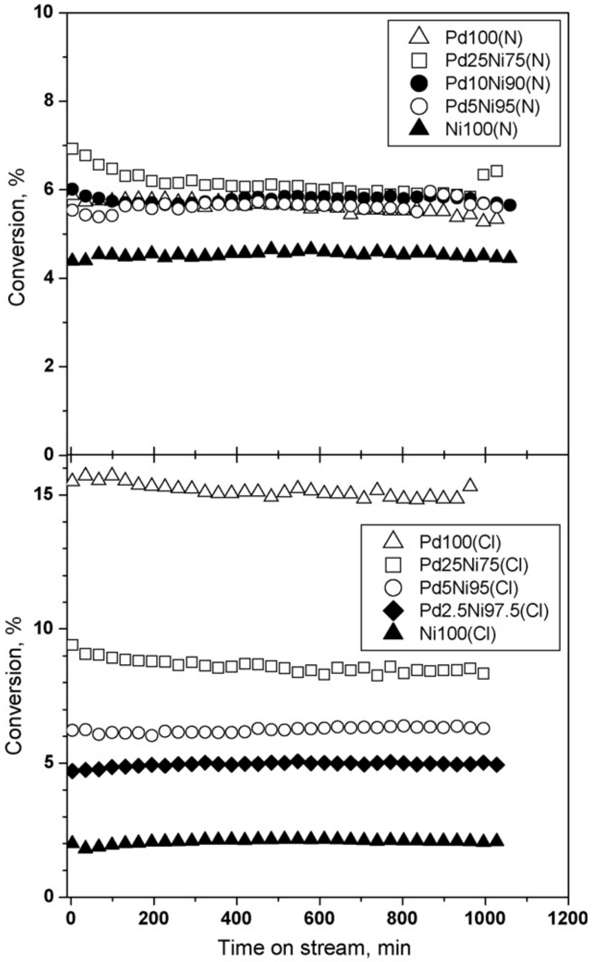

Fig. 6. Conversion changes in 1,2-dichloroethane hydrodechlorination on 2 wt.% Pd–Ni/Sibunit catalysts at 230 °C. Ex-nitrate series—top section, ex-chloride series—bottom section.

The values of turnover frequencies of all tested catalysts are rather similar (Tables 2 and 3). The ratio of TOF values for the most active-to-the least active catalyst at 230 °C is only slightly higher than 2. Taking into account a potential uncertainty in assessing metal dispersion by hydrogen chemisorption in carbon-supported catalysts [17], we are not in a position to consider a possible relation between TOF and at.% Pd. However, variations in product selectivity are very large and, therefore, will be discussed (Fig. 7). In the case of Ni100(Cl) and all bimetallic samples the selectivity toward ethene ($S_{C_2H_4}$) slightly decreases with TOS. In the case of the monometallic catalyst such a selectivity decrease results from the fact that this catalyst becomes gradually more active in producing vinyl chloride (Table 3). Independent long-term experiments showed that the selectivity for vinyl chloride reaches ∼30%. However, in the case of Pd–Ni/C catalysts the decrease in $S_{C_2H_4}$ is compensated almost exclusively by increase of $S_{C_2H_6}$. Very high selectivity for ethane, at the expense of ethene, is characteristic for Pd catalysts at a low temperature of HdCl of 1,2-DCE (Tables 2 and 3, and Ref. [21]). Therefore, the decrease of $S_{C_2H_4}$ with TOS can be interpreted by some additional surface enrichment with palladium accompanying the reaction carried at 230 °C for ∼20 h. Such a suggestion is supported by recent Monte-Carlo simulations in the temperature range from 327 to 727 °C which showed a pronounced segregation of Pd for all Pd–Ni compositions, but at lower equilibration temperatures the Pd segregation was more pronounced [13]. Our Pd–Ni/C catalysts were prereduced at 400 °C for 3 h and subjected to reaction at 230 °C for ∼20 h. It is suggested that during reaction a prereduced sample of Pd–Ni would be additionally enriched with palladium, if, of course,

