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Nitrous oxide in oxidation chemistry and catalysis: application and production

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Abstract

An overview is given on extensive studies, which are targeted to involve N_2O into organic synthesis as an oxidant. Due to unique oxidative properties, nitrous oxide provides remarkable prospects in catalytic and non-catalytic oxidation chemistry in both gas and liquid phases. The interest to new oxidant resulted in appearance of a new technology for the production of inexpensive N_2O too.

Keywords: Nitrous oxide; Catalysis; Oxidation

1. Introduction

The involvement of new feed stocks and reagents into large-scale chemical industry is always a very important event for the industry and its economics and often results in dramatic consequences. It was the case, e.g., when coal, a main feed stock for the industrial organic synthesis in the 19th century, had been substituted by oil in the 20th century. The same is expected for the further substitution of oil by natural gas (light alkanes) in the 21st century. In petrochemistry of the 20th century, an extremely important consequence of the mentioned changes in the feed stock basis had resulted from the substitution of extremely reactive but dangerous acetylene and its derivates, which were produced in the past mainly from the coal, by olefins.

For sophisticated synthesis, which includes partial oxidation of various organic substrates, one can recognize utilization initially of air oxygen, then a set of inorganic compounds like transition metal ions in a high oxidation state, then the substitution of these oxidants by a "green chemistry" oxidant hydrogen peroxide.

Indeed, the final choice of real chemical industry is basing not only on chemical properties of a particular reagent but also (and often mainly) on comparative assessments of its cost, availability, etc.

One of the most difficult fields of catalytic chemistry is selective oxidation of hydrocarbons. The main difficulty here consists in the creation of selective catalysts. Such catalysts should perform a dual function: to activate dioxygen and generate some catalyst-bound oxygen species of a proper reactivity, and to activate organic molecule so as to direct the reaction to the desired products [1,2]. The optimization of both these parameters simultaneously is a very difficult task, since one cannot tune them independently. Modifying the catalyst composition, we often find ourselves in the situation when gaining in one aspect we are losing in the others. That is why for many catalytic oxidation reactions we fail to get a reasonable selectivity. Instead, we have to use complex multi-step processes.

Two simple reactions of the above type are the partial oxidation of methane to methanol and that of benzene to phenol. These reactions are often included into the top 10 most difficult challenges of modern chemistry. At present, to produce methanol, methane is first converted to a mixture of H_2 and CO and after that the latter mixture is converted to methanol. As to the benzene oxidation to phenol, it is carried usually via the three-step "cumene process" leading to acetone as byproduct. Theoretically, the both selective oxidations could be done in a single step, simply adding one oxygen atom to the starting molecule.

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Application of alternative oxidants in the form of various oxygen-containing molecules opens new possibilities. The idea of this approach is as follows. Variation of the oxidant chemistry should change the state of surface oxygen, while the activation of organic molecules may remain unchanged or affected to a smaller degree, thus providing new opportunity for controlling the selectivity.

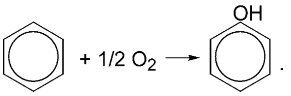
During the last decades, one of the most intriguing new reagents for the selective oxidation has appeared to be nitrous oxide, N_2O. This compound is used in medicine due to its light narcotic effect (‘‘laughing gas’’) but in chemistry it was considered mostly as a not very toxic but practically useless compound. Moreover, in the last two decades even some special environmental restrictions were issued to prevent the emission of N_2O into the atmosphere, since the compound has been recognized as a both greenhouse and ozone depleting agent.

Our brief review is devoted to nitrous oxide as an oxidant, which remarkable oxidation chemistry promises a significant progress in the field. The paper includes four parts comprising the following subjects: a gas phase catalytic oxidation with nitrous oxide, a liquid phase non-catalytic oxidation with nitrous oxide, the development of a pilot-scale process for direct oxidation of benzene to phenol (‘‘AlphOx^{TM}’’), and the production of N_2O via catalytic selective oxidation of ammonia with dioxygen.

2. Gas phase catalytic oxidation with N_2O

In the late 1970s–early 1980s, nitrous oxide has attracted a significant attention of researchers involved in searching for new ways in selective transformation of methane. In particular, research groups of Lunsford [3,4] and Somorjai [5,6] showed that application of N_2O oxidant over supported MoO_3 and V_2O_5 oxides provided high selectivity of methane oxidation to methanol and formaldehyde, especially at low conversions.

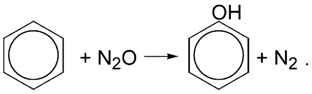
First practical interest to nitrous oxide as an oxidant has appeared in relation to phenol problem, which is one of the most bulky chemicals, with the annual world production exceeding 6 million tons. Its present-day cumene technology includes three steps: (i) alkylation of benzene with propylene to produce cumene; (ii) oxidation of the cumene to cumene hydroperoxide; and (iii) decomposition of the latter to the target product phenol and a co-product acetone. An ideal solution of the problem would be, indeed, a direct oxidation of benzene to phenol with dioxygen:



(1)

However, many attempts to accomplish this reaction were unsuccessful. The interaction with O_2 in the presence of known catalysts leads mainly to the destruction of the aromatic ring and low phenol selectivity.

In 1983, Iwamoto et al. [7] were the first to use N_2O for the oxidation of benzene:



(2)

This reaction over a vanadia catalyst allowed achieving much better selectivity as compared to the oxidation by dioxygen. At 550 °C, the reaction selectivity exceeded 70%. These results were recognized as a promising lead to a long awaited one-step direct process. However, a pilot test performance did not meet the expectations since the selectivity proved to be too low for a commercial development.

Nevertheless, work [7] has stimulated further efforts in searching for new more effective catalytic systems. As a result, in 1988, three groups of researchers [8–10] independently distinguished the ZSM-5 zeolites to be the best catalysts for reaction (2). The catalysts allowed the reaction to proceed at much lower temperature and, which is even more important, with the selectivity approaching 100%. Further studies involved the active participation of many other groups [11–33] and contributed to the improvement of the zeolite catalyst performance. Also, this approach was expanded to the oxidation of various benzene derivatives [34–39] as well as other type of hydrocarbons [20,40–45].

On this basis, a new phenol process has been developed jointly by Solutia Inc. (formerly a chemical business of Monsanto separated in 1997) and the Boreskov Institute of Catalysis (BIC). Below this process will be discussed in more details. The remarkable oxidation activity of ZSM-5 gave rise to numerous discussions concerning the origin of the mentioned untypical zeolite activity as well as the reasons for an amazing specificity of the N_2O oxidant compared to O_2.

As for the nature of the catalytic activity, two different approaches were suggested. One of them is based on a traditional notion that zeolites are the acidic catalysts with strong Brönsted and Lewis sites. The other one relates to the common oxidation catalysis, which might be provided by the presence of a transition metal admixture. After many efforts, this catalytic admixture has been identified and proved to be iron [46–49], which is present practically always in zeolites at least at the level of a few hundred ppm [50]. In the micropore space of the high silica zeolite matrix, iron can form some active sites, which catalyze the reaction and were called α-sites. Recently, several groups of researchers [50–53] conducted most conclusive studies on this subject, including preparation of virtually Fe-free zeolites, which is a quite difficult task. Presently, one may conclude that the iron idea seems to be generally accepted, although the detailed structure and composition of α-sites till now are not perfectly clear and thus are the subject of many theoretical [54–60] and experimental [58,61–69] studies.

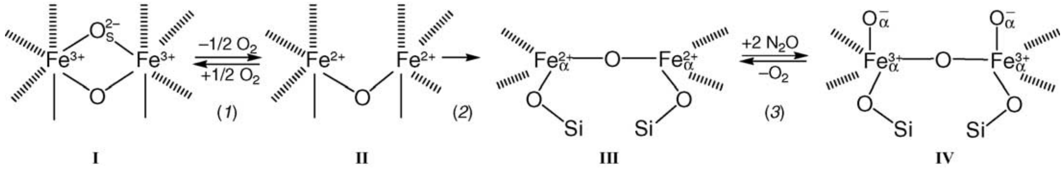


Fig. 1. An assumed mechanism of the α-sites' formation [70].

Fig. 1 shows a possible mechanism of the α-site formation as it is suggested in [70]. An initial binuclear iron complex (I) may form via both a Fe atom migration from tetrahedral positions of the zeolite lattice or an "external" Fe insertion from $FeCl_3$ (e.g., at a solid ion exchange, sublimation, CVD, etc.). The existence of such complexes inside Fe-containing zeolites of various structure including FeZSM-5, Fe-silicalite and Fe-β was suggested and well documented by many authors [61,71–81]. Upon oxygen desorption at elevated temperatures, complex (I) may transform into a reduced complex (II) (step 1). This transformation seems to proceed rather readily. If this oxygen evolution appears to be reversible, the α-site formation does not occur and, at cooling, the system returns to its initial state, thus restoring complex (I). Such reversibility of the iron redox transformation was noted in several works with FeZSM-5 zeolites, especially with those having a high concentration of iron (1–5 wt.%) [62,73–75,80]. For the α-site formation to occur, the reduced Fe^{2+} atoms should convert into a new stable state, in which they lose their ability to react with O_2 and thus make the step (1) irreversible. The process of the Fe^{2+} stabilization appeared to depend on the chemical composition of the matrix and is strongly facilitated by the presence of water vapor [20,26,30,71,78]. Presumably, the stabilization can occur in the form of complex (III), in which Fe_2^{2+} entities are strongly incorporated into a silicate fragment of the zeolite matrix and have a more distant position as compared to complex (II), thus making impossible their reoxidation into the latter complex.

The reduced iron atoms of complex (III) appear to be inert to dioxygen. However, they are readily oxidized at elevated temperatures (over 200 °C) by nitrous oxide into complex (IV) to give adsorbed $O^{\bullet-}_{\alpha}$ species. Namely, this reversible redox transition $Fe_{\alpha}^{2+} \leftrightarrow Fe_{\alpha}^{3+}$ between complexes (III) and (IV) is considered to provide a selective transfer of oxygen atoms from N_2O to hydrocarbon molecules to be oxidized.

2.1. N_2O specificity

A remarkable specificity of N_2O is proved to relate to a particular state of anion radical oxygen species O_{α}^{-} (called α-oxygen), which forms on the α-sites from N_2O, but cannot form from O_2 as it is illustrated by Fig. 1. A number of thorough studies were devoted to investigation of properties of α-oxygen including its reactivity tests, IR-spectroscopy isotope labeling, and step-response experiments [53,58,64,66–69,81–85]. Among the specific features of α-oxygen, its very high reactivity seems to be the most remarkable one. For example, it easily oxidizes various organic molecules, including methane, even at room temperature. This allows one to conduct a single turn-over synthesis of, e.g., phenol according to the following scheme [82]:

$$N_2O + (\,)_{\alpha} \xrightarrow{200-250\,^{\circ}C} (O^-)_{\alpha} + N_2, \tag{3}$$

$$C_6H_6 + (O^-)_{\alpha} \xrightarrow{25\,^{\circ}C} (C_6H_5OH)_{\alpha}, \tag{4}$$

$$(C_6H_5OH)_{\alpha} \xrightarrow[\text{extraction}]{25\,^{\circ}C} C_6H_5OH + (\,)_{\alpha}, \tag{5}$$

This scheme includes first the α-oxygen loading (Eq. (3)). Then, after the reactor cooling, the α-oxygen interaction with benzene is allowed at room temperature (Eq. (4)). The phenol product can be finally extracted from the catalyst surface, e.g., with methanol (Eq. (5)). In all experiments of this type, the extract analysis revealed nearly the theoretical yield of phenol. No other products were detected. These results approve clearly the α-oxygen participation, which is further confirmed by using the $^{18}O_{\alpha}$ isotope [45,82].

