ELSEVIER

Catalysis Today 75 (2002) 277–285

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Oxidation of unsymmetrical dimethylhydrazine over heterogeneous catalysts

Solution of environmental problems of production, storage and disposal of highly toxic rocket fuels

Z.R. Ismagilov[a,*], M.A. Kerzhentsev[a], I.Z. Ismagilov[a], V.A. Sazonov[a], V.N. Parmon[a], G.L. Elizarova[a], O.P. Pestunova[a], V.A. Shandakov[b], Yu.L. Zuev[c], V.N. Eryomin[c], N.V. Pestereva[c], F. Garin[d], H.J. Veringa[e]

[a] *Boreskov Institute of Catalysis, Prospekt Akademika Lavrentieva 5, Novosibirsk 630090, Russia*
[b] *Federal Research and Production Center "Altai", Biysk 659322, Russia*
[c] *State Rocket Center "Academician V.P. Makeyev Design Bureau", Miass 456300, Russia*
[d] *Louis Pasteur University, Strasbourg 67070, France*
[e] *Netherlands Energy Research Foundation (ECN), Petten 1755ZG, The Netherlands*

Abstract

The catalytic oxidation of unsymmetrical dimethylhydrazine (UDMH) by air has been studied in a vibro-fluidized catalyst bed laboratory kinetic setup over catalysts $Cu_xMg_{1-x}Cr_2O_4/\gamma\text{-}Al_2O_3$, 32.9%$Ir/\gamma\text{-}Al_2O_3$ and $\beta\text{-}Si_3N_4$ in a temperature range 150–400 °C. The catalyst $Cu_xMg_{1-x}Cr_2O_4/\gamma\text{-}Al_2O_3$ was found to be optimal regarding high yields of CO_2 and low yields of NO_x. A probable mechanism of UDMH heterogeneous catalytic oxidation is proposed. Catalyst $Cu_xMg_{1-x}Cr_2O_4/\gamma\text{-}Al_2O_3$ has been further used in the pilot plant specially designed for the destruction of UDMH. Results of testing the main fluidized bed catalytic reactor for UDMH oxidation and the reactor for selective catalytic reduction of NO_x with NH_3 are presented. These results prove that the developed UDMH destruction technology is highly efficient and environmentally safe. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Rocket fuels; Unsymmetrical dimethylhydrazine; Catalytic oxidation; Oxide catalysts; Noble metal catalysts; Nitride catalysts; Fluidized bed reactor; NO_x reduction

---

1. Introduction

Reduction and conversion of the weapons production in Russia have made extremely topical finding solution of the problems of development and implementation of environmentally safe and efficient processes for the disposal of rocket fuel components (RFCs). One of the most pressing problems is development of the destruction process for extremely toxic 1,1-dimethylhydrazine $(CH_3)_2N\text{–}NH_2$ (unsymmetrical dimethylhydrazine-UDMH, technical name-"heptyl"). There are no industrial facilities for the UDMH treatment in Russia and CIS, as well as no reliable treatment technologies that meet economical and environmental requirements. Therefore, the solution of the problems of destruction of the sub-standard UDMH and other RFCs, industrial wastes containing RFC, spills of RFC on soil, etc., is a very urgent task.

---

[*] Corresponding author. Tel.: +7-3832-341219; fax: +7-3832-397352.
E-mail address: zri@catalysis.nsk.su (Z.R. Ismagilov).

PII: S0920-5861(02)00080-9

Conventional thermal methods of the RFC destruction, such as the incineration in flame and the plasma method, consume much energy and lead to the formation of large amounts of secondary pollutants. The need of additional purification of the exhaust gas from NO_x and other pollutants makes these methods complicated for practical application.

Methods of processing UDMH and other toxic RFCs into useful products are not yet promoted to the state of industrial application, and cannot solve the problem of UDMH utilization due to the lack of interest of enterprises to work with such flammable and toxic chemicals.

At the same time, the problem of UDMH destruction can be solved by creation of a treatment plant based on UDMH oxidation in a fluidized catalyst bed reactor [1,2]. The unique feature of this method is the possibility of flameless total oxidation of organic compounds in a near stoichiometric ratio with oxygen at relatively low temperatures (500–750 °C), which suppresses the formation of “thermal” and “fuel” nitrogen oxides. This is achieved by the use of highly active catalysts in a fluidized bed, having rather high heat transfer coefficients and providing an efficient removal of reaction heat. Pilot and industrial plant tests on the combustion and processing of different types of organic wastes have shown high efficiency and environmental safety of this technology [1–6].

An important advantage of the catalytic fluidized bed waste destruction technology is a small size of the apparatus. A compact installation designed as a mobile unit will allow treatment of UDMH at distant locations, Navy bases, etc., and thus will exclude hazardous (and sometimes impossible) transportation of rockets or RFC to the centralized treatment facilities.

2. Experimental

In order to select the optimal catalyst and process parameters for UDMH catalytic oxidation, the experiments were first conducted in the laboratory setup, and then technology was tested in the pilot plant.

