ELSEVIER

Catalysis Today 75 (2002) 219–225

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Detoxication of water containing 1,1-dimethylhydrazine by catalytic oxidation with dioxygen and hydrogen peroxide over Cu- and Fe-containing catalysts

Oxana P. Pestunova*, Galina L. Elizarova, Zinfer R. Ismagilov, Mikhail A. Kerzhentsev, Valentin N. Parmon

Boreskov Institute of Catalysis, Prosp. Akad. Lavrentieva 5, Novosibirsk 630090, Russia

Abstract

A number of Cu- and Fe-hydroxide containing catalysts, supported on oxide carriers, were prepared to provide the removal of 1,1-dimethylhydrazine from aqueous solutions via its oxidation by hydrogen peroxide and air oxygen. The Cu-containing samples as well as Fe/ZSM-5 are the most active catalysts in this reaction. The reaction products were analyzed by gas chromatography and UV–Vis spectroscopy. The effect of nature of the oxidizer and catalyst, pH and temperature on both the reaction rate and product composition was studied. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: 1,1-Dimethylhydrazine; Hydrogen peroxide; Catalyst; Oxidation; Wastewater treatment

1. Introduction

For the last decade, neutralization of highly toxic propellants in waste waters and spills has become a problem of great concern. 1,1-Dimethylhydrazine (unsymmetrical dimethylhydrazine, UDMH), which is the main propellant for space rockets and missiles, is a highly toxic substance whose maximum allowable concentration in water is 0.01 ppm. Unfortunately, to date there were no methods providing an efficient removal of UDMH from diluted aqueous solutions. At the UDMH detoxication via direct oxidation with Cl-containing oxidants, radiolysis, etc., the main problem is a lot of parallel oxidation processes, involving participation of free radicals. This results in the transformation of ca. 10% of UDMH into 1,1-dimethylnitrosoamine (DMNA). The latter is more stable and toxic than UDMH.

In our recent works we proposed to use Cu, Fe, Mn and Co hydroxides of transition metals as catalysts for oxidation of UDMH with air oxygen [1,2] and hydrogen peroxide [3] in aqueous solutions. In the present study we investigated more closely the influence of both the oxidant and catalyst nature, as well as of reaction pH (7–11) and temperature (298–348 K) on the rate of UDMH oxidation and yields of the main products.

2. Experimental

2.1. Catalyst preparation

In this study, Cu- and Fe-hydroxide compounds supported on SiO_2, TiO_2, Al_2O_3 or NaX, NaA and ZSM-5 zeolites as well as bulk iron oxide α-Fe_2O_3 were used as catalysts. The active metal content was not higher than 2 wt.% for supported catalysts.

---

* Corresponding author. Tel.: +7-3832-342563;
fax: +7-3832-343056.
E-mail address: oxanap@catalysis.nsk.su (O.P. Pestunova).

PII: S0920-5861(02)00072-X

We used commercial SiO_2 ($S_{BET} = 300\,m^2\,g^{-1}$), TiO_2 ($10\,m^2\,g^{-1}$) and zeolites NaX ($600\,m^2\,g^{-1}$), NaA ($400\,m^2\,g^{-1}$) and ZSM-5 ($280\,m^2\,g^{-1}$). α-Al_2O_3 ($S_{BET} = 10\,m^2\,g^{-1}$) and γ-Al_2O_3 ($230\,m^2\,g^{-1}$) were prepared at the Boreskov Institute of Catalysis [4]. To prepare the supported catalysts, NaOH was added to suspension of a carrier in aqueous solutions of either nitrate or chloride of the active metal. After that the suspension was vigorously stirred to attain pH 7–8 [5,6]. The procedure provides the rapid quantitative deposition of hydroxide on the support. The catalyst was dried and calcinated at 573 K. α-Fe_2O_3 was prepared from commercial Fe_3O_4 by heating at 573 K in air for 4 h [7].