The Eqs. (3)–(5) seem to be the main steps of the reaction mechanism at the benzene oxidation with N_2O.

The similar reactions can be conducted with other organic substrates too. These single turn-over reactions, beside a mechanistic importance, happened to be a convenient way for estimating the potentialities of the oxidation with α-oxygen. For that, a variety of organic substrates were tested for their interaction with α-oxygen at room temperature to identify primary oxidation products [84,85]. The list of investigated substrates includes alkanes, cycloalkanes, alkenes and aromatics (Table 1). The analysis of the products extracted from the catalyst surface showed that the interaction with O_{α} in all cases leads to the selective formation of hydroxylated products, thus revealing a remarkable N_2O potential as a selective oxidant.

Table 1
Substrates investigated in the stoichiometric oxidation by α-oxygen at room temperature [84,85]

Alkanes	Cycloalkanes	Alkenes	Aromatics
Methane	Cyclohexane	Cyclohexene	Benzene
Ethane	Methylcyclohexane		Toluene
Propane			Ethylbenzene
Hexane			1-Propylbenzene
2-Methylhexane			Chlorobenzene
			Fluorobenzene
			Trifluorotoluene

Table 2
Oxidation of various substrates (except for benzene) with N_2O over zeolite catalysts

Substrate	Temperature (°C)	Substrate conversion (%)	Hydroxylated products selectivity (%)	Reference
Non-aromatic				
Methane	275	–	ca. 2	[58]
Ethane	390	<10	0	[40]
Propane	450	51.7	11.5	[42]
	500	50	0	[43]
Cyclohexane	300	ca. 3	0	[20]
Cyclododecane	400	20	0	[41]
Cyclohexene	300	ca. 3	0	[20]
Aromatic				
Toluene	350	24	27	[35]
	320	36.6	41.5	[36]
	450	25	40	[38]
Chlorobenzene	330	6.7	100	[8]
	350	23	58	[35]
Fluorobenzene	350	9.2	90.4	[9]
	400	45	94	[14]
	350	19	68	[35]
Phenol	350	11.5	92	[44]
	475	8.9	97	[45]
Benzaldehyde	300	12	0	[35]
Nitrobenzene	350	5	0	[35]
Anisole	350	53	ca. 1	[35]
Aniline	500	13	29	[35]
Difluorobenzenes	397	25–30	80–85	[37]
1,3,5-Trimethylbenzene	350	0	–	[20]
Biphenyl	350	6	70	[35]
	400	12	95	[39]
Naphthalene	350	1	43	[35]

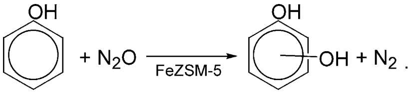
2.2. Other catalytic reactions at elevated temperatures

Presently, many researchers are trying to use N_2O for conducting various oxidation reactions by the catalytic way at elevated temperature. Quite good selectivities were achieved in the oxidative dehydrogenation of alkanes [40,42,43] and in the epoxidation of propylene to propylene oxide [86]. The data presented in Table 2 demonstrate the selectivities toward hydroxylation products obtained in the oxidation of various substrates over zeolite catalysts. One can see that with alkane and alkene substrates, nearly no hydroxylated products were obtained. Two exceptions are works by Bulanek et al. [42] and Wood et al. [58]. In [42], the selectivity of ca. 11.5% has been reported in the hydroxylation of propane to propanol. In [58], even the catalytic hydroxylation of methane to methanol has been observed but the selectivity was only 2%.

The situation with aromatics is much more promising. In some cases, the selectivities are high, over 90%. This is the case for the hydroxylation of chlorobenzene, fluorobenzene, phenol and biphenyl. However, in many cases the resulted selectivity appeared to be much lower than it might be expected from the room temperature stoichiometric data. One can assume that this is a result of side transformations taking place inside zeolite cavities when performing catalysis at elevated temperatures. To suppress such side transformations and especially coking, leading to a heavy problem of the catalyst deactivation, the researchers are trying to neutralize various functional groups on the zeolite surface but leaving intact the α-sites. This is a difficult challenge. Nevertheless, in some cases this approach leads to significant improvements, which can be illustrated by an example of hydroxylation of phenol to dihydroxybenzenes.

2.3. Hydroxylation of phenol

Fig. 2 shows a 40-h run for the hydroxylation of phenol by N_2O over the FeZSM-5 zeolite [87]:



(6)

The total selectivity of the reaction to the sum of dihydroxybenzenes (DHB) is 95%. The upper picture presents the distribution of the DHB isomers versus time on stream. One can see that the fractions of resorcinol (RS) and benzoquinone (BQ) are always small, while hydroquinone (HQ) and catechol (CH) are the two main products subjected to a redistribution with the time-on-stream. At the initial period, the HQ fraction comprises 85 mol%, and

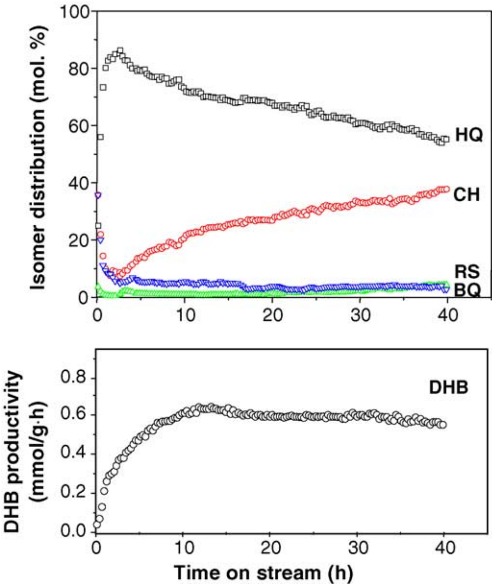


Fig. 2. Phenol hydroxylation by N_2O over FeZSM-5 zeolite [87]. HQ, hydroquinone; CH, catechol; RS, resorcinol; BQ, benzoquinone. The reaction conditions: feed mixture 2.3 vol.% N_2O, 4.6 vol.% C_6H_5OH, 19 vol.% C_6H_6, helium balance, temperature 475 °C, contact time 2 s.

decreases after 40 h to less than 60%, while there is a compensating growth of CH. The lower picture in Fig. 2 shows the total productivity of DHBs. After reaching the plateau, the productivity stays nearly constant for many hours.

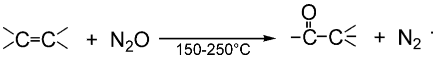
Note that presently there are three liquid phase industrial processes practiced in a direct hydroxylation of phenol to HQ and CH. All these processes use H_2O_2 as an oxidant and catalysts of different types. Rhone Poulenc uses strong acids, while Brichima—Fenton-type reagent, and Enichem—titanosilicalite TS-1. Table 3 presents a comparison of the phenol hydroxylation by H_2O_2 and N_2O for the preparation of HQ and CH. In relation to the phenol conversion, the hydroxylation by N_2O is inferior to Enichem process, but it is superior with other parameters: better selectivities based on both phenol and the oxidant, less tars (or coke) formation and a more favorable isomer distribution in respect to HQ. N_2O forms mainly HQ, which is considered usually as a more valuable product. Its amount averaged for 40 h run is 2.6 times greater than the amount of catechol. With H_2O_2, the amounts of HQ and CH are equal in the best case. Thus, the phenol oxidation with N_2O may be considered as a lead to an alternative process for the HQ and CH production.

2.4. Summary

Summarizing the consideration of the gas phase catalytic oxidation by N_2O, one should note, on the one hand, a remarkable potentiality of nitrous oxide as a selective oxygen donor, and on the other hand, difficulties that often arise when trying to realize this potentiality. The main difficulty is slow desorption of the desired hydroxylated product from the catalyst. For that one should increase the temperature, which can lead to side reactions inside zeolites as well as the catalyst deactivation due to its coking. So, there is still a big room for further studies and improvements in this field.

3. Liquid phase oxidation with N_2O

As a possible way to resolve the difficulties with the catalytic gas phase oxidation discussed above, the authors of [89] suggested an idea to transfer the reaction into a liquid phase. This would facilitate the product removal from the catalyst surface, thus increasing the number of possible catalytic reactions. The idea was confirmed only in part. However, instead, it brought the authors of [89] to the unexpected discovery of a non-catalytic oxidation of alkenes to carbonyl compounds:



$$>C=C< \; + \; N_2O \xrightarrow[150\text{-}250^\circ C]{} -\overset{\overset{O}{\|}}{C}-C< \; + \; N_2 \; . \qquad (7)$$

Actually, this type of the oxidation was first described much earlier, in 1951, by Bridson-Jones et al. [90,91]. However, due to low selectivities obtained by these authors (not exceeding 64%) and very harsh reaction conditions, which are difficult to provide in the laboratory practice, no attempt has been made since 1951 to reproduce or to improve the results of [90,91].

The important distinctions of the work [89] were much milder experimental conditions and a higher selectivity toward the target carbonyls, which in many cases comprises 95–100%.

Table 3
Hydroquinone and catechol synthesis via the hydroxylation of phenol with H_2O_2 and N_2O (the catalysts used are given in parentheses)

Process parameters	H_2O_2 oxidant [88]			N_2O oxidant [87]
	Rhone Poulenc ($HClO_4$, H_3PO_4)	Brichima (Fe^{2+}/Co^{2+})	Enichem (TS-1)	(FeZSM-5)
Phenol conversion (%)	5	10	25	9
Selectivity (%) based on the consumption of				
Phenol	90	80	90	95
Oxidant	70	50	70	15 (89)[a]
Tars, coke (%)	10	20	12	<5
HQ:CH ratio	0.71	0.43	1.0	2.6

[a] Since the hydroxylation is performed in a phenol–benzene mixture, the N_2O selectivities are based on the DHB formation (15%), and on the sum of the DHB and phenol formation (89%).

Table 4
Liquid phase oxidation of cyclopentene to cyclopentanone [92] and cyclohexene to cyclohexanone [89] with N_2O[a]

Run no.	Temperature (°C)	Reaction time (h)	Conversion (%)	Selectivity (%)
Oxidation of cyclopentene				
1	200	2	9.7	99.0
2	200	5	20.4	99.5
3	200	10	41.1	98.5
4	200	20	67.5	98.5
		+20 (add. N_2O)	94.2	97.8
Oxidation of cyclohexene				
1	200	12	7.5	98.5
2	220	12	16.8	98.0
3	250	12	61.7	96.0
4	280	3	46	96.5

[a] The initial N_2O pressure at room temperature in an autoclave Parr reactor was 25 atm.