2.1. Laboratory setup

The laboratory setup for the study of UDMH catalytic oxidation reaction consists of the following principal units: systems of compressed gas (N_2 as a UDMH carrier, air as an oxidizer) and UDMH supply, a flow mixer for combining the air flow with the flow of N_2 saturated with UDMH vapor, a gradientless quartz catalytic reactor with a vibro-fluidized catalyst bed, and a system for the reaction mixture analysis based on a gas chromatograph Kristall 2000M. Separation and analysis of UDMH and organic reaction products were carried out in a Teflon column (1.5 m long, 2 mm in diameter) with a polymer sorbent HayeSep C modified by 5% KOH, using FID and He as carrier gas (30 ml/min) at a temperature of 155 °C. Air, CO_2 and N_2O were separated and analyzed in a stainless steel column (1.5 m long, 3 mm in diameter) with a carbon sorbent SKT, using TCD and He as carrier gas (30 ml/min) at a temperature of 155 °C. An ECOM SG Plus automatic gas analyzer was used to measure $C(NO)$ and $C(NO_2)$.

The experiments in the reactor with vibro-fluidized catalyst bed can be conducted under the following conditions: catalyst temperature, 20–500 °C; C(UDMH) in the initial reaction mixture, 0.1–2 mmol/l (0.2–4 vol.%); reaction mixture flow rate, 10–100 l/h; catalyst loading, 0.1–2 cm^3; reaction mixture space velocity, 5000–72 000 h^{-1}.

Characteristics of the catalysts used in the laboratory UDMH oxidation experiments are given in Table 1. Catalysts $Cu_xMg_{1-x}Cr_2O_4/\gamma\text{-}Al_2O_3$ and $32.9\%Ir/\gamma\text{-}Al_2O_3$ were developed at the Boreskov Institute of Catalysis (BIC) and prepared using the method of $\gamma\text{-}Al_2O_3$ spherical support wet impregnation with metal salts, followed by drying and calcination. The catalyst $\beta\text{-}Si_3N_4$ was received from the V.N. Bakul’ Institute of Superhard Materials (Kiev, Ukraine) as a monolith support, and a part of it was crushed and sieved to obtain granules.

2.2. Pilot plant

The schematic diagram of a pilot plant for fluidized bed UDMH destruction is shown in Fig. 1. The mixture to be treated (e.g. mixture of water and UDMH, or sub-standard UDMH) is supplied from the tank (10) to the catalytic fluidized bed reactor (1). Compressed air is fed to the reactor in a quantity necessary for the complete oxidation of UDMH in the catalyst bed at 500–700 °C. The electric heater, nichrome wire coiling around the reactor wall, is used for pre-heating

Table 1
Characteristics of the catalysts used in the laboratory experiments on UDMH oxidation

Catalyst	Active components loading (wt.%)	S_{BET} ($m^2\,g^{-1}$)	Bulk density ($g\,cm^{-3}$)	Average mechanical strength (MPa)	Granule size (mm)
$Cu_xMg_{1-x}Cr_2O_4/\gamma$-$Al_2O_3$	Cr_2O_3-17.0; MgO-3.6; CuO-1.7	130	1.1	49	0.25–0.5
32.9%Ir/γ-Al_2O_3	Ir-32.9	–	0.9	–	0.5–1.0
β-Si_3N_4	Si_3N_4-100	0.4	1.0	26	0.5–1.0

the catalyst bed in order to start the process of catalytic oxidation. Gas leaving the reactor may contain small quantities of nitrogen oxides (NO and NO_2), trace amount of unreacted UDMH, and solid particles of variable size resulting from the catalyst attrition and the mineral part of treated wastes. Gas temperature at the reactor outlet is lowered to 350–500 °C using the heat exchanger immersed in the catalyst bed. From the reactor, the gas enters the cyclone (3), where large particles of the size >30 μm are separated and the gas temperature is decreased to 250–350 °C.

At the second stage, the gas passes through the reactor with two monolith catalysts (4), the first one used for the selective catalytic reduction (SCR) of nitrogen oxides with ammonia, and the second one-for the oxidation (afterburning) of excess NH_3 and residual UDMH in the gas stream (for simplicity, we will term this unit as "SCR reactor"). For the further gas purification from UDMH and medium-size particles (3–30 μm), a foam jet scrubber No. 1 (5) is used, which acts both as a gas and particle trap, and as a regenerative heat exchanger. In this apparatus, a highly turbulent foam layer with a constantly refreshed surface provides the separation of medium-size particles and toxic admixtures from the gas, with concomitant gas cooling to 70–90 °C. For further treatment, the gas

