CATALYTIC OXIDATION OF METHANOL IN THE CENOSPHERIC FLUIDIZED BED

by

Gabriela BERKOWICZ[a*], Jan WRONA[b], Jerzy BARON[a], Dariusz BRADLO[a], and Witold ZUKOWSKI[a]

[a]Faculty of Chemical Engineering and Technology, Cracow University of Technology,
Cracow, Poland
[b]Faculty of Environmental Engineering, Cracow University of Technology, Cracow, Poland

The process of oxidation of gaseous CH_3OH by N_2O was carried out over an Ag–Fe_2O_3-cenosphere catalyst whose structure can be defined as double shell-core catalyst. Preparation of the catalyst was carried out in two stages: thermal decomposition of $Fe(CO)_5$ at above 160 °C and then electroless Ag plating. The process of methanol degradation by N_2O was carried out in a fluidized bed reactor. The study confirms that it is possible to achieve complete degradation of N_2O and CH_3OH for the obtained catalyst at above 450 °C when the contact time of the reactants with the catalyst is approximately 6 second and when the substrates are used in stoichiometric ratios. More than 60% of the hydrogen contained in CH_3OH can be converted to molecular hydrogen at 500 °C with a ratio of N_2O/CH_3OH not greater than 0.6 and with a contact time of reactants with the catalyst of approx. 6 seconds.

Key words: *nitrous oxide, methanol decomposition, core-shell catalyst,
Ag/Fe_2O_3-coated cenospheres, catalytic fluidised bed*

Introduction

Nitrous oxide as a greenhouse gas and an oxidant

Greenhouse gases of anthropogenic origin are the main cause of global climate change. The first symptoms of these changes are phenomena noted in the recent years: record average annual temperatures, heat waves, reduction of the surface area of the polar ice cap, permafrost, and glaciers but also forest fires, violent storms, tornadoes and floods of uncommon scale [1, 2].

After CO_2 and CH_4, nitrous oxide is the third most abundant GHG which is released to the atmosphere [3]. Although concentration of N_2O in the troposphere is more than a thousand times less than CO_2, N_2O is its important component because one molecule of N_2O has the same greenhouse warming power as 298 molecules of CO_2 [4]. Atmospheric N_2O is very stable. It is estimated that its lifetime in the atmosphere is approximately 120 years [5]. In the stratosphere, N_2O reacts with ozone. This reaction significantly decreases ozone concentration; thereby the amount of UV radiation reaching the Earth's surface is increasing [6].

---

* Corresponding author, e-mail: gabriela.berkowicz@pk.edu.pl

S1232

Berkowicz, G., *et al*.: Catalytic Oxidation of Methanol in the Cencspheric ...
THERMAL SCIENCE: Year 2019, Vol. 23, Suppl. 4, pp. S1231-S1240

Nitrous oxide is released into the atmosphere as a result of the processes of nitrification and denitrification occurring in soils and oceans. However, since the beginning of the industrial revolution, industrial and agricultural activities have resulted in a significant increase in its concentration. Nitrous oxide has increased approximately linearly by about 0.8 ppb per year over the past few decades [7]. Permanent increase in N_2O concentration in the atmosphere resulted in a search for an effective catalytic method of its decomposition [8-18]. The U.S. Environmental Protection Agency reported that in the years 1990-2014, almost 80% of N_2O emitted in the US. had its source in agricultural production (mainly emissions from the soil and intestinal processes) [19]. It is impossible to reduce N_2O contained in this stream. On the other hand, N_2O emissions associated with the industrial activity can be restricted. The most important industrial processes, which introduce significant amounts of N_2O into the atmosphere, are the production of adipic acid and nitric acid [20-23]. The other important sources of N_2O emissions include: combustion of fossil fuels, fluidised bed combustion (FBC), non-catalytic selective reduction (NCSR) of NO_x, and using chemicals such as ammonia or urea [24]. The N_2O emissions in industrial plants may be reduced *e. g.* in catalytic reduction. Due to its oxidation potential, N_2O can be used as an oxidant of other air pollutants such as simple hydrocarbons, alcohols, aldehydes, ketones, acids, ethers, organic compounds of chlorine or fluorine [25-27].

In this paper N_2O was used as an oxidant of methanol – an example air pollutant. After CH_4, methanol is the second most abundant organic compound in the atmosphere [28]. The process of catalytic oxidation of methanol enjoys great interest, mainly due to the possibility of hydrogen generation [29-33]. The necessity of rapid removal of heat generated in this process is the premise for carrying it out in a fluidised bed. Intensive mixing, very good conditions of heat exchange, and good temperature equalization inside the bed should contribute to finding the temperature at which it will be possible to carry out optimal decomposition of N_2O and CH_3OH. An additional advantage of the fluidised bed is its tolerance to dust, which can be contained in the air used in the process. Being an active metal catalyst in the oxidative decomposition of methanol, silver was used in the experiments in the form of a catalytic layer coated on a carrier [34].