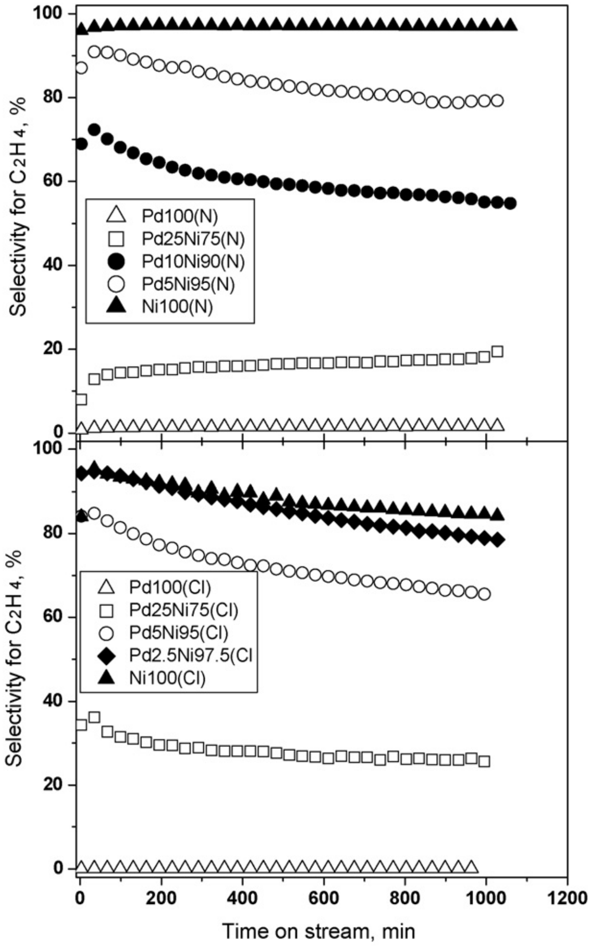

Fig. 7. Time on stream behavior in 1,2-dichloroethane hydrodechlorination on 2 wt.% Pd–Ni/Sibunit catalysts at 230 °C. Ex-nitrate series—upper section, ex-chloride series—bottom section.

one does not consider a possible effect of reaction environment, especially that of chlorine/chloride species. In any case, our hypothesis constitutes a challenge for an in situ surface spectroscopy verification.

A closer comparison of product selectivities (Fig. 7) is straightforward for the Pd–Ni(N) catalysts because all of them exhibited similar overall conversions (Fig. 6, upper subsection), and somewhat more difficult for the ex-chlorides series, where differences in the overall conversions were larger (Fig. 6, bottom subsection). Nevertheless, it is seen that the selectivity for ethene is very high for Ni100 and Ni very rich samples and negligible for Pd100 or small for Pd25Ni75 catalysts (Tables 2 and 3). The turnover frequency for ethene formation, $\mathrm{TOF}_{\mathrm{C_2H_4}}(= \mathrm{TOF}_{\mathrm{total}} \times S_{\mathrm{C_2H_4}})$ as a function of bulk composition of Pd–Ni is presented in Fig. 8. One can see a remarkable decrease of $\mathrm{TOF}_{\mathrm{C_2H_4}}$ with Pd content. In interpretation of this relation one should consider the effect of the surface concentration, so Fig. 8 also contains relevant data considering the surface composition of Pd–Ni alloys, based on the literature [13]. Very similar character of both curves indicates that surface Ni atoms are the active sites of hydrogen-assisted chlorine removal from 1,2-dichloroethane, without unwanted hydrogenation of ethene to ethane. However, a modest synergistic effect, seen as maximum in $\mathrm{TOF}_{\mathrm{C_2H_4}}$ versus Pd–Ni alloy composition, is conceivable because of the behavior of Pd2.5Ni97.5(Cl) catalyst, marked as the uppermost empty square in Fig. 8. The inset in Fig. 8, where $\mathrm{TOF}_{\mathrm{C_2H_4}}$ is correlated with the inferred surface composition of Pd–Ni, visualizes the speculation given above, however further studies with a more careful control of metal dispersion, alloy homogeneity and surface composition, at the range 0–5 at.% Pd, are needed to verify this issue.