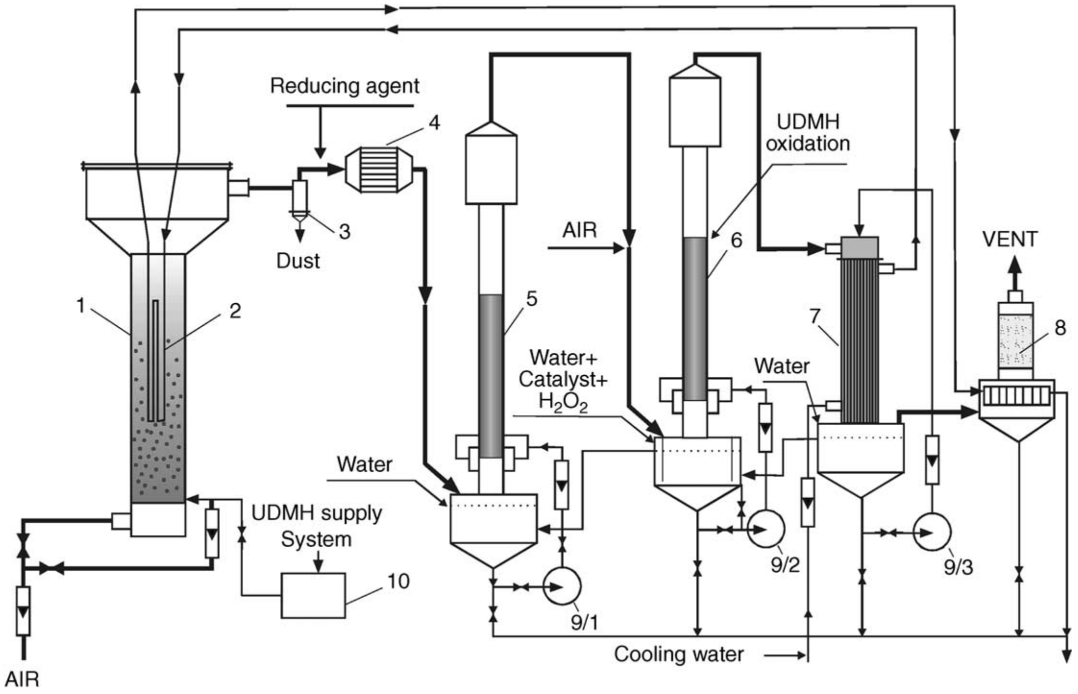

Fig. 1. Scheme of the pilot plant for the process of UDMH catalytic destruction: 1—catalytic-fluidized bed reactor; 2—water heat exchanger; 3—cyclone; 4—SCR reactor; 5 and 6—jet scrubbers; 7—absorber-condenser; 8—aerosol filter; 9—pumps; 10—tank for UDMH.

is directed to the jet scrubber No. 2 (6), where the complete destruction of UDMH traces is conducted over powder catalysts for the liquid-phase UDMH oxidation, which are added to the scrubber liquid [7]. If necessary, additional air or hydrogen peroxide can be fed into this scrubber.

Then the gas saturated with water vapor enters the absorber-condenser (7), where its purification from the small-size particles (0.1–3 μm) takes place with the final removal of the trace amounts of UDMH and the gas cooling to 30–40 °C. UDMH accumulated in the absorber-condenser will be oxidized in the scrubber liquid using the above-mentioned liquid-phase catalysts.

The fluidized bed reactor was loaded with the catalyst $Cu_xMg_{1-x}Cr_2O_4/\gamma\text{-}Al_2O_3$ (6 dm^3) in the form of spherical 1.4–2.0 mm granules. The SCR catalyst was prepared using the oxide-containing paste extrusion technique, while the afterburning catalyst was prepared using the technique of aluminosilicate support wet impregnation with metal salts, both finished by monolith drying and calcination. These two catalysts have the following characteristics: active component loadings (wt.%)-$Fe_2O_3 + Cr_2O_3 + ZnO$ (total of 30–50) and CuO 1.89, Co_3O_4 1.87, Cr_2O_3 6.74; S_{BET} ($m^2\,g^{-1}$)-20 and 14; channel size (mm^2)-4 × 4 and 2 × 2; wall thickness (mm)-0.8–1.2 and 0.3; catalyst volume loaded in the SCR reactor (dm^3)-10 and 5.

3. Results and discussion

3.1. Catalytic oxidation of UDMH in the laboratory setup

The first series of experiments were carried out using the $Cu_xMg_{1-x}Cr_2O_4/\gamma\text{-}Al_2O_3$ catalyst, which was specially developed for catalytic combustion in the fluidized bed reactors. In the temperature range 200–300 °C, in addition to the products of deep UDMH oxidation (CO_2, H_2O, N_2), 14 peaks corresponding to various partial oxidation products were revealed on the FID gas chromatograms. A typical example of the GC analysis of UDMH oxidation products formed over the $Cu_xMg_{1-x}Cr_2O_4/\gamma\text{-}Al_2O_3$ catalyst at 270 °C is given in Fig. 2. The main compounds identified are: methane CH_4 (17 s), dimethylamine $(CH_3)_2NH$-DMA (2 min 40 s), formaldehyde dimethylhydrazone $(CH_3)_2N{-}N{=}CH_2$ (alias methylenedimethylhydrazine-MDMH) (10 min 16 s), residual UDMH (8 min 25 s). The remaining peaks correspond to small quantities of ethane, methanol, formaldehyde and traces of other organic compounds present among the products.