Cenospheres as a catalyst carrier

Because the process was carried out in a fluidised bed, it was decided to embed the catalyst on the surface of fly ash cenospheres. An aluminosilicate sphere filled with gas (N_2, CO_2) was the core of the active layer of the catalyst. These hollow spherical particles are formed during the combustion of bituminous coal in pulverized fuel boilers used in the power industry, and as a fraction of fly ash are retained in electrofilters [35]. Globally, approximately 750 million tons of fly ash per annum are produced, most of which in China [36]. The large scale of use of coal in energy processes results in large quantities of cenospheres in fly ash, constituting 0.3-1.5 wt.% [37]. In order to minimize cenospheres impact on the environment, the method of its application is looking for [38]. Cenospheres can be easily separated from the other components of fly ash, because of their apparent density of 0.4-0.8 g/cm^3 [39], which makes them float on the water surface. Cenospheres are used primarily as fillers. Cenospheres have a high strength and thermal stability of the mould and thus may be an interesting carrier on which an active layer of *e. g.* a catalyst can be deposited. Spherical cenospheres have low apparent density and therefore can be easily introduced into a fluidised state [40].

Depositing a layer of a catalyst on cenospheres facilitates significant reduction in density of the target particle of the catalyst. As a consequence, the minimum fluidisation ve-

locity of grains of the catalyst is reduced and the contact time between fluidising medium and grains is increased. Previous studies have shown that oxidation of methanol can be successfully carried out on Ag-coated cenospheres having a core-shell structure [41]. It turned out, however, that the silver deposited on aluminosilicate microsphere is not resistant to abrasion, which resulted in silver particles of the shell being removed from the fluidised bed.

In this paper, the process of removing CH_3OH and N_2O from a gas stream was carried out over an Ag-Fe_2O_3-cenospheres whose structure can be defined as: core-double shell catalyst. Studies on the oxidation of CH_3OH using N_2O seem to be important not only from theoretical, but also from the environmental point of view.

Experimental part

Catalyst preparation

A schematic diagram of the core-double shell cenospheric catalyst is shown in fig. 1. The process of obtaining this catalyst was carried out in two stages. First, a uniform layer of iron was deposited by thermal decomposition of iron pentacarbonyl $Fe(CO)_5$ at above 160 °C. In order to ensure uniform iron coating of cenospheres, the process was carried out in a fluidised bed reactor. Iron pentacarbonyl was decomposed according to the reaction: $Fe(CO)_5 \rightarrow Fe + 5CO\uparrow$ [42].

In this manner, 99% yield of iron deposition process was achieved. The obtained product was designated as Fe-Cenospheres. The SEM images of Fe-coated cenospheres are shown in figs. 2(a) and 2(b). In the SEM pictures, there was a uniform layer of iron covering the almost entire surface of a cenosphere, fig. 2(a). The BSE (backscattered electrons) imaging indicated on iron as the only chemical component of coating. The XRD and ICP methods confirmed the presence of metallic iron on the surface of cenospheres, fig. 3, and determined that the resulting material contains 18 wt.% Fe.

Figure 1. A schematic diagram of Ag-Fe_2O_3-conosphere catalyst;
1 – gas-filled interior of cenosphere,
2 – glassy matter (160-200 μm in diameter and
2-5 μm in thickness), 3 – Fe_2O_3 coating,
4 – silver coating

In the second step, the method of electroless plating of silver on the iron coating of Fe-cenospheres was applied. Fe-coated cenospheres were introduced into 130 cm^3 methanolic solution of silver nitrate (concentration of 0.1 mol/dm^3). Reduction of silver was carried out by dropping sodium hypophosphite solution to achieve three-fold excess of the precipitating agent. Silver precipitation process is described by the equation:

$$2AgNO_3 + NaH_2PO_2 + H_2O \rightarrow NaH_2PO_4 + 2Ag + 2HNO_3$$
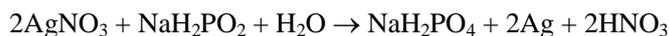
Precipitation of silver was carried out at 80 °C. The obtained product was filtered, dried at 100 °C for 2 hours, and calcined for 1 hour at 140 °C and then for 4 hours at 600 °C. The SEM images of Ag-Fe_2O_3-cenospheres were compared with images of Fe-cenospheres in fig. 2(c). The new shell has of a completely different nature. In fig. 2(c) it can be seen that the new silver is deposited on cenospheres in the form of granular aggregates. That kind of

