Transformation of alumina supported nickel catalysts during hydrodechlorination of 1,2-dichloroethane[*]

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Our previous work with Sibunit carbon supported nickel catalysts investigated in the reaction of 1,2-dichloroethane hydrodechlorination showed the transformation of nickel to an fcc NiC_x solution and/or even to an hcp Ni_3C carbide phase during reaction. Carbon entering to nickel was considered to originate from the organic molecule, not from the carbon support. To substantiate this interpretation we decided to carry out the title reaction in the presence of alumina supported nickel catalysts. Hydrodechlorination of 1,2-dichloroethane performed on differently metal loaded Ni/Al_2O_3 catalysts resulted in a massive carbiding of nickel, leading to the Ni_3C carbide phase. This effect was better marked for the catalysts with a higher Ni loading (≥ 2 wt.%). However, for very high Ni loading (20 wt.%) characterized by bigger metal crystallites (~30 nm), only a portion of Ni was carbided.

1. INTRODUCTION

Catalytic hydrodechlorination (HdCl) offers an exceptional advantage over all oxidative (noncatalytic and catalytic) methods of destruction of harmful chlorinated compounds. This is because the carbon skeleton of a chlorine-

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[*]This article is dedicated to Professor Dobiesław Nazimek on the occasion of his 65th birthday

containing organic molecule is not irreversibly lost (i.e. not converted to CO_2), but several useful and less harmful products could be achieved in effect of catalytic transformation. However, search for active, selective and durable catalysts is still on. Nickel, in addition to platinum and palladium, is regarded as an efficient hydrodechlorination catalyst [1-9]. In the case of vicinal dichlorocarbons, Ni is even better than Pt and Pd, because in its presence the hydrodechlorination products are unsaturated compounds, more valuable than their saturated analogs.

There are different opinions as to the fate of nickel (active) phase during HdCl reactions. Some recent papers occasionally report a (partial) transformation of the fcc Ni phase into either hcp α-Ni [2,3] or hcp Ni_3C phase [10], or no Ni phase change [11,12] during HdCl reactions. Our recent work on HdCl of 1,2-dichloroethane (DCE) on Sibunit carbon nickel catalyst showed a massive transformation of nickel to nickel carbide phases (fcc NiC_x and hcp Ni_3C), [13-15]. Carbon incorporated into Ni was considered to originate from the organic molecule. To confirm this hypothesis, the present hydrodechlorination study was carried out on alumina supported Ni catalysts.

2. MATERIAL AND METHODS

The 1, 2, 5 and 20 wt.% metal-loaded nickel catalysts were prepared by incipient wetness impregnation of γ-alumina from Sasol (150-200 mesh, specific surface area 196 m^2/g). Nickel (II) chloride ($NiCl_2*6H_2O$, of analytical purity from POCh, Gliwice, Poland) was used in catalyst preparation. 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^oC and stored in a desiccator.

Crystallite size of Ni in the catalysts was assessed from X-ray diffraction (XRD). XRD experiments were performed on a Siemens D5000 diffractometer using Ni-filtered CuK_α radiation. Several samples of Ni/Al_2O_3 catalysts (reduced and after reaction) were scanned by a step-by-step technique, at 2θ intervals of 0.02°. The catalytic conversion of DCE was investigated using a glass flow reaction system [13-15]. After reduction at 500^oC for 3 h in $10\%H_2$/Ar flow (25 cm^3/min), the catalysts were investigated in the reaction of DCE with hydrogen (1:1 ratio) at 230^oC. Total flow of the reaction mixture was 41.1 cm^3/min (H_2: 1.15 cm^3/min, DCE: 1.15 cm^3/min, Ar: 38.8 cm^3/min). The mass of the catalyst used ranged between 0.1 and 0.4 g, depending on the metal loading, in order to not exceed conversion levels beyond 10%. In all kinetic runs, the activities of all

catalysts declined with time on stream.   A typical run lasted ca. 24 h. The reaction was followed by gas chromatography (HP 5890 series II with FID, a 5% Fluorcol/Carbopack B column (10 ft) from Supelco).

3. RESULTS AND DISCUSSION

Crystallite sizes of nickel assessed from XRD (using the Scherrer formula) are shown in Table 1.

Tab. 1. Ni crystallite sizes in alumina supported catalysts after reduction at 500^oC for 3h.

Ni loading, wt.%	Reflection	Ni crystallite size[a], nm	Average Ni crystallite size[b], nm
1	111	14.4	12.6
	200	6.1	
	220	17.2	
2	111	20.0	17.1
	200	13.5	
	220	17.9	
5	110	20.7	15.6
	200	13.1	
	220	13.0	
20	111	36.5	29.7
	200	28.6	
	220	23.9	

[a] From the Scherrer formula.
[b] From three basic XRD reflections (111, 200 and 220) of Ni.