2.2. Catalysts testing

UDMH was oxidized in a batch reactor with a reflux condenser at atmospheric pressure, various pH and temperatures ranging from 298 to 323 K. The solutions to be oxidized contained 1.5 wt.% ($0.25\,mol\,l^{-1}$) of UDMH. Hydrogen peroxide in concentration ranging from 1.6 to 6.8 wt.% (0.5–$1\,mol\,l^{-1}$) or air oxygen were used as the oxidizers. A known reaction between UDMH and formaldehyde was used for the spectrophotometric analysis of UDMH [1]. The final solutions were analyzed with a Kristall-2000M gas–liquid chromatograph (Russia) equipped with a flame ionization detector and a stainless steel column $1.5\,m \times 2\,mm$ with Hayesep C modified with 1% KOH. To monitor the reaction products by absorption in the UV–Vis region, a Shimadzu UV-300 (Japan) spectrometer was used. The absorption bands were identified basing on data from literature sources. Also a number of probable products were prepared and their spectra were recorded.

The concentrations of Cu and Fe in solution after reaction were determined using standard spectrophotometric methods with biquinoline and phenantroline [8], respectively.

3. Results and discussion

3.1. The influence of the reaction conditions on the rate and selectivity of the UDMH oxidation

Table 1 presents the half-time of the UDMH conversion in the presence of different catalysts. The half-times of the UDMH oxidation without catalysts are more than 24 h if air is used as the oxidizer and about 600 min if hydrogen peroxide is used. Thus all tested catalysts are active at the oxidation of 1,1-dimethylhydrazine with oxygen and hydrogen peroxide, but their activities are different. Note that the reaction rate is much lower if air is used as the oxidizer (compare nos. 1 and 2, and 9 and 10). According to Table 1, the sample 2% Cu/SiO_2 (nos. 1 and 2) is the most active catalyst, and all other Cu-containing catalysts have nearly the same activity. In contrast to the Cu-containing catalysts, the Fe-based catalysts are less active. However, the Fe-based catalysts are more environmentally benign. The Fe-containing catalysts based on ZSM-5 and NaA (Table 1, nos. 14–16) exhibit the highest activity. The initial zeolite ZSM-5 contains 0.55 wt.% of iron and it is also active in the UDMH oxidation. It should be noted that the bulk iron oxide α-Fe_2O_3 is less active than the supported iron catalysts, though the concentration of the active component in it is much higher (Table 1, no. 11).

The active metal leaching measured at basic pH is negligible—less than 0.5%. As pH is raised to 7, iron leaching remains insignificant, while that of copper increases up to 30%. Therefore, it can be concluded that the contribution of homogeneous catalysis is negligible when Fe-containing catalysts are used, but it is possible with Cu-containing catalysts at pH 7.

Undoubtedly, the support essentially affects the catalyst activity. However, its influence is not directly related to the support surface area. Thus, the catalysts based on α-Al_2O_3 and γ-Al_2O_3 (nos. 3, 4 and 12, 13) have almost equal activity, in spite of a great difference in their surface areas S_{BET} (10 and $230\,m^2\,g^{-1}$, respectively). On the other hand, the catalysts 2% Fe/ZSM-5 and 2% Fe/SiO_2 have approximately equal specific surface areas of supports but they essentially differ in their catalytic activity.

Table 1 suggests that pH of the UDMH solutions does not significantly affect the rate of the UDMH oxidation and influences mostly the amount and composition of the oxidation products. The composition and yields of the intermediate reaction products, which are detected by UV–Vis spectroscopy, depend significantly on pH. Fig. 1 shows the evolution of UV–Vis spectra of the UDMH solutions during the oxidation with H_2O_2. Thus, in the neutral medium, formaldehyde 1,1-dimethylhydrazone

Table 1
Half-times of the 1,1-dimethylhydrazine decomposition ($\tau_{1/2}$) in the presence of various catalysts[a]

No.	Catalysts	Oxidizer	pH	Catalyst load (g)	$\tau_{1/2}$ (min)
1	2% Cu/SiO_2	Air	7	0.5	81
		Air	9	0.5	88
2	2% Cu/SiO_2	H_2O_2	7	0.25	1
		H_2O_2	9	0.25	1
3	2% $Cu/\alpha\text{-}Al_2O_3$	H_2O_2	7	0.25	4
4	2% $Cu/\gamma\text{-}Al_2O_3$	H_2O_2	7	0.25	2
5	2% Cu/TiO_2	H_2O_2	7	0.25	4
6	2% Cu/zeolite (NaA)	H_2O_2	7	0.25	4
7	2% Cu/zeolite (NaX)	H_2O_2	7	0.25	6
8	1% Cu/zeolite (ZSM-5[b])	H_2O_2	7	0.25	4
9	2% Fe/SiO_2	Air	7	1.5	110
		Air	9	1.5	>300
10	2% Fe/SiO_2	H_2O_2	7	1	120
		H_2O_2	9	1	28
11	$\alpha\text{-}Fe_2O_3$	H_2O_2	7	1	38
		H_2O_2	9	1	25
12	2% $Fe/\alpha\text{-}Al_2O_3$	H_2O_2	9	1	31
13	2% $Fe/\gamma\text{-}Al_2O_3$	H_2O_2	7	1	25
		H_2O_2	9	1	24
14	2% Fe/ZSM-5[b]	H_2O_2	7	1	3
		H_2O_2	9	1	6
15	1% Fe/ZSM-5[b]	H_2O_2	9	1	3
16	2% Fe/NaA	H_2O_2	7	1	6
		H_2O_2	9	1	16
17	ZSM-5[b]	H_2O_2	9	1	5