Presently, the oxidation of cyclopentene [92] and cyclohexene [89] with N_2O to corresponding cyclic ketones is studied in more details. Using these examples, one can demonstrate this new aspect of the oxidation chemistry of N_2O.

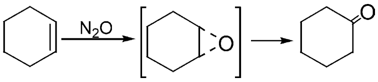
3.1. Oxidation of cyclopentene and cyclohexene

Presently, cyclohexanone (together with cyclohexanol) is produced mostly via a simple but still ineffective large-scale technology: the oxidation of cyclohexane by dioxygen. This is the reaction of a radical type, and its selectivity decreases strongly with increasing the substrate conversion over 3–5%. The similar oxidation of cyclopentane is even less selective. As a result, cyclopentanone is produced via much more complicated ways, mainly via the adipic acid decomposition, which theoretical yield is only 58 wt.%.

Table 4 shows that the liquid phase oxidation of cyclopentene and cyclohexene by nitrous oxide leads to much better results. The selectivities of both reactions are high (96–99%) even at the high conversion of the organic substrates. Thus, in case of cyclopentene, nearly 98% selectivity was obtained at the 94% conversion. Such a high selectivity can be explained by a non-radical type reaction mechanism as well as by a remarkable feature of nitrous oxide to react solely with the alkene C=C bonds. Therefore, the oxidation products having no such bonds are not subjected to the overoxidation even at the high substrate conversion.

3.2. The mechanism of the N_2O reaction with olefins

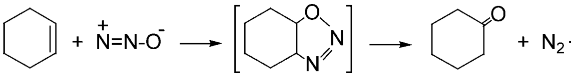
The possible mechanism of oxygen transfer from nitrous oxide to an unsaturated carbon atom seems to be of a special interest. As a probable hypothesis one may assume an intermediate formation of alkenoxide, which isomerizes further into a carbonyl compound. For cyclohexene, e.g., it means:



(8)

However, this hypothesis was not supported by the experiment, since neither cyclopentene oxide nor cyclohexene oxide undergo the isomerization or any other transformation under the reaction conditions.

Another hypothesis [90,93] seems to be more adequate. The oxygen transfer is assumed to occur via the 1,3-dipolar cycloaddition mechanism. This mechanism has been convincingly substantiated by both experimental [89–93] and theoretical studies [94,95] and implies the formation of an intermediate 1,2,3-oxadiazoline complex:



(9)

3.3. The organic substrates screening

To estimate prospects and limitations of nitrous oxide for the liquid phase oxidation, the authors of [96] performed a wide screening of the alkene oxidation including alkenes of various types. Further we give some examples and make short comments on the results obtained in [96].

3.3.1. Cycloalkenes

In addition to cyclopentene and cyclohexene discussed above, the hydrocarbon cycles comprising 8 and 12 carbon atoms were studied too. Due to the symmetrical location of the double bond, the only one type of resulting ketones is possible with these molecules, which forms in all cases with the high selectivity (96–99%). The availability of a substituent in the ring leads to the formation of two isomeric ketones differing by the position of oxygen.

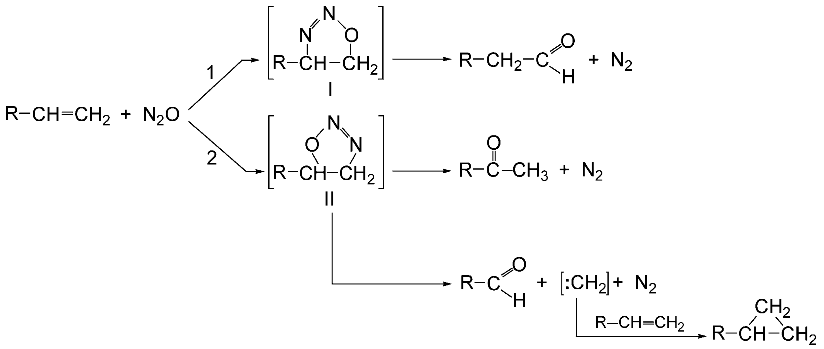
3.3.2. Linear alkenes

The oxidation of linear alkenes (Table 5) exhibits particular features depending on the position of the double bond in the substrate molecule and the config-

Table 5
Oxidation of linear alkenes with N_2O in liquid phase (220 °C, reaction time 12 h, the initial N_2O pressure at room temperature 10 atm) [96,97]

Entry	Substrate	Conversion (%)	Product composition (mol%)
1	Ethylene, 0.08 mol in 50 ml benzene	27	Acetaldehyde, 91; cyclopropane, 4; cycloheptatriene, 3
2	Propylene, 0.08 mol in 50 ml benzene	26	Propanal, 23; acetone, 31; acetaldehyde, 22; methylcyclopropane, 4; cycloheptatriene, 15
3	1-Hexene, 0.08 mol in 50 ml benzene	35	Hexanal, 15; 2-hexanone, 29; pentanal, 27; butylcyclopropane, 14; cycloheptatriene, 12
4	1-Octene, 0.06 mol in 50 ml benzene	30	Octanal, 13; 2-octanone, 28; heptanal, 26; hexylcyclopropane, 9; cycloheptatriene, 18
5	2-Butene		Methylethylketone, 87; 2-methylpropanal, 3; acetaldehyde, 6; trimethylcyclopropane, 3
6	2-Pentene, 0.14 mol in 50 ml benzene	22	2-Pentanone, 41; 3-pentanone, 47; acetaldehyde, 5; propanal, 3; cyclopropanes, 1

uration of the intermediate oxadiazoline complexes. For the case of terminal alkenes, the intermediate complex may have configuration (I) or (II) as shown in Eq. (10):



(10)

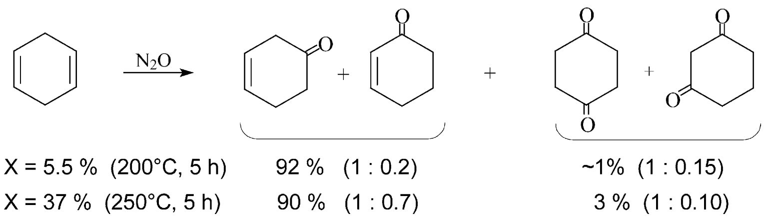
In complex (I), the oxygen of N_2O is bound to the terminal carbon atom; consequently, the decomposition of such intermediate leads to an aldehyde. In complex (II), the oxygen is bound to the second carbon atom and the decomposition of the intermediate leads to a ketone. Also, with complex (II) there exists another possible way of the decomposition which involves the cleavage of the C–C bond. The latter way leads to an aldehyde with a smaller number of carbon atoms and the equivalent amount of the methylene species, $:CH_2$, which is intercepted immediately by the alkene or solvent molecules. Thus, the oxidation of propylene in the benzene solvent (Table 5, entry 2) provided the following results: the non-cleavage way of the reaction resulted in the formation of 23 mol% of propanal and 31 mol% of acetone; the cleavage way resulted in the formation of 22 mol% of acetaldehyde and methylene, which, upon the reaction with propylene, forms 4 mol% of methylcyclopropene and, upon the reaction with benzene, 15 mol% of cycloheptatriene.

With non-terminal alkenes, the cleavage path of the oxidation is less pronounced and the oxidation leads to a rather selective ketone formation. Thus, the oxidation of 2-butene (Table 5, entry 5) provides methylethylketone with the 86% selectivity, while the oxidation of 2-pentene (entry 6) provides 2- and 3-pentanones with the 88% total selectivity.

3.3.3. *Cycloalkadienes*

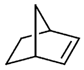
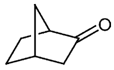
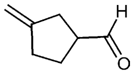
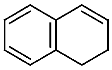
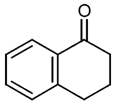
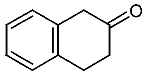
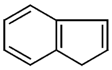
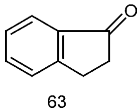
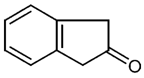
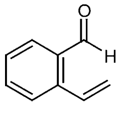
These compounds contain two double bonds, which can react with N_2O consecutively, thus yielding accordingly unsaturated monoketones and diketones. 1,4-Cyclohexadiene and 1,5-cyclooctadiene, which have the isolated double bonds, as well as 1,3-cyclohexadiene with the conjugated double bonds were studied [96].

The obtained distribution between mono- and diketones gives an interesting feature of the reaction. At the oxidation of 1,4-cyclohexadiene (Eq. (11)), 3- and 2-cyclohexen-1-ones are the main products comprising 90–92% of the yield:



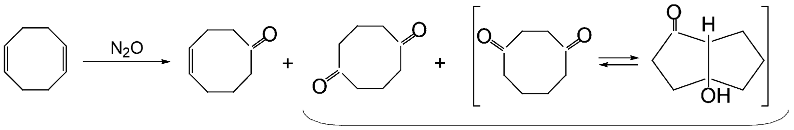
(11)

Table 6
Oxidation of bicyclic alkenes with N_2O in liquid phase (the initial N_2O pressure at room temperature 10 atm) [96]

Entry	Substrate	T (°C)	Reaction time (h)	Conversion (%)	Product composition (mol%)
1	 0.053 mol in 45 ml cyclohexane	180	4	42	 28  29
2	 0.039 mol in 20 ml benzene	250	5	46	 65  28
3	 0.043 mol in 20 ml benzene	250	5	35	 63  14  10

(Note that with 1,4-cyclohexadiene, 20–25% of the converted alkene is consumed by a polymerization process, which is not taken into account at calculating the product composition shown in Eq. (11). With 1,5-cyclooctadiene, no polymerization was noted.) The concentration of diketones is very small and at conversion $X = 37\%$ comprises only 3% instead of statistically expected 9%. This low yield of diketones may indicate that the insertion of the first carbonyl group into 1,4-cyclohexadiene deactivates the remaining double bond and makes it more resistant to the further oxidation. Approximately, a 10-fold predominance of 1,4-versus 1,3-cyclohexanedione is observed.

The oxidation of 1,5-cyclooctadiene also leads to the formation of mono- and diketones (Eq. (12)):



X = 13 % (200°C, 5 h) 88 % 4.5 % (1 : 0.9 : 0.15)
X = 42 % (220°C, 5 h) 80 % 13 % (1 : 0.5 : 0.5)

(12)

However, unlike 1,4-cyclohexadiene, this diene forms only one monoketone isomer. Besides, no deactivation effect of the C=O group is observed, so that in this case the diketone fraction is much greater and close to its statistically expected value. These distinctions are probably explained by a more distant location of the double bonds in the 1,5-cyclooctadiene molecule.

Interestingly, that among the oxidation products of 1,5-cyclooctadiene, a thorough NMR analysis identifies reliably 3α-hydroxyhexahydro-1(2H)-pentalenone. Most probably, this compound forms as a result of an intramolecular aldol condensation of 1,4-cyclooctanedione, which contribution increases with the temperature and at 220 °C consumes 50% of the latter compound (Eq. (12)).

