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The effect of copper and gold on the catalytic behavior of nickel/alumina catalysts in hydrogen-assisted dechlorination of 1,2-dichloroethane

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ABSTRACT

Two series of alumina-supported Ni–Cu and Ni–Au catalysts were prepared by incipient wetness co-impregnation and characterized using nitrogen adsorption at −196 °C, X-ray diffraction, hydrogen chemisorption, and temperature-programmed reduction methods. The presence of different alloy phases found in reduced Ni–Cu and Ni–Au catalysts was in fair agreement with the phases predicted by the thermodynamics of these systems suggesting that a reasonable extent of alloying was achieved for both alloy systems. The $Ni–Cu/Al_2O_3$ and $Ni–Au/Al_2O_3$ catalysts were tested in the reaction of hydrodechlorination of 1,2-dichloroethane at 250 and 270 °C. Adding Cu or Au to Ni/Al_2O_3 introduces substantial, although different, changes in the catalytic behavior, especially in the product selectivity. The presence of copper enhances the propensity of nickel towards vinyl chloride formation (from ~60% to ~85%), whereas addition of gold increases the selectivity to ethene (~20% to ~60%), at 250 °C. Differences in catalytic behavior of both alloy systems are discussed.

1. Introduction

We have recently reported [1] that carbon-supported nickel catalysts appeared active in hydrodechlorination (HdCl) of 1,2-dichloroethane, producing ethene with very high selectivity (up to 97%) at relatively low reaction temperatures (210–230 °C). Interestingly, in the case of Ni catalysts characterized by lesser metal dispersion (prepared from nickel chloride and nickel acetate), the selectivity to vinyl chloride increased gradually with time-on-stream, at the expense of ethene, even up to 30%. Because the used Ni catalysts contained large amounts of incorporated carbon (detected as Ni_3C and $NiC_{x\leq 0.1}$), the catalytic behavior of Ni/C seemed to be largely regulated by the population of surface carbon species. A higher surface carbon content (implied by a higher carbon content in Ni_3C than in $NiC_{x\leq 0.1}$) was linked with an enhanced selectivity to vinyl chloride. Alternatively, the Ni/C samples which were most selective towards ethene (and characterized by a smaller Ni particle size) contained only tiny amounts of carbon in the form of NiC_x solution. It is suggested that, in such conditions, a new reaction route leading to vinyl chloride via a concerted elimination of HCl is feasible.

Surprisingly, the literature dealing with HdCl application of modified nickel catalysts, especially with Ni–Cu and Ni–Au catalysts is rather scarce. One respects a series of reports from the group of Keane, who investigated silica, titania and alumina-supported Ni–Au in HdCl of 2,4-dichlorophenol and obtained a higher dechlorination rate over the bimetallic system in comparison with Ni [2–4]. Similarly, an isolated paper which describes the catalytic behavior of $Ni–Cu/SiO_2$ in HdCl came from Choi and Lee [5]. They showed that $Ni–Cu/SiO_2$ catalysts efficiently converted 1,1,2-trichloroethane into vinyl chloride with ≥95% selectivity. Copper introduction to Ni/SiO_2 reduced the metal particle size and weakened the adsorption strength of Ni, and led to low conversion of 1,1,2-trichloroethane and a high selectivity to vinyl chloride [5]. Palladium-modified Ni catalysts were investigated in HdCl of hexachlorobenzene [6] and 1,2-dichloroethane [7]. It was shown that the degree of dechlorination of hexachlorobenzene is regulated by the Ni content in Pd–Ni/C [6]. Śrębowata et al. [7] reported the results for HdCl of 1,2-dichloroethane on Pd–Ni/C: the selectivity for ethene is very high for pure nickel (>90%) and negligible for pure palladium, which produces mainly ethane and ethyl chloride. In general, addition of Pd to Ni drastically reduces the turnover frequency for ethene formation, although very small amounts of palladium would be beneficial for this reaction.

In this paper, we provide the first reported application of Al_2O_3-supported Ni–Cu and Ni–Au in HdCl of 1,2-dichloroethane. This represents an extension to our earlier studies [1] where we established interesting HdCl catalytic properties for Ni/carbon.

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Table 1
Characteristics of alumina-supported Ni, Ni–Cu and Ni–Au catalysts.