S1234

Berkowicz, G., *et al*.: Catalytic Oxidation of Methanol in the Cencspheric …
THERMAL SCIENCE: Year 2019, Vol. 23, Suppl. 4, pp. S1231-S1240
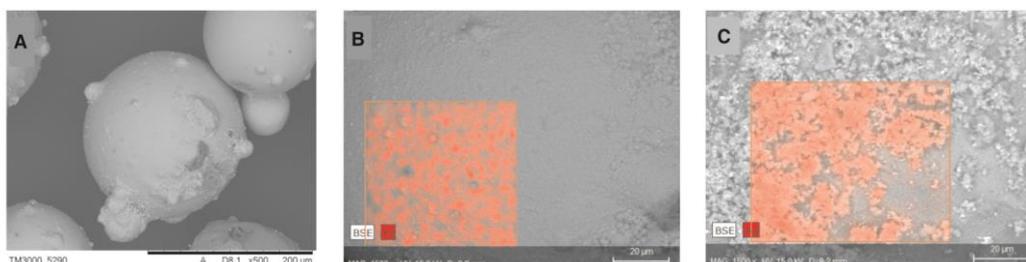
Figure 2. The SEM images of (a), (b) Fe- cenospheres (c) Ag-Fe$_2$O$_3$-Cenospheres
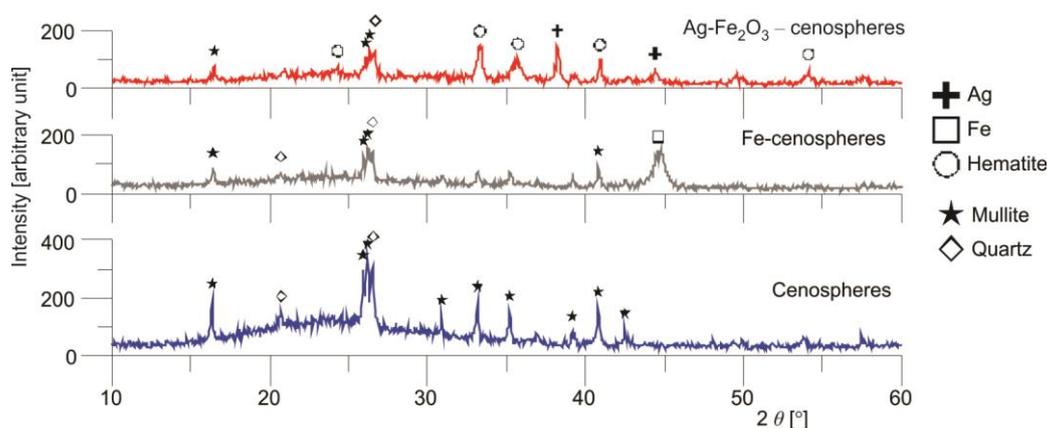
Figure 3. The XRD patterns of Fe-coated cenospheres and Ag-Fe$_2$O$_3$-coated cenospheres

roughened layer is preferred due to increased surface area of the material, which ultimately will be a catalyst. Backscattered electron (BSE) imaging confirms the presence of Ag and also Fe and O in the layer of the catalyst. Based on the results of ICP and XRD analyses of the obtained grains, it was demonstrated that the catalyst contains silver (7.10 wt.%) and hematite (12.51 wt.%) and does not contain iron. It proves that the yield of silver coating process is high and that there is another parallel process of oxidation of iron. The process of silver precipitation on Fe-coated cenospheres using sodium hypophosphite can be described by the equation which also takes into account the oxidation of Fe:

$$10AgNO_3 + NaH_2PO_2 + 2Fe + 5H_2O \rightarrow NaH_2PO_4 + 10Ag + 10HNO_3 + Fe_2O_3$$
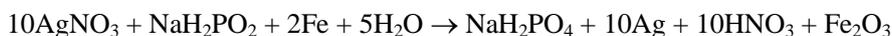
Bowker *et al*. [43] have demonstrated that hematite also exhibits catalytic activity in oxidation of methanol. Its presence in the surface layer of the core–double shell catalyst is not undesirable.

