



Catalytic oxidation of cyanides in an aqueous phase over individual and manganese-modified cobalt oxide systems

St. Christoskova*, M. Stoyanova

Department of Physical Chemistry, University of Plovdiv, 24 Tzar Assen St, Plovdiv 4000, Bulgaria

ARTICLE INFO

Article history:

Received 18 July 2007

Received in revised form 29 July 2008

Accepted 14 October 2008

Available online 1 November 2008

Keywords:

Cyanides

Catalytic oxidation

Cobalt oxide systems

Kinetics

ABSTRACT

The possibility for purification of wastewaters containing free cyanides by applying of a new method based on cyanides catalytic oxidation with air to CO₂ and N₂ at low temperature and atmospheric pressure was investigated. On this purpose, individual and modified with manganese Co-oxide systems as active phase of environmental catalysts were synthesized. The applied method of synthesis favours the preparation of oxide catalytic systems with high active oxygen content (total-O* and surface-O*_s) possessing high mobility, and the metal ions being in a high oxidation state and in an octahedral coordination-factors determining high activity in reactions of complete oxidation. The catalysts employed were characterized by powder X-ray diffraction, Infrared spectroscopy, and chemical analysis. The effect of pH of the medium and catalyst loading on the effectiveness of the cyanide oxidation process, expressed by the degree of conversion (α , %), by the rate constant (k , min⁻¹), and COD was studied. The results obtained reveal that using catalysts investigated a high cyanide removal efficiency could be achieved even in strong alkaline medium. The higher activity of the manganese promoted catalytic sample could be explained on the basis of higher total active oxygen content and its higher mobility both depending on the conditions, under which the synthesis of catalyst is being carried out.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Wastewaters generated by metallurgical operations, electroplating, steel hardening, synthetic rubber production, organic synthesis, gold and silver mining, etc. usually contain free and metal-complex cyanides. All cyanide species are considered to be acute hazardous materials for living organisms and have therefore been designated as P-Class hazardous wastes (i.e. the most regulated waste) when being disposed of. Therefore, the treatment of cyanide wastewaters before they are discharged into the waterways is attracting public and regulatory attention [1,2].

Different methods are currently available for cyanide destruction with different effectiveness, namely biological treatment [3,4], chemical oxidation [5,6], electrochemical oxidation [7–9], photocatalytic [10–12], and catalytic oxidation [13,14]. The most common method for destruction of cyanides is alkaline chlorination. The main drawback of this method is the formation of highly toxic cyanogen chloride intermediate, which together with the residual chlorine, create additional environmental problems. Consequently, there is a growing need for alternative, non-chlorine methods for destroying cyanides. Biological treatment is limited to

a very low concentration of cyanides and therefore is not applicable on wastewater effluents from most industrial sites [15]. Photocatalytic degradation of cyanides using several powdered semiconductors—TiO₂, ZnO, Fe₂O₃, ZnS and CdS has been studied extensively during the last years. It was found that these metal oxides worked best because of their chemical stability; however, anatase, a polymorph of TiO₂ was preferred due to its high quantum efficiency for photoconversion, and its stable formation of electron-hole pair. However, the present drawbacks for TiO₂ photocatalysis in the treatment of wastewater include: (a) the rapid unfavourable charge carrier recombination reaction in TiO₂ compared to the redox reactions resulting in low quantum yield; (b) the high band gap energy of 3.2 eV which limits its application from using solar energy; and (c) the main oxidation products are reported to be cyanate and nitrate, which presence in industrial effluents also imposes environmental problems on the public domain.

Cyanide remediation can be accomplished with high effectiveness using electrochemical methods but this technique is limited in its applicability to the treatment of cyanide on a practical scale owing to high energy requirements and cost of equipment.

An environmentally friendly method for destruction of cyanide in aqueous solutions is based on heterogeneous catalytic reactions providing complete oxidation. Using both suitable catalytic systems and reaction conditions a high selectivity towards envi-

* Corresponding author. Tel.: +359 32 261 469; fax: +359 32 635 049.
E-mail address: christ@argon.acad.bg (St. Christoskova).

ronmentally harmless products can be achieved at mild conditions (room temperature and atmospheric pressure).