The temperature dependence of UDMH oxidation products concentrations presented in Fig. 3 shows that a noticeable increase of conversion to CO_2 begins at 200 °C, and at temperatures above 300 °C, practically complete UDMH transformation into the deep oxidation products CO_2, H_2O and N_2 is observed.

The influence of the initial C(UDMH) on the composition of oxidation products at 300 °C is shown in Fig. 4. It can be seen that in the C(UDMH) range 0–0.7 mmol/l practically complete UDMH conversion following the deep oxidation route takes place, and the $C(CO_2)$ grows proportionally to the C(UDMH). Upon further C(UDMH) increase over 0.7 mmol/l, the efficiency of UDMH transformation into the deep oxidation products decreases, and significant quantities of the partial oxidation products appear in the exhaust gas.

Methane and MDMH are present in the reaction products in a wide temperature range (Figs. 3 and 4). They are already formed in significant quantities at 150 °C. Based on the presence of these compounds at the reactor outlet, it is possible to suggest a probable mechanism of UDMH heterogeneous catalytic oxidation, proceeding via the following principal steps:

$$(CH_3)_2N{-}NH_2 + [\ ] \rightarrow [(CH_3)_2N{-}NH_2]_{ads} \quad (1)$$

$$[(CH_3)_2N{-}NH_2]_{ads} + [O]_{ads} \rightarrow [(CH_3)_2N{=}N]_{ads} + [H_2O]_{ads} \quad (2)$$

$$[(CH_3)_2N{=}N]_{ads} + [(CH_3)_2N{=}N]_{ads} \rightarrow [(CH_3)_2N{-}N{=}CH_2]_{ads} + [CH_3N{=}NH]_{ads} \quad (3)$$

$$[(CH_3)_2N{-}N{=}CH_2]_{ads} \rightarrow (CH_3)_2N{-}N{=}CH_2 + [\ ] \quad (4)$$

$$[(CH_3)_2N{-}N{=}CH_2] + [O]_{ads} \rightarrow (CH_3)_2NH + CO_2 + H_2O + N_2 + NO_x \quad (5)$$