Experimental arrangement

The diagram of laboratory system for continuous monitoring of the process of methanol and nitrous oxide degradation on Ag-Fe$_2$O$_3$-cenosphere catalyst is shown in fig. 4. The system included: a liquid methanol evaporation node, a chemical reactor with the fluidised catalyst bed, a dilution node for the post reaction mixture with FTIR analyser. Quantitative analyses of CH$_3$OH, HCHO, N$_2$O, NO, NO$_2$, NH$_3$, CO, CO$_2$, CH$_4$, C$_2$H$_2$, C$_2$H$_4$, C$_2$H$_6$, (CH$_3$)$_2$CO, (CH$_3$)$_2$O, CH$_3$COOH, HCOOH, (C$_2$H$_5$)$_2$O, and CH$_3$COC$_2$H$_5$ were carried out us-
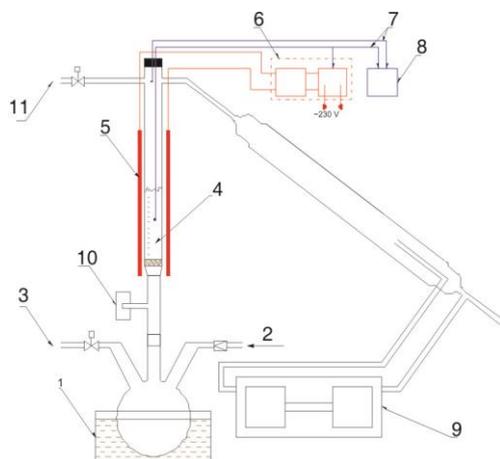
Figure 4. The diagram of laboratory system for continuous monitoring of the process of methanol and nitrous oxide degradation on Ag-Fe₂O₃-cenosphere catalyst;
1 – glycerin bath, 2 – CH₃OH, 3 – N₂O in N₂,
4 – fluidised bed of Ag-Fe₂O₃-Cenospheres,
5 – heater, 6 – set of temperature regulation,
7 – regulatory thermocouples, 8 – PID temperature regulator RE72, 9 – FTIR analyser, 10 – subwoofer,
11 – air inlet

ing the FTIR analyser equipped with a gas cuvette heated up to 180 °C. The FTIR analyses of composition of the products were performed with a frequency of 0.2 Hz.

The process of methanol degradation by N_2O was carried out in a fluidized bed tubular reactor having a diameter of 35 mm. In the lower part of the reactor, there was a distributor – a G0 glass filter on which 20 g of Ag-Fe₂O₃-cenosphere catalyst was placed. The catalyst bed was heated by external heating element in the range of 250-500 °C at a rate of 5 °C/min. The fluidisation process was supported by sounds emitter with a frequency of 45 Hz. It facilitated achieving the minimum fluidisation velocity at low flow speed of gas [40] and also prevented formation of channels in the bed, local areas of overheating of the catalyst [41]. Liquid methanol (2-18 cm³/h) and a solution of N_2O (72 cm³/min.) in N_2 (0.6-2 dm³/min.) were dosed to the round bottom flask acting as a node of methanol evaporation and as a mixing chamber for reagents. The flask was immersed in a glycerin bath at 140 °C. The flows of gas streams were regulated by mass flow controllers. The gaseous post–reaction mixture was fed to more than one hundred times larger volume of air flow, causing a dilution of the mixture to levels which are suitable for FTIR analysis.

Results and discussion

Degradation of N_2O and CH_3OH under various molar ratios of reactants

A study of the degradation of methanol and nitrous oxide were carried out by passing those compounds through the fluidised bed of Ag-Fe₂O₃-cenosphere catalyst heated from 250 to 500 °C. The process temperature was varied in a continuous manner to maintain a constant temperature rise of 5 °C/min. Based on the results of the FTIR analysis, the molar steams of CH_3OH, N_2O, CO, CO_2, CH_4, and $HCHO$ in the product mixture were calculated. The remaining components taken into account in the analysis may have occurred at a concentration lower than the detection limit of the analytical method. In addition, the molar flows of hydrogen and water were calculated from the balance of chemical elements, according to the following equations:

$$\dot{n}_{H_2O} = \dot{n}_{CH_3OH\_in} + \dot{n}_{N_2O\_in} - \dot{n}_{CH_3OH\_out} - 2\dot{n}_{CO_2\_out} + \dot{n}_{CO\_out} - \dot{n}_{HCHO}$$
$$\dot{n}_{H_2} = 2\dot{n}_{CH_3OH\_in} - 2\dot{n}_{CH_4\_out} - 2\dot{n}_{CH_3OH\_out} - \dot{n}_{HCHO} - \dot{n}_{H_2O}$$

The process of mutual degradation of CH_3OH and N_2O can be described by equation, wherein the starting materials used in the proportions of 1 to 3 are decomposed into carbon dioxide, water and nitrogen.