It is well known that free cyanides are strong catalytic poison therefore the catalyst's surface active sites available for the oxygen (used as oxidant) are reduced. Based on this reason only few catalytic systems used for the low-temperature complete oxidation of cyanides are described in the literature [16–18].

Development of effective catalytic method for destruction of cyanides in an aqueous medium requires preparation of new oxide catalysts which should satisfy certain criteria, the more essential among them being as follows:

- to contain high active oxygen content (total-O* and surface-O*s) possessing high mobility—an important factor providing the activity of oxide systems in oxidation processes;
- the metal ions being in a high oxidation state and in an octahedral coordination;
- to exhibit high catalytic activity with respect to low-temperature complete oxidation of cyanides in strong alkaline medium;
- to be stable against metal leaching which may cause secondary pollution of the waters.

The preparation of catalysts with predetermined chemical composition and properties (bulk, surface and morphological) is strongly dependent on both initial compositions and on experimental conditions of the synthesis procedure.

The present paper aims to synthesize new cobalt oxide systems satisfied the above mentioned criteria and to investigate their catalytic activity in the low-temperature degradation of free cyanides in alkaline solutions.

2. Experimental

2.1. Catalyst preparation

The individual Co-oxide system was prepared by oxidation-precipitation method in an aqueous solution using NaOCl as oxidant, according to the procedure described in [19]. The synthesis of Co-oxide system modified with Mn was carried out by drop wise addition of an aqueous solution of $\text{Co}(\text{NO}_3)_2$ (0.4 M) to the mixture of KMnO_4 (0.4 M) and KOH (4 M) under vigorous stirring at ambient temperature and $\text{pH} > 10$. The Co to Mn ratio should be 3:1. The black precipitate formed was kept digesting in the mother liquor for 120 min, washed several times (until disappearance of nitrate and neutral pH), then dried at 70°C in air until constant mass was obtained. The washed precipitate was dried at 60°C in air until constant mass and calcinated at 120°C for 2 h.

2.2. Characterization

The synthesized Co- and Co–Mn-systems were characterized by means of chemical analysis, X-ray diffraction (XRD), infrared spectroscopy (IR), and atomic emission spectrometry with inductively coupled plasma (ICP-OES).

Chemical analysis of the synthesized catalysts includes determination of the active oxygen content as well as determination of Co and Mn content.

The total active oxygen content O^* (it is considered that active oxygen content is the amount of oxygen above the stoichiometrical content in the oxide, corresponding to the lowest stable valence state) was determined iodometrically [20]. The relative standard deviation of the method is 4.71%. The content of the surface active oxygen O_s^* has been determined by the method described by

Kanungo [21]. The relative standard deviation of the method is 5.02%.

The Co to Mn ratio in the studied samples was estimated from the data of ICP-OES analysis. Each result is an average of five parallel measurements. The relative standard deviation of determination of Co was 5.96%, and that of Mn—7.96%.

IR-spectra were recorded with a PerkinElmer model 1750 spectrophotometer in KBr tablets (2 mg of the sample in 200 mg KBr).

X-ray analysis of the catalysts was performed using X-ray instrument TURMA (Germany), with $\text{Co K}\alpha$ irradiation. Diffraction patterns were recorded according to the method applied to polycrystalline samples—the samples were ground and pressed on organic glass supports.

2.3. Oxidation reaction

The catalytic oxidation of cyanides was carried out isothermally at 308 K in a thermostatic batch reactor of 250 cm^3 volume provided with three ports for gas inlet and outlet, and sampling. For a typical run, the desired amounts of catalyst in powder form were suspended in 200 cm^3 distilled water. The initial pH of the solutions was adjusted to 9.5 or 12 with NaOH to prevent volatilization of cyanide as toxic HCN ($\text{p}K_a[\text{HCN}]$ 9.21 at 298 K). The suspension was saturated by bubbling air at atmospheric pressure for 30 min; then the required amount of KCN was added to adjust the CN^- ions concentration to 3 mM. The mixture was stirred vigorously, slurring the catalyst uniformly throughout the liquid. During the runs continuous air purging of the solution was performed so that the fraction of catalyst surface covered by oxygen can be assumed constant in the batch reactor. Consequently, the concentration of oxygen in the solution is constant during the experiments.

