Decomposition of gaseous HCN in the presence of Ni-containing catalysts

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Abstract This work is devoted to the decomposition of gaseous HCN by oxidation with air catalyzed by different nickel containing catalysts. The presence of metallic nickel does not cause the decomposition of cyanide at 400 °C, but NiO, electrochemical prepared nickel oxides $\text{Ni}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ and $(\beta, \gamma)\text{-NiOOH}$ exhibit distinctly high catalytic activity at this temperature. The effect of HCN decomposition for electrochemically prepared nickel oxides was over 90 %. Nickel deposited on activated carbon also demonstrated catalytic behavior during the destruction of HCN with an air mixture at the temperature 400 °C. Nickel oxide mixed with activated carbon showed a small increase of catalytic activity in the destruction of HCN in comparison with NiO.

Keywords Gaseous HCN destruction · Oxidation · Nickel-impregnated activated carbon · Nickel oxides

Introduction

Cyanides are discharged by various industries, particularly in metallurgical processes (extraction of gold and silver), plating and surface finishing. They are considered among the most dangerous compounds for the environment and their toxicity is mainly due to their aptitude to release free cyanides. Different processes are proposed and used for the removal of cyanides in solutions and slurries [1–12].

Hydrogen cyanide (HCN) is a very toxic gas (ca. 30 times more toxic than carbon monoxide) that already affects human beings at ppm level in air whereas 1 min of exposure to concentrations of ca. 300 ppm is lethal [13]. However, to my

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knowledge, there are only a few publications focused on the catalytic decomposition of HCN in the gas phase, as reviewed by Kröcher and Elsner [14]. Iron oxide, Al_2O_3 or Pt, Pd, Rh, Ag, V_2O_5 , WO_3 , $\text{CuSO}_4/\text{TiO}_2$ each supported on TiO_2 pellets [15] and $\text{Pt}/\text{Al}_2\text{O}_3$ [16] were studied as catalysts in this reaction.

The activated carbons, which are known as an excellent adsorbents, are widely used as catalysts and supports of catalysts [10, 12, 17–19], in the mining industry for precious metal recovery and in polishing processes to remove low level cyanide concentration. For cyanide treatment, activated carbon and activated carbon impregnated with some transition metals have showed their effectiveness as an adsorbent and catalyst for the heterogeneous oxidation of cyanides and other pollutants. Although studies concerning cyanide adsorption with activated carbon have already been performed, the oxidation of HCN in the gas phase by nickel, nickel oxide and nickel-impregnated activated carbon has not yet been investigated.

HCN is ubiquitously produced from the pyrolysis of plastic wastes and solid fuels containing some organic nitrogen. The studies of HCN oxidation are justified due to the method of thermal decomposition of industrial waste, including hazardous waste, which very often contains cyanides because they are applied increasingly. It is worth taking into account that galvanic waste is also utilized by admixturing to ceramic building materials [20–24]. For this reason, there is a danger that trace quantities of cyanides can be released with waste gas.

Nickel hydroxide can be one of the post-galvanic waste components. Therefore, it is important to explain if the addition of nickel hydroxide to ceramics along with other galvanic waste can perform the function of catalyst in the oxidation of HCN within the ceramic material. Because the burned ceramic material has an alkaline reaction and conditions are oxidizing in a furnace [24], these are conducive to the oxidation of both nickel and HCN.

This work is dedicated to the removal of HCN emissions by oxidation using nickel, nickel oxides and nickel-impregnated activated carbon and silica, with the aim of finding new and improved catalysts for this reaction.

Materials and methods

Preparation of catalysts

Nickel powder (Inco-Europe Ltd.) type 255 grain-size distribution of 2.2–2.8 μm , nickel foam (Nitech-Spraprec) thickness 1.6 mm, density 500 g/m^3 and porosity over 95 % and NiO (Aldrich) $d < 10 \mu\text{m}$ was used as catalyst.

The starting material acting as a carrier was activated carbon NORIT RO 0.8 Supra No 92-70937 and silica SYLOID 244 (specific surface 300–350 m^2/g).