$$CH_3OH + 3N_2O \rightarrow CO_2 + 2H_2O + 3N_2$$

S1236

Berkowicz, G., *et al*.: Catalytic Oxidation of Methanol in the Cencspheric …
THERMAL SCIENCE: Year 2019, Vol. 23, Suppl. 4, pp. S1231-S1240
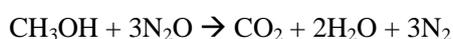
Studies of degradation of methanol and nitrous oxide were carried out at different N_2O/CH_3OH molar ratios in the range from 0.45 to 3.63. It was found that the degree of methanol conversion increased with increasing ratio of N_2O/CH_3OH, fig. 5. Under condition near to stoichiometry, complete conversion of methanol was obtained at a temperature of approx. 400 and 450 °C for the experiments in which the ratios of N_2O/CH_3OH were equal 3.63 and 2.40, respectively. As methanol content in the stream of substrates increased (*i. e.* N_2O/CH_3OH ratio decreased), depletion of the oxidizing agent was evident and methanol was present in the product stream. When the N_2O/CH_3OH ratio was equal to 1.44, *i. e.* when there was a 2-fold molar excess of methanol, there was 9.5% of unreacted methanol in products at 500 °C. At 500 °C, the lowest degree of N_2O conversion of 77.6% was achieved in the experiment with the lowest N_2O/CH_3OH ratio of 0.45, fig. 5.
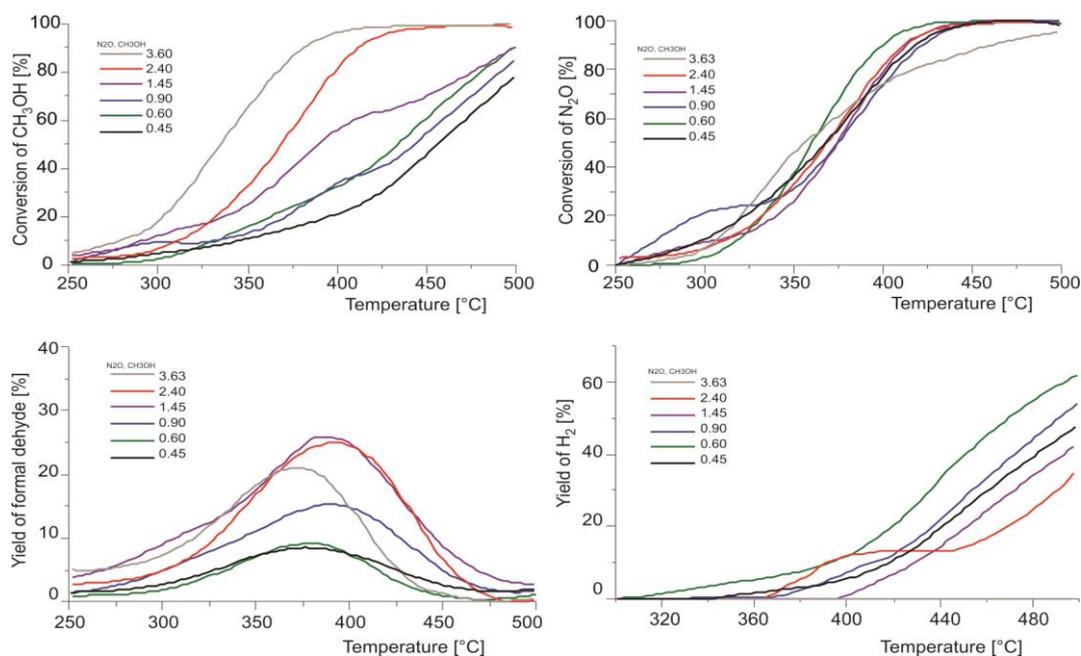
Figure 5. Conversion of substrates and efficiency of formaldehyde and hydrogen, as a function of temperature and substrate ratio

The degree of N_2O conversion remained at a high level in most of the experiments. Total N_2O conversion was usually achieved at over 450 °C, fig. 5. Only during the experiment in which a molar excess of N_2O was used ($N_2O/CH_3OH = 3.63$), the total conversion of nitrous oxide was not obtained, although it reached 94.9% at 500 °C. During the experiments with a stoichiometric excess of N_2O, there was no CH_4 and CO among the products of the process.

Small quantities of formaldehyde were found in the product stream during all the experiments. The maximum concentration of formaldehyde was reached in the range of 370-390 °C. The smaller the ratio N_2O/CH_3OH, the greater the maximum yield of formation of formaldehyde, fig. 5. The highest efficiency of formaldehyde of 21% at 370 °C was achieved for the lowest N_2O/CH_3OH ratio of 0.45. There is no formaldehyde among the products of the process above 450 °C. In the processes of removal of methanol from gas, formaldehyde is an undesirable product, due to its toxicity and carcinogenicity [44].

With increased share of methanol in the mixture of substrates CO was noted and increase of H_2 as per balance of elements. These compounds can be formed by the reaction:

$$CH_3OH + 2N_2O \rightarrow H_2 + CO + H_2O + 2N_2$$

When the N_2O/MeOH ratio decreased in the range between 3.63 and 0.6, the yield of H_2 formation was increased. However, when the N_2O/MeOH ratio was 0.45, the H_2 yield was not significantly different from the yield obtained when the ratio was 0.6, fig. 5. During the experiment with the N_2O/MeOH ratio equal to 0.45, the hydrogen yield in the temperature range of 450-500 °C was lower by 15% in relation to the experiment where the ratio was 0.60. It can therefore be concluded that the experiment with N_2O/MeOH ratio of 0.6 is the most favourable in terms of hydrogen production.