Catalyst notation[a]	Nominal metal content (wt.%)			S_{BET} (m^2/g)	V_p (cm^3/g)	d_p (nm)
	Ni	Au	Cu			
Ni100	2.0	–	–	196	0.49	9.9
Ni90Cu10	2.0	–	0.24	n.m.[b]	n.m.[b]	n.m.[b]
Ni50Cu50	2.0	–	2.2	184	0.47	9.9
Ni25Cu75	2.0	–	6.5	n.m.[b]	n.m.[b]	n.m.[b]
Ni90Au10	2.0	0.75	–	193	0.48	9.9
Ni67Au33	2.0	3.3	–	189	0.47	10
Ni50Au50	2.0	6.7	–	183	0.46	9.9
γ-Al_2O_3[c]	–	–	–	204	0.52	10.2

[a] In catalyst notation Ni*X*Cu(Au)*Y*, *X* and *Y* mean atomic percentages of Ni and Cu(Au) in supported metal phase.
[b] Not measured.
[c] Subjected to the same pretreatment as all metal catalysts (reduction at 500 °C for 3 h, see Section 2.2).

Chlorine-containing metal precursors were chosen because of two reasons. First, as mentioned earlier, our previous study with Ni/C catalyst prepared from $NiCl_2$ showed a better selectivity to vinyl chloride than in the case of using $Ni(NO_3)_2$ as an impregnating salt [1]. Second, avoidance of chloride (which is strongly held on alumina) would not be workable in the HdCl reaction where a lot of HCl is produced. Furthermore, deposition of gold was planned by using a chlorine-containing salt (NH_4AuCl_4 precursor).

The results presented herein extend the limited reaction data for modified Ni catalytic applications and allow to find out Ni–Cu/Al_2O_3 and Ni–Au/Al_2O_3 as effective HdCl catalysts.

2. Experimental

2.1. Catalyst preparation and characterization

The Al_2O_3 support was obtained from Sasol (Puralox SCCA, 150/200 mesh), characterized by surface area 202 m^2/g, total pore volume 0.53 cm^3/g, and high purity (Si – 81 ppm, and Fe – 114 ppm, Na – 3 ppm, Ti – 18 ppm), according to the specification of manufacturer. The Al_2O_3-supported Ni, Ni–Cu and Ni–Au catalysts were prepared by (co)impregnation of alumina with an aqueous solution of the metal chloride containing precursors ($NiCl_2{\cdot}6H_2O$ and $CuCl_2{\cdot}2H_2O$, both of analytical purity from POCh, Gliwice, Poland and NH_4AuCl_4, specpure from Johnson Matthey) via the incipient wetness technique. In each case, the overall nickel loading was 2 wt.%, whereas the amounts of copper and gold were so adjusted as to meet specific atomic percentages shown in Table 1. During impregnation and preliminary drying with infrared lamps, a proper mixing was assured by the rotary motion of a beaker containing the catalyst precursor. Then, the solid was further dried overnight at an air oven at 90 °C and stored in a desiccator.

Temperature-programmed reduction (TPR) of the catalysts was performed in flowing 10% H_2/Ar (25 cm^3/min), ramping the temperature at 8 °C/min and using a Gow-Mac thermal conductivity detector (TCD). Injections of known amounts of hydrogen into the hydrogen–argon flow were provided for calibration (before and after each TPR run). In the case of a few hardly reducible samples (i.e., exhibiting TPR peaks at above 500 °C) the TPR experiments were also performed on the samples which were subjected to a standard reduction procedure used prior to catalytic tests (i.e., at 500 °C for 3 h, see next section). Such "difference" TPR profiles allowed to estimate the degree of reduction [8,9].

Surface areas and pore volumes of selected catalysts were measured with an ASAP2020 instrument from Micromeritics, employing the BET and BJH methods and using nitrogen as adsorbate.

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 500 °C (at 8 °C/min) and kept at 500 °C for 3 h. After a subsequent purge in argon flow at 450 °C for 1 h, the catalyst was saturated with flowing H_2 at 150 °C, following the procedure of Znak et al. [10]. 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 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 450 °C (TCD, Gow-Mac), giving the dispersion of nickel on assumption of $H_{ad}/Ni_{surf} = 1$ chemisorption stoichiometry.

XRD experiments were performed on a Siemens D5000 diffractometer using Ni-filtered CuK_α radiation. Freshly reduced and used in HdCl samples of Ni, Ni–Cu and Ni–Au catalysts were scanned by a step-by-step technique, at 2θ intervals of 0.05°. After the reaction, the catalyst sample was quickly cooled in a flow of reaction mixture from 270 to ~100 °C, then the flow of 1,2-dichloroethane was stopped, and the further cooling to room temperature was done in a H_2/Ar flow.