$$[CH_3N{=}NH]_{ads} \rightarrow CH_4 + N_2 \quad (6)$$

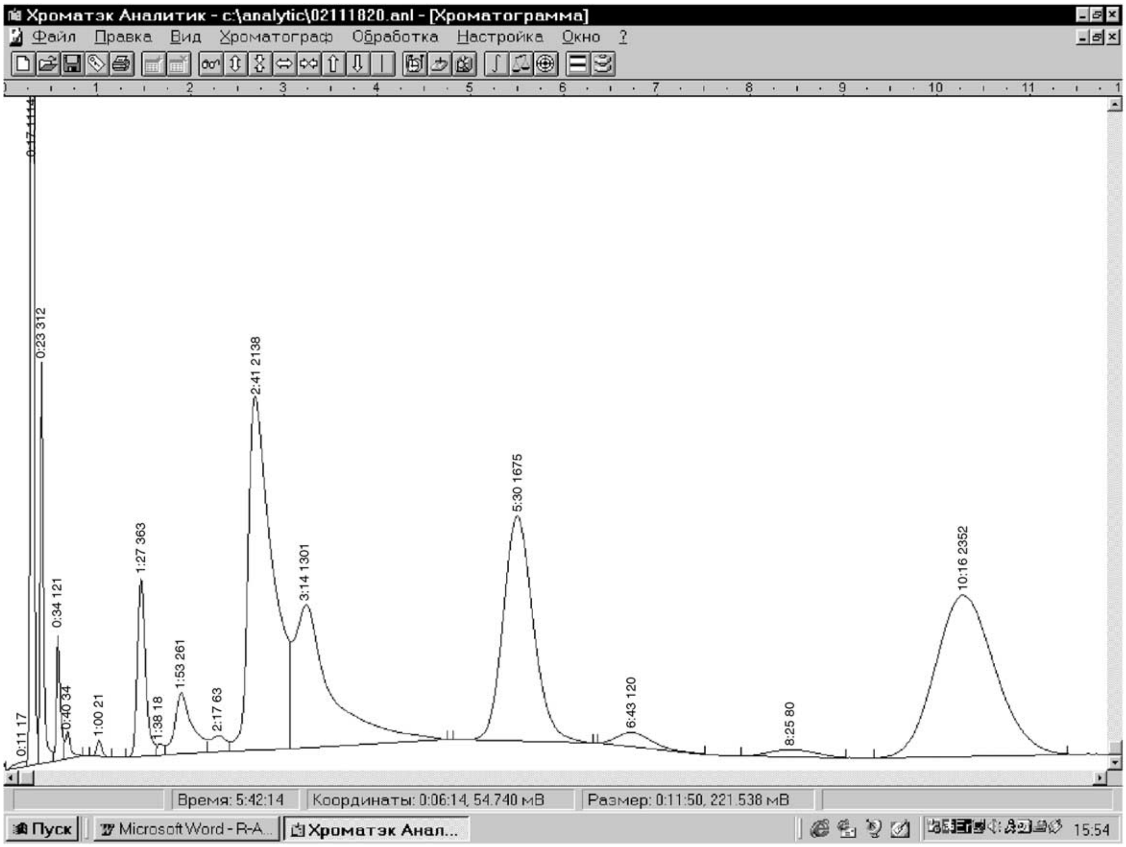

Fig. 2. Chromatogram of the UDMH oxidation products formed over $Cu_xMg_{1-x}Cr_2O_4/\gamma\text{-}Al_2O_3$ catalyst at 270 °C.

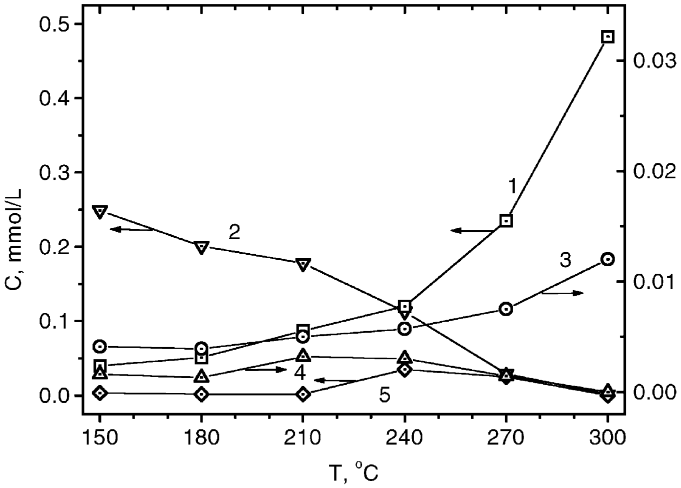

Fig. 3. Temperature dependencies of the concentrations of UDMH oxidation products over $Cu_xMg_{1-x}Cr_2O_4/\gamma\text{-}Al_2O_3$ catalyst at the initial *C*(UDMH) 0.26 ± 0.02 mmol/l and space velocity of 6000 h^{-1} (catalyst volume 1.0 cm^3): 1—CO_2; 2—MDMH; 3—CH_4; 4—UDMH, 5—DMA.

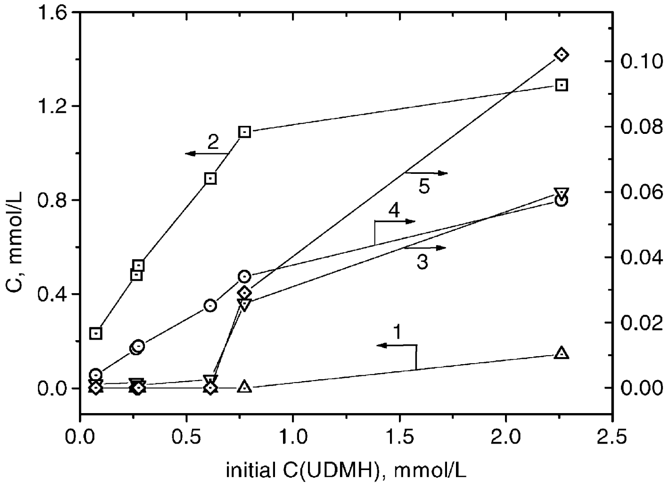

Fig. 4. Dependencies of concentrations of the UDMH oxidation products on the initial C(UDMH) over $Cu_xMg_{1-x}Cr_2O_4/\gamma\text{-}Al_2O_3$ catalyst at 300 °C and space velocity of 6000 h^{-1} (catalyst volume 1.0 cm^3): 1—UDMH; 2—CO_2; 3—MDMH; 4—CH_4; 5—DMA.

$$[CH_3N{=}NH]_{ads} + [O]_{ads} \rightarrow CO_2 + H_2O + N_2 + NO_x \quad (7)$$

The proof of this mechanism and its elucidation require additional research.

It is well known that iridium metal is a principal active component of catalysts used in spacecraft engines for the decomposition of a liquid propellant-hydrazine (N_2H_4) [8,9]. There is also information in literature that this type of catalysts is active in the reaction of UDMH oxidation by ozone [10]. Therefore, it was interesting to study the dependencies of UDMH oxidation by air over the iridium-containing catalyst 32.9%Ir/γ-Al_2O_3 which had been previously prepared and studied at BIC in the frame of a classified aerospace propulsion research program. Recently it was reported that the activity of nitrides and carbides of some metals, e.g. Mo and W, in the hydrazine decomposition reaction is comparable with the activity of Ir/γ-Al_2O_3 in the same reaction [11]. Because, in addition to the reported high activity of Ir/γ-Al_2O_3 in hydrazine decomposition, the 32.9%Ir/γ-Al_2O_3 catalyst also proved to be very active in the UDMH deep oxidation, by analogy it was decided to study the possibility of UDMH oxidation over nitrides. The β-Si_3N_4 catalyst was used for the experiments, since there is information that the silicon nitride surface is active in the UDMH decomposition [12]. Finally, we will compare the results of UDMH oxidation over 32.9%Ir/γ-Al_2O_3 and β-Si_3N_4 catalysts with some of our results obtained previously using the 0.64%Pt/γ-Al_2O_3 catalyst [13].