The changes in the yield of hydrogen by changing the contact time of the reactants with the catalyst were examined at the N_2O/CH_3OH ratio of 0.60. Results of the investigations are shown in fig. 6. Changes of contact time were made by regulation of N_2 flow in the range of 0.25 to 2.00 L/min, while stream of N_2O had a constant value. In previous experiments, the stream of nitrogen was constant and equalled to 0.60 L/min. It was found that the reduction of the contact time by increase of N_2 flow to the value of 1.04 and 2.00 L/min reduced hydrogen yield two and three times, respectively at 500 °C. Extension of the contact time of the reactants with the catalyst did not result in a growth of H_2 yield. Efficiency of hydrogen generation in the range of the highest test temperatures did not change for experiments in which stream of N_2 was changed in the range of 0.25–0.6 L/min.

Figure 6. Hydrogen efficiency as a result of a change in the contact time of the reactants with the catalyst during degradation of N_2O and CH_3OH

The mechanism of catalytic oxidation depends on the type of the catalyst. It is known, that both N_2O and CH_3OH can be adsorbed reversibly on the silver surface [45, 46]. The adsorbed substrates can interact with each other to form surface methoxy and surface hydroxy fragments. In addition, adsorbed methanol can undergo dissociation which leads to formation of surface methoxy and also surface hydrogen. According to Schwaner *et al.*, [46] there is no dissociation of adsorbed N_2O on silver. Taking into account the number of registered products, the following sequence of reactions is proposed. In the proposed mechanism, *, means active site of the catalyst:

$$N_2O + * \rightarrow N_2O* \qquad (r.1)$$
$$CH_3OH + * \rightarrow CH_3OH* \qquad (r.2)$$
$$CH_3OH* + N_2O* \rightarrow CH_3O* + OH* + N_2 \qquad (r.3)$$
$$CH_3OH* + * \rightarrow CH_3O* + H* \qquad (r.4)$$
$$CH_3OH* + OH* \rightarrow CH_3O* + H_2O_{(g)} + * \qquad (r.5)$$
$$2CH_3O* \rightarrow 2CH_2O_{(g)} + 2H* \qquad (r.6)$$
$$CH_2O + OH* \rightarrow HCOO* + H_2 \qquad (r.7)$$
$$HCOO* \rightarrow CO_{(g)} + OH* \qquad (r.8)$$

S1238

Berkowicz, G., *et al*.: Catalytic Oxidation of Methanol in the Cencspheric …
THERMAL SCIENCE: Year 2019, Vol. 23, Suppl. 4, pp. S1231-S1240

$$HCOO* \rightarrow CO_{2(g)} + H* \qquad (r.9)$$

$$N_2O* + CO \rightarrow CO_{2(g)} + N_2 + * \qquad (r.10)$$

$$CH_3OH* + H* \rightarrow CH_{4(g)} + O* \qquad (r.11)$$

$$2H* \rightarrow H_{2(g)} \qquad (r.12)$$
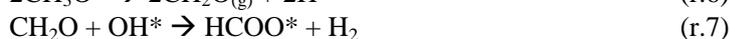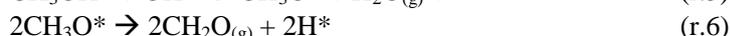
Additionally, in the case of two layer catalyst (as used here) the Fe_2O_3 can also act as an active ingredient. Probably, this p-type oxide plays additional important role in mechanism, because there are various types of oxygen present on its surface: O_2^-, atomic O^-, regular O^{-2}. Basically, there are two types of conventional catalysts used for oxidation reactions: metal oxide and noble metal. Ag-Fe_2O_3-cenospheres catalyst contains both of the two types of active compounds.

Conclusions

Cenospheres can be successfully coated with a layer of iron by thermal decomposition of iron pentacarbonyl in a fluidised bed of cenospheres. The obtained core-double shell Ag-Fe_2O_3-cenosphere catalyst proved to be active during oxidation of methanol by nitrous oxide. It is possible to achieve complete degradation of N_2O and CH_3OH for the obtained catalyst at a temperature above 450 °C when the contact time of the reactants with the catalyst is approximately 6 second and when the substrates are used in stoichiometric ratios. The use of N_2O excess makes it is impossible to achieve complete degradation of N_2O, but above 450 °C it is possible to achieve complete conversion of methanol. Then the only products of its conversion are CO_2 and H_2O. The use of more than double excess of methanol in relation to the stoichiometry of the reaction prevents total conversion of methanol, but significant amounts of CO, CH_4 and H_2 begin to appear among process products.