Activated carbon and silica was modified by the deposition of the catalyst on their surface. This was a three-stage process. In the first stage, NORIT was degreased in the solution of mersolan in an ultrasonic washer at a temperature 70–80 °C for 30 min, silica was degreased for 15 min. Then the materials were thoroughly washed and filtered. After that, in the second stage, carbon and silica were activated for 30 min in the mixture of PdCl_2 and SnCl_2 in hydrochloric acid

solution in an ultrasonic shaker. Such prepared materials were washed, filtered and dried. Ambient drying was preliminarily performed at room temperature for 20 h and further drying was continued at 80 °C for the next 2 h. In the next stage, dried samples were covered by a layer of nickel. The nickel layer was deposited using a chemical method. This process involved the immersing of the obtained materials in chemical nickel bath. All samples were ultrasonically stirred for 30 min at 70–80 °C. Afterwards, they were washed, filtered and dried at room temperature for 20 h and further at 80 °C to constant mass. The amount of deposited nickel onto carbon was about 25 %. Silica prepared in this way consisted of about 30 % of nickel, but ultrasonic stirring caused significant size reduction and inhomogeneity of the silica carrier. For this reason, the second part of the silica was covered by nickel using mechanical stirring. As a result of this process, silica with 18 % of nickel was obtained.

Additionally, a sample containing NiO powder mixed with carbon NORIT (in a 1:1 ratio) was prepared as a catalyst.

The $\text{Ni}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ and $(\beta, \gamma)\text{-NiOOH}$ samples were prepared by the anodic oxidation of NiO and $\beta\text{-Ni(OH)}_2$ following the procedure outlined by Skowroński [25] and Czerwiński [26].

Experimental setup for HCN destruction

Catalytic HCN destruction measurements were carried out in a closed system consisting of three glass reactors, i.e. generation of HCN, oxidation and absorption reactors, a furnace NABERTHERM with programmable regulation of temperature and a water aspirator. The HCN generation reactor consisted of a distillation flask (1000 ml) with a dropping funnel, a capillary tube for bubbling air, and a reflux condenser with a pipe for carrying away the generated HCN. The oxidation reactor consisted of two parts. The bottom part included glassy foam. Catalysts were placed on this foam. The top part of the oxidation reactor possessed a pipe for carrying away gas products formed during HCN destruction to the absorption reactor, which consisted of three absorption bulbs with 1 % NaOH solutions (150 ml). The oxidation reactor was placed in the furnace.

Procedure of HCN destruction

The catalyst was placed in the reactor and in the furnace then NaCN solution (500 ml) containing 500 mg CN^- was poured into the distillation flask. The water aspirator was started and the air was blown by the capillary tube which was immersed in NaCN solution. Then the furnace was turned on and after the proper temperature was reached, for 30 min (every 5 min), 10 ml of sulfuric acid solution (1:1) was poured through the dropping funnel. The total amount of added acid was 60 ml, and at this point, the distillation flask was heated up. The solution was boiled for 1 h. Next, the heating was turned off and the flask was cooled down for 0.5 h. Afterwards the capillary tube was removed and the system was aired for 0.5 h and then the furnace was turned off. The airflow was continued for another 0.5 h. Then the total content of cyanide in the absorption bulbs was determined.

Analytical procedure

The concentrations of cyanide in the reaction mixture were determined spectrophotometrically at $\lambda_{\text{max}} = 578$ nm using piryidinebarbituric acid in the presence of Chloramine-T [27]. The UV-spectral analyses of cyanide were performed using a UV–VIS/MINI-1240 type photometer (SHIMADZU). All the chemicals used were analytical reagent grade.

Results and discussion

HCN oxidation by metallic nickel

The decomposition of HCN over nickel powder and nickel foam was investigated. These catalysts were placed in the oxidation reactor and the HCN/air mixture was let through. The data of these trials are reported in Table 1. It is shown that in a majority of cases, metallic nickel does not reveal catalytic behavior in the decomposition of cyanide. Only in one case of using nickel with a mass of 2.0087 g was the efficiency 14 %. In this case, one could observe that the powder glowed during the preliminary heating. It can mean that metallic nickel was partly oxidized to nickel oxide. The confirmation of this phenomenon is my subsequent studies with nickel oxide, which exhibited its catalytic behavior in the oxidation of HCN.