The oxidation of conjugated 1,3-cyclohexadiene is strongly complicated by the Diels-Alder side reaction. Therefore, the main part of the diene is consumed by a dimerization process, and only 25–30% are involved in the oxidation, thus yielding cyclic ketones.

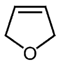
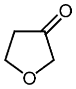
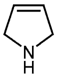
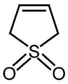
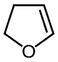
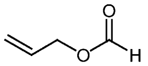
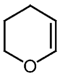
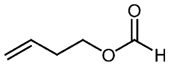
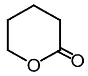
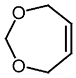
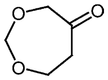
3.3.4. Bicyclic alkenes

The results of the oxidation for this type alkenes are presented in Table 6. The oxidation of norbornylene (entry 1) leads to the formation of both ketone (norcamphor) and aldehyde (1-formyl-3-methylenecyclopentane) in approximately equal amounts, thus indicating a significant cleavage of the double bond to occur.

The oxidation of 1,2-dihydronaphthalene proceeds with a minor cleavage and yields α- and β-tetralones with the total selectivity 93% (entry 2). The oxygen adds predominantly to the α-position, and the amount of α-tetralone is approximately twice that of β-tetralone.

At the oxidation of indene, where the double bond locates in a 5-membered cycle (entry 3), the oxygen also adds to the both positions, but the preference of the α-position becomes even greater. The ratio of α-indanone to β-indanone is 4.5:1. Presumably, 2-ethenylbenzaldehyde

Table 7
Oxidation of heterocyclic alkenes with N_2O in liquid phase [96]

Entry	Substrate	$P^0_{N_2O}$ (atm)[a]	T (°C)	Reaction time (h)	Conversion (%)	Product composition (mol%)
1	 0.13 mol in 50 ml benzene	10	220	12	16	 94
2	 0.13 mol in 30 ml benzene	25	180	10	13	Unidentified products
3	 0.085 mol in 50 ml acetonitrile	10	210	5	8	Butadiene, ~50
4	 0.13 mol in 60 ml cyclohexane	10	200	5	34	 71
5	 0.11 mol in 50 ml benzene	25	240	5	20	 48  31
6	 0.10 mol in 15 ml benzene	25	220	5	16	 94

[a] The initial N_2O pressure at room temperature.

also forms (~10%) as a result of the double bond cleavage in the indene molecules.

3.3.5. Heterocyclic alkenes

Among alkenes of this type, the cycles containing oxygen, nitrogen and sulfur were tested (Table 7). 5-Membered heterocycles with a similar structure of their molecules (2,5-dihydrofuran, 3-pyrroline, butadiene sulfone) exhibit different reaction patterns depending on the nature of the heteroatom. The oxygen-containing cycle of 2,5-DHF (entry 1) is oxidized selectively yielding a corresponding ketone (94%), while the cycles containing nitrogen (entry 2) and sulfur (entry 3) show a strong tendency toward side reactions resulting in a set of unidentified products.

The comparison of several oxygen-containing cycles presented in Table 7 allows one to follow an effect of the double bond location in the heterocycle molecules. Results with 2,3-DHF (entry 4) and 3,4-dihydro-2H-pyran (entry 5) show that the double bonds of the nearest to the oxygen atom location exhibit an increased disposition toward the cleavage. Indeed, the oxidation of 2,3-DHF proceeds exclusively via the cleavage route. It leads to 71% of allyl formate in the products. No sign of an expected butyrolactone was detected. The oxidation of 3,4-dihydro-2H-pyran also proceeds primarily via the cleavage route, giving 48% of 3-butenyl formate. But in this case, a significant contribution of a non-cleavage route is also observed, which is evidenced by the presence of 31% of δ-valerolactone in the products.

Unlike that, the oxidation of 2,5-DHF (entry 1) and 4,7-dihydro-1,3-dioxepin (entry 6), having a more distant location of the double bonds (position 3), proceeds essentially without a cleavage leading in both cases to the formation of corresponding ketones with 94% selectivity.

3.4. Summary

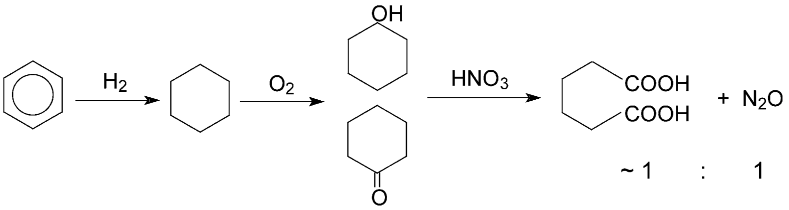
The presented data show that the liquid phase oxidation of alkanes with nitrous oxide into carbonyl compounds can be applied to a variety of substrates including aliphatic, cyclic, heterocyclic alkenes and their derivatives. By an analogy with "epoxidation", this type of reactions may be called "carboxidation". The carboxidation proceeds non-catalytically in the temperature range of 150–250 °C yielding ketones and aldehydes as the main products. Although the reaction selectivity depends significantly on the alkene structure and its composition, each type of alkenes was shown to include substrates whose carboxidation proceeds selectively yielding 90–99% of carbonyl compounds.

Due to release of high reaction energy at the N_2O oxidation, it can cause also a cleavage of the alkene molecule over the reactive double bond. This undesirable process increases the number of the reaction products and decreases the selectivity. But in the case of terminal alkenes, where this process is most intensive, it may deserve a special interest as a way for generating carbenes, which can be used for conducting some fine synthetic reactions.

4. The development of a new phenol process

The development of a new phenol process based on the direct oxidation of benzene by N_2O (reaction (2)) has been made jointly by BIC and Solutia Inc. The interest of Solutia to the remarkable oxidation chemistry of nitrous oxide follows from the fact that Solutia is one of the major world producers of adipic acid, which is an intermediate for the Nylon-6,6 production.

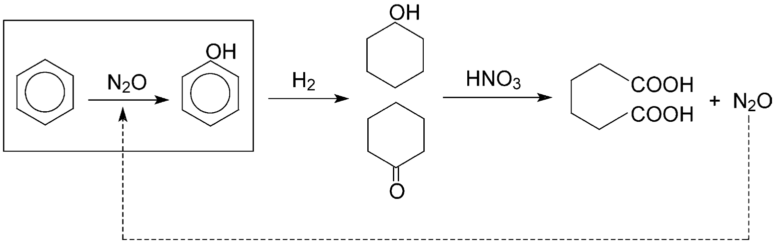
The production of adipic acid includes several steps (see Scheme (13)): the hydrogenation of benzene to cyclohexane, the oxidation of cyclohexane to a mixture of cyclohexanol and cyclohexanone, and finally the oxidation of the latter mixture to adipic acid with the use of nitric acid:



(13)

The last stage yields a large amount of concentrated waste nitrous oxide, which is formed in a ca. 1:1 mole ratio to adipic acid.

Nitrous oxide is not considered as an innocent "laughing gas" any more. It may contribute to a global climate change due to its green house and ozone depleting effects [98]. In a recent review [99], various approaches for abating the N_2O emissions were discussed. Regarding this situation, Solutia suggested to use waste nitrous oxide for the oxidation of benzene to phenol, incorporating this reaction as a key stage in a new modified adipic acid production scheme [100–102]:



(14)

This scheme also starts with benzene. In this case, benzene is first oxidized to phenol, and only then goes to hydrogenation. Nitrous oxide, which is produced at the last stage, returns to the front end of the overall process thus closing the cycle.

The new phenol process uses a Fe-containing zeolite catalyst and was called the AlphOx™ process after the name of α-oxygen (see Section 2). The process has been successfully tested at a pilot plant (Fig. 3) erected by Solutia in Pensacola (Florida). The reaction was performed in a simple adiabatic reactor, which is an essential feature of this process economy. Table 8 presents typical parameters describing the pilot reactor performance. One can see that the new process provides high selectivity as referred to both benzene and nitrous oxide. Its productivity is 400 g of phenol per 1 kg of catalyst per hour, which is at the top end of the best industrial catalysts for selective oxidation reactions.

The AlphOx™ process shows several advantages when compared to the cumene process, i.e., one step only, low capital expenses, no acetone byproduct, and no highly reactive intermediates. There are also outstanding safety features. The operating conditions ensure that the whole process is non-flammable throughout, including the reaction step, the separation system and the recycling loop. The process has also very good environmental features. Instead of spending efforts and money on the N_2O neutralization, the new phenol process uses N_2O as a valuable raw material.

5. The catalytic production of inexpensive N_2O

Extensive studies in the field of the application of nitrous oxide for the selective oxidation of hydrocarbons make development of new processes for synthesis of the inexpensive on purpose N_2O of vital importance too. The high capacity for the products of selective oxidation of hydrocarbons, for example, phenol, needs technological processes for the of nitrous oxide synthesis at the unit capacity up to 100,000 t/y. The existing commercial-scale

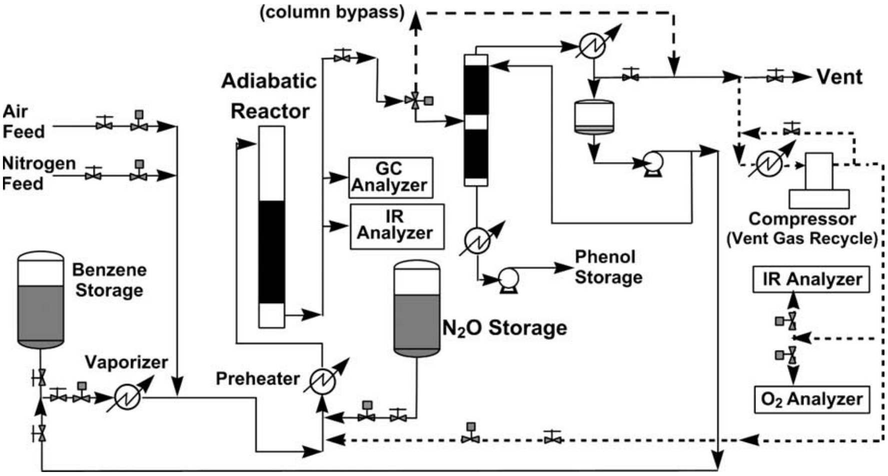


Fig. 3. A flowsheet of the AlphOx^{TM} pilot plant at Solutia facilities in Pensacola [100].

N_2O production technologies implemented in the industry by the moment are based mostly on the thermal decomposition of nitrite–nitrate salts mixtures [103] via the reaction:

$$NH_4NO_3 \xrightarrow{250\,^\circ C} N_2O + 2H_2O$$

and can only provide one tenth of the required capacity to N_2O. At the same time, for the large-scale production of nitrous oxide, catalytic technologies seem to be much more promising.

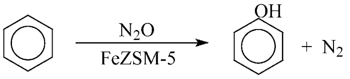
Below we consider the recent development of a new large-scale catalytic process for the synthesis of nitrous oxide via selective oxidation of ammonia over a Mn–Bi–O/α-Al_2O_3 catalyst. The catalyst was found to be active in the temperature range 315–370 °C and to provide a high selectivity (up to 90%) towards the N_2O formation. The process has been developed by BIC in a tight cooperation with Solutia Inc., USA.