More than 60% of the hydrogen contained in methanol can be converted to molecular hydrogen at a temperature of 500 °C with a ratio of N_2O/CH_3OH not greater than 0.6 and with a contact time of reactants with the catalyst of approx. 6 seconds. Increasing the contact time does not affect the efficiency of the process. The study confirms that environmentally harmful nitrogen oxide (I) can be successfully used for oxidation of methanol to purify the air from vapours of the alcohol.

References

[1] Venkataramanan, M., *et al*. Causes and Effects of Global Warming, *Indian Journal of Science and Technology*, *4* (2011), 3, pp. 226-229
[2] ***, American Meteorological Society, Climate Change, https://www.ametsoc.org/ams/index.cfm/about-ams/ams-statements/statements-of-the-ams-in-force/climate-change/
[3] ***, US Environmental Protection Agency, *Overview of Greenhouse Gases*, https://www3.epa.gov/climatechange/ghgemissions/gases.html
[4] ***, US Environmental Protection Agency, *Emission Factors for Greenhouse Gas Inventories*, https://www.epa.gov/sites/production/files/2015-11/documents/emission-factors_nov_2015.pdf
[5] Zabilskiy, M., *et al*., N_2O Decomposition Over CuO/CeO_2 Catalyst: New Insights into Reaction Mechanism and Inhibiting Action of H_2O and NO by Operando Techniques, *Applied Catalysis B: Environmental, 197* (2016), Nov., pp. 146-158
[6] Ravinshakara, A. R., *et al*., Nitrous Oxide (N_2O): the Dominant Ozone-Depleting Substance Emitted in the 21st Century, *Science, 326* (2009), 5949, pp.123-125
[7] ***, European Environment Agency, *Atmospheric Concentration of Nitrous Oxide (ppb)*, 2015 http://www.eea.europa.eu/data-and-maps/figures/atmospheric-concentration-of-n2o-ppb-1
[8] Abu-Zied, B. M., *et al*., Pure and Ni-Substituted Co_3O_4 Spinel Catalysts for Direct N_2O Decomposition, *Chinese Journal of Catalysis, 35* (2014), 7, pp. 1105-1112
[9] Zhang, B., *et al*., Role of Aggregated Fe Oxo Species in N_2O Decomposition Over Fe/ZSM-5, *Chinese Journal of Catalysis, 35* (2014), 12, pp. 1972-1981

[10] Ul-Ain B., *et al.*, Catalytic Decomposition of N_2O on Cobalt Substituted Barium Hexaferrites, *Chinese Journal of Catalysis, 34* (2013), 7, pp. 13571362

[11] Wu, M., *et al.*, Effects of Acid Pretreatment on Fe-ZSM-5 and Fe-Beta Catalysts for N_2O Decomposition, *Chinese Journal of Catalysis, 37* (2016), 6, pp. 898-907

[12] Zhang, F., *et al.*, Promotion by Co of a $NiO-BaCO_3$ Catalyst for N_2O Decomposition, *Chinese Journal of Catalysis, 36* (2015), 3, pp. 344-347

[13] Pietrogiacomi, D., *et al.*, N_2O Decomposition on CoO_x, CuO_x, FeO_x or MnO_x Supported on ZrO_2: The Effect of Zirconia Doping with Sulfates or K+ on Catalytic Activity, *Applied Catalysis B: Environmental, 187* (2016), June, pp. 218-227

[14] Pachatouridou, E., *et al.*, N_2O Decomposition Over Ceria-Promoted Ir/Al_2O_3 Catalysts: The Role of Ceria, *Applied Catalysis B: Environmental, 187* (2016), Jan., pp. 259-268

[15] Melian-Cabrera, I., *et al.*, Tail Gas Catalyzed N_2O Decomposition Over Fe-Beta Zeolite. On the Promoting Role of Framework Connected AlO_6 Sites in the Vicinity of Fe by Controlled Dealumination During Exchange, *Applied Catalysis B: Environmental, 203* (2017), Apr., pp. 218-226

[16] Yu, H., *et al.*, $Pb_{0.04}Co$ Catalyst for N_2O Decomposition in Presence of Impurity Gases, *Applied Catalysis B: Environmental, 185* (2015), Dec., pp. 110-118

[17] Zabilskiy, M., *et al.*, Small CuO Clusters on CeO_2 Nanospheres as Active Species for Catalytic N_2O Decomposition, *Applied Catalysis B: Environmental, 163* (2015), Feb., pp. 113-122

[18] Franken, T., *et al.*, Investigation Of Potassium Doped Mixed Spinels $Cu_xCo_{3-x}O_4$ as Catalysts for an Efficient N_2O Decomposition in Real Reaction Conditions, *Applied Catalysis B: Environmental, 176-177* (2015), Oct., pp. 298-305