Sampling a sufficient number of aliquots (0.5 cm^3) and analyzing them for residual content of cyanides and oxidation products (cyanate, nitrate, ammonium, and carbon dioxide) followed the progress of the reaction.

The catalytic activity was expressed both by the rate constant (k , min^{-1}), overall degree of CN^- conversion (α , %), and chemical oxygen demand.

2.4. Analytical methods

The total cyanide concentration was followed spectrophotometrically at $\lambda_{\text{max}} = 585\text{ nm}$ using pyridine–barbituric acid reagent (Merckoquant[®] cyanides test, Merck AG). The concentration of cyanate was determined spectrophotometrically employing a modified method of Guillon and Karst based on the reaction between cyanate ions and 2-aminobenzoic acid under buffered conditions [22]. The extent of the complete degradation of cyanides was also monitored by the chemical oxygen demand (COD) determination using COD Cell Test Spectroquant[®], Merck AG. The UV-spectral analyses of cyanide and cyanate, as well as determination of COD were performed using a Spectroquant NOVA 400, Merck photometer.

The amount of CO_2 generated during the experiments was determined by absorption of gas outlet stream in a NaOH solution of known concentration.

Leaching of catalysts in the reaction mixture at different pH was assessed by measuring the concentration of dissolved metal ions with Spectro-Flama ICP-AES model spectrometer. Experiments were carried out as follows: aliquots of the reaction mixture were taken 2 h after the start of the process (operating parameters: temperature 308 K; catalyst concentration $0.5\text{--}2\text{ g dm}^{-3}$; pH interval 9.0–12.0). The catalyst was filtered and the filtrate analysed for dissolved Co and Mn content.

Table 1
Chemical analysis of the synthesized catalysts.

Catalyst	Active oxygen content				Metal content ($\times 10^3$ g at g $^{-1}$)	
	Total (O *)		Surface (O *s)		Co	Mn
	(%)	($\times 10^3$ g at g $^{-1}$)	(%)	($\times 10^3$ g at g $^{-1}$)		
Co-oxide	6.40	4.00	2.56	1.60	5.22	0
Co–Mn-oxide	8.80	5.51	2.64	1.65	5.14	1.72

3. Results and discussion

3.1. Samples preparation and characterization

In this study precipitation was carried with reverse addition of the precipitant to the system. Such an approach facilitates the production of hydrophilic precipitates. Moreover, it is known that decomposition of the oxidant used—NaOCl (for Co-oxide system) or KMnO $_4$ (for Co–Mn-oxide) in strongly alkaline medium produced nascent oxygen. The chemisorption of the last on the precursor surface results in the incorporation of overstoichiometric (i.e. active) oxygen into oxide catalysts. As a result the oxidation state of metal ions in the oxide system increases and high concentration of ionic oxygen species (O $^-$, O $^{2-}$) on the surface is provided [19,23]. The latter play a basic role in oxidation catalysis.

KOH was used as a precipitating agent instead of NH $_4$ OH in order to avoid the formation of water soluble ammonia complexes of Co. In addition, our preliminary investigations revealed that M(OH) $_2$ (used as precursors in the synthesis of corresponding oxides), prepared through precipitation of M(II) with NH $_4$ OH exhibited lower specific area and weaker adsorption ability as compared to those precipitated with KOH.

The chemical analysis data of the synthesized catalysts are listed in Table 1. The content of cobalt and manganese found in the synthesized catalysts shows atomic Co/Mn ratio = 3 (R.S.D. 5%).

Analysis of the results presented in Table 1 reveals that modification of individual Co-oxide system with Mn leads to an increase of the total active oxygen content in the catalyst composition. The reason is the fact that Co–Mn-fresh oxide systems is bicomponent catalyst comprising higher oxide of cobalt and γ -MnO $_2$ with greatly defected structure provided by incorporation of the overstoichiometric oxygen in its composition.

It is also evident from the Table 1 that a decrease in the relative percentage content of O * is observed at commensurable values of Co content (in g-at metal/g of catalysts) in both individual and modified catalytic samples. This gives grounds to suggest that the active oxygen bonded to manganese ions is mainly located in the lattice of Co–Mn-oxide system, while the surface active oxygen is bonded to Co ions.