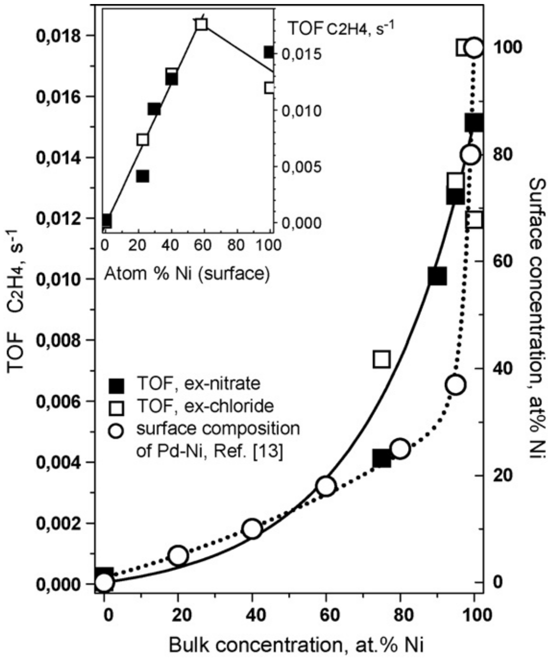

Fig. 8. The steady state (after 20 h) turnover frequency to ethene as a function of the nominal Ni content (at.%) in Pd–Ni/Sibunit catalyst in 1,2-dichloroethane hydrodechlorination (solid line) and the surface vs. bulk composition in Pd–Ni alloys based on Ref. [13] (dotted line). Inset: turnover frequency to ethene as a function of the surface composition inferred from [13].

X-ray diffraction appeared very useful in assessing variations in the structure and phase composition of Pd–Ni/Sibunit carbon samples prior to and after reaction. We return to Figs. 2–5 which illustrate variations in the phase composition of representative samples. Both Pd/C catalysts experienced a partial, albeit rather small, transformation to PdC_x solution (Fig. 2). Similar, but much stronger change was found in HdCl of dichlorodifluoromethane, where carbon incorporation led to the formation of $\mathrm{PdC}_{0.13}$ solution [14,22,23]. Nevertheless, palladium carbiding does not have any special effect on the catalytic behavior or this phase variation occurs at an initial stage of reaction. Some presence of unalloyed palladium in both Pd25Ni75 catalysts diagnosed by TPHD (Fig. 1) and confirmed by XRD (Fig. 3) resulted in a partial transformation of this phase into PdC_x. Much more intense is the bulk transformation of both Ni100 catalysts (Fig. 4). For Ni100(Cl)/C after reaction the presence of an hcp phase of $\mathrm{Ni_3C}$ is detected, in addition to some formation of an fcc NiC_x ($x \leq 0.1$) solution. For Ni100(N)/C only the fcc NiC_x phase was found. Similarly, the remaining Pd–Ni samples show some phase carbiding, exemplified by NiC_x formation in Pd5Ni95 (Fig. 5).

Temperature programmed hydrogenation (TPH) runs performed with the catalysts which had been subjected to reaction

Table 2
Representative kinetic data of 1,2-dichloroethane hydrodechlorination over 2 wt.% Pd–Ni/C catalysts prepared from metal nitrates: overall conversions, turnover frequencies, product selectivities and activation energies