2.2. Catalytic tests

The reaction of hydrodechlorination of 1,2-dichloroethane (1,2-DCA) was carried out at atmospheric pressure, in a glass flow reactor equipped with fritted disk to place a catalyst charge. Prior to the reaction (as before adsorption and XRD experiments), the catalyst was dried in Ar flow at 120 °C for 0.5 h, reduced in flowing 10% H_2/Ar (25 cm^3/min), ramping the temperature from 20 to 500 °C (at 8 °C/min) and kept at 500 °C for 3 h.

In the catalytic conversion of 1,2-DCA (HPLC grade, 99.8% pure from Sigma–Aldrich, Germany), the flows of all gases, except 1,2-DCA, were fixed by using mass flow controllers. After the reduction, the catalyst was cooled to 250 °C, then contacted with the reaction mixture, i.e., with a flow of hydrogen + argon + 1,2-DCA at 41.2 cm^3/min (1.2 + 38.8 + 1.2, respectively). 1,2-DCA was provided from a saturator kept at 0 °C (partial pressure = 2.9 kPa). The partial pressure ratio $P_{H2}/P_{1,2\text{-DCA}}$ was 1:1. The reaction progress was followed by gas chromatography (HP 5890 series II with FID, a 5% Fluorcol/Carbopack B column (10 ft) from Supelco). The total FID signal from the first two analyses was somewhat reduced compared to that observed in subsequent GC analyses. A satisfactory carbon balance (within ~95%) was found for further GC analyses. After catalyst screening at 250 °C, the temperature of reaction was increased to 270 °C, and new experimental points were collected. Reproducibility of results (checked on a few samples of Ni100/Al_2O_3) was fair, ±10% (total activity) or good, ±2% (product selectivities towards ethene and vinyl chloride). In each case the mass of catalyst was 0.2 g. A typical run lasted ~20 h, for each reaction temperature.

3. Results and discussion

Table 1 lists the catalysts used in this work. As it was expected, loading alumina with such relatively small amounts of nickel and

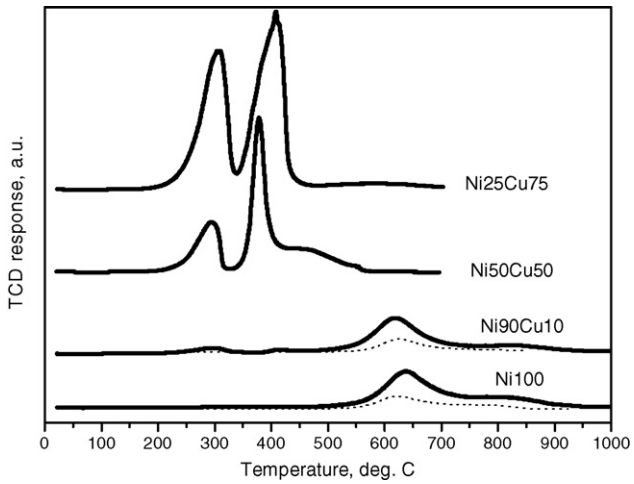

Fig. 1. TPR profiles of Ni–Cu/Al_2O_3 catalysts. Broken lines show "difference" TPR spectra, i.e., obtained after pre-reduction at 500 °C for 3 h.

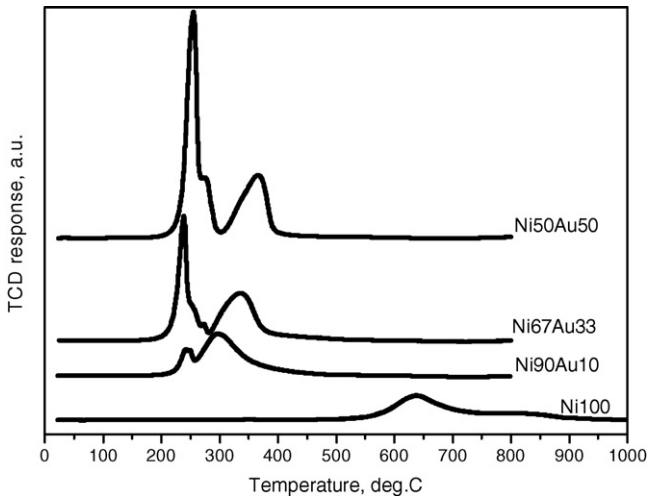

Fig. 2. TPR profiles of Ni–Au/Al_2O_3 catalysts.

copper (gold) as used in this work only marginally changed the overall surface area and pore volume of the support. Thus, the textural characteristic of our catalysts remained practically unchanged compared to the unloaded alumina support. In view of this fact and very fine grain size of catalysts (150–200 mesh), a close comparison between catalytic properties of all used catalysts should not be affected by internal diffusion problems.