Results obtained about the effect of temperature of the thermal treatment of catalytic systems on the active oxygen content reveal that the amount of O * in Co-oxide systems thermally treated up to 473 K remains unchanged and is sharply reduced on heating of the sample above 573 K (O * \sim 1%) (Table 2). Incorporation of Mn in the individual oxide system leads to increase of their thermal stabil-

Table 2
The effect of temperature on the active oxygen content.

Temperature (K)	Total active oxygen (%)	
	Co-oxide	Co–Mn-oxide
473	6.40	8.60
523	3.24	7.60
573	2.17	6.25
623	0.96	5.80
823	0.76	5.00

ity. At that Co–Mn-catalyst preserves 56% of its total active oxygen content on heating up to 823 K. This extends the possibilities for practical application of the modified catalytic system in reactions of complete oxidation of toxic substances in gas phase that require higher reaction temperatures.

The results of X-ray diffraction analysis reveal that both individual and manganese modified Co-oxide systems are amorphous substances. The amorphous character of the catalysts suggests that the active sites are isostructural and chemically identical, which is a prerequisite to high sensitivity in oxidation reactions. It worth noting in recent years amorphous catalysts attract special interest due to their important features, namely: presence of a great number of unsaturated coordination centres and defects, isotropic structural and chemical properties [24].

The bonding energy of oxygen to metal ions on the catalyst surface is the main factor providing the activity of oxide catalysts. With decrease of the bond strength between the surface cation and oxygen the catalytic activity is increased and the selectivity of the process against products of complete oxidation enhanced [25]. IR spectral characterization of catalytic systems can provide information about the way of oxygen bonding to metal ions on the surface of oxide catalysts as well as about energy uniformity and reactivity of catalytic systems.

In Fig. 1 the IR-spectra of the studied catalytic samples are presented. The presence of a wide and intense absorption band at 586 cm $^{-1}$ (Co-oxide) and 579 cm $^{-1}$ (Co–Mn-oxide), respectively is characteristic feature of the IR spectra of studied freshly prepared oxide systems. The discussed band (recorded at frequencies higher than that associated with the vibrations of the M–O bond in corresponding hydroxides) is provided by stretching vibrations of the bond cation–oxygen on the surface of catalytic sample and indicates the presence of active oxygen [23]. Thereupon the intensity of the indicated bands is proportional to the content of O * . The spectral range of appearance of these bands is an evidence for the covalent character of oxygen bonding to the metal ions of the surface, which in its turn justifies the assumption of high activity of the synthesized samples in reactions of complete oxidation.

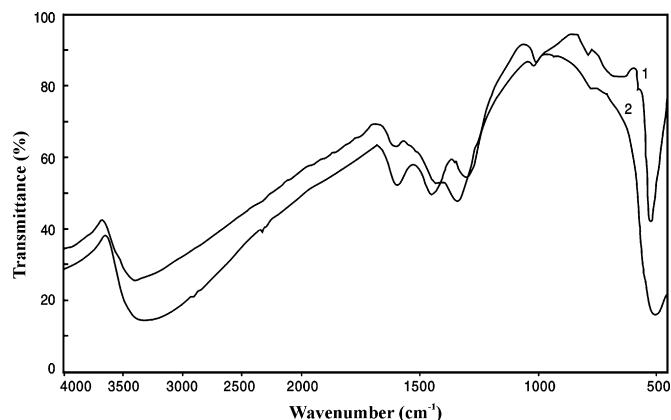


Fig. 1. IR-spectra of the studied catalytic samples: (1) Co-oxide system and (2) Co–Mn-oxide system.

Evidently, the inclusion of manganese in the composition of Co-oxide system causes a shift of the band at 586 cm^{-1} towards lower frequencies (with $\sim 7\text{ cm}^{-1}$), which is an evidence for the decrease of the surface Co–O bond strength. The increase of the width of the same band in Co–Mn-oxide, i.e. the growth in its integral intensity is another confirmation of the fact that the ionic feature of the bond is growing stronger. Data of the IR spectral analysis give us grounds to assume that Mn additive influences the mobility of the reacting oxygen, the latter contributing to activity of oxide systems in oxidation processes.