5.1. Catalysts for the oxidative synthesis of N_2O

At present, several catalytic methods for the N_2O synthesis are known. This knowledge originates partly from the extensive studies on numerous deNOX processes. Among the known methods are:

Table 8

Performance of the AlphOx pilot plant adiabatic reactor in Pensacola [100]



Reaction parameters	Values
Temperature (°C)	400–450
Contact time (s)	1–2
Degree of conversion (mol%)	
Benzene to phenol	97–98
Benzene to CO_x	0.2–0.3
Benzene to diols	1
N_2O to phenol	85
Phenol productivity (kg/kg catalyst per h)	0.4

(1) Catalytic reduction of NO with CO in the presence of homogeneous catalysts [104].

(2) Catalytic reduction of NO either with CO, or with H_2, or with a mixture of carbon monoxide and hydrogen (synthesis gas) in the presence of heterogeneous catalysts such as supported platinum group metals, for example (1–5) wt.% Ru, Pt/Al_2O_3 (or SiO_2, ZrO_2, TiO_2) [105].

(3) Catalytic oxidation of ammonia with dioxygen in the presence of heterogeneous catalysts based on bulk metal oxides:

$$2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O. \qquad (15)$$

In the latter situation, manganese dioxide was considered in the literature as the most active and selective. More complex mixed oxide systems based on manganese dioxide were developed as well: MnO_2–Bi_2O_3 [106,107], MnO_2–CuO [108], MnO_2–Bi_2O_3–Fe_2O_3 [106,108], MnO–CoO–NiO [108]. The catalysts free of manganese oxides were also proposed, e.g., Co_3O_4–Al_2O_3 [109], Pr_2O_3–Nd_2O_3–CeO_2 [108]. Some of the tested systems were bulk catalysts [106,107], while the other were suggested as both bulk catalysts and catalysts impregnated to an inert support (silica, graphite or another binding material) [108].

A number of disadvantages of the above mentioned catalysts imposed serious restrictions upon their large-scale applications. The main of these disadvantages are: (i) a low activity and selectivity toward the formation of N_2O (no more than 84% at the molar ratio $O_2/NH_3 \approx 1$ in the reaction mixture); (ii) a relatively high (up to 3%) selectivity toward the formation of undesirable nitrogen oxide NO; (iii) a low mechanical strength and low catalyst effectiveness.

In order to eliminate the above disadvantages, a number of supported oxide catalysts were developed and tested in

Table 9
New supported catalytic systems for the N_2O production tested in BIC at the catalyst screening [118]

Support	Active component	X_{NH_3} (%)	S_{N_2O} (%)
α-Al_2O_3	Mn–Y–O	96.2	85.7
	Mn–Ce–O	96.7	78.2
	Mn–Sm–O	97.3	86.0
	Mn–Bi–O	97.1	89.2
γ-Al_2O_3	Mn–Y–O	96.8	80.0
	Mn–Ce–O	97.1	62.7
	Mn–Sm–O	97.0	76.6
	Mn–Bi–O	97.0	54.0

Experimental conditions: initial mixture 8 vol.% NH_3, 9 vol.% O_2, rest helium. Temperature, 350 °C.

BIC (see Table 9). A supported Mn–Bi–O catalyst has been selected as having a good activity and needed level of selectivity toward nitrous oxide combined with a low yield of NO [110] through the undesirable side reaction:

$$2NH_3 + 2.5O_2 \rightarrow 2NO + 3H_2O.$$

The procedure for the catalyst preparation includes the double impregnation of an α-alumina support with a solution of manganese(II) and bismuth(III) nitrates followed by the calcination at 400–750 °C [110]. The prepared catalyst appears to be mechanically strong and highly selective toward nitrous oxide (up to 90%) at a wide range of operating conditions.

5.2. Studies on the kinetic properties of the Mn–Bi–O/-α-Al_2O_3 catalyst for the NH_3 oxidation

The kinetic studies of the synthesized catalysts were the initial stage in the development of a large-scale process of the N_2O production. Two types of the laboratory scale reactors were used for these studies: (i) an isothermal plug flow reactor and (ii) a gradient-less CSTR equipped with an external circulation loop to provide the regime of the ideal mixing.

The kinetic properties of the Mn–Bi–O/α-Al_2O_3 catalyst were studied at temperatures 270–400 °C in the following range of the operation conditions: pressure 1–6 atm, contact time 0.03–12 s, the inlet mixture concentrations of ammonia 1.0–50 vol.%, dioxygen 3.0–83 vol.%, water (steam) 0.0–43 vol.%.

The main pathways of the ammonia oxidation with O_2 over Mn–Bi–O/α-Al_2O_3 which were detected under the studied conditions appeared to be the desirable reaction (15) and the reaction:

$$2NH_3 + 1.5O_2 = N_2 + 3H_2O. \qquad (16)$$

One-parameter dependencies of the rates of reactions (15) and (16) on the reactant concentrations and temperature were obtained by a series of experiments using the gradient-less reactor (Figs. 4 and 5). The overall rate of the ammonia oxidation was found to increase on increasing the concentrations of NH_3 and O_2. Water was found to decrease the rate of the ammonia oxidation. The selectivity toward N_2O increases on increasing the concentrations of dioxygen and water and decreases on increasing the ammonia concentration (Fig. 4). Thus, the maximal selectivity to nitrous oxide is achieved at high concentrations of dioxygen and water and at a low concentration of ammonia. At excess oxygen, the selectivity toward N_2O was as high as 90%. It should be mentioned that only a minor decrease (to no less

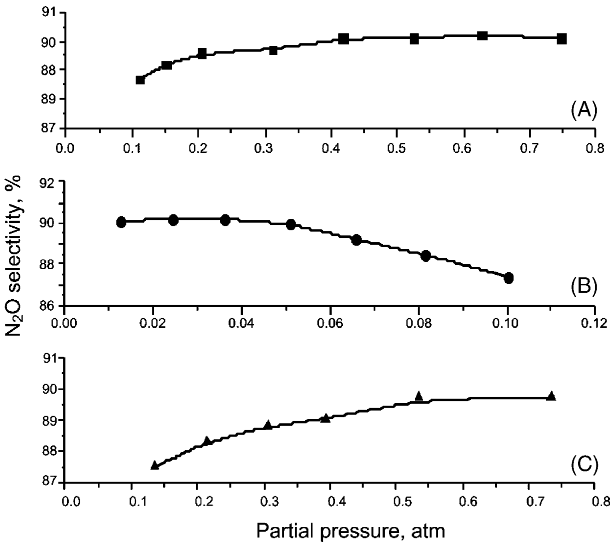


Fig. 4. One-parameter dependences of the selectivity of the Mn–Bi–O/α-Al_2O_3 catalyst toward N_2O on the partial pressures of dioxygen (A), ammonia (B) and water (C). Experimental conditions: composition of the mixture in the reactor, vol.%: O_2–4.6–31.1; NH_3–0.5–4.2; H_2O–5.7–30.6; balance helium. Temperature 370 °C; pressure 2.7 atm; contact time 0.05 s; NH_3 conversion 31–63% (according to [115]).

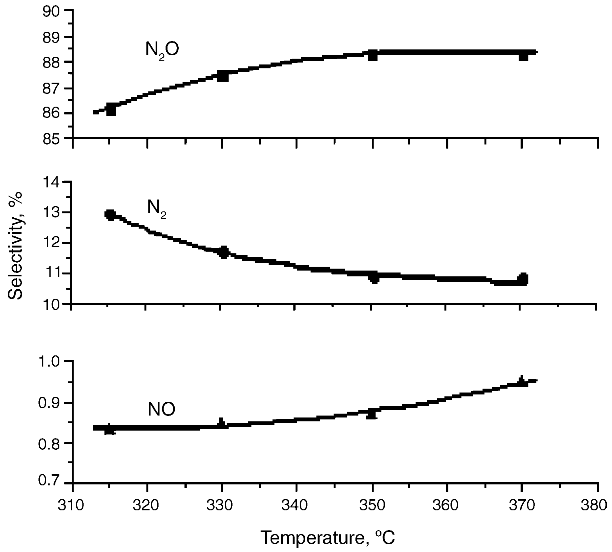


Fig. 5. Temperature dependence of the selectivity of the Mn–Bi–O/α-Al_2O_3 catalyst toward N_2O, N_2 and NO. The gradientless CSTR reactor, the concentrations in the reactor, vol.%: ammonia, 2.88; oxygen, 7.1; water, 11.5. Experimental conditions: composition of the mixture in the reactor, vol.%: NH_3–2.88; O_2–7.1; H_2O–11.5; balance helium; pressure 2.7 atm; contact time 0.05–0.5 s, NH_3 conversion 36–73% (according to [115]).

than 88%) in the selectivity to nitrous oxide was observed at the stoichiometric dioxygen/ammonia ratio. At the whole range of the inlet composition and operation temperature, the selectivity toward N_2O was found to increase on increasing the NH_3 conversion. The latter observation could be explained via the independence of the parallel pathways (15) and (16) of the NH_3 oxidation [110]. So, N_2O is the final product of reaction pathway (15), and thus the rate of the N_2O formation should decrease on increasing the NH_3 conversion in a less extent than the rate of the N_2 formation.

The selectivity to N_2O rises on increasing the temperature from 315 to 370 °C. The further temperature increase results in decreasing the N_2O selectivity due to a significant formation of NO. Thus, the preferable temperature range for achieving the maximal selectivity toward nitrous oxide has appeared to be 340–370 °C (Fig. 5).

A mathematical processing of the obtained experimental data allowed a phenomenological kinetic model to be suggested for the steady state rates of the formation of both N_2O and N_2 at the temperature range from 315 to 370 °C. The model provides the minimal mean deviation of the experimental and calculated data, i.e. ca. 9% for the rates of N_2O and N_2 formation and ca. 1% for the selectivity to nitrous oxide.

5.3. The development of a technology for the catalytic synthesis of nitrous oxide via the ammonia oxidation

Theoretical and experimental work done has shown the possibility of the N_2O production in the both fluidized and fixed bed reactors. Below, some results of the pilot testing and mathematical modeling of the new N_2O production process are summarized.

5.3.1. Fluidized bed reactor for the N_2O production

To arrange a large-scale production of concentrated nitrous oxide at as high as 100,000 t/y unit capacity, it seems promising to use the concentrated inlet reaction mixture consisting of NH_3 and O_2 at the molar ratio of ca. 1:1. The adiabatic temperature rise is 80–90 °C per percent of the inlet ammonia. Thus, the synthesis of nitrous oxide at the high inlet concentrations of ammonia and dioxygen can be provided using a fluidized catalyst bed reactor only.

Due to a considerable structural inhomogeneity of the fluidized bed, a relatively long contact time is required for the complete ammonia conversion. Theoretical estimations have shown to be appropriate to restrict the ammonia conversion in the fluidized bed reactor to ca. 98% in order to provide the further conversion of the reaction mixture using an adiabatic fixed bed reactor.