TPR of Ni100 showed a relatively low reducibility of alumina-supported $NiCl_2$ precursor (Fig. 1). However, the "difference" TPR profile obtained in the separate experiment on pre-reduced Ni100 (at 500 °C, for 3 h) showed a significant degree of reduction (~65%, Table 2). An earlier study of Wang and Lu [11] showed much lower degree of reduction of $NiCl_2/Al_2O_3$ (<30%). However, in contrast to Wang and Lu, our alumina-supported catalysts were not precalcined at 500 °C for 4 h before reduction. Wang and Lu [11] indicate that higher calcination temperatures increase the nickel–alumina interactions which are seen as the formation of hardly reducible nickel aluminate.

The "difference" TPR profile obtained for Ni90Cu10 catalyst shows that reduction at 500 °C for 3 h leads to a considerable degree of reduction, ~76% (Fig. 1 and Table 2). Higher amounts of added copper resulted in a complete reduction of metal phase. This result might suggest that some, reasonable proximity between both metal components (Cu and Ni) was achieved by simple co-impregnation. It must be mentioned that the TPR of pure 2% Cu/Al_2O_3 catalyst showed two forms of Cu species (one reducible at nearly 285 °C, the other at ~375 °C, TPR profile not shown), suggesting that the enhancement of Ni reducibility (in Ni–Cu catalysts) would also be realized by spillover of hydrogen species from a more readily reducible copper sites [11–13].

Much better reducibility of nickel dichloride was achieved after gold addition. All tested Ni–Au catalysts, i.e., even Ni90Au10, were completely reduced at below 500 °C (Fig. 2). NH_4AuCl_4/Al_2O_3 is reduced at ~210 °C (TPR not shown), in good agreement with [14]. Therefore, also in this case the presence of another IB metal facilitates reduction of Ni dichloride.

X-ray diffraction (XRD) was found a useful method for characterization of metal (alloy) phase(s) after catalyst reduction. Fig. 3 demonstrates the XRD profiles obtained for reduced and used in HdCl Ni–Cu/Al_2O_3 catalysts, whereas Fig. 4 shows analogous data for Ni–Au/Al_2O_3 samples. Analysis of XRD profiles provided essential data concerning the phase composition and metal crystallite size, collected in Table 2. It is seen that in both alloy cases, a reasonable but not complete alloy miscibility was achieved. For Ni–Cu system a miscibility gap occurs below 354 °C [15], so one should expect rather good component intermixing after reduction at 500 °C for 3 h. Based on earlier estimations for Ni–Cu system [16], the root-mean-square displacement [taken as $(2Dt)^{1/2}$, where D and t are diffusion coefficient and time, respectively] at 500 °C for 3 h should be at least 11.5 nm. Because this quantity is comparable with metal crystallite sizes obtained for the reduced Ni–Cu catalysts (Table 2), it is concluded that complete mixing should be obtained for bimetallic particles after applying our reduction conditions. The fact, that such an ideal case was not achieved (Table 2) must follow from the catalyst preparation method employed in this study (co-impregnation technique). Nevertheless, the Ni–Cu alloy compositions of dominant phases do not differ much from nominal compositions, therefore we believe that screening of these catalysts should reflect the effect of alloy composition on the behavior in HdCl of 1,2-DCA.

Table 2
Characteristics of Ni–Cu and Ni–Au catalysts by XRD and TPR.

Catalyst notation[a]	XRD results		TPR results	
	Metal phase analysis at % (% contribution in metal phase)	Metal crystallite size (nm)	TPR peaks (°C)	Degree of reduction[b] (%)
Ni100	100% Ni (100%)	Two fractions (20 + ~3)	635, 820	65.7
Ni90Cu10	14.5% Cu (91%) + 57.5% Cu (9%)	16.4	618	76.5
Ni50Cu50	62% Cu (72.5%) + 31% Cu (27.5%)	12	295, 379	100
Ni25Cu75	83% Cu (90%) + 18.5% Cu (10%)	21.1	305, 408	100
Ni90Au10	1% Au (90%) + 90% Au (10%)	<2	245, 308	100
Ni67Au33	2% Au (60%) + 95% Au (40%)	9.4	238, 335	100
Ni50Au50	1% Au (50%) + 92% Au (50%)	13.4	255, 271, 365	100

[a] As in Table 1.
[b] After reduction at 500 °C for 3 h. Degrees of reduction of Ni100 and Ni90Cu10 were estimated from "difference" TPR spectra, see text and Fig. 1.

