

WYRÓŻNIONE PRACE DOKTORSKIE

CATALYTIC DECOMPOSITION OF N₂O USING A NEW GENERATION OF FUNCTIONALIZED MICROPOROUS AND MESOPOROUS INORGANIC MATERIALS

KATALITYCZNY ROZKŁAD N₂O Z ZASTOSOWANIEM NOWOCZESNYCH, FUNKCJONALIZOWANYCH MIKRO- I MEZOPOROWATYCH MATERIAŁÓW NIEORGANICZNYCH

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Abstract

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prowadzi obecnie badania naukowe w Zespole Chemicznych Technologii Środowiskowych pod kierownictwem dr hab. Lucjana Chmielarza, prof. UJ w Zakładzie Technologii Chemicznej na Wydziale Chemii UJ. Zainteresowania naukowe autorki dotyczą syntezy nowoczesnych materiałów porowatych o właściwościach zeolitów i ich aktywności katalitycznej w procesach środowiskowych.

ABSTRACT

In the framework of the presented doctoral thesis, different groups of a new generation of functionalized microporous and mesoporous inorganic materials were prepared. The studies included synthesis and post synthesis modification of: mesoporous silica (SBA-15) modified with metals by MDD method, hydrotalcite-like materials, nanostructured Co-Ce-O systems, hierarchical materials originated from mesoporous silicas and Beta zeolite nanoparticles, mesoporous Beta zeolite obtained using mesotemplate-free method, ZSM-5 and Y zeolites calcined at different temperatures.

Physicochemical properties of the obtained materials were studied by various techniques such as: low-temperature N₂ sorption, X-ray diffraction, TG and ICP analyzes, EPR, IR-DRIFT and UV-vis-DR spectroscopies, SEM and TEM images, X-ray photoelectron spectroscopy, NH₃-TPD and H₂-TPR.

The obtained samples were tested as catalysts in low-temperature (250–500°C) N₂O decomposition. Nitrous oxide is one of the greenhouse gases with a very long lifetime in the atmosphere (about 150 years) and high Global Warming Potential (about 310 times of GWP of CO₂). Nitric acid plants are the main source of N₂O emission among chemical industry and the commercial technology for reduction of this emission, fulfilling all industrial needs, is still not available. Thus, extensive studies in this area are necessary to reduce the harmful impact of N₂O on the environment.

All the tested catalysts were active in N₂O decomposition, however the best results were achieved over nanostructured Co-Ce-X systems obtained using reverse microemulsion method and SBA-15 modified with Rh and Cu, Fe, Ti or Al by MDD method. Over the Co-Ce-X samples 100% of N₂O conversion was obtained at about 400°C, while for Rh modified SBA-15 at about 450°C. It was found that Co₃O₄ spinel (redox centers) is responsible for high activity of Co-Ce-X systems. However, activity of this catalyst was enhanced by the presence of ceria increasing the oxygen mobility on the catalyst surface.

Keywords: nitrous oxide, catalytic decomposition, micro-mesoporous materials, zeolites

Słowa kluczowe: podtlenek azotu, rozkład katalityczny, materiały mikro-mezoporo-
rowate, zeolity

STRESZCZENIE

W ramach niniejszej rozprawy doktorskiej wykonano syntezę i modyfikację nowoczesnych, funkcjonalizowanych mikro- i mezoporowatych materiałów nieorganicznych. Badaniami objęto takie materiały jak: mezoporowata krzemionka (SBA-15) modyfikowana metalami przy użyciu metody MDD, materiały tlenkowe uzyskane na bazie hydrotakitu, nanometryczne układy tlenkowe Co-Ce-O, materiały o hierarchicznej strukturze porowatej otrzymane w wyniku impregnacji mezoporowatych krzemionek (typu SBA-15 i MCF) nanoziarnami zeolitu Beta, mezoporowaty zeolit Beta otrzymany metodą bez użycia szablonu mezoporów oraz zeolity ZSM-5 i Y kalcynowane w różnych temperaturach.

Właściwości fizyko-chemiczne otrzymanych materiałów określono za pomocą takich technik jak: niskotemperaturowa sorpcja N_2 , dyfrakcja promieniowania rentgenowskiego, analizy TG i ICP, spektroskopie EPR, IR-DRIFT i UV-vis-DR, mikroskopia SEM i TEM, spektroskopia fotoelektronów wzbudzonych rentgenowsko (XPS) oraz techniki temperaturowo-programowane (NH_3 -TPD i H_2 -TPR).