A broad band in the region $3600\text{--}2600\text{ cm}^{-1}$ (O–H stretching) with a maximum centred about 3400 cm^{-1} , together with a band at 1640 cm^{-1} (H–O–H bending) are also observed in both spectra. The band centered at 3400 cm^{-1} can be attributed to the lattice modes of hydrogen bonded hydroxyl groups, whereas the band at 1640 cm^{-1} corresponds to adsorbed molecular water. These results indicate that the samples are hydrated/hydroxylated. It is evident from the IR spectra that the hydrate in the samples is not bonded in a form of oxyhydroxide (CoOOH should display a sharp peak around 3600 cm^{-1}).

3.2. Catalytic activity

Application of heterogeneous catalysts in purification of wastewaters requires they should be stable towards metal ion exchange between the catalyst and the liquid phase under the operating conditions. It is important to study the solubility of heterogeneous catalyst because continuous (gradual) leaching of the catalyst should lead to its progressive deactivation. Moreover dissolved metal ions, included in the catalyst composition, could cause the occurrence of homogeneous catalytic reactions. In these cases one could assume the presence of homogeneous-heterogeneous catalytic reaction rather than of pure heterogeneous process.

Preliminary experiments were carried out with a view to investigate the leaching of the oxide systems in the course of cyanide catalytic oxidation. The results obtained show that the Co and Mn content in the reaction mixture after long-term runs (2 h) was always below 1 ppm, the latter being a strong evidence in support of heterogeneous catalysis.

With a view to finding optimum conditions for complete degradation of cyanide to harmless products the effect of the following parameters on both the cyanide conversion efficiency, expressed through k , min^{-1} and α , and the reaction selectivity was investigated: (a) initial pH (9.5; 12); (b) catalyst concentration ($0.5\text{--}2.0\text{ g dm}^{-3}$). The results of the kinetic investigations are illustrated in Figs. 2–5.

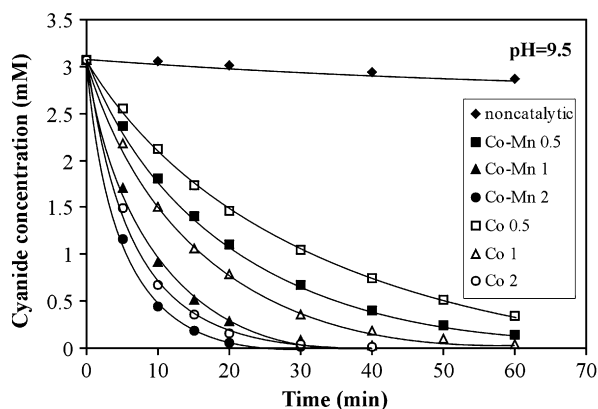


Fig. 2. Concentration change of cyanides during catalytic oxidation over studied catalytic samples.

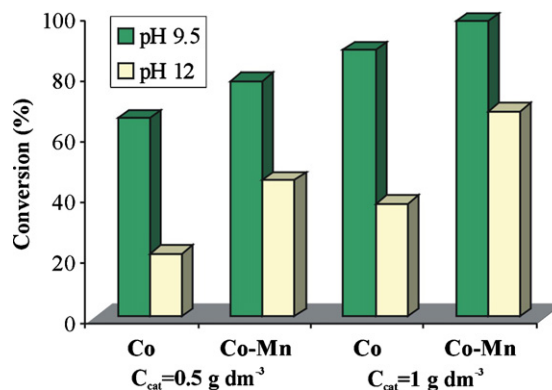


Fig. 3. Effect of the catalyst concentration and pH on the degree of cyanide conversion (α_{30}).

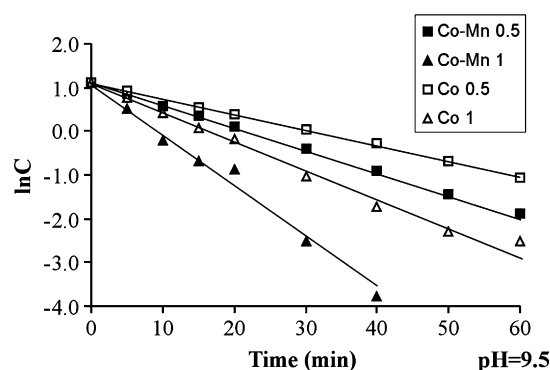


Fig. 4. Linear transformation $\ln C = f(t)$ of the kinetic curves of cyanide catalytic degradation.