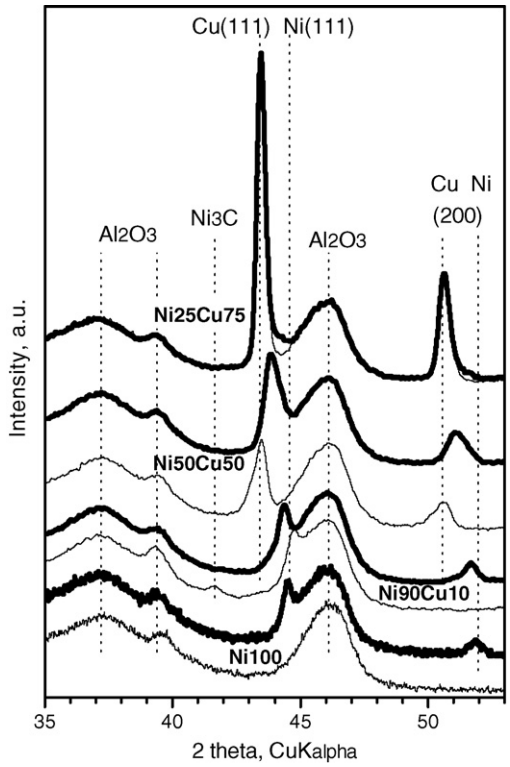

Fig. 3. XRD profiles of Ni–Cu/Al_2O_3 catalysts. Reduced catalysts – thick lines, catalysts after HdCl – thin lines.

In the case of Ni–Au system, a complete miscibility of two metal components cannot be achieved because of thermodynamics reasons. Instead, a two-phase system is expected, where very rich in Au phase coexists with that composed of a nearly pure nickel

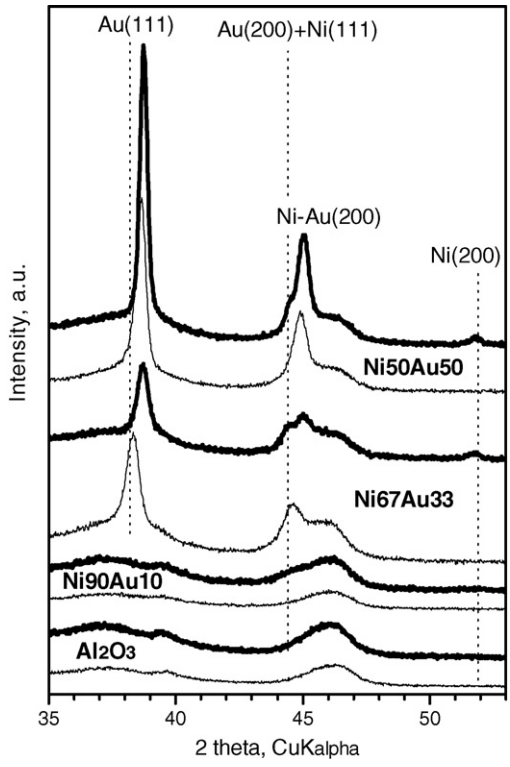

Fig. 4. XRD profiles of Ni–Au/Al_2O_3 catalysts. Reduced catalysts – thick lines, catalysts after HdCl – thin lines.