Otrzymane materiały zostały przebadane w roli katalizatorów niskotemperaturowego (250–500°C) rozkładu N_2O . Podtlenek azotu jest jednym z gazów cieplarnianych o długim czasie życia w atmosferze (ok. 150 lat) i wysokim współczynniku GWP (ok. 310 razy większy od GWP dla CO_2). Fabryki produkujące kwas azotowy(V) stanowią największe źródło emisji N_2O spośród przemysłu chemicznego, a komercyjne technologie zmniejszające emisję tego szkodliwego tlenku do atmosfery nie są dostępne.

Wszystkie przebadane katalizatory były aktywne w procesie rozkładu N_2O , aczkolwiek największą aktywnością odznaczały się dwie grupy materiałów: nanometryczne układy Co-Ce-X otrzymane metodą odwróconej mikroemulsji oraz SBA-15 modyfikowany Rh i Cu, Fe, Ti albo Al metodą MDD. 100% konwersji N_2O w obecności katalizatora Co-Ce-X osiągnięto w temperaturze ok. 400°C, a przy użyciu mezoporowatej krzemionki modyfikowanej Rh w temperaturze ok 450°C. Stwierdzono, że za wysoką aktywność próbek z serii Co-Ce-X odpowiedzialny jest spinel Co_3O_4 (centrum redox). Aczkolwiek jego aktywność została wzmocniona obecnością ceru zwiększającego mobilność tlenu na powierzchni katalizatora.

1. HARMFUL IMPACT OF N_2O ON THE ENVIRONMENT

The harmful impact of N_2O on the environment has been neglected for a very long time, mainly on account of its relatively small emission. More advanced research motivated by rapid growth of chemical industry and road traffic in the second half of the 20th century revealed the harmful impact of N_2O on the environment [1]. Nitrous oxide, due to strong absorbance of infrared radiation is (together with CO_2 and CH_4) one of the main greenhouse gases. In practice it means that N_2O molecules trap infrared radiation (heat) emitted from the Earth's surface, simulta-

neously increasing the temperature on Earth [2]. Its contribution to global warming is estimated to be about 6%. The GWP index (Global Warming Potential) of nitrous oxide is 310 and 21 times higher than GWP of CO₂ and CH₄, respectively. This fact explains why even the relatively small emission of N₂O in comparison to other greenhouse gases (about 10% of CO₂ emission) is very dangerous for environment. Moreover, the lifetime of N₂O molecule in the atmosphere is very long, approximately 150 years. Nitrous oxide is also one of the gases depleting the ozone layer, however its interaction with O₃ is indirect. N₂O is one of main sources of other nitrogen oxides NO_x in the stratosphere, which directly deplete ozone layer. However, there is still no consensus in quantitative values of its complex ozone depleting potential [3].

2. EMISSION SOURCES

Nitrous oxide, being a part of the Earth's nitrogen cycle, is one of the gases naturally present in the environment. The natural sources of N₂O in the atmosphere are processes in lands and oceans, however the emission from anthropogenic sources is becoming increasingly important. The emission coming from human activities is about 40% of the total N₂O emission (8% of total greenhouse gases emission in EU). Despite the fact that about 60% of nitrous oxide emission comes from natural sources, the problem is in high concentration of anthropogenic N₂O emission sources which can result in a local exceeding of emission standards. The anthropogenic sources can be divided into three main sections: (i) agriculture (land cultivation, fertilizers), (ii) transportation (by-product of nonselective catalytic reduction of NO_x (NSCR) and three-way catalysis (TWC)) and (iii) chemical industry (adipic acid, nitric acid and fertilizers production). Other, more dispersed sources are fossil fuels, biomass burning and waste incineration. Among the mentioned sources, the highest contribution to N₂O emission comes from agriculture, about 1000–2200 kt per year [2, 4, 5].

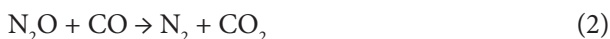
The main emission of N₂O in terms of chemical industry is assigned to adipic acid, nitric acid, caprolactam, glyoxal and acrylonitrile production plants. Moreover, nitrous oxide is also produced in all processes involving ammonia oxidation, or where nitric acid acts as oxidizing agent [3].

The emission of nitrous oxide to the atmosphere caused by human activities disturbs the natural balance in the environment. The reduction of anthropogenic N₂O emission by about 70–80% is necessary to stabilize its concentration in the atmosphere. This goal can be achieved in two ways, by prevention of N₂O formation or by after-treatment solutions. The type of undertaken method is strongly influenced by the construction of the existing installations and economic issues [4].