The Van Deemter two phase model [111] was used to describe hydrodynamics of the fluidized bed. The following assumptions underlay the model: (1) the plug flow regime is assumed for a gas in the bubble phase; (2) axial gas backmixing in the dense catalyst phase is taken into consideration; (3) the chemical reaction occurs in the dense phase only; (4) there are no temperature gradients in the bed.

Table 10
Operation conditions used for modeling the fluidized bed reactor

Temperature (°C)	350
Pressure (atm)	5
Axial gas dispersion coefficient (m^2/s)	3.0
Inlet composition (vol.%)	50 NH_3, 50 O_2

Table 11
Summary of the fluidized bed reactor parameters of the specified capacity for nitrous oxide equal to 100,000 t/y

Catalyst charge (m^3)	31.5
Ammonia conversion (%)	98
Selectivity to N_2O (%)	85.6

The primary goal of the modeling of the fluidized bed reactor was to investigate the influence of the operation conditions on the reactor performance. The fluidized bed properties such as the bed expansion, dense phase gas holdup and transition to turbulent fluidization were studied using the cold flow model of 0.15 m i.d. [114]. The results of these cold flow studies were used during the modeling of the fluidized bed reactor. Table 10 presents the reference operation conditions used for the modeling.

It has been established by the modeling that the rate of the ammonia transformation in the fluidized catalyst bed reactor is determined under the given operation conditions by the interphase mass transfer and catalyst activity. The bed height providing the 98% ammonia conversion decreases by 20–30% on increasing twice the interphase exchange coefficient or the catalyst activity. The axial dispersion of the gas in the dense phase affects the reactor performance only moderately. The neglecting of the axial dispersion leads to a 10% decrease in the calculated bed height providing the ammonia conversion equal to 98% and to a decrease in the calculated selectivity to N_2O by 1%.

Some parameters of the fluidized catalyst bed reactor estimated for the specified capacity for nitrous oxide equal to 100,000 t/y are summarized in Table 11.

The results of the above mathematical modeling were used for a pilot testing of the catalyst for the N_2O synthesis in the fluidized bed reactors of 4.1–7.0 cm i.d. The test studies were carried out both in the Solutia Research Center and in BIC.

The catalyst with a wide particle size distribution (10–120 μm) for the fluidized bed was prepared at BIC by the above spoken procedure. The performance of the catalyst samples for the fluidized bed synthesis of N_2O was tested using a laboratory isothermal plug flow reactor; the selectivity to N_2O was equal to 87–88%.

The pilot testing in the fluidized bed reactor [116] was carried out with the maximal catalyst loading 6 kg under the following conditions:

Reactor temperature (°C)	350–380
Pressure in the reactor (atm)	2.0
Inlet reactant concentrations (vol.%)	17–49.5 NH_3, 17–50.5 O_2

The obtained conversion of NH_3 was 62–99.5%, selectivity to N_2O 83–88%, selectivity to NO 0.2–0.5%. The total time of the pilot testing was 710 h.

Testing the catalyst in the pilot fluidized bed installation revealed only a minor difference between the catalyst selectivity to N_2O observed with the either fluidized bed or plug flow reactors. The catalyst was found to be stable, no catalyst activity losses were observed during the whole test period.

5.3.2. Tubular reactor for the N_2O production

The oxidation of ammonia to nitrous oxide is accompanied by the evolution of a considerable heat. This allows the process to be conducted in a tubular reactor at far lower concentrations of ammonia and dioxygen than those in the fluidized bed reactor. The maximal inlet ammonia concentration to provide the steady operation heat regimes in the tubular reactor was determined by the tube diameter, the catalyst particle size and geometry of the catalyst granules, as well as the catalyst activity and process conditions. The preliminary estimations reveal the maximal admissible concentrations of ammonia of 4–7 vol.% at the tubular reactor inlet.

The modeling of the nitrous oxide synthesis in the tubular reactor was mainly aimed at searching for the optimal operation parameters and stable working regimes to provide the maximal inlet ammonia concentration and the largest possible diameter of the reactor tube. The modeling was based on a quasihomogeneous steady-state approximation for the processes of heat and mass transfer in a two-dimensional tubular reactor [112,117].

The imposed limitations for the choice of optimal operation regimes were the following: (i) the hot spot temperature in the reactor must not be higher than 400 °C in order to prevent the selectivity losses; (ii) the hot spot to cooling agent (HSCA) sensitivity of the reactor, which is defined as the ratio of the hot spot temperature variation (ΔT_{HS}) to the variation of the cooling agent temperature (ΔT_{CA}):

$$\mathrm{HSCA} = \frac{\Delta T_{HS}}{\Delta T_{CA}},$$

must not exceed 4 for a spherical catalyst and 5 for a Rashig ring catalyst; (iii) the pressure drop through the bed is not higher than 0.8 atm.

The following parameters were optimized at the modeling: the superficial gas velocity, temperature of the cooling agent, temperature of the inlet reaction mixture, the activity and particle size of the catalyst. It was discovered during the modeling that the temperature of the heat carrier, the catalyst activity and the inlet ammonia concentration are the main parameters which affect the temperature profile in the reactor.

The results of the mathematical modeling gave rise to a pilot testing of the ammonia oxidation process using an installation consisting of a single tube of 4.5 m length [117].

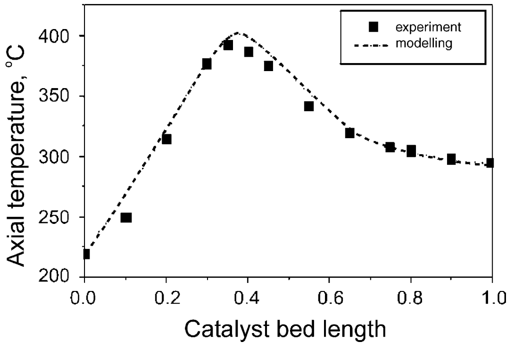


Fig. 6. Temperature profile measured along the axis of the pilot tubular reactor at the stationary regime. The operation conditions: flow velocity 3.1 m/s (STP); absolute pressure 2.2 atm; inlet NH_3 concentration 4 vol.%; the spherical catalyst of diameter 5 mm (according to [115]).

The tube was immersed into a thermostat made of an air-fluidized bed of fine γ-Al_2O_3 particles. A typical steady-state temperature profile measured along the axis of the tubular reactor is shown in Fig. 6. It is seen that the longitudinal temperature profiles in the reactor obtained by mathematical modeling are in a good agreement with the experimental data.

The mathematical modeling has demonstrated the possibility to improve the tubular reactor performance using the Rashig ring catalysts instead of spherical catalysts. At the use of a Rashig ring catalyst, it was shown possibility to increase the inlet ammonia concentration from 4.5 to 8 vol.% at the constant tube diameter due to increasing the radial heat conductivity of the bed and the wall heat transfer coefficient (see Table 12).

5.4. The process flowsheet for the large-scale production of nitrous oxide via selective oxidation of ammonia

The data obtained at both the pilot testing of the BIC developed catalyst and mathematical modeling of the oxidation have allowed to suggest the following schemes for the synthesis of concentrated nitrous oxide (Fig. 7) [113,115,117].

Ammonia and dioxygen are co-fed at the molar ratio 1:1 into the main reactor, where the selective oxidation of ammonia to N_2O proceeds at 350–370 °C and 5 atm. The main reactor could be of either a tubular fixed bed or fluidized bed type. In the case of the tubular reactor, the inlet

Table 12
Performance of a tubular reactor for the specified capacity for nitrous oxide equal to 100,000 t/y

	Spherical catalyst	Rashig ring catalyst
Maximal inlet concentration of NH_3 (mol%)	4.5	8
Theoretical adiabatic temperature rise (°C)	360	640
HSCA	<5	<5
Bed height (m)	5	8.5

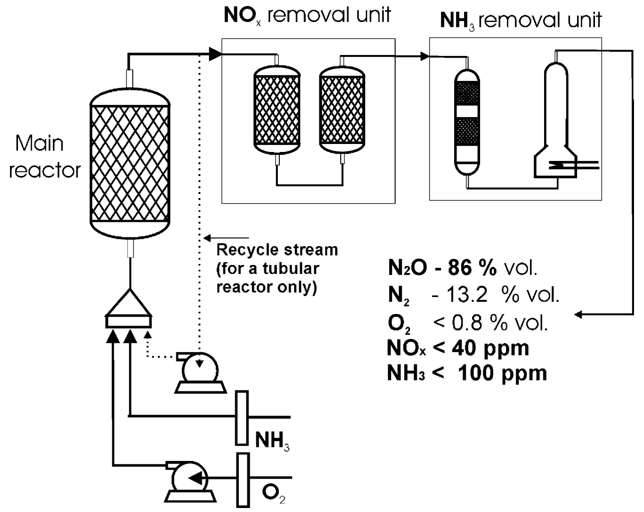


Fig. 7. A process flowsheet for production of N_2O via selective oxidation of ammonia over Mn–Bi–O/α-Al_2O_3 catalyst.

reaction mixture is diluted by the recycle stream in order to decrease the inlet ammonia concentration down to 8 vol.%. The conversion of ammonia in the main reactor reaches ca. 98%. The gas which escapes the main reactor is supplied to a NO_x removal unit consisting of two consecutive adiabatic fixed bed reactors. In the first reactor, the formation of N_2O takes place from residual reactants. In the second reactor, the products are cleaned from NO_x via the selective reduction of nitrogen oxides with ammonia in the presence of oxygen to produce molecular nitrogen. The outlet gas from the NO_x removal unit is cooled and fed to a NH_3 removal unit which consists of an ammonia absorber and a stripping tower. The gas product mixture at the outlet of NH_3 removal unit contains mainly nitrous oxide (86% mol) and molecular nitrogen (13.2% mol). The fraction of residual oxygen in the gas product mixture is O_2:N_2O < 1:100.

Some engineering data for the process of synthesis of nitrous oxide at the capacity 100,000 t/y are given in Table 13.

5.5. Summary for the catalytic N_2O production

An α-alumina supported manganese–bismuth oxide catalyst is developed for the oxidation of ammonia into nitrous oxide. The catalyst can be used both in the fixed and fluidized bed conditions. The pilot testing of the catalyst for 600–800 h under conditions of the fixed and fluidized bed revealed that the catalyst properties are retained during the whole test period. At the temperature range of 340–370 °C, the catalyst provides the selectivity for the oxidation of ammonia into nitrous oxide no less than 86%. The data obtained by the pilot testing of the developed catalyst and mathematical modeling of the fluidized bed and tubular reactors for the ammonia oxidation allow a process flowsheet to be suggested for the 100,000 t/y production of nitrous oxide. The process provides the synthesis of nitrous oxide comprising 86% of the target product (the rest is N_2). Ammonia contributes the main part (ca. 70%) to the prime cost of the produced N_2O.

Table 13
Main characteristics of the N_2O synthesis at the N_2O capacity 100,000 t/y

Consumption of ammonia	13500 m^3/h (STP)
Consumption of oxygen	13000 m^3/h (STP)
Operation temperature	330–370 °C
Selectivity to N_2O	86%
Consumption coefficients	
Ammonia	0.9 kg/kg
Oxygen	1.63 kg/kg
Production of steam	13,000 kJ/kg

6. General conclusions

At the last decade, the application of N_2O in the laboratory practice became a fast growing field. It is evidenced, not only by a large number of research groups (according to our estimations, over 40) involved in the N_2O studies, but also by a significant number of recent reviews dedicated to the oxidation chemistry of nitrous oxide [34,119–124].