Temperature dependencies of the concentrations of various UDMH oxidation products formed over the 32.9%Ir/γ-Al_2O_3 and β-Si_3N_4 catalysts are presented in Figs. 5 and 6. Table 2 also gives the comparison of

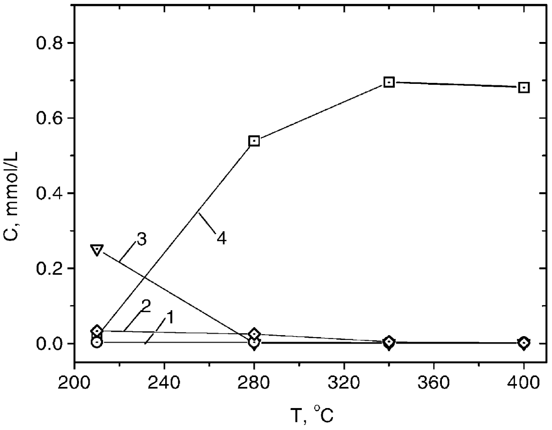

Fig. 5. Temperature dependencies of the concentrations of UDMH oxidation products over 32.9%Ir/γ-Al_2O_3 catalyst at the initial C(UDMH) 0.35 ± 0.03 mmol/l and space velocity of 72 000 h^{-1} (catalyst volume 0.1 cm^3): 1—CH_4; 2—DMA; 3—MDMH; 4—CO_2.

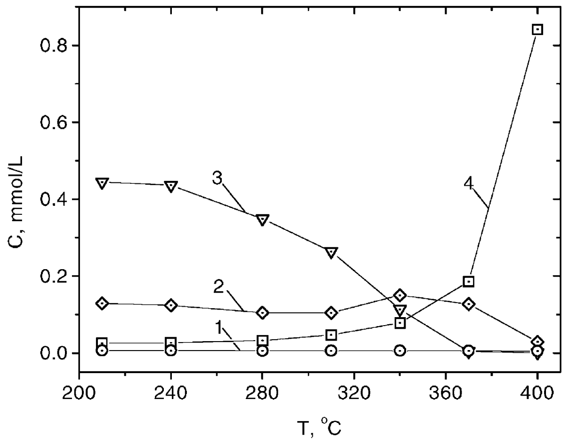

Fig. 6. Temperature dependencies of the concentrations of UDMH oxidation products over β-Si_3N_4 catalyst at the initial C(UDMH) 0.60 ± 0.05 mmol/l and space velocity of 7200 h^{-1} (catalyst volume 1.0 cm^3): 1—CH_4; 2—DMA; 3—MDMH; 4—CO_2.

C(N_2O) and C(NO), and corresponding selectivities for these two catalysts.

It can be seen from Fig. 5 that in a wide temperature range (340–400 °C) and at high space velocity (72 000 h^{-1}), practically total UDMH oxidation to CO_2 (curve 4) takes place over 32.9%Ir/γ-Al_2O_3 (at the initial C(UDMH) of 0.35 mmol/l, the expected C(CO_2) is 0.7 mmol/l, and the experimental values are 0.68–0.70 mmol/l). Only one of the partial oxidation products-MDMH is found in a significant concentration (curve 3) at temperatures below 280 °C.

As it follows from Fig. 6, over β-Si_3N_4 UDMH conversion to CO_2 (curve 4) attains only 70% at 400 °C (0.60 mmol/l of UDMH gives 0.84 mmol/l of CO_2, compared to 1.2 mmol/l of CO_2 calculated for the total UDMH oxidation). MDMH (curve 3) prevails among the partial oxidation products.

It is interesting to note that C(CH_4) for both 32.9%Ir/γ-Al_2O_3 and β-Si_3N_4 (curve 1 in Figs. 5 and 6, respectively) is ca. 0.005 mmol/l, which is noticeably lower than the values found for $Cu_xMg_{1-x}Cr_2O_4$/γ-Al_2O_3 around 300 °C in this study, and for the previously studied 0.64%Pt/γ-Al_2O_3 catalyst [13]. In the case of 32.9%Ir/γ-Al_2O_3, this can be explained by its high activity, sufficient for CH_4 oxidation in the entire temperature range studied. In the case of β-Si_3N_4, this may be interpreted in terms of the increased selectivity of formation of partial oxidation products, retaining two methyl groups at the nitrogen atom-MDMH and DMA (curve 2 in Fig. 6), and, as a consequence, decreased selectivity of CH_4 formation.