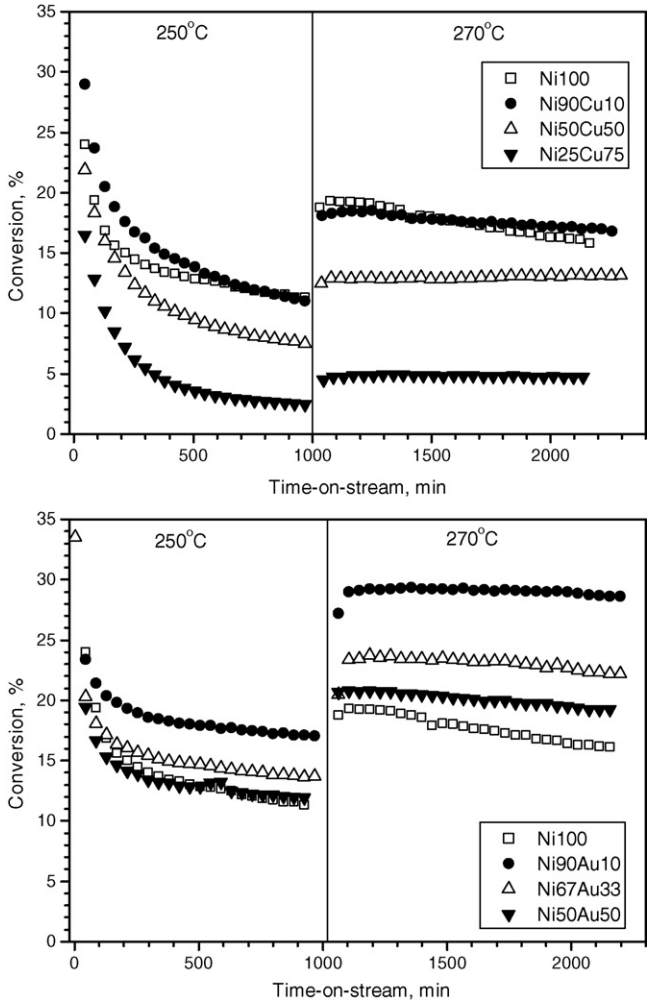

Fig. 5. Time-on-stream behavior of Ni–Cu/Al_2O_3 (top) and Ni–Au/Al_2O_3 (bottom) catalysts in HdCl of 1,2-DCA at 250 and 270 °C.

[17]. In good agreement with it, our XRD showed the presence of two phases composed of nearly pure component metals (Fig. 4 and Table 2).

Metal dispersion of Ni100/Al_2O_3, assessed from hydrogen chemisorption, was 0.15 (H/Ni). Attempts to measure metal dispersions of Ni-containing bimetallic catalysts gave very small quantities, roughly 5–7 times lower than that of Ni and will not be reported here because they are subjected to a considerable error. Very low hydrogen uptakes by Ni–Cu and Ni–Au alloys are not surprising because a pronounced surface segregation of the IB metal was established for Ni–Cu [18–29] and Ni–Au alloys [30]. On the other hand, catalyst screening in HdCl of 1,2-DCA showed that the overall conversion level on bimetallic catalysts is similar to that found for Ni/Al_2O_3, the analysis of kinetic data will be based on the activity expressed per mass of Ni. Therefore, our attention was focused at the effect of the composition of active phase on catalytic properties in HdCl of 1,2-dichloroethane.

The results obtained for hydrodechlorination of 1,2-DCA over alumina-supported Ni–Cu and Ni–Au are shown in Figs. 5–8. Fig. 5 shows the time-on-stream behavior of these catalysts. It is seen that the initial high activity of all samples is reduced by a factor of 3–4 for Ni–Cu and ~2 for Ni–Au, at 250 °C. Most probably, surface carbiding and chloriding are responsible for such a drop of conversion. Interestingly, after increasing the reaction temperature to 270 °C, further changes of conversion with time are much smaller, especially for the bimetallic catalysts (Fig. 5).

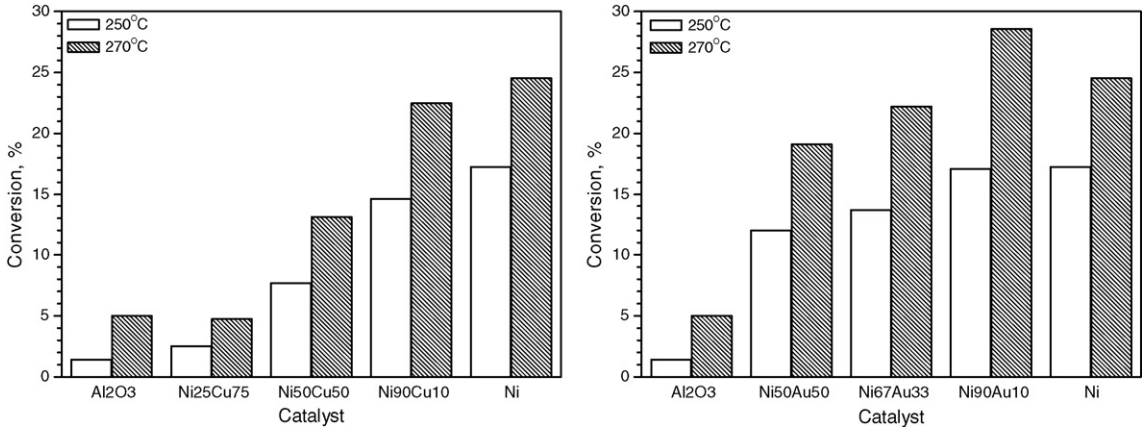

Fig. 6. HdCl of 1,2-DCA over Ni–Cu/Al_2O_3 and Ni–Au/Al_2O_3 catalysts (mass of catalyst 0.2 g). Conversions: after ~1000 min at 250 °C and at steady state at 270 °C. Left side Ni–Cu/Al_2O_3, right side Ni–Au/Al_2O_3.