[a] Reaction conditions: $T = 297\,K$; $[UDMH] = 0.25\,mol\,l^{-1}$; $[H_2O_2] = 0.4\,mol\,l^{-1}$.

[b] Zeolite ZSM-5 contains 0.55 wt.% of iron.

and sym-tetrazine were the intermediate products (Fig. 1, curve a), with absorption bands at 235 and 500 nm, respectively. The intensity of these absorption bands increases initially during the reaction and then decrease. The spectrum of the final solution exhibits only the absorption band of the cation of 1,1,5,5-tetramethylformazanium (360 nm) (Fig. 1, curve b). For pH 9–11, the following intermediate products are observed: formaldehyde monomethylhydrazone (235 nm), 1,1,4,4-tetramethyltetrazene (280 nm), sym-tetrazine (500 nm) (Fig. 1, curve c). At the reaction completion, the absorption bands of 1,1,5-trimethylformazane (320 nm) and DMNA (230 nm) are observed (Fig. 1, curve d). If oxygen provides the oxidation at ambient temperature, the evolution of the spectra is approximately the same, but at pH 7 the yield of the cation of 1,1,5,5-tetramethylformazane (360 nm) is smaller, and sym-tetrazine (500 nm) is not observed.

Table 2 presents the yields of the main final products of the UDMH oxidation detected by gas chromatography for a number of catalysts under different reaction conditions. At 348 K, the rate of the UDMH oxidation with hydrogen peroxide is rather high even in the absence of a catalyst. In this case, more than 10 products are simultaneously formed irrespective of the solution pH. DMNA and dimethylformamide (DMFA) are the main products (see Table 2; nos. 1 and 2). For pH 9–11, the catalytic oxidation with oxygen and hydrogen peroxide yields 10–15% of DMNA (Table 2; nos. 4, 6 and 11).

If the catalytic oxidation with hydrogen peroxide is performed at pH 7 and lower, the yields of DMNA are from 0.1 to 3% (Table 2). At ambient temperature, the main product is the 1,1,5,5-tetramethylformazanium cation (∼20–30%), which is not toxic (Table 2; nos. 5, 8 and 12). At 348 K, the yield of the tetramethylformazanium cation significantly decreases while the