3. CATALYTIC N₂O DECOMPOSITION AND REDUCTION

The non-catalytic decomposition of nitrous oxide to nitrogen and oxygen starts at about 600°C (Eq. 1). The N-O bond order (1.6) is lower than the order of N-N bond (2.7), so the breaking of N-O bond is expected to occur easier. Due to the spin-forbidden route of this reaction (N₂O is diamagnetic and the product of its decomposition – oxygen is paramagnetic) the activation energy of this process is very high – about 250–270 kJ/mol (Fig. 1). During the reaction 82 kJ of heat is produced per one mole of N₂O molecules (exothermic reaction), however to exceed the activation energy barrier heat income is necessary [6, 7].

The N₂O molecule can be also decomposed by the use of the reducing agents such as CO (Eq. 2), H₂, light hydrocarbons or carbon [1].



The temperature necessary to nitrous oxide destruction can be decreased in the presence of a catalyst. The electron transfer to antibonding 3π orbital in N₂O molecule can be facilitated in the presence of strong electron donors (changing the oxidation state during the catalytic cycle) e.g. transition metals, mixed oxides, zeolites [4].

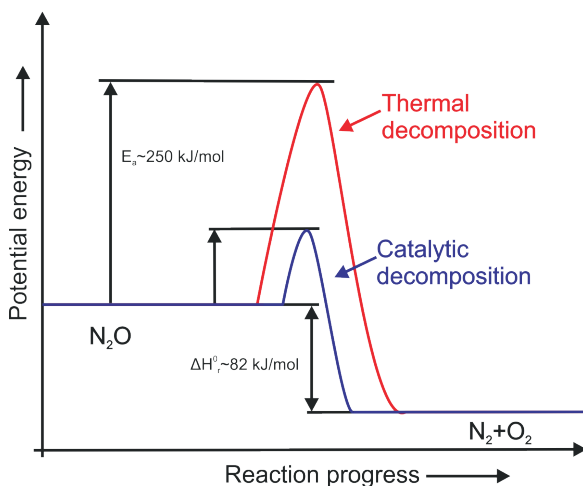
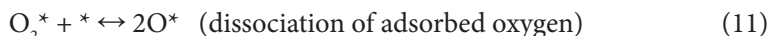


Figure 1. Energy diagram for N₂O decomposition reaction

The mechanism of N₂O decomposition is complex and, despite extensive studies, still not definitively established. Numerous elementary steps are considered as taking part in this reaction (Eqs. 3–11) [8]





* – active center

The general concept assumes dissociative chemisorption of the N₂O molecule with the evolution of the N₂ molecule (Eq. 3), followed by desorption of molecular oxygen (Eq. 4). Some scientists proposed adsorption of nitrous oxide on the catalyst surface (Eq. 5) and the surface reaction (Eq. 6) as possible elementary steps, however the majority agreed that the adsorbed N₂O molecule does not take part in the reaction. Oxygen desorption from the catalyst surface is considered as a rate determining step and can proceed according to (Eq. 4) and by the reaction with N₂O molecule from the gaseous phase (Eqs. 7 and 9) (Fig. 2) [8]. It must be taken into account that the contribution of the particular elementary reactions in the overall mechanism strongly depends on the type of catalyst used. E.g. Obalova et al. [8, 9] indicated that recombination of adsorbed oxygen species over mixed metal oxides (prepared from LDHs) proceeds through the Eley-Rideal mechanism.

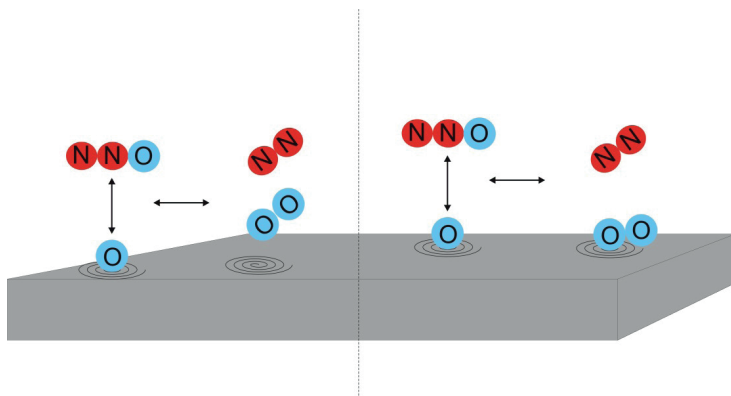
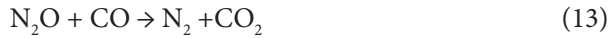


Figure 2. Removal of surface oxygen by reaction with N₂O molecule (by Eley-Rideal mechanism)

In case of SCR of N_2O with CO the presence of a reducing agent facilitates the removal of oxygen atoms adsorbed on the catalyst surface (surface scavenging) (Eq. 12). Therefore, the slowest, rate determining step is accelerated and the reaction proceeds at lower operation temperatures. Generally, it is suggested that CO acts as a stoichiometric reductant in the presence of N_2O (Eq. 13). N_2O reduction with CO could be applied especially in case of sources, where CO is already present, such as oxalic acid $((COOH)_2 \cdot 2H_2O)$ plants [10–14].