Catalyst	Reaction temperature (°C)	Conversion, % (TOF, s^{-1})[a]	Product selectivity (%)					Activation energy (kJ/mol)
			C_2H_4	C_2H_6	C_2H_3Cl	C_2H_5Cl	Other products[b]	
Ni100	210	2.36 (0.0076)	96.8	2.0	0.4	0.6	0.2	63.9 ± 1.3
	220	3.37 (0.0107)	96.9	1.9	0.5	0.5	0.2	
	230	4.96 (0.0144)	97.0	1.6	0.6	0.6	0.2	
Pd5Ni95	210	3.03 (0.0086)	67.4	30.9	0.2	1.3	0.2	62.2 ± 1.6
	220	4.22 (0.0120)	73.1	25.4	0.2	1.2	0.1	
	230	5.69 (0.0160)	79.3	19.1	0.3	1.0	0.3	
Pd10Ni90	210	3.05 (0.0093)	37.9	58.7	–	3.2	0.2	60.6 ± 1.5
	220	4.24 (0.0134)	45.7	51.3	–	2.9	0.1	
	230	5.71 (0.0180)	55.0	42.2	0.1	2.5	0.2	
Pd25Ni75	210	3.23 (0.0119)	9.8	80.1	0.1	9.9	0.1	59.6 ± 4.8
	220	4.83 (0.0178)	13.3	77.5	0.1	8.9	0.2	
	230	6.34 (0.0234)	19.5	72.5	–	7.8	0.1	
Pd100	210	2.88 (0.0081)	0.7	72.5	–	26.6	0.2	64.1 ± 1.3
	220	3.99 (0.0112)	1.0	73.8	–	24.9	0.3	
	230	5.28 (0.0148)	1.6	75.6	–	22.5	0.3	

H_2-to-1,2-DCE ratio 1:1.

[a] TOF based on metal dispersion (H/M) from Table 1.

[b] Mainly C_1, C_3 and C_4 hydrocarbons.

showed negligible HCl evolution but large amounts of liberated CH_4 (TPH spectra not shown). It means that the reaction of 1,2-DCE hydrodechlorination carried out at a relatively low temperature (210–230 °C) does not lead to an irreversible deposition of Cl and, at the same time, clarifies the absence of catalyst's deactivation with time on stream. On the other hand, methane liberated from the catalysts during TPH reveals some presence of carbon on and/or in the samples. A high temperature maximum, at >500 °C, similar for all catalysts, indicates gasification of Sibunit carbon. On the other hand, a low temperature maximum (350–450 °C) is probably associated with carbon removal from the metal.

Fig. 6 shows that the overall conversion obtained for Ni(Cl)/C is roughly 2.5 times higher than that for Ni(N)/C. A relatively small difference in metal dispersion between both catalysts (Table 1) does not permit to explain such a large conversion difference in terms of metal dispersion. On the other hand, one has to consider that hydrogen chemisorption would not

Table 3
Representative kinetic data of 1,2-dichloroethane hydrodechlorination over 2 wt.% Pd–Ni/C catalysts prepared from metal chlorides: overall conversions, turnover frequencies, product selectivities and activation energies

Catalyst	Reaction temperature (°C)	Conversion, % (TOF, s^{-1})[a]	Product selectivity (%)					Activation energy (kJ/mol)
			C_2H_4	C_2H_6	C_2H_3Cl	C_2H_5Cl	Other products[b]	
Ni100	210	1.07 (0.0075)	88.3	2.1	8.0	0.4	1.2	66.4 ± 1.1
	220	1.53 (0.0106)	86.5	1.9	9.8	0.3	1.5	
	230	2.08 (0.0145)	84.0	1.6	12.0	0.3	2.1	
Pd2.5Ni97.5	210	2.76 (0.0123)	65.9	32.5	0.2	1.2	0.2	61.1 ± 0.9
	220	3.74 (0.0165)	71.7	26.7	0.3	1.1	0.2	
	230	4.97 (0.0222)	78.5	19.9	0.3_3	0.9	0.3_7	
Pd5Ni95	210	3.55 (0.0112)	49.7	48.1	0.1_2	2.0	<0.1	58.6 ± 1.0
	220	4.81 (0.0151)	56.9	41.2	0.1	1.8	–	
	230	6.32 (0.0199)	65.6	32.7	0.1_3	1.5	<0.1	
Pd25Ni75	210	4.60 (0.0153)	14.8	77.8	–	7.4	–	60.5 ± 0.2
	220	6.33 (0.0212)	19.7	73.7	–	6.5	0.1	
	230	8.53 (0.0284)	25.6	68.5	–	5.7	0.2	
Pd100	210	7.82 (0.0168)	0.1	64.9	–	34.9	0.1	65.2 ± 0.4
	220	11.0 (0.0236)	0.1	67.4	–	32.4	0.1	
	230	15.3 (0.033)	0.2	69.9	–	29.7	0.2	

H_2-to-1,2-DCE ratio 1:1.