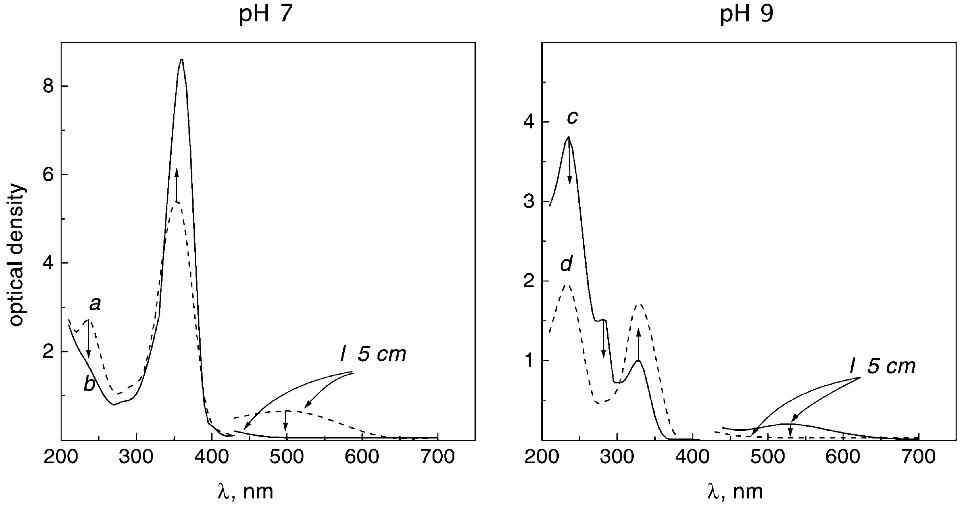

Fig. 1. Time evolution of the UV–Vis absorption spectra of the UDMH solutions during the oxidation with H_2O_2. Catalyst: 0.2 g 2% Cu/SiO_2; [UDMH] $= 0.25\,mol\,l^{-1}$; $[H_2O_2] = 1\,mol\,l^{-1}$. The spectra are recorded at the 100-fold dilution, optical length = 1 cm. (a) pH 7, 1 min; (b) pH 7, 60 min; (c) pH 9, 1 min; (d) pH 9, 60 min.

yield of methanol increases (Table 2, nos. 3 and 10). For the ZSM-5 based catalysts, the final solution contains less amount of the reaction products (Table 2, nos. 8 and 13). That can be probably associated with the higher activity of these catalysts in comparison with the other ones. A two-fold increase in the initial concentration of hydrogen peroxide does not result in a considerable decrease in the product yield. This is probably associated with the fact that the major part of hydrogen peroxide is consumed for the side

Table 2
The main products of the UDMH oxidation without catalysts and in the presence of the Cu- and Fe-containing catalysts

No.	Catalyst	Oxidizer	T (K)	pH	Products yield (%)			
					CH_3OH	DMNA[a]	DMFA[a]	F^+ or F^0[b]
1	None	H_2O_2	348	7	16	4	4	6
2	None	H_2O_2	348	9	7	13	3	4
3	2% Cu/SiO_2	H_2O_2	348	7	10	0.7	2	0.4
4	2% Cu/SiO_2	H_2O_2	348	9	3	13	6	0.1
5	2% Cu/SiO_2	H_2O_2	298	7	1	0.9	6	31
6	2% Cu/SiO_2	H_2O_2	298	9	3	10	13	11
7	2% Cu/SiO_2	Air	298	7	1	0.03	0.04	30
8	1% Cu/ZSM-5	H_2O_2	298	7	3	0.4	1.8	18
9[c]	1% Cu/ZSM-5	H_2O_2	298	7	2.3	0.1	0.01	0.2
10	2% Fe/α-Al_2O_3	H_2O_2	348	7	11	3	None	16
11	2% Fe/α-Al_2O_3	H_2O_2	348	9	4	12	None	10
12	2% Fe/α-Al_2O_3	H_2O_2	298	7	4	2	None	25
13	1% Fe/ZSM-5	H_2O_2	298	7	1.3	1	1.1	0.2
14[c]	1% Fe/ZSM-5	H_2O_2	298	7	3.6	0.3	0.8	0.1
15	1% Fe/ZSM-5	Air	298	7	3.2	0.07	None	1

[a] DMNA: dimethylnitrosoamine, DMFA: dimethylformamide.

[b] F^+: 1,1,5,5-tetramethylformazanium cation (under pH 7), F^0: 1,1,5-trimethylformazane (under pH 9).

[c] New portion of the H_2O_2 was added when UDMH had been consumed.

reaction of its catalytic decomposition. However, if a fresh portion of hydrogen peroxide is added to the final solution, the reaction product concentration decreases (nos. 9 and 14). Particularly remarkable is the decrease in the concentrations of formazane and DMFA, which is undoubtedly associated with their easy oxidation.

If oxygen provides the oxidation at ambient temperature in the presence of Cu-containing catalysts, the main product is the 1,1,5,5-tetramethylformazanium cation, which is not toxic. The yields of DMNA, DMFA and methanol are, respectively, 0.03, 0.04 and 1% (Table 2, no. 7). We found much less final product 1,1,5,5-tetramethylformazanium cation with Fe-containing catalysts (Table 2, no. 15), but the rate of the UDMH oxidation was much slower.

In the gas phase, methane and nitrogen were detected in the all cases.