The studies reviewed in this paper showed that, due to remarkable features of N_2O, this oxidant opens new prospects in the oxidation chemistry in both gas and liquid phases. At present, advances in the gas phase reactions relate mainly to the hydroxylation of benzene and other aromatic compounds over Fe-containing zeolites. Much efforts are being taken currently to study the mechanisms of the oxidation with N_2O and to search for new reactions and new types of the catalysts.

In the liquid phase reactions, nitrous oxide exhibits another aspect of its unique oxidative chemistry, providing a particular type of the non-catalytic oxidation of alkenes to carbonyl compounds (i.e., the carboxidation reactions). The possibility to conduct such reactions without a catalyst mediation suggests a significant technological advantage. But actually it does not mean that there are no needs for catalysis here. On the contrary, one could see that not all carboxidation reactions considered above showed sufficient selectivities. For improving the selectivity, a decrease of the reaction temperature without decreasing the reaction rate would be highly appreciated. Evidently, this can be achieved only with the aid of catalysis.

Studies on the catalytic liquid phase oxidation with N_2O are already initiated [125–131]. The most interesting results in the field were obtained by the research groups of Yamada [127,128], Neumann [129,130], and Kozhevnikov [131]. Using various types of catalysts (Ru porphyrene complexes, polyoxometallates, and supported metals), these authors managed to conduct a selective oxidation of alkenes to epoxides as well as alcohols to aldehydes. Although the reaction temperature still was rather high (up to 150–200 °C), these data showed that the catalytic activation of N_2O in the liquid phase is certainly feasible. Thus, this approach may lead to new breakthrough results in the future.

As for the catalytic carboxidation of alkenes, no successful results in either liquid or gas phases were reported in the literature until now. One may think that this promising type of oxidative reactions may happen to be a difficult challenge for the catalytic research.

Generally, N_2O is considered as an expensive and quite ‘‘exotic’’ compound which application in chemical industry is economically unreasonable. At the thorough consideration it appeared to be not correct. Indeed, the production of unexpensive N_2O seems to be easy arranged as a large-scale catalytic process too, the starting materials being widely available and unexpensive ammonia and air. The economic estimations based on the results of the pilot units tests demonstrated that the specific cost of active oxygen in N_2O obtained by the new technology, is about four times lower than the cost of active oxygen in the widely accepted oxidant H_2O_2 [101]. No doubt this finding will provide an additional driving force for searching new applications of nitrous oxide in various fields of chemistry.

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References

[1] G.K. Boreskov, Catalytic activation of dioxygen, in: J. Andersen, M. Boudart (Eds.), Catalytic Science and Technology, vol. 3, Springer-Verlag, Berlin, 1982, p. 39.
[2] A. Belansky, J. Haber, Oxygen in Catalysis, Marcel Dekker, New York, 1966.
[3] R.S. Liu, M. Iwamoto, J.H. Lunsford, J. Chem. Soc. Chem. Commun. 78 (1982) 78.
[4] H.F. Liu, R.S. Liu, K.Y. Liew, R.E. Johnson, J.H. Lunsford, J. Am. Chem. Soc. 106 (1984) 4117.
[5] M.M. Khan, G.A. Somorjai, J. Catal. 91 (1985) 263.
[6] K.J. Zhen, M.M. Khan, C.H. Mak, K.B. Lewis, G.A. Somorjai, J. Catal. 94 (1985) 501.
[7] M. Iwamoto, K. Matsukami, S. Kagawa, J. Phys. Chem. 87 (1983) 903.
[8] E. Suzuki, K. Makashiro, Y. Ono, Chem. Soc. Jpn. Chem. Commun. (1988) 953.
[9] M.H. Gubelmann, P.J. Tirel, Fr. Pat. 2630735 (filed May 2, 1988).
[10] A.S. Kharitonov, T.N. Aleksandrova, L.A. Vostrikova, V.I. Sobolev, K.G. Ione, G.I. Panov, USSR Pat. 1805127 (filed June 22, 1988).
[11] R. Burch, C. Howitt, Appl. Catal. A: Gen. 86 (2) (1992) 139.
[12] V. Zholobenko, Mendeleev Commun. 1 (1993) 28.
[13] J.S. Yoo, A.R. Sohail, S.S. Grimmer, C.-F. Chin, Catal. Lett. 29 (1994) 299.
[14] V.I. Bogdan, L.M. Kustov, D.B. Batizat, A.M. Sakharov, V.B. Kazansky, Stud. Surf. Sci. Catal. 94 (1995) 635.
[15] J.L. Motz, H. Heinichen, W.F. Hölderich, Stud. Surf. Sci. Catal. 105 (1997) 1053.
[16] N. Häfele, A. Reitzmann, D. Roppelt, G. Emig, Appl. Catal. A: Gen. 150 (1997) 153.
[17] S. Kowalak, K. Nowinska, M. Swiecicka, M. Sopa, A. Jankowska, G. Emig, E. Klemm, A. Reitzmann, in: Proceedings of the 12th International Zeolite Conference, vol. 4, Baltimore, MRS 4, 1998, p. 2847.
[18] S.N. Vereshchagin, N.P. Kirik, N.N. Shishkina, A.G. Anshits, Catal. Lett. 56 (1998) 145.
[19] A. Reitzmann, E. Klemm, G. Emig, Chem. Eng. J. 90 (2002) 149.
[20] A. Ribera, I.W.C.E. Arends, S. de Vries, J. Perez-Ramirez, R.A. Sheldon, J. Catal. 195 (2000) 287.
[21] S.S. Shevade, B.S. Rao, Catal. Lett. 66 (2000) 99.
[22] S. Perathoner, F. Pino, G. Genti, G. Giordano, A. Katovic, J.B. Nagy, Top. Catal. 23 (2003) 125.
[23] B. Wichterlova, Z. Sobalik, J. Dedecek, Appl. Catal. B: Environ. 41 (2003) 97.
[24] S.N. Vereschagin, N.P. Kirik, N.N. Shishkina, S.V. Moroz, A.I. Vyalkov, A.G. Anshits, Catal. Today 61 (2000) 129.
[25] T. Ren, L. Yan, X. Zhang, J. Suo, Appl. Catal. A: Gen. 244 (2003) 11.
[26] E.J.M. Hensen, Q. Zhu, M.M.R.M. Hendrix, A.R. Overweg, P.J. Kooyman, M.V. Sychev, R.A. van Santen, J. Catal. 221 (2004) 560.
[27] Q. Zhu, R.M. van Teeffelen, R.A. van Santen, E.J.M. Hensen, J. Catal. 221 (2004) 575.
[28] A. Waclaw, K. Nowinska, W. Schwieger, Appl. Catal. A: Gen. 270 (2004) 151.
[29] J. Jia, K.S. Pillai, W.M.H. Sachtler, J. Catal. 221 (2004) 119.
[30] K.S. Pillai, J. Jia, W.M.H. Sachtler, Appl. Catal. A: Gen. 264 (2004) 133.
[31] S.I. Reshetnikov, S.B. Ilyin, A.A. Ivanov, A.S. Kharitonov, React. Kinet. Catal. Lett. 83 (2004) 157.
[32] A.A. Ivanov, V.S. Chernyavsky, M.J. Gross, A.S. Kharitonov, A.K. Uriarte, G.I. Panov, Appl. Catal. A: Gen. 249 (2003) 327.
[33] P. Notte, Top. Catal. 13 (2000) 387.
[34] G.I. Panov, A.S. Kharitonov, V.I. Sobolev, Appl. Catal. A 98 (1993) 1.
[35] J.L. Motz, H. Heinichen, W.F. Hölderich, J. Mol. Catal. A: Chem. 136 (1998) 175.
[36] B.I. Halas, K. Frey, K. Varga, I. Kiricsi, React. Kinet. Catal. Lett. 74 (2001) 377.
[37] L.M. Kustov, A.L. Tarasov, V.I. Bogdan, A.A. Tyrlov, J.W. Fulmer, Catal. Today 61 (2000) 123.
[38] B. Vogel, C. Schneider, E. Klemm, Catal. Lett. 79 (2002) 107.
[39] D.P. Ivanov, L.V. Pirutko, V.I. Sobolev, Neftekhimiya 44 (2004) 359 (in Russian).
[40] S.N. Vereschagin, L.I. Baikalova, A.G. Anshits, Izv. Acad. Sci. USSR, Ser. Khim. 8 (1988) 1718 (Russ.).
[41] M. Stockenhuber, R.W. Joyner, J.M. Dixon, M.J. Hudson, G. Grubert, Microporous Mesoporous Mater. 44/45 (2001) 367.
[42] R. Bulanek, B. Wichterlova, K. Novoveska, V. Kreibich, Appl. Catal. A: Gen. 264 (2004) 13.
[43]- E.V. Kondratenko, J. Perez-Ramirez, Appl. Catal. A: Gen. 267 (2004) 181.
[44] K.A. Dubkov, V.I. Sobolev, G.I. Panov, Kinet. Catal. 38 (6) (1997) 1 (in Russian).
[45] K.A. Dubkov, V.I. Sobolev, E.P. Talzi, M.A. Rodkin, et al. J. Mol. Catal. A: Chem. 123 (1997) 155.
[46] A.S. Kharitonov, G.A. Sheveleva, G.I. Panov, V.I. Sobolev, Ye.A. Paukshtis, V.N. Romannikov, Appl. Catal. A 98 (1993) 33.
[47] V.I. Sobolev, G.I. Panov, A.S. Kharitonov, V.N. Romannikov, A.M. Volodin, K.G. Ione, J. Catal. 139 (1993) 435.
[48] G.I. Panov, V.I. Sobolev, A.S. Kharitonov, in: S. Yoshida, N. Takazawa, T. Ono (Eds.), Catalysis Science and Technology, vol. 1, Kodansha, Tokyo, 1991, p. 171.
[49] G.I. Panov, G.A. Sheveleva, A.S. Kharitonov, V.N. Romannikov, L.A. Vostrikova, Appl. Catal. A 82 (1992) 31.
[50] L.V. Pirutko, V.S. Chernyavsky, A.K. Uriarte, G.I. Panov, Appl. Catal. 227 (2002) 143.
[51] P. Kubanek, B. Wichterlova, Z. Sobalik, J. Catal. 211 (2002) 109.
[52] D. Meloni, R. Monaci, V. Solinas, G. Berlier, S. Bordiga, I. Rossetti, C. Oliva, L. Forni, J. Catal. 214 (2003) 169.
[53] J. Perez-Ramirez, F. Kapteijn, J.C. Groen, A. Domenech, G. Mul, J.A. Moulijn, J. Catal. 214 (2003) 33.
[54] N.A. Kachurovskaya, G.M. Zhidomirov, E.J.M. Hensen, R.A. van Santen, Catal. Lett. 86 (2003) 25.
[55] A.L. Yakovlev, G.M. Zhidomirov, R.A. van Santen, J. Phys. Chem. B 105 (2001) 12297.