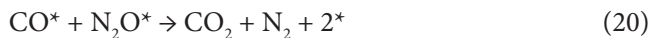
Similarly to N_2O decomposition, many different mechanisms of N_2O reduction with CO have been proposed. The two most popular are called ‘redox’ and ‘associative’ mechanisms.

First, redox mechanism starts with oxidation of the catalyst surface by N_2O decomposition (oxygen atoms chemisorb on the catalyst surface) followed by its reduction with CO (also adsorbed on the surface, or from gaseous phase) with the formation of CO_2 (Eqs. 14–17). Second, associative mechanism assumes simultaneous oxidation and reduction of the catalyst surface by reaction of both adsorbed N_2O and CO molecules, or adsorbed CO and N_2O from gaseous phase (Eqs. 18–21) [14].

Redox mechanism:

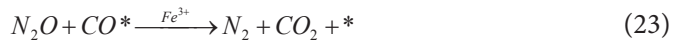


Associative mechanism:



Moreover the mechanism of N_2O reduction by CO depends on the used catalyst and form of active phase. Pérez-Ramírez [15] stated that over Fe modified ZSM-5

zeolites the mechanism depends on the iron distribution. Over isolated Fe site CO adsorbs on the iron centers and in the next step reacts with N₂O from gaseous phase (Eqs. 22 and 23). While in case of oligomeric Fe clusters CO reacts with adsorbed oxygen species (Eq. 24).



4. CATALYSTS FOR N₂O DECOMPOSITION AND REDUCTION

Materials catalytically active in N₂O decomposition and reduction can be divided into a few groups: pure metals, pure oxides, mixed oxides, hydrotalcites derived materials, spinels, perovskites, transition metals supported on alumina, silica and zirconia and zeolites [1].

Over pure metals (Pt, Pd, Ag, Au, Ge) N₂O decomposition starts at about 370°C [16, 17]. Metal catalysts decrease the activation energy from 250–270 kJ/mol to about 130 kJ/mol. An important drawback of this group of catalysts is their high price and poorly developed surface area [1].

Pure metal oxides (transition and rare earth metals) such as CuO, CoO, CeO₂, Cr₂O₃, Fe₂O₃, CaO, SrO, V₂O₃, MnO exhibit high activity in N₂O decomposition (activation energy between 80–170 kJ/mol) [18, 19]. However, their activity depends on the metal oxidation state. E.g. MnO and V₂O₃ are much more active in comparison to Mn₂O₃ and V₂O₅. An additional inconvenience connected with this group of materials is the possibility of the oxidation state changing under reaction conditions [1].

Studies related to catalytic activity of metal oxides lead to the conclusion that mixed oxides systems such as doped oxides, LDOs (derivatives of hydrotalcites), supported oxides, perovskites and spinels are more active and stable [1]. Layered oxide systems obtained by calcination of hydrotalcites (minerals with general formula $[M^{2+}_{1-x}M^{3+}_x + (OH)_2]^{x+}A^{-n}_{x/n} \cdot mH_2O$, where M are di- and trivalent cations, A interlayer anions and x can take values in the range of 0.2–0.35) are recently under great scientist interest [20]. The catalyst such as e.g. Co/Mg-Mn/Al [21], Ni-(Mg)-Al and Ni-(Mg)-Mn [22], Co-Mn-Al promoted with alkali metals (Li, Na, K) [23, 24] enable decrease of activation energy of N₂O decomposition to about 45–55 kJ/mol.

Another very wide group of catalysts for N₂O decomposition and reduction are zeolites. Zeolites such as ZSM-5, ZSM-11, Beta, Y, A, X, Mordenite and Ferrierite, modified by ion exchange with transition metal ions, such as Fe, Co, Ni, Cu, Mn,

Ce, Ru, Rh or Pd, exhibit catalytic activity even below 300 °C (activation energy about 75–170 kJ/mol) [25–27]. The most extensive studies were focused on iron modified ZSM-5, which additionally shows increased activity in the presence of NO (natural component of waste gases emitted from nitric acid plants) [28, 29].

Despite numerous studies up-till-now, the catalytic systems fulfilling all parameters needed for their commercialization (high activity, selectivity and stability, low price, nontoxic components) have not been developed yet. To meet the environmental protection standards further research, based on current knowledge, is required to develop catalysts for commercial application.