Data obtained reveal that under the investigated conditions a low-temperature liquid phase oxidation of cyanide proceeds involving the participation of both individual and manganese modified oxide systems. It was established that in runs carried out without catalyst in the system the degree of cyanide conversion is insignificant (approx. 3% in 60th minute), i.e. the homogeneous oxidation does not contribute considerably to the overall reactant conversion (Fig. 2). Evidently cyanide oxidation proceeds more effectively in the presence of Co–Mn-oxide system. At pH 9.5 and $C_{\text{cat}} = 1\text{ g dm}^{-3}$ almost complete conversion of cyanide is attained in 40 min over manganese-modified sample, while using Co-oxide system the same conversion degree is achieved even at the 60th minute (Figs. 2 and 3).

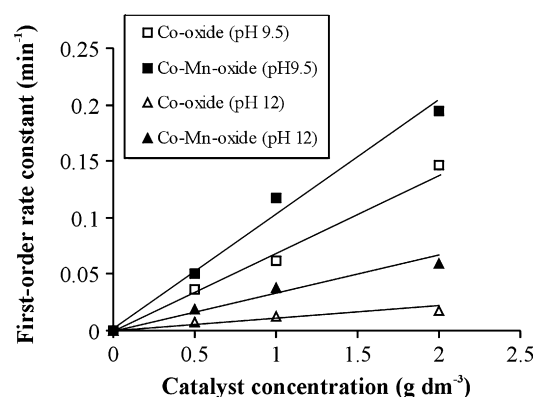


Fig. 5. First-order rate constant as a function of catalyst concentration.

It is evident from the kinetics curves that an exponential line fits the experimental data at all the catalyst loading, regardless of pH of the solution. Obviously, the cyanide catalytic oxidation proceeds according to pseudo-first-order kinetics. The linearity of the $\ln C$ vs. reaction time plots (Fig. 4) confirms the above statements. Under studied conditions the reaction rate becomes independent of the oxygen concentration owing to the fact that all experiments were performed with continuously bubbling air through the liquid phase, thus assuming that the oxygen coverage of the catalyst surface is kept constant throughout the oxidation process.

The influence of both catalyst concentration and pH of the medium on the cyanide conversion efficiency was investigated. From the reactivity data presented in Figs. 2 and 3 it may be noted that the conversion efficiency and the pseudo-first-order rate constant increase notably with catalyst loading, regardless of pH. In fact, at pH 9.5 for Co–Mn-oxide system with $C_{\text{cat}} = 2 \text{ g dm}^{-3}$ about 95% removal efficiency is achieved for 15 min, while with $C_{\text{cat}} = 0.5 \text{ g dm}^{-3}$ the similar conversion degree is achieved even at the 60th minute (Fig. 2). In strong alkaline medium using 2 g dm^{-3} Co-oxide system almost complete conversion of cyanide is attained at the 40th minute, while with $C_{\text{cat}} = 0.5 \text{ g dm}^{-3}$ only 75% of initial cyanide are degraded for the same reaction time. The established linear relationship between the rate constants (calculated from the slopes of the plots $\ln C$ vs. reaction time presented in Fig. 4) and the concentration of the catalysts (Fig. 5), regardless of pH indicates that the reaction is not controlled by external diffusion and moreover that the process runs on the surface of the catalysts.

The rate of cyanide oxidation is also affected by pH of the solution as indicated by the results at pH 9.5 and 12 (Fig. 3). As the pH of the solution increases (with other constant parameters), the cyanide conversion becomes less favourable over both catalytic systems considered. In fact, the calculated pseudo-first-order reaction rate constants for the reaction carried out at pH 9.5 and pH 12 for the individual Co-oxide system ($C_{\text{cat}} = 1 \text{ g dm}^{-3}$) are 0.062 and 0.012 min^{-1} , respectively. The oxidation experiments carried out with doped catalyst ($C_{\text{cat}} = 2 \text{ g dm}^{-3}$) show that increase of the alkalinity of the reaction medium (with other constant parameters) causes a decrease in the rate constant by a factor of 3.2. The reason of the observed lower cyanide degradation rate at high pHs could be due to the unfavourable adsorption of cyanide ions onto the more negative charged surface of oxide systems induced by the adsorption of OH^- ions at high pH.