It is seen that the three less loaded Ni catalysts (1, 2 and 5 wt.%) were characterized by roughly similar metal particles, whereas the most Ni loaded catalyst (20 wt.%) had much larger Ni crystallites. This difference will have an effect on the extent of phase transformations during hydrodechlorination (discussed later).

Figure 1 shows the X-ray diffractogrammes of 1 wt.% Ni/Al_2O_3 catalyst subjected to reduction at 500^oC and reaction at 230^oC. At first glance, both diffractogrammes are very similar, suggesting no big change in the structure of catalyst caused by reaction. The situation is complicated by overlapping the main Ni reflection (111) with the (400) reflection from alumina. However, the absence of (200) reflection of Ni at $2\theta \approx 51.8^o$ in the profile of used catalyst suggests that the fcc phase of Ni has been transformed into another species. Somewhat better developed XRD reflection at $2\theta \approx 39^o$ and a slight irregularity in the course of descending branch at $2\theta \approx 41^o$ would result from the contribution of hcp phase of

Ni$_3$C. However, at so low Ni loading, the overall XRD picture is dominated by reflections from the alumina support.
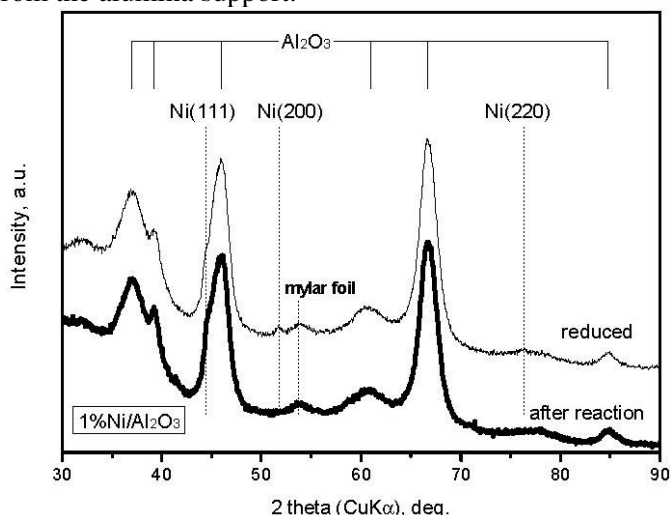

Fig. 1. Comparison of XRD profiles of 1 wt.% Ni/Al$_2$O$_3$ catalysts: reduced (thin line) and subjected to HdCl of 1,2-dichloroethane (thick line). Dotted lines indicate basic XRD reflections of Ni (fcc phase) and solid lines indicate positions of basic XRD reflections of γ-alumina.

Much better insight into the problem of Ni transformation during HdCl follows from studying the Ni/Al$_2$O$_3$ catalysts characterized by a higher metal loading (2, 5 and 20 wt.%). A complete disappearance of the (200) reflection of Ni observed for 2 and 5 wt.% Ni/Al$_2$O$_3$ catalysts (Figs. 2 and 3) is now accompanied by a distinct development of XRD reflections characteristic of Ni$_3$C (hcp) phase (represented by stars in Figs. 2, 3 and 4). Partial carbiding leading to the formation of the fcc NiC$_x$ phase detected in our previous studies with Ni/C catalysts [13-15] is not observed here. However, in the present case a serious overlap of the (111) reflection of Ni with the (400) reflection from alumina makes such observation very difficult. Much less intense (200) and (220) Ni reflections observed for the reduced catalysts practically disappear after HdCl (Figs. 2 and 3), so it is impossible to make speculations about their shift towards lower diffraction angles, which would be suggestive of some presence of carbided fcc NiC$_x$ phase.