5. EXPERIMENTAL

Catalytic studies of N₂O decomposition were performed in a fixed-bed quartz microreactor. For each experiment 0.1 g of catalyst (particle sizes in the range of 0.160–0.315 mm) was placed on quartz wool plug in microreactor and outgassed in a flow of pure helium. The composition of outlet gases was analyzed using a gas chromatograph (equipped with TCD detector) or a quadruple mass spectrometer.

The N₂O conversion was determined according to Eq. 25, where XN₂O – conversion of N₂O, c⁰N₂O – concentration of N₂O at reactor inlet, cN₂O – concentration of N₂O at reactor outlet.

$$X_{N_2O} = \frac{c_{N_2O}^0 - c_{N_2O}}{c_{N_2O}^0} \cdot 100\% \quad (25)$$

The above equation was used assuming that the total volumetric flow along the reactor could be considered as constant. During N₂O decomposition from one mole of N₂O molecules 1.5 moles of N₂ and O₂ are formed, what causes an increase of the outlet molar flow [30–32].

6. RESULTS AND DISCUSSION

The research aim was the synthesis and catalytic functionalization of different types of porous materials such as: (i) mesoporous silica (SBA-15) modified with Rh, Cu, Fe, Ti and Al by MDD method [33], (ii) hydrotalcite-like materials containing Cu, Co, Ni and Fe [34], (iii) nanostructured Co-Ce-O systems obtained using reverse microemulsion method [35], (iv) hierarchical materials originated from MCF and SBA-15 materials and Beta zeolite nanoparticles modified with Fe [36, 37], (v) mesoporous Beta zeolite obtained using mesotemplate-free method modified with Fe [37] and (vi) Fe modified ZSM-5 and Y zeolites calcined at different temperatures [38].

The first group of catalysts examined in N₂O decomposition was mesoporous silica modified with transition metals by MDD method [33]. Rh and Cu, Fe, Ti or

Al were introduced on the surface of SBA-15 silica (micro-mesoporous material with uniform, hexagonally ordered mesopores (Fig. 3.)), with different loadings, by Molecular Designed Dispersion method. Using this method we obtained the following series of the samples: SBA-15; Rh(0.05–0.30)-SBA-15; X-SBA-15, where X: Ti, Al, Cu, Fe; Rh-X-SBA-15, where X: Ti, Al, Cu, Fe. MDD method consists of two steps: (i) reaction of metal acetylacetonate complex with silica hydroxyl groups and (ii) thermal decomposition of surface adsorbed complex. This method leads to deposition of metal oxide species in the highly dispersed form. Deposition of rhodium did not produced any new reflexes in XRD patterns, characteristic of Rh or its compounds. Therefore, it could be concluded that the size of rhodium species deposited on the SBA-15 support was below detection level of the XRD method. All the samples (parent SBA-15 and SBA-15 modified with metals by MDD method) exhibited type IV adsorption-desorption isotherms, which are typical of mesoporous materials. We did not observe the blocking of mesopores what proves the high dispersion of deposited metals. Rh was introduced into the samples in the range of values of 0.40 to 1.50%. It was found that with increasing loading of Rh the dispersion of metal species on the silica surface decreased. However, even for the highest loading of noble metal deposited by the MDD method its dispersion did not drop below 70%. The rhodium-modified samples were active in N₂O decomposition. The conversion of N₂O began at temperature as low as 200°C. At higher temperatures the performance of catalysts depended on Rh-loading. Increasing loading of rhodium led to an increase in activity of the catalysts. For the most active catalyst the total N₂O conversion was obtained at 450°C.

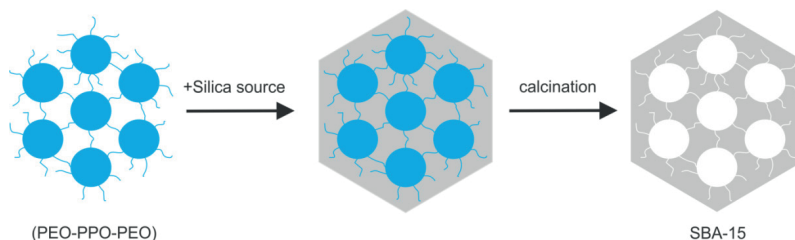


Figure 3. Schematic representation of SBA-15 synthesis

The second group of catalysts analyzed was hydrotalcite derived mixed metal oxides (Fig. 4.) [34]. The samples contained beside Mg and Al also Cu, Co, Fe and Ni. The compositions and atomic ratios of the obtained hydrotalcite-like samples are presented in Tab. 1. Calcined hydrotalcites containing iron and nickel proved to be the least active and therefore, the optimization of the chemical and phase composition was limited only to the Cu and Co-containing catalysts. The optimization consisted of: (i) modification of transition metals content, (ii) modification of calcination temperature, (iii) impregnation with different amounts of alkali metal.