Experiments performed with the aim of determining the chemical nature of stable intermediates and final products of cyanide oxidation showed that cyanate, CO_2 and N_2 are the products formed in the course of reaction over the studied catalytic samples. At pH 12 and $C_{\text{cat}} = 2 \text{ g dm}^{-3}$ about 83% degree of cyanide conversion is achieved on Co–Mn-oxide within the first 30 min with high selectivity to CO_2 (approx. 75%). Under the same conditions the conversion on Co-oxide system is only 41% and the ratio between the concentration of CNO^- and CO_2 is almost 1:1. It was established that when the oxidation was carried out at pH 9.5 for 2 h a very low concentration of cyanate is detected. The results obtained reveal that after complete degradation of cyanides the determined COD is less than $10 \text{ mg O}_2/\text{L}$, implying that complete oxidation of cyanides is achieved under given conditions as well as that the reaction proceeds according to a consecutive scheme in which cyanide is first oxidized to intermediate product CNO^- , which undergoes further oxidation to form an end product CO_2 .

4. Conclusions

A comparative study on the catalytic properties of individual and modified with Mn Co-oxide systems with respect to liquid-phase oxidation of free cyanides in an alkaline medium shows that

the mixed Co–Mn-catalyst exhibits higher activity in this reaction. The results obtained reveal that catalysts investigated appear to be promising as active phase of environmental catalysts for oxidative destruction of free cyanides in wastewaters. The higher activity of the manganese promoted catalytic sample could be explained on the basis of higher total active oxygen content and its higher mobility both depending on the conditions, under which their synthesis is being carried out.

The effectiveness of the cyanide oxidation process is affected by pH of the solution. As the medium alkalinity increases (with other constant parameters), the cyanide conversion becomes less favourable and the effect is much weaker for Co–Mn-oxide system. At catalyst concentration higher than 1 g/L a high cyanide removal efficiency could be achieved even in strong alkaline medium (pH higher than 12). Thus using manganese promoted oxide system no preliminary correction of pH is necessary. The reaction rate also increases notably with catalyst loading, regardless of pH. At catalyst loading of 2 g/L the maximum cyanide removal efficiency is attained for the reaction time, allowing practical application of the proposed catalytic method for purification of wastewaters containing free cyanides. The basic advantage of this method in comparison with alkaline chlorination—the most common method for treating cyanides is the fact that formation of the highly toxic cyanogen chloride is prevented.

Acknowledgements

Authors gratefully acknowledge the financial support by the National Science Fund at the Ministry of Education and Science of Bulgaria (Project VUX-1105) and from the University of Plovdiv Research Fund (Project 07-X-70).