A rough comparison of peak widths in reduced catalysts (Ni reflections) and after reaction (Ni$_3$C reflections) suggests no metal sintering caused by hydrodechlorination. Also an apparent absence of XRD reflections characteristic of nickel dichloride indicates that bulk chloriding of nickel does not occur during hydrodechlorination of 1,2-dichloroethane at 230°C.
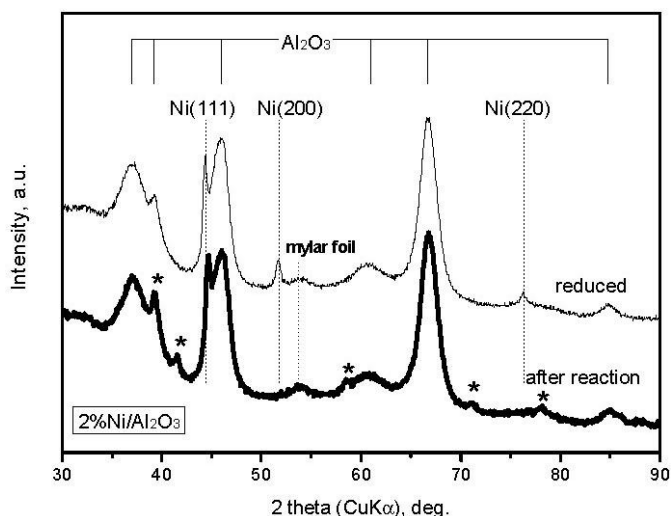
Fig. 2. Comparison of XRD profiles of 2 wt.% Ni/Al$_2$O$_3$ catalysts: reduced (thin line) and subjected to HdCl of 1,2-dichloroethane (thick line). Dotted lines indicate basic XRD reflections of Ni (fcc phase) and solid lines indicate positions of basic XRD reflections of γ-alumina. Stars symbolize positions of XRD reflections of Ni$_3$C (hcp).
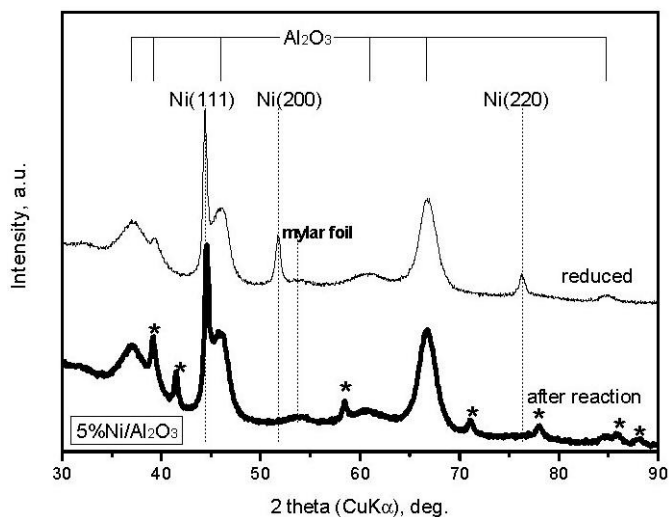

Fig. 3. Comparison of XRD profiles of 5 wt.% Ni/Al$_2$O$_3$ catalysts: reduced (thin line) and subjected to HdCl of 1,2-dichloroethane (thick line). Dotted lines indicate basic XRD reflections of Ni (fcc phase) and solid lines indicate positions of basic XRD reflections of γ-alumina. Stars symbolize positions of XRD reflections of Ni$_3$C (hcp).

Interestingly, Figure 4 representing the behavior of 20 wt.% Ni/Al_2O_3 catalyst, shows that a considerable part of nickel is not transformed into Ni_3C after hydrodechlorination. Such conclusion follows from the presence of (200) and (220) Ni reflections in used catalysts. In addition, HdCl does not result in shift of these reflections towards lower diffraction angles, which would be suggestive of some carbon incorporation. Therefore, it appears that this "unaffected" nickel material represents the interior of metal crystallites, not reached by carbon species during reaction. It is recalled that the 20 wt.% Ni/Al_2O_3 catalyst was characterized by very big metal crystalites (~30 nm in size). Apparently, such large Ni crystallites are not easily carbided due to limited diffusion of carbon at $230^{o}C$.
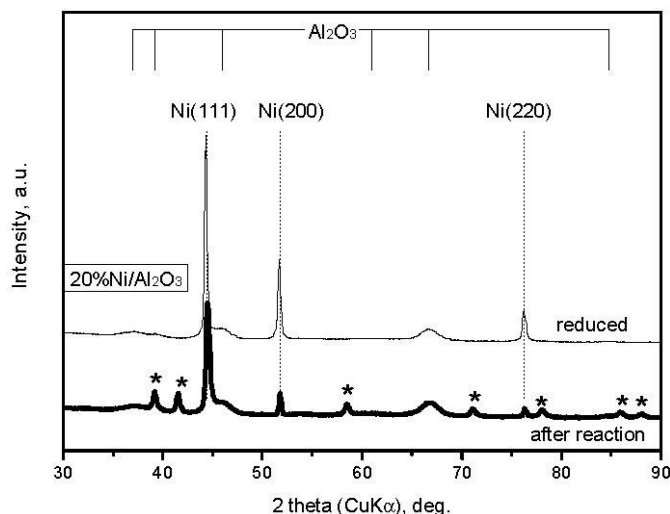

Fig. 4. Comparison of XRD profiles of 20 wt.% Ni/Al_2O_3 catalysts: reduced (thin line) and subjected to HdCl of 1,2-dichloroethane (thick line). Dotted lines indicate basic XRD reflections of Ni (fcc phase) and solid lines indicate positions of basic XRD reflections of γ-alumina. Stars symbolize positions of XRD reflections of Ni_3C (hcp).

4. CONCLUSIONS

Hydrodechlorination of 1,2-dichloroethane studied on differently metal loaded Ni/Al_2O_3 catalysts led to a massive carbiding of nickel dectected by formation of the Ni_3C carbide phase. Carbon entering nickel bulk originated from the organic molecule. Unexpectedly, the presence of previously seen partly carbided Ni fcc phase (NiC_x) was not confirmed. Carbiding was much better

detected for the catalysts with a higher Ni loading (≥2 wt.%). However, for very high Ni loading (20 wt.%) characterized by bigger metal crystallites, only a portion of Ni was carbided.

5. REFERENCES

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