3.2. The proposed mechanism of the UDMH oxidation

Production of the tetramethylformazanium cation from 1,1-dimethylhydrazine using a copper(II) halogenide as an oxidizer in acid solutions was described elsewhere [9]. We propose the following mechanism of the UDMH oxidation at pH 7: UDMH interacts with the copper(II) (iron(III)) cations of the hydroxide catalyst to yield copper(I) (iron(II)) and a tetramethylformazanium cation; then low-valent copper (Fe) is re-oxidized with air oxygen (hydrogen peroxide) to give the high valent state:

$$5(CH_3)_2NNH_2+16\,Cu_{hydr}{}^{2+}\rightarrow 2(CH_3)_2NN{=}CH{-}N{=}N(CH_3)_2{}^{+}+N_2+16\,Cu_{hydr}{}^{+}+14H^{+}$$

$$\underline{16Cu_{hydr}{}^{+}+4O_2+16H^{+}\rightarrow 16Cu_{hydr}{}^{2+}+8H_2O}$$

$$5(CH_3)_2NNH_2+4O_2+2H^{+}\rightarrow 2(CH_3)_2NN{=}CH{-}N{=}N(CH_3)_2{}^{+}+N_2+8\,H_2O$$

Note, that the complex tetramethylformazanium cation cannot be formed in one step. We propose that this cation is formed through formaldehyde dimethylhydrazone, since the concentration of the latter increases and then decreases in the course of the reaction (as evidenced by spectrophotometric measurements). Formaldehyde dimethylhydrazone interacts with UDMH in the presence of catalysts, as we observed in Ref. [1], to produce a cation of tetramethylformazanium:

$$(CH_3)_2NNH_2+(CH_3)_2NN{=}CH_2+O_2+H^{+}\overset{cat}{\rightarrow}(CH_3)_2NN{=}CH{-}N{=}N(CH_3)_2{}^{+}+2H_2O$$

Formaldehyde dimethylhydrazone can result from the reaction between UDMH and formaldehyde:

$$3(CH_3)_2NNH_2+CH_2O\rightarrow (CH_3)_2NN{=}CH_2+H_2O$$

One may assume that formaldehyde is formed by the oxidation of some part of UDMH via the reaction:

$$(CH_3)_2NNH_2+2O_2\rightarrow 2CH_2O+N_2+2H_2O$$

Both in alkaline and neutral media, the oxidation of UDMH starts from its interaction with the metal ions on the catalyst surface to produce low-valent metal. However, the reaction of the copper(I) (or Fe(II)) re-oxidation slows down in the alkaline medium because of a deficiency of protons, but Cu(I) (or Fe(II)) can interact under these conditions with oxygen or hydrogen peroxide in the hydroxide polymer to yield a peroxide complex. A molecule of UDMH may be coordinated at the same active center. Then the coordinated oxygen is transferred to the UDMH molecule to form 1,1-dimethylhydrazine hydroperoxide (Fig. 2, reaction 1) [10,11]. Hydrazine hydroperoxide can convert into dimethyldiazene (Fig. 2, reaction 2) or *N*,*N*-DMNA (Fig. 2, reaction 3) [10,11].

Dimethyldiazene is known to be a highly active compound with the propensity for different transformations such as decomposition to hydrocarbons and nitrogen, isomerization to formaldehyde monomethylhydrazone (reaction 4), and dimerization yielding 1,1,4,4-tetramethyltetrazene (reaction 5) [11]. The appearance of tetrazenes in the reaction mixture proves that unsymmetrical hydrazines are oxidized to diazenes acting as intermediates [11].

In its turn, formaldehyde monomethylhydrazone may be subjected to the oxidative coupling with UDMH in the presence of the catalyst to yield 1,1,5-trimethylformazane (reaction 6) [1].

In the alkaline medium, formaldehyde monomethylhydrazone can be also dimerized to 1,4-dimethylhexahydrotetrazine (reaction 7), which may be further oxidized to sym-tetrazine (reaction 8) [12].