Table 1. Sample codes, compositions and atomic ratios of hydrotalcite-like materials

Sample code	Composition	Atomic ratio
HT600-Cu10	Cu/Mg/Al	10/61/29
HT600-Cu15	Cu/Mg/Al	15/56/29
HT700-Cu15	Cu/Mg/Al	15/56/29
HT800-Cu15	Cu/Mg/Al	15/56/29
HT600-Co10	Co/Mg/Al	10/61/29
HT600-Co15	Co/Mg/Al	15/56/29
HT700-Co15	Co/Mg/Al	15/56/29
HT800-Co15	Co/Mg/Al	15/56/29
HT600-Cu10Co10	Cu/Co/Mg/Al	10/10/51/29
HT700-Cu10Co10	Cu/Co/Mg/Al	10/10/51/29
HT800-Cu10Co10	Cu/Co/Mg/Al	10/10/51/29
HT600-Cu15Co15	Cu/Co/Mg/Al	15/15/41/29
HT600-Fe10	Fe/Mg/Al	10/61/29
HT600-Ni10	Ni/Mg/Al	10/61/29

It was shown that an increase in calcination temperature promoted the formation of the oxide and spinel phases such as MgO, $MgAl_2O_4$, CuO, $CuAl_2O_4$, CoO and Co_3O_4 . Among the samples calcined at 600°C the best results were obtained for the copper-containing catalysts. An increase in calcination temperature to 700°C significantly activated the cobalt-containing catalysts, while an opposite effect was found for the samples containing copper. Among the samples calcined at 800°C the best results were obtained for the catalysts containing simultaneously both cobalt and copper. The activation of the cobalt-containing samples was related to the formation of the catalytically active spinel phases.

It was reported in the literature that modification of the sample with alkaline promoter, potassium in this case, should result in catalyst activation. This effect is related to increased oxygen desorption rate (O_2 produced during N_2O decomposition) through the presence of a strong electron donor [9, 23, 24, 35–37]. In case of a series of the samples modified with Cu deposition of potassium significantly increased their catalytic activity. Moreover, activity increased with increasing potassium content and for HT800-Cu15/K0.9 100% of N_2O conversion was achieved at 500°C.

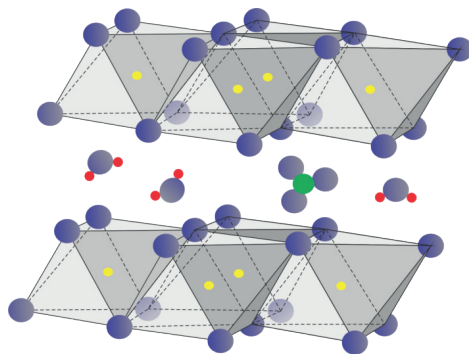


Figure 4. Schema of hydrotalcite structure

The third group of materials examined were nanostructured Co-Ce-O oxide systems obtained using reverse microemulsion method [38]. Two series of oxide systems based on cobalt and cerium were obtained by mixing two water-in-oil microemulsions. The first microemulsion contained cerium and cobalt salts, while the second one a precipitating agent (Fig. 5.). The applied method resulted in the formation of nanosized solid solutions of Co in CeO_2 with different loadings. The formation of reversed solid solutions (Ce in Co_3O_4) was not detected, probably because of faster crystallization of the Co_3O_4 phase. The obtained catalysts were active in N_2O decomposition and the synergetic effect of both metals significantly increased their activity in comparison to pure Ce and Co oxides. In case of a Ce-Co-X series the activity increased with increasing Co content. Such dependence was not observed in case of Co-Ce-X series.

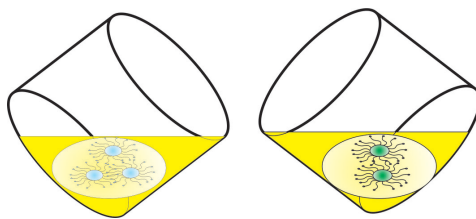


Figure 5. Schema of Co-Ce-O oxide systems synthesis by reverse microemulsion method

An important part of the doctoral thesis was dedicated to the materials with zeolitic properties, such as micro-mesoporous composites with properties of Beta zeolite [39, 40] and ZSM-5 and Y zeolites modified with iron [41].

Combined materials with micro- and mesoporosity, so-called materials with the hierarchical porous structure or hierarchical materials [39, 40], have been synthesized to overcome the diffusion limitations caused by the presence of small channels in zeolites, but also to increase the accessibility of acid centers present inside of the zeolite pore system (influencing the form and amount of introduced transition metal). Both factors mentioned contribute to the improvement of the properties of

mesoporous zeolites in comparison to conventional microporous ones. Hierarchical micro-mesoporous materials with properties of Beta zeolite were obtained by impregnation of mesoporous silica materials such as MCF [39] and SBA-15 [40] with a solution of Beta nanoseeds. Figure 6. presents the schema of SBA-15 impregnation with zeolite nanoseeds.