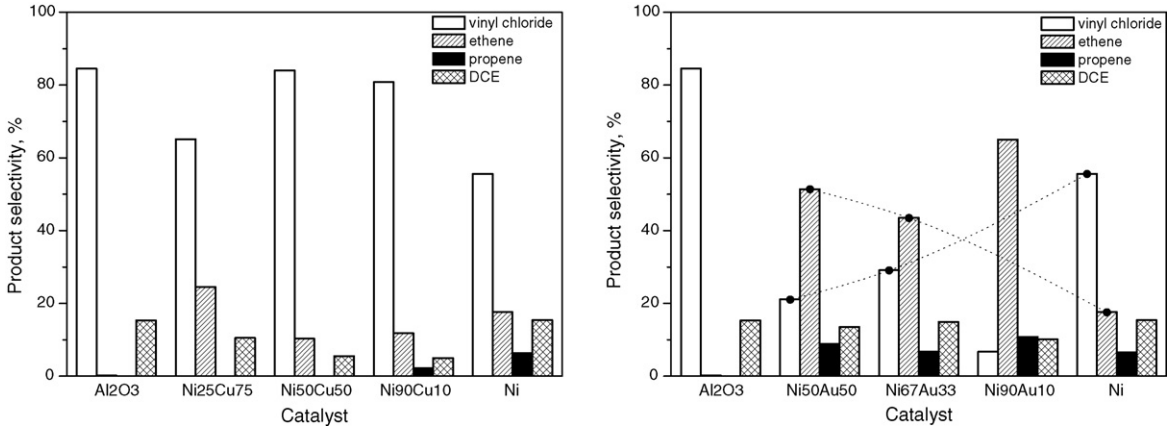

Fig. 7. Product selectivity at 250 °C in HdCl of 1,2-DCA. DCE denotes the sum of dichlorinated ethenes. Left side Ni–Cu/Al_2O_3, right side Ni–Au/Al_2O_3.

Fig. 6 shows the conversions achieved on the same charges of catalysts (0.2 g). Because each catalyst contained the same amount of Ni (2 wt.%), Fig. 6 reflects the catalytic activity referred to the same mass of Ni. In the case of Ni100 and Ni90Cu10 catalysts the overall conversions were corrected for the extent of catalyst (Ni) reduction (last column in Table 2). It is seen that Ni100 and Ni-rich catalysts are more active than those with larger amount of copper and gold. Interestingly, the Ni90Au10 catalyst shows higher activity than Ni100 (at 270 °C), the result which can be regarded as an indication of synergistic effect of alloying Ni with Au. Similar results were obtained by the group of Keane, who investigated silica, titania and alumina-supported Ni–Au in HdCl of 2,4-dichlorophenol and obtained a higher dechlorination rate over the bimetallic system in comparison with Ni [2–4].

Previous reports on HdCl of 1,2-dichloroethane over Pd–Ag [31] and Pt–Cu [32] catalysts suggested that the C–Cl bond scission would take place on the IB metal sites. Active hydrogen (from Pt or Pd) is needed for regeneration of the chlorinated silver or copper surfaces into metallic silver and copper. A similar situation would take place in the case of Ni modified by Cu and Au. However, another

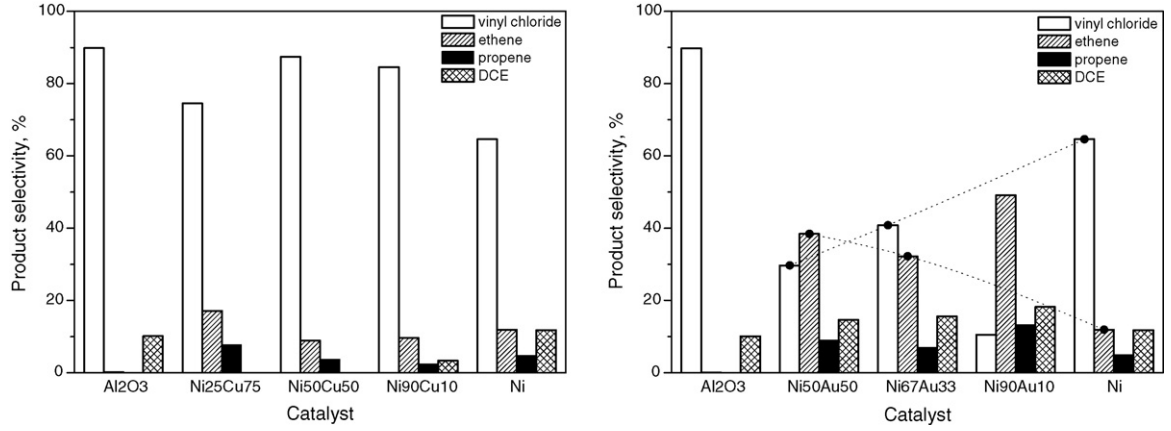

Fig. 8. Product selectivity at 270 °C in HdCl of 1,2-DCA. DCE denotes the sum of dichlorinated ethenes. Left side Ni–Cu/Al_2O_3, right side Ni–Au/Al_2O_3.