According to the literature data, 1,1-dimethylhydrazine can be also subjected to a number of other

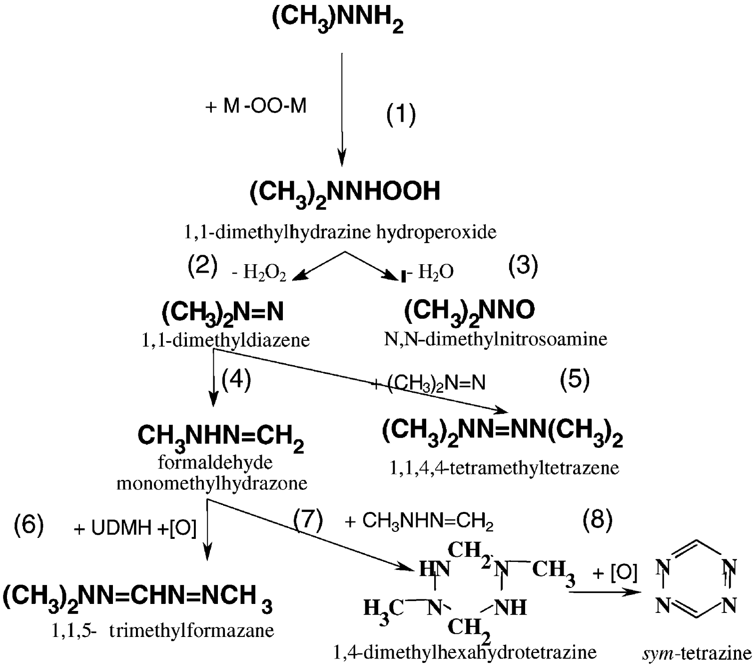

Fig. 2. Possible pathways of the products formation under catalytic UDMH oxidation in alkaline media.

transformations. Thus, ethanol, dimethyl ether [13] and gaseous hydrocarbons [14] were observed in the products of its non-catalytic and catalytic oxidation at pH 9–11.

4. Conclusion

The experimental results give evidence that UDMH can be efficiently oxidized in aqueous solutions both by hydrogen peroxide and oxygen in the presence of metal hydroxide catalysts. The process can proceed via different mechanisms depending on the pH of the solution. In the neutral medium the non-toxic 1,1,5,5-tetramethylformazanium cation is predominantly formed (up to 30% yield), further decomposing to other products with low toxicity. In the alkaline medium the reaction is not selective. In this case toxic and stable products, such as DMNA and DMFA are formed with rather high yields (up to 15%).

It is shown that iron-containing catalysts are more resistant to the action of the reaction medium because during the UDMH oxidation less than 0.5% of the active metal are washed from the catalyst, whereas in the course of Cu-containing catalysts up to 30% of copper can be leached from the catalyst at pH 7.

Thus, the detoxication of aqueous UDMH solutions should be carried out in neutral media in the presence of iron-containing catalysts.

This process will be used for UDMH removal from the scrubbing liquids in the technology for UDMH oxidative destruction in a fluidized bed of catalyst followed by the off gas treatment system, developed under project #959 of the International Science and Technology Center (ISTC).

Acknowledgements

The financial support of this study by the ISTC under project #959 is gratefully acknowledged.

References

[1] G.L. Elizarova, L.G. Matvienko, O.P. Pestunova, et al., Kinet. Catal. 39 (1998) 44.
[2] Russian Federation Patent No. 2 063 385 (1998).

[3] O.P. Pestunova, G.L. Elizarova, V.N. Parmon, Russ. J. Appl. Chem. 72 (1999) 1209.

[4] R.A. Shkrabina, Yu.K. Vorob’ev, E.A. Moroz, et al., Kinet. Catal. 22 (1981) 332.

[5] G.L. Elizarova, L.G. Matvienko, V.L. Kuznetsov, et al., J. Mol. Catal. 103 (1995) 43.

[6] G.L. Elizarova, L.G. Matvienko, O.L. Ogorodnikova, V.N. Parmon, Kinet. Catal. 41 (2000) 332.

[7] C.M. Flynn, Chem. Rev. 84 (1984) 31.

[8] G. Charlot, Methods of Analytical Chemistry, Khimiya, Leningrad, 1965 (in Russian).

[9] J.R. Boehm, A.L. Balch, K.F. Bizot, et al., J. Am. Chem. Soc. 97 (1975) 501.

[10] M.A. Mathur, H.H. Sisler, Inorg. Chem. 20 (1981) 426.

[11] B.V. Ioffe, M.A. Kuznetsov, A.A. Potekhin, Chemistry of Organic Derivates of Hydrazine, Khimiya, Leningrad, 1979 (in Russian).

[12] W.M. Tolles, W.R. McBride, W.E. Thun, J. Am. Chem. Soc. 91 (1969) 2443.

[13] Germany Patent No. 1 517 654 (1973).

[14] E.V. Schmidt, Hydrazine and Its Derivatives, Wiley, New York, 1984, p. 340.