Table 2 shows that the increase of C(NO) and C(N_2O) with temperature correlates with the increase of UDMH conversion to CO_2 (curve 4 in Figs. 5 and 6). C(NO) values over 32.9%Ir/γ-Al_2O_3 (2000–3000 ppm) in the temperature range of total UDMH oxidation are comparable with those obtained previously for the 0.64%Pt/γ-Al_2O_3 (1600–2200 ppm), but are significantly higher than C(NO) values measured over $Cu_xMg_{1-x}Cr_2O_4$/γ-Al_2O_3 (30–470 ppm) [13].

The catalyst $Cu_xMg_{1-x}Cr_2O_4$/γ-Al_2O_3 has been extensively studied previously [1–5] and was found to be one of the best for nitrogen-containing compounds oxidation in the fluidized bed reactors. Recently, we also determined that its performance in UDMH oxidation is superior in comparison with other catalysts, such as 0.64%Pt/γ-Al_2O_3, Fe_2O_3/γ-Al_2O_3 and zeolite-supported catalysts [13] regarding a high conversion of UDMH to deep oxidation products and low yields of NO_x. The results of this study also demonstrate the advantage of $Cu_xMg_{1-x}Cr_2O_4$/γ-Al_2O_3 in UDMH oxidation when it is compared with 32.9%Ir/γ-Al_2O_3 and β-Si_3N_4. Thus, $Cu_xMg_{1-x}Cr_2O_4$/γ-Al_2O_3 was chosen

Table 2
Temperature dependencies of NO and N_2O concentrations and selectivities of formation over 32.9%Ir/γ-Al_2O_3 and β-Si_3N_4 catalysts

T (°C)	32.9%Ir/γ-Al_2O_3				β-Si_3N_4			
	C(NO) (ppm)	S(NO) (%)	C(N_2O) (ppm)	S(N_2O) (%)	C(NO) (ppm)	S(NO) (%)	C(N_2O) (ppm)	S(N_2O) (%)
400	2890	17.2	238	2.8	2263	8.4	303	2.2
370	2670	15.9	–	–	170	0.6	142	1.0
340	1948	11.6	242	2.9	108	0.4	91	0.7
310	880	5.2	–	–	153	0.6	33	0.2

Table 3
Results of testing the main reactor with fluidized catalyst bed

Experiment no.	Main air flow (m^3/h)	Air flow through injectors (m^3/h)	UDMH flow rate (l/h)	Oxygen excess coefficient, α	T in the reactor (°C)	Gas composition at the main reactor outlet (mg/m^3)		
						NO_x	CO	UDMH
1	16.2	1.6	1.08	2.7	630	6000	<5	<0.05
2	16.2	1.6	2.24	1.31	675	6000	<5	<0.05
3	16.2	1.6	2.56	1.14	735	6000	<5	0.075

Table 4
Results of the SCR reactor testing

Experiment no.	Initial concentration of UDMH (mg/m^3)	Initial concentration of NO_x (mg/m^3)	Initial concentration of NH_3 (g/m^3)	NH_3 flow rate (m^3/)h	T in the SCR reactor (°C)	Gas composition at the SCR reactor outlet (mg/m^3)			
						UDMH	NO_x	CO	NH_3
4	2.14	2000	7.86	0.20	420	0.095	80	<5	<5

for further studies in the pilot plant for UDMH destruction.

3.2. Pilot plant testing of the UDMH destruction technology

The series of pilot plant experiments were accomplished in two stages-testing of the main catalytic reactor with a fluidized catalyst bed (Table 3, experiments 1–3), and testing during the simultaneous operation of the main reactor and the off-gas treatment system: the SCR reactor and the wet gas cleaning units (example-Table 4, experiment 4).

In experiments 1–3, process parameters providing the most total UDMH oxidation were determined. In experiment 4, the process parameters of the main reactor were specially chosen to provide the presence of some residual UDMH at the reactor outlet. That was done in order to study the efficiency of UDMH removal from the gas stream by the units of the off-gas treatment system.

Taking into account the data from [13,14], the pilot plant testing results can be summarized as follows:

- In a temperature range 600–720 °C, practically complete UDMH catalytic oxidation takes place in the fluidized catalyst bed. C(CO) at the main reactor outlet does not exceed the detection limit-5 mg/m^3.
- During the catalytic oxidation of UDMH at 630–735 °C using an optimal regimes with oxygen excess coefficient $\alpha > 1$, C(UDMH) at the main reactor outlet does not exceed 0.1 mg/m^3, which corresponds to the UDMH oxidation efficiency of not less than 99.9998%.
- During the catalytic oxidation of UDMH, concentrations of nitrogen oxides at the main reactor outlet are 2000–6000 mg/m^3 with NO_2 to NO ratio of ca. 2:1.
- Monolith SCR catalyst provides no less than 90% efficiency of the gas purification from nitrogen oxides in a temperature range 405–420 °C and in the excess of NH_3.
- Monolith afterburning catalyst, placed after the SCR catalyst in the SCR reactor, provides oxidation of excess NH_3 with the efficiency of no less than 99.9% and UDMH oxidation at low concentrations (2 mg/m^3) with the efficiency of ca. 80%.