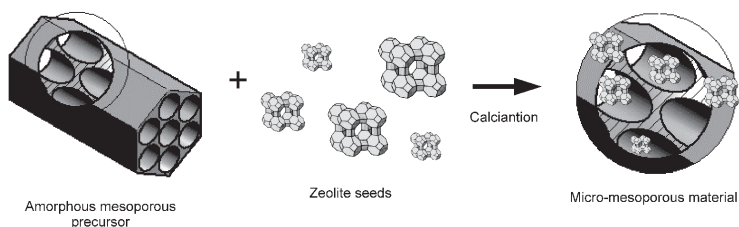


Figure 6. Schema of the impregnation method

Impregnation resulted in introduction of the zeolitic phase on the external surface of mesoporous matrix, as well as inside the mesopore channels. The slurry of zeolite Beta seeds used for impregnation was obtained by shortening of the crystallization time of the parent Beta zeolite solution. MCF material was impregnated with Beta nanoseeds using four different methods [39]: (i) wet impregnation, (ii) wet impregnation with acidification of Beta nanoseeds suspension, (iii) incipient wetness impregnation and (iv) incipient wetness impregnation with acidification of Beta nanoseeds suspension. All the samples were modified with Fe by ion-exchange method. Introduction of Beta nanoseeds to MCF silica significantly increased its catalytic activity in N_2O decomposition, however the activity of combined materials was lower in comparison to conventional Fe-Beta. It is worth to notice that despite significantly lower content of the crystalline (zeolitic) active phase in the hierarchical samples in comparison to conventional zeolite the temperature of effective operation of the impregnated samples is lower only by about 50°C. This fact makes this group of materials very interesting for future applications in catalysis. SBA-15 mesoporous materials [40] were impregnated using two methods: (i) wet impregnation without acidification and (ii) wet impregnation with acidification (methods chosen as more effective than incipient wetness impregnation). Lower content of the zeolitic phase was detected in the acidified sample, what also resulted in its lower catalytic activity in N_2O decomposition.

A second series of the micro-mesoporous samples with Beta zeolite properties [40], was obtained by mesotemplate-free method. This method is based on controlled aggregation of Beta zeolite nanoparticles with the formation of interparticle porosity (Fig. 7.). The generated mesoporosity influenced the process of ion exchange by enhanced accessibility of ion-exchange positions. The coordination and aggregation of introduced into the samples iron was investigated by the UV-vis-DRS and EPR measurements. Iron was introduced to the micro-mesoporous samples mainly in the

form of monomeric Fe³⁺ cations and small oligomeric Fe_xO_y species. While, in case of conventional Beta zeolite iron was present in more aggregated forms such as oligomeric Fe_xO_y species and bulky Fe₂O₃ oxide crystallites. It is worth to mention that the catalytic activity of Fe in N₂O decomposition depends on its aggregation form and more active species were generated in the micro-mesoporous sample [41, 42].

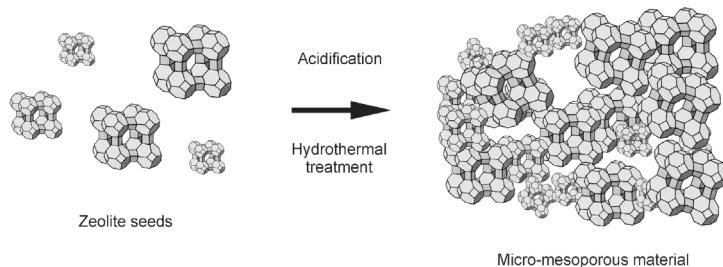


Figure 7. Schema of mesotemplate-free method

The last group of materials examined in the framework of this doctoral thesis was related to ZSM-5 and Y zeolites calcined at different temperatures (500, 600, 700 and 800°C) [43]. The obtained results showed that the type of zeolite structure influenced the form of introduced iron species. Wider pores present in FAU structure (12 MR channels) than in MFI structure (10 MR channels) favored generation of less aggregated iron forms (Fe³⁺ cations and oligomeric Fe_xO_y species), more active in N₂O decomposition. Thus, the FeY series was found to be significantly more active than the Fe-ZSM-5 series.

CONCLUSIONS

In the framework of this doctoral thesis different groups of a new generation of functionalized microporous and mesoporous inorganic materials modified with transition metals were synthesized and tested as catalyst in N₂O decomposition. Results of the performed research were published in six manuscripts.