particular aspect of Au and Cu addition should be considered. The addition of Au to Ni increases the selectivity to ethene (probably by reducing coking of Ni–Au), whereas the addition of Cu to Ni increases the selectivity to vinyl chloride (probably because of a lesser effect of Cu on coking). Figs. 7 and 8 show these trends. Much more interesting are the results of product selectivities, calculated as the percentages of 1,2-DCA consumed in the formation of a designated product (Figs. 7 and 8). In this respect, both bimetallic systems showed quite different behavior. Addition of Au to Ni leads to an increase of selectivity to ethene, at the expense of vinyl chloride. It suggests that chloride removal (as HCl) from the catalyst surface is enhanced due to gold presence. This is not the case when copper is added to nickel. For Ni–Cu/Al_2O_3 catalysts, vinyl chloride monomer is the dominant product (Figs. 7 and 8). These figures also show very high selectivity to vinyl chloride of γ-alumina, but its activity is rather low (Fig. 6). Choi and Lee [5] showed that Ni–Cu/SiO_2 catalysts efficiently converted 1,1,2-trichloroethane into vinyl chloride with ≥95% selectivity. They suggested that copper introduction to Ni/SiO_2 reduced the metal particle size and weakened the adsorption strength of Ni, and led to low conversion of 1,1,2-trichloroethane and a high selectivity to vinyl chloride [5]. We are of opinion Ni–Cu mixed ensembles are more suited for a concerted removal of H and Cl atoms from the molecule of 1,2-DCA than unmodified Ni surface. Different extent of surface carbiding (more pronounced for Ni–Cu than for Ni–Au) should also have effect on the catalytic behavior. It seems that due to the presence of Au, the Ni–Au surface is less prone both to carbiding as well to chloriding. Preliminary temperature-programmed hydrogenation study of post-reaction deposits confirm such a supposition (detailed results not shown). Rapid removal of HCl and carbonaceous species from Ni–Au catalysts during HdCl run makes their surface better disposed for stripping of all chloride atoms from the molecule of 1,2-DCA. This is not the case for Ni–Cu, where carbiding and chloriding are more pronounced than for Ni–Au.

The trends in the selectivities to vinyl chloride and ethene with Au content (presented as two dotted lines in Figs. 7 and 8) show that by adding more gold, the selectivity to ethene is increased at the cost of vinyl chloride. However, the data for Ni95Au5 are omitted in this correlation. Much higher metal dispersion of this catalyst (compared to the rest, Table 2) would be responsible for such a behavior. We found that nickel catalysts (prepared from Ni nitrate) characterized by a higher metal dispersion give more ethene, compared to low dispersed Ni catalysts (from Ni chloride or Ni acetate), which give relatively larger amounts of vinyl chloride [1].

The post-reaction samples of all tested catalysts were investigated by XRD (thin lines in Figs. 3 and 4). It is seen that in several cases (1 1 1) reflections of fcc metal (alloy) phase were shifted towards lower diffraction angles. In agreement with earlier findings [1,7], such changes are ascribed to carbon (originating from 1,2-DCA molecule) incorporation to a Ni-rich phase.

4. Conclusions

Incipient wetness co-impregnation of γ-alumina with chloride solutions of Ni and Cu/Au, followed by a prolonged hydrogen treatment at 500 °C yielded reasonable degree of alloying for both alloy systems, in a fair agreement with the thermodynamics of these solid alloy systems. For Ni–Au, a significant intermixing was not feasible because of thermodynamics constraints. Introduction of copper (or gold) to nickel brought about interesting changes in the catalytic behavior in HdCl of 1,2-dichloroethane (synergistic effects). The presence of copper enhances the predisposition of nickel towards vinyl chloride formation, whereas addition of gold increases the selectivity to ethene. It is argued that this difference is associated with a decreased tendency of surface chloriding and carbiding when nickel is alloyed with gold compared to Ni–Cu.

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