[56] N.A. Kachurovskaya, G.M. Zhidomirov, R.A. van Santen, J. Phys. Chem. B 108 (2004) 5944.
[57] J.A. Ryder, A.K. Chakraborty, A. Bell, J. Catal. 220 (2003) 84;
J.A. Ryder, A.K. Chakraborty, A. Bell, J. Catal. 106 (2002) 7059.
[58] B.R. Wood, J.A. Reimer, A. Bell, M.T. Janicke, K.C. Ott, J. Catal. 224 (2004) 148.
[59] J.A. Ryder, A.K. Chakraborty, A. Bell, J. Phys. Chem. B 106 (2002) 7059.
[60] K. Yoshizawa, Y. Shiota, T. Yumura, T. Yamabe, J. Phys. Chem. B 104 (2000) 734.
[61] M. Mauvezin, G. Delahay, B. Coq, S. Kieger, J.C. Jumas, J. Olivier-Fourcade, J. Phys. Chem. B 105 (2001) 928.
[62] G. Berlier, G. Spoto, G. Ricchiardi, S. Bordiga, C. Lamberti, A. Zecchina, J. Mol. Catal. A 182/183 (2002) 359.
[63] G. Berlier, A. Zecchina, G. Spoto, G. Ricchiardi, S. Bordiga, C. Lamberti, J. Catal. 215 (2003) 264.
[64] L. Kiwi-Minsker, D.A. Bulushev, A. Renken, J. Catal. 219 (2003) 273.
[65] B. Louis, C. Terel, L. Kiwi-Minsker, A. Renken, Catal. Today 69 (2001) 365.
[66] I. Yuranov, Z. Bulushev, L. Kiwi-Minsker, J. Catal. 227 (2004) 138.
[67] G.D. Pirngruber, J. Catal. 219 (2003) 456.
[68] P.K. Roy, G.D. Pirngruber, J. Catal. 227 (2004) 164.
[69] S. Komeoka, T. Nobukova, S.-I. Tanaka, I. Shin-ichi, K. Tomishige, K. Kunimori, Phys. Chem. Chem. Phys. 5 (2003) 3328.
[70] E.V. Starokon, K.A. Dubkov, L.V. Pirutko, G.I. Panov, Top. Catal. 23 (2003) 137.
[71] K.A. Dubkov, N.S. Ovanesyan, A.A. Shteinman, E.V. Starokon, G.I. Panov, J. Catal. 207 (2002) 341.
[72] G.M. Zhidomirov, A.L. Yakovlev, M.A. Milov, N.A. Kochurovskaya, I.V. Yudanov, Catal. Today 51 (1999) 397.
[73] K. Lazar, A.N. Kotasthane, P. Fejes, Catal. Lett. 57 (1999) 171.
[74] T.V. Voskoboinikov, H.-Y. Chen, W.M.H. Sachtler, Appl. Catal. B 19 (1998) 279.
[75] P. Fejes, J.B. Nagy, K. Lazar, J. Halasz, Appl. Catal. A: Gen. 190 (2000) 117.
[76] P. Marturano, L. Drozdova, A. Kogelbauer, R. Prins, J. Catal. 192 (2000) 236.
[77] A.A. Battiston, J.H. Bitter, W.M. Heijboer, F.M.F. de Groot, D.S. Koningsberger, J. Catal. 215 (2003) 279.
[78] A.R. Overweg, M.W.J. Craje, A.M. van der Kraan, I.W.C.E. Arends, A. Ribera, R.A. Sheldon, J. Catal. 223 (2004) 262.
[79] El-M. El-Malki, R.A. van Santen, W.M.H. Sachtler, J. Catal. 196 (2000) 212.
[80] G. Berlier, G. Spoto, S. Bordiga, G. Ricchiardi, P. Fisicaro, A. Zecchina, I. Rossetti, E. Selli, L. Forni, E. Giamello, C. Lamberti, J. Catal. 208 (2002) 64.
[81] K.A. Dubkov, Ye.A. Paukshtis, G.I. Panov, Kinet. Katal. 42 (2001) 205.
[82] G.I. Panov, V.I. Sobolev, K.A. Dubkov, A.S. Kharitonov, Stud. Surf. Sci. Catal. 101 (1996) 493.
[83] G.I. Panov, V.I. Sobolev, K.A. Dubkov, V.N. Parmon, N.S. Ovanesyan, A.E. Shilov, A.A. Shteinman, React. Kinet. Catal. Lett. 61 (2) (1997) 251.
[84] M.A. Rodkin, V.I. Sobolev, K.A. Dubkov, N.H. Watkins, G.I. Panov, Stud. Surf. Sci. Catal. 130 (2000) 875.
[85] P.P. Knops-Gerrits, W.J. Smith, Stud. Surf. Sci. Catal. 130 (2000) 3531.
[86] V. Duma, D. Hönicke, J. Catal. 191 (2000) 93.
[87] D.P. Ivanov, V.I. Sobolev, L.V. Pirutko, G.I. Panov, Adv. Synth. Catal. 344 (2002) 986.
[88] B. Notari, Stud. Surf. Sci. Catal. 37 (1988) 413.
[89] G.I. Panov, K.A. Dubkov, E.V. Starokon, V.N. Parmon, React. Kinet. Catal. Lett. 76 (2002) 401.
[90] F.S. Bridson-Jones, G.D. Buckley, L.H. Cross, A.P. Driver, J. Chem. Soc. (1951) 2999.
[91] F.S. Bridson-Jones, G.D. Buckley, J. Chem. Soc. (1951) 3009.
[92] K.A. Dubkov, G.I. Panov, E.V. Starokon, V.N. Parmon, React. Kinet. Catal. Lett. 77 (2002) 197.
[93] R. Huisgen, Angew. Chem. Int. Ed. Engl. 2 (1963) 562.
[94] M.D. Su, H.Yi. Liao, W.S. Chung, S.Y. Chu, J. Org. Chem. 64 (1999) 6710.
[95] V.I. Avdeev, S.Ph. Ruzankin, G.M. Zhidomirov, Chem. Commun. (2003) 42.
[96] E.V. Starokon, K.A. Dubkov, D.E. Babushkin, V.N. Parmon, G.I. Panov, Adv. Synth. Catal. 346 (2004) 268.
[97] S.V. Semikolenov, K.A. Dubkov, E.V. Starokon, D.E. Babushkin, G.I. Panov, Izv. Russ. Akad. Sci., Ser. khim., No. 4 (2005) (Russ.).
[98] B. Delmon, Appl. Catal. B: Environ. 1 (1992) 139;
F. Kapteijn, J. Rodrigues-Mirasol, J.A. Moulijn, Appl. Catal. B: Environ. 9 (1996) 25.
[99] G. Centi, S. Parathoner, F. Vazzana, Chem. Tech. 3 (1999) 48.
[100] A.K. Uriarte, M.A. Rodkin, M.J. Gross, A.S. Khartinov, G.I. Panov, Catal. Stud. Surf. Sci. Catal. 110 (1997) 857.
[101] A.K. Uriarte, Stud. Surf. Sci. Catal. 130 (2000) 743.
[102] G.I. Panov, A.K. Uriarte, M.A. Rodkin, V.I. Sobolev, Catal. Today 41 (1998) 365.
[103] I.L. Knuniyantz (Ed.), Chemical Encyclopedy, vol. 1, Khimiya, Moscow, 1988 , p. 94 (in Russian).
[104] EP 0054965, C01B 21/22 (1982).
[105] EP 1036761, C01B 21/22 (2000).
[106] Pat. DE, N 503200 (1930).
[107] Pat. CSR. N 158091 (1973).
[108] EP 0799792, C01B 21/22 (1997).
[109] V.A. Roiter (Ed.), Handbook on Catalytic Properties of Substances, Naukova Dumka, Kiev, 1968 (Russ.)
[110] E.M. Slavinskay, S.A. Veniaminov, P. Notte, A.S. Ivanova, A.I. Boronin, Yu.A. Chesalov, I.A. Polukhina, A.S. Noskov, J. Catal. 222 (2004) 129.
[111] J.J. Van Deemter, Chem. Eng. Sci. 13 (1961) 143.
[112] M.G. Slin'ko, Mathematical Modeling of Chemical Reactors, Novosibirsk, Institute of Catalysis, 1968 (Russ.).
[113] WO 00/01654 (2001).
[114] V.N. Kashkin, V.S. Lakhmostov, I.A. Zolotarskii, A.S. Noskov, J.J. Zhou, Chem. Eng. J. 91 (2003) 215.
[115] A.S. Noskov, I.A. Zolotarskij, S.A. Pokrovskaya, V.N. Korotkikh, I.A. Polukhina, Kataliz v Promyslennosty (Catal. Ind.) 1 (2004) 5 (in Russian).
[116] A.S. Noskov, I.A. Zolotarskij, S.A. Pokrovskaya, V.N. Korotkikh, in: Proceedings of XVI International Conference on Chemical Reactors (Chemreactor-16), Berlin, Germany, December 1–3, 2003, Novosibirsk: BIC, 2003, p. 198.
[117] A.S. Noskov, I.A. Zolotarskij, S.A. Pokrovskaya, V.N. Korotkikh, E.M. Slavinskay, V.V. Mokrinskij, V.N. Kashkin, Chem. Eng. J. 91 (2003) 235.
[118] Pat. RF 2185237 (2004).
[119] A. Kharitonov, G. Panov, V. Sobolev, Usp. Khim. 11 (1992) 2062.
[120] A. Reizman, M. Häfele, G. Emig, Trends Chem. Eng. 3 (1996) 63.
[121] G. Panov, A. Uriarte, M. Rodkin, V. Sobolev, Catal. Today 4 (1998) 365.
[122] F. Kaptejn, J. Rodriguez-Mirazol, J. Moulijn, Appl. Catal. B: Environ. 9 (1996) 25.
[123] G. Panov, CATTECH 4 (2000) 8–32.
[124] A. Leontiev, O. Fomicheva, M. Proskurina, N. Zefirov, Usp. Khim. 70 (2001) 107 (in Russian).
[125] B. Ohtani, S. Takamiyk, Y. Hirai, M. Sudoh, S. Nishimoto, T. Kagiya, J. Chem. Soc. Perkin Trans. 2 (1992) 175.
[126] J.T. Groves, J.S. Roman, J. Am. Chem. Soc. 117 (1995) 5594.
[127] T. Yamada, K. Hashimoto, Y. Kitaichi, K. Suzuki, Chem. Lett. (2001) 922.
[128] K. Hashimoto, H. Tanaka, T. Ikeno, T. Yamada, Chem. Lett. (2002) 582.
[129] R. Ben-Daniel, L. Weiner, R. Neumann, J. Am. Chem. Soc. 124 (2002) 8788.
[130] R. Ben-Daniel, R. Neumann, Angew. Chem. Int. Ed. 42 (2003) 92.
[131] T.L. Stuchinskaya, I. Kozhevnikov, Catal. Commun. 4 (2003) 609.