The novel porous materials such as mesoporous silica (SBA-15) modified with transition metals by MDD method, hydrotalcite derived mixed metal oxides, nanostructured Co-Ce-O systems, hierarchical materials originated from mesoporous silicas and Beta zeolite nanoparticles, mesoporous Beta zeolite obtained using mesotemplate-free method and ZSM-5 and Y zeolites calcined at different temperatures were successfully synthesized and modified with transition metal ions. Various techniques were used for physicochemical characterization of the obtained samples, such as: low-temperature N₂ sorption, X-ray diffraction, TG and ICP analyzes, EPR, IR-DRIFT and UV-vis-DR spectroscopies, SEM and TEM, X-ray photoelectron spectroscopy, NH₃-TPD and H₂-TPR measurements.

All the tested samples were active in low-temperature nitrous oxide decomposition reaction. The comparison of the samples activity is presented in Fig. 8. The desired activity of catalysts for commercial application in this process (in nitric acid plants) should be in the range of 250–500°C. From each group of catalysts one sample, exhibiting the highest activity in N₂O decomposition in the presence of oxygen (the strongest reaction inhibitor) was chosen. The temperature region of their activity was marked with an empty rectangle, while the region of 100% of N₂O conversion was filled with color.

The best results among all tested groups of materials were obtained for nanostructured Co-Ce-O systems obtained using reverse microemulsion method. These catalysts were active in all range of low-temperature N₂O decomposition. High activity of Co-Ce-X systems can be explained by the presence of Co₃O₄ spinel (Co²⁺/Co³⁺ redox sites) strengthened by ceria, which is responsible for increased oxygen mobility on the catalyst surface (oxygen desorption from the catalyst surface is considered as a rate determining step).

Another group of materials potentially interesting for application in this reaction is mesoporous silica (SBA-15) modified with Rh and other metals (Cu, Fe, Ti or Al) deposited by Molecular Design Dispersion method. These catalysts are active in all range of low-temperature N₂O decomposition, however 100% of N₂O conversion was achieved only in 20% of this range.

The other groups of materials tested in the framework of this doctoral thesis were active in the desired range of temperatures (for application in low-temperature N₂O decomposition emitted from nitric acid plants), however they did not result in 100% of N₂O conversion.

Among different groups of functionalized microporous and mesoporous inorganic materials modified with transition metals, tested in N₂O decomposition in the framework of this doctoral thesis, Co-Ce-X systems were found to be the most active. The obtained materials are very attractive for possible application as catalysts for low-temperature N₂O decomposition in nitric acid plants.

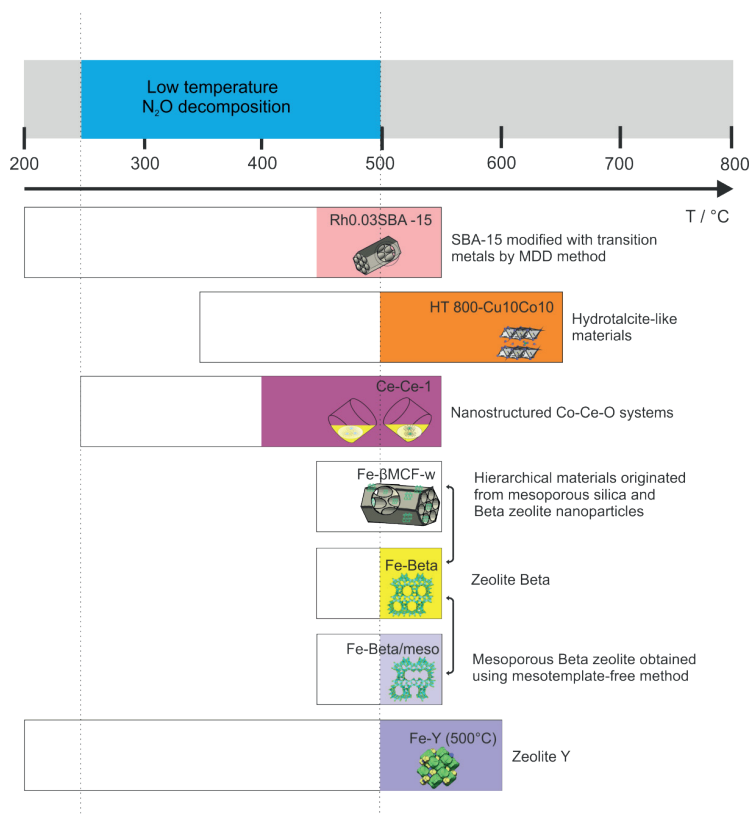


Figure 8. Comparison of the samples activity from different groups of tested materials in N₂O decomposition

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