HCN oxidation by nickel oxides

In consecutive tests, NiO samples were placed in the catalytic vessel and HCN oxidation was studied at different temperatures (Table 2). At a temperature of 200 °C, the decomposition of HCN was not found, whereas at 300 and 350 °C, the decomposition ratio was significant. At the temperature 400 °C, this effect was over 90 %.

A similar relationship for electrochemically prepared $\text{Ni}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ was observed (Table 3). $\text{Ni}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ also exhibited distinctly high catalytic activity at this temperature.

In order to become convinced if in the process of HCN decomposing a nickel oxide sample loses its catalytic behavior, 9 trials with the same NiO weighed

Table 1 Thermal decomposition of HCN using nickel powder and nickel foam as catalysts

Catalyst	Dose of catalyst (g)	Temperature (°C)	Residual CN^- concentration (mg)	The rate of cyanide decomposition (%)
Ni powder	0.5039	400	500	0
	2.0087	400	430	14
Ni foam	0.0854	400	500	0
	0.0704	400	500	0

The initial mass of cyanide = 500 mg

Table 2 Thermal decomposition of HCN using NiO as a catalyst

	Dose of catalyst (g)	Temperature (°C)	Residual CN [−] concentration (mg)	The rate of cyanide decomposition (%)
The initial mass of cyanide = 500 mg	0.6162	200	500	0
	0.5536	300	78.35	84.33
	2.0190	300	17.40	96.52
	0.5203	350	61.68	87.66
	0.5827	400	38.1	92.38
	2.0282	400	0.112	99.98
	0.5769	500	0.014	99.997

Table 3 Thermal decomposition of HCN using electrochemically prepared Ni₂O₃·xH₂O and (β,γ)-NiOOH as catalysts

Catalyst	Dose of catalyst (g)	Temperature (°C)	Residual CN [−] concentration (mg)	The rate of cyanide decomposition (%)
Ni ₂ O ₃ × H ₂ O	0.5125	200	500.00	0
	2.0371	300	21.75	95.65
	0.5537	350	77.67	84.47
	6.5366	400	0.48	99.90
(β,γ)-NiOOH	0.5261	200	445.00	10.00
	0.5229	300	93.00	81.40
	0.5002	400	2.30	99.54

The initial mass of cyanide = 500

amount (2.0282 g) were carried out. Through this NiO sample, a total amount of 4.5 g HCN was let through (Fig. 1). As can be seen in Fig. 1, the catalytic activity of nickel oxide was not decreased in these trials. The decomposition of HCN was over 99 % in every test.

In the next series, the catalytic behavior of (β,γ)-NiOOH (as powder) was tested. In this case, only a smaller amount of electrode material was used (about 500 mg) in order to assure a low flow resistance through the layer of catalyst. The data shown in Table 3 prove unambiguously that electrochemically prepared (β,γ)-NiOOH has a high catalytic activity in the destruction of HCN. During further measurements (Fig. 1), the sample (β,γ)-NiOOH did not lose its catalytic activity.

HCN oxidation by nickel deposited on NORIT

The studies concern catalytic removal of cyanide ions in aqueous solutions using nickel catalyst—NiO exhibits its high catalytic activity at low temperatures [28] and investigations which had been carried out earlier into the decomposition of HCN in the gas phase confirmed its catalytic activity also in this case. Therefore, it was revealed purposely to develop a method of increasing NiO catalytic activity. With

Fig. 1 The rate of HCN decomposition with number of use various catalysts ($T = 400\text{ }^{\circ}\text{C}$, doses of CN^- 500 mg)

this aim, trials with a porous carrier coated in partly oxidized nickel were carried out. Activated carbon NORIT and silica SYLOID were the carriers.

First of all, the trials of HCN decomposition on carrier free nickel (NORIT and SYLOID) were carried out and their results are shown in Tables 4 and 5. It can be seen that HCN, without nickel catalyst, passed through the oxidation reactor with porous material present at the set, it did not decay and the decomposition is insignificant.