4. Conclusions

1The catalyst $Cu_xMg_{1-x}Cr_2O_4/\gamma\text{-}Al_2O_3$ is shown to have a superior performance in UDMH deep oxidation as compared to the catalysts 32.9%$Ir/\gamma\text{-}Al_2O_3$

and β-Si_3N_4. Both $Cu_xMg_{1-x}Cr_2O_4/\gamma$-$Al_2O_3$ and 32.9%Ir/γ-Al_2O_3 exhibit high activity in UDMH deep oxidation with minimal formation of the partial oxidation products. But the oxide catalyst provides much lower conversion of fixed nitrogen to nitrogen oxides. The catalyst β-Si_3N_4 has a lower activity in the deep oxidation of UDMH, and the reaction is accompanied by the formation of DMA and MDMH at high concentrations in the low-temperature region. Besides, rather high NO concentrations are observed over this catalyst. Thus, the catalyst $Cu_xMg_{1-x}Cr_2O_4/\gamma$-$Al_2O_3$ has been chosen for further pilot plant studies.

Testing of the pilot plant for UDMH destruction has shown high efficiency and environmental safety of the developed UDMH destruction technology.

Acknowledgements

Financial support of the International Science and Technology Center (ISTC, Project No. 959), Moscow, Russia, is gratefully acknowledged.

References

[1] Z.R. Ismagilov, M.A. Kerzhentsev, Catal. Rev. Sci. Eng. 32 (1990) 51–103.

[2] Z.R. Ismagilov, M.A. Kerzhentsev, Catal. Today 47 (1999) 339–346.

[3] Z.R. Ismagilov, N.A. Koryabkina, R.A. Shkrabina, V.A. Ushakov, Catal. Today 29 (1996) 427–431.

[4] Z.R. Ismagilov, React. Kinet. Catal. Lett. 60 (2) (1997) 215–218.

[5] Z.R. Ismagilov, in: Proceedings of the Second World Congress on Environmental Catalysis (AIChE), November 15–20, 1998, Miami, FL, pp. 94–96.

[6] Z.R. Ismagilov, R.A. Shkrabina, N.A. Koryabkina, New technology for production of spherical alumina supports for fluidized bed combustion, Catal. Today 47 (1999) 51–71.

[7] O.P. Pestounova, G.L. Elizarova, Z.R. Ismagilov, M.A. Kerzhentsev, V.N. Parmon, Detoxication of water containing 1,1-dimethylhydrazine by catalytic oxidation with dioxygen and hydrogen peroxide over Cu- and Fe-containing catalysts, in: Abstracts of the Third European Workshop on Environmental Catalysis- “Environmental Catalysis: A Step Forward”, Maiori (Amalfi Coast), Italy, May 2–4, 2001, p. 137.

[8] T.P. Gaidei, V.N. Novgorodov, I.Ya. Tiuryaev, Zh. Prikl. Khim. 70 (7) (1997) 1125–1132 (in Russian).

[9] T.P. Gaidei, I.Ya. Tiuryaev, Zh. Prikl. Khim. 70 (8) (1997) 1319–1322 (in Russian).

[10] L.Ye. Gorelenko, B.V. Strakhov, G.I. Yemelyanova, Vestn. Mosk. Un-ta, Ser. 2 28 (4) (1987) 359–362 (in Russian).

[11] J.A.J. Rodrigues, G.M. Cruz, G. Bugli, M. Boudart, G. Djega-Mariadassou, Catal. Lett. 45 (1997) 1–3.

[12] J.L. Armstrong, Y.-M. Sun, J.M. White, Appl. Surf. Sci. 120 (1997) 299–305.

[13] Z.R. Ismagilov, V.N. Parmon, M.A. Kerzhentsev, V.A. Sazonov, I.Z. Ismagilov, G.L. Elizarova, O.P. Pestunova, L.N. Rolin, V.N. Eryomin, Yu.L. Zuev, N.V. Pestereva, G.V. Sakovich, Environmentally friendly method for the utilization of heptyl and wastes containing heptyl, in: Proceedings of the Scientific and Technical Seminar on “Problematic Questions in the Methodology of Utilization of Composite Solid Rocket Propellants, Wastes and Residues of Liquid Rocket Propellants in the Elements of Rocket and Space Technology”, Federal Research and Production Center “Altai”, Biysk, Russia, November 16–17, 1999, pp.13–27 (in Russian).

[14] Z.R. Ismagilov, M.A. Kerzhentsev, Catalysis for solving environmental problems of disarmament, in: Abstracts of the Fourth European Congress on Catalysis, Rimini, Italy, September 4–9, 1999, p. 93.