[a] TOF based on metal dispersion (H/M) from Table 1.

[b] Mainly C_1, C_3 and C_4 hydrocarbons.

necessarily reflect a real metal dispersion in carbon supported palladium catalysts [24]. It is hypothesized that some part of palladium in the 2 wt.% Pd(Cl)/C catalyst is very highly dispersed, and not detected by XRD. If it is so, modification of very highly dispersed Pd by neighboring carbon species should be more marked than in the case of larger Pd particles, the fact which results in a more severe underestimation of palladium surface area by H_2 chemisorption. Some our results suggest that it would be the case. XRD data for the used Pd(Cl)/C catalyst (Fig. 2) show that a considerable part of palladium was transformed into PdC_x. The large crystallite Pd material does not appear to be carbided [a sharp (1 1 1) reflection at ∼40°]. However, the fraction at ∼39.3° suggests a deeper Pd carbiding in this catalyst than in the used Pd(N)/C, where the respective (1 1 1) reflection is at ∼39.7°. Therefore a bulk carbiding is considered to be more intense for smaller Pd particles. This conclusion seems to be in conflict with our earlier suggestion that larger Pd crystallites are prone to a deeper carbiding in HdCl of CCl_2F_2 [23]. However, in the case of 1,2-dichloroethane hydrodechlorination we do not dispose such a very efficient carbiding agent like CCl_2F_2, which after stripping off of all halogens easily enters palladium bulk. In the present case, the C_2 molecule must be split of into C_1 fragments before bulk carbiding. Palladium, in general, is not a very efficient metal in alkane hydrogenolysis, however a few earlier papers indicate a higher C–C splitting activity for higher metal dispersions [25,26]. It leads to a conclusion, that a deeper carbiding of Pd(Cl)/C than Pd(N)/C would result from a higher hydrogenolysis activity of the former catalyst. This, in turn, would result from a higher Pd dispersion of the 2 wt.% Pd(Cl)/C catalyst. Therefore, a higher overall conversion obtained for the 2 wt.% Pd(Cl)/C catalyst would result from its higher metal dispersion and, simultaneously, from a higher extent of bulk carbiding. It has already been suggested that carbided palladium [23] and nickel [27] catalysts are more active than their noncarbided analogues. All this tentative hypothesis should be verified by testing a more highly loaded Pd/C catalysts (by XRD and, preferably, TEM) subjected to different degrees of carbiding.

Finally, the results presented in this work indicate that a considerable, although certainly far from ideal, degree of Pd–Ni mixing in our catalysts resulted from their preparation method and pretreatment. It should also be marked that even more sophisticated preparation route of Pd–Ni/Sibunit carbon which employed the use of an organometallic compound of nickel not always leads to entirely homogenized Pd–Ni particles (see Table 2 in Ref. [11], data for catalyst Pd51Ni49/C; with other bimetallic catalysts well-mixed).

4. Conclusions

1. Sibunit carbon supported Pd–Ni catalysts showed good and stable activity in the hydrodechlorination of 1,2-dichloroethane at low reaction temperatures (∼230 °C).
2. Selectivity for ethene is very high for pure nickel (>90%) and negligible for pure palladium, which produces mainly ethane and ethyl chloride.
3. In general, addition of Pd to Ni drastically reduces the turnover frequency for ethene formation, however small amounts of palladium would be beneficial for this reaction.
4. Changes in the catalytic behavior of Pd–Ni/Sibunit carbon catalysts supported by characterization data (XRD, TPHD) suggest that the surface of Pd–Ni catalysts is strongly enriched with palladium.

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