In connection with this, in the next trials in this reactor, a porous carrier with deposited nickel on it was placed. Because oxygen as well as HCN was also present in the stream flow and the decomposition process was carried out at relatively high temperatures (over $300\text{ }^{\circ}\text{C}$), an assumption that the formation of a nickel oxide layer took place on the nickel surface is justified. The data of trials with activated carbon/nickel catalyst are shown in Table 4. It can be seen that the presence of Ni/NiO on

Table 4 Thermal decomposition of HCN using NORIT without nickel, NORIT with deposited Ni and NORIT mixed with NiO

Catalyst	Dose of catalyst (g)	Temperature ($^{\circ}\text{C}$)	Residual CN^- concentration (mg)	The rate of cyanide decomposition (%)
NORIT without nickel	0.4982	400	497	0.6
NORIT with deposited Ni (25 %)	2.0045	300	120.92	75.82
	2.0004	350	44.07	91.19
	2.0003	400	90.92	81.82
NORIT mixed with NiO (1:1)	1.0000	400	2.89	99.42

The initial mass of cyanide = 500 mg

Table 5 Thermal decomposition of HCN using SYLOID without nickel and SYLOID with deposited Ni

Catalyst	Dose of catalyst (g)	Temperature (°C)	Residual CN ⁻ concentration (mg)	The rate of cyanide decomposition (%)
SYLOID without nickel	0.8180	400	500	0
SYLOID with deposited Ni (18 %)	1.3858	400	129.00	74.20
SYLOID with deposited Ni (30 %)	1.1860	400	126.88	74.62

The initial mass of cyanide = 500 mg

the carbon surface improves the rate of HCN removal significantly. At the temperature 300 °C, the efficiency of HCN decomposition was over 75 %. In the attempt at 350 °C the efficiency was over 91 %. Further studies at the temperature 400 °C continued with the same sample of Ni impregnated NORIT (Fig. 1) proved that the efficiency of HCN decomposition increases in comparison to the 0.5 g NiO sample and was over 80 % in the first two trials, but after subsequent trials, carbon in the reactor was burned.

The next studies were conducted using carbon NORIT mixed with NiO powder (in 1:1 ratio) and their results are shown in Fig. 1. The results demonstrate that the catalytic activity of NiO mixed with NORIT is higher than for a comparable sample of NiO without activated carbon but lower than for carbon covered with nickel using this chemical method.

HCN oxidation by nickel deposited on SYLOID

The results obtained for the second studied carrier silica SYLOID are presented in Table 5. In these cases, the layer of catalyst deposited in the reactor was higher than catalytic layers in previous studies. For this reason, sometimes disturbances of the process appeared affected, probably by the increase of HCN flow resistance through a thicker layer of catalysts. It can make gas penetration through the layer of catalyst difficult and it is possible that it was forming channels and as a result, the catalyst had a smaller contact with the faster flowing gas. Sometimes a flowing gas carries away silica particles. This phenomenon was especially visible for silica covered with 30 % of nickel. It was connected with its considerable size reduction during the ultrasonic stirring.

Taking into account that mixing cyanides with nickel ions is avoided due to the generation of a very stable complex (the stability product of $\text{Ni}(\text{CN})_4^{2-}$ is $10^{31.3}$), the next trials examined if the observed loss of HCN was connected to its bonding with nickel. With this end in view, the samples of catalysts were investigated for cyanide content. In these studies, the samples were placed into a distillation flask and the whole procedure of cyanide absorption was conducted, except that there was no catalyst in the oxidation reactor and the furnace was not turned on. If the samples of catalyst contained cyanide bonding with nickel, the emission of HCN after the

addition of concentrated sulfurous acid (1:1) would be unavoidable. But the presence of cyanide was not found in any samples.

Conclusion

Metallic nickel does not reveal catalytic behavior in the decomposition of cyanide with an air mixture at 400 °C, but NiO and electrochemically prepared nickel oxides $\text{Ni}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ and $(\beta, \gamma)\text{-NiOOH}$ exhibit distinctly high catalytic activity at this temperature. The amount of HCN decomposition with electrochemically prepared nickel oxides was over 90 %. It is a reasonable assumption that Ni(III) ion present at the oxide surface take part in HCN heterogenous destruction and their catalytic activity depends on both their superficial concentration and reaction temperature.

Nickel deposited on activated carbon also demonstrates catalytic behavior during the destruction of HCN with air mixture at the temperature 400 °C. But activated carbon is burned during the measurements.

NiO mixed with activated carbon in the destruction of HCN showed a small increase of catalytic activity in comparison with NiO.

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