References

- [1] D.W. Grosse, Treatment technologies for hazardous wastes. 4. A review of alternative treatment processes for metal bearing hazardous-waste streams, *J. Air Pollut. Control Assoc.* 36 (1986) 603–614.
- [2] S.Q. Hassan, M.P. Vitello, M.J. Kupferle, D.W. Grosse, Treatment technology evaluation for aqueous metal and cyanide bearing hazardous wastes (F007), *J. Air Waste Manage.* 41 (1991) 710–715.
- [3] D.A. Kunz, R.F. Fernandez, P. Parab, Evidence that bacterial cyanide oxygenase is a pterin-dependent hydroxylase, *Biochem. Biophys. Res. Commun.* 287 (2001) 514–518.
- [4] C.S. Wang, D.A. Kunz, B.J. Venables, Incorporation of molecular oxygen and water during enzymatic oxidation of cyanide by *Pseudomonas fluorescens* NCIMB 11764, *Appl. Environ. Microbiol.* 62 (1996) 2195–2197.
- [5] M. Futakawa, H. Takahashi, G. Inoue, T. Fujioka, Treatment of concentrated cyanide waste-water, *Desalination* 98 (1994) 345–352.
- [6] N. Costarramone, A. Kneip, A. Castetbon, Ferrate(VI) oxidation of cyanide in water, *Environ. Technol.* 25 (2004) 945–955.
- [7] L. Szpyrkowicz, F. Ricci, S. Daniele, Removal of cyanides by electrooxidation, *Ann. Chim.* 93 (2003) 833–840.
- [8] M.R.V. Lanza, R. Bertazzoli, Cyanide oxidation from wastewater in a flow electrochemical reactor, *Ind. Eng. Chem. Res.* 41 (2002) 22–26.
- [9] J. Lu, D.B. Dreisinger, W.C. Cooper, Anodic oxidation of copper cyanide on graphite anodes in alkaline solution, *J. Appl. Electrochem.* 32 (2002) 1119–1129.
- [10] K. Chiang, R. Amal, T. Tran, Photocatalytic degradation of cyanide using titanium dioxide modified with copper oxide, *Adv. Environ. Res.* 6 (2002) 471–485.
- [11] B. Dabrowski, A. Zaleska, M. Janczarek, J. Hupka, J. Miller, Photo-oxidation of dissolved cyanide using TiO_2 catalyst, *J. Photochem. Photobiol. A: Chem.* 151 (2002) 201–205.
- [12] A. Bozzi, I. Guasaquillo, J. Kiwi, Accelerated removal of cyanides from industrial effluents by supported TiO_2 photo-catalysts, *Appl. Catal. B: Environ.* 51 (2004) 203–211.
- [13] A. Alicilar, M. Komurcu, M. Guru, The removal of cyanides from water by catalytic air oxidation in a fixed bed reactor, *Chem. Eng. Process.* 41 (2002) 525–529.
- [14] B. Basu, S. Satapathy, A.K. Bhatnagar, Merox and related metal phthalocyanine catalyzed oxidation processes, *Catal. Rev. Sci. Eng.* 35 (1993) 571–609.
- [15] L.P. Salomonson, in: B. Vennesland, E. Conn, F. Wissing (Eds.), *Cyanide in Biology*, Academic Press, New York, 1981.
- [16] Y. Malatov-Meytal, M. Sheintuch, Catalytic abatement of water pollutants, *Ind. Eng. Chem. Res.* 37 (1998) 309–326.

- [17] M. Kitis, E. Karakaya, N.O. Yigita, G. Civelekoglu, A. Akcil, Heterogeneous catalytic degradation of cyanide using copper-impregnated pumice and hydrogen peroxide, *Water Res.* 39 (2005) 1652–1662.
- [18] M. Stoyanova, St. Christoskova, M. Georgieva, Aqueous phase catalytic oxidation of cyanides over iron-modified cobalt oxide system, *Appl. Catal. A: Gen.* 274 (2004) 133–138.
- [19] St. Christoskova, M. Stoyanova, M. Georgieva, D. Mehandjiev, Preparation and characterization of a higher Co-oxide, *Mater. Chem. Phys.* 60 (1999) 39–43.
- [20] K. Nakagava, R. Konaka, T. Nakata, Oxidation with nickel peroxide. I. Oxidation of alcohols, *J. Org. Chem.* 27 (1962) 1597–1601.
- [21] S.B. Kanungo, Physicochemical properties of MnO_2 -CuO and their relationship with the catalytic activity for H_2O_2 decomposition and CO oxidation, *J. Catal.* 58 (1979) 419–435.
- [22] M. Guilloton, K. Karst, A spectrophotometric determination of cyanate using reaction with 2-aminobenzoic acid, *Anal. Biochem.* 149 (1985) 291–295.
- [23] A. Bielanski, J. Haber, *Oxygen in Catalysis*, Marcel Dekker Inc., New York, 1991.
- [24] W. Wang, M. Qiao, H. Li, W. Dai, J. Deng, Study on the deactivation of amorphous NiB/SiO₂ catalyst during the selective hydrogenation of cyclopentadiene to cyclopentene, *Appl. Catal. A: Gen.* 168 (1998) 151–157.
- [25] A. Davidov, IR Spectroscopy in The Chemistry of Oxide's Surface, Khimia, Novosibirsk, 1984.