[19] ***, U.S. Environmental Protection Agency, Inventory of U.S. Greenhouse Gas Emissions and Sinks:1990 – 2014, 1-558 Raport EPA 430-R-16-002, https://www.epa.gov/sites/production/files/2016-04/documents/us-ghg-inventory-2016-main-text.pdf

[20] Reimer, R. A, *et al.*, Abatement of N_2O Emissions Produced in the Adipic acid Industry, *Environ. Prog., 13* (1994), 2, pp. 134-137

[21] Stefanova, M., *et al.* Technical Engineering for Catalytic Reduction of Nitrous Oxide Emissions, *GSTF Journal of Engineering Technology (JET), 3* (2015), 2, pp. 89-94

[22] Castellan, A., *et al.*, Industrial Production and Use of Adipic Acid, *Cat. Today, 9* (1991), 3, pp. 237-254

[23] Perez-Ramirez, J., Prospects of N_2O Emission Regulations in the European Fertilizer Industry, *Applied Catalysis B: Environmental, 70* (2007), 1-4, pp. 31-35

[24] ***,AEA Technology Environment, Options to Reduce Nitrous Oxide Emissions (Final Report) A report produced for DGXI, 1998 http://ec.europa.eu/environment/enveco/climate_change/pdf/nitrous_oxide_emissions.pdf

[25] Held, A., *et al.*, Propane-to-Propene Oxide Oxidation on Silica-Supported Vanadium, *Journal of Catalysis, 336* (2016), Apr., pp. 23-32

[26] Woods, M. P., *et al.*, Oxygen and Nitrous Oxide as Oxidants: Implications for Ethane Oxidative Dehydrogenation over Silica-Titania-Supported Molybdenum, *The Journal of Physical Chemistry C, 113* (2009), 23, pp. 10112-10119

[27] ***,United State Environmental Protection Agency, The original list of hazardous air pollutants. https://www3.epa.gov/airtoxics/188polls.html

[28] Jacob, D. J., *et al.*, Global Budget of Methanol: Constraints from Atmospheric Observations, *Journal of Geophysical Research, 110 (D08303)* (2005) Apr., pp. 1-17

[29] Araiza, D. G., *et al.*, Partial Oxidation of Methanol Over Copper Supported on Nanoshaped Ceria for Hydrogen Production, *Catalysis Today, 282* (2017), 2, pp. 185-194

[30] Chen, W.-H., *et al.*, Hydrogen Production from Methanol Partial Oxidation Over Pt/Al_2O_3 Catalyst with Low Pt Content, *Energy, 88* (2015), Aug., pp. 399-407

[31] Chang, F. W., *et al.*, *Applied Catalysis A: General, 302* (2006), 2, pp. 157-167

[32] Tsoncheva, T., *et al.*, Nanostructured Copper-Zirconia Composites as Catalysts for Methanol Decomposition, *Applied Catalysis B: Environmental, 165* (2015), Apr., pp. 599-610

[33] Marban, G., *et al.*, A Highly Active, Selective and stable Copper/Cobalt-Structured Nanocatalyst for Methanol Decomposition, *Applied Catalysis B: Environmental*, 99 (2010), 1-2, pp. 257-264

[34] Mo, L., *et al.*, Selective Production of Hydrogen from Partial Oxidation of Methanol Over Supported Silver Catalysts Prepared by Method of Redox Coprecipitation, *C. Today, 148* (2009), 1-2, pp. 124-129

[35] Tian, C., *et al.*, Understanding of Physicochemical Properties and Formation Mechanisms of fine Particular Matter Generated from Canadian Coal Combustion, *Fuel, 165* (2016), Feb., pp. 224-234

S1240

Berkowicz, G., *et al*.: Catalytic Oxidation of Methanol in the Cencspheric …
THERMAL SCIENCE: Year 2019, Vol. 23, Suppl. 4, pp. S1231-S1240

[36] Yao, Z. T., *et al*., A Comprehensive Review on the Applications of Coal Fly Ash, *Earth-Science Reviews, 141* (2015), Feb., pp. 105-121

[37] Vassilev, S. V., *et al*., Phase-Mineral and Chemical Composition of Coal Fly Ashes as a Basis for their Multicomponent Utilization. 2. Characterization of Ceramic Cenosphere and Salt Concentrates, *Fuel, 83* (2004), 4-5, pp. 585-603

[38] Aixiang, Z., *et al*., Electroless Ni-P Coating of Cenospheres Using Silver Nitrate Activator, *Surface & Coatings Technology, 197* (2005), 2-3, pp. 142-147

[39] Li, Y., Ash Cenosphere Formation, Fragmentation and its Contribution to Particulate Matter Emission during Solid Fuels Combustion 2012, Ph. D. thesis, Department of Chemical Enginering, Curtin University, Perth, western Australia, Australia

[40] Berkowicz, G., *et al*., Cenospheres as an Innovative Fluidised Bed Material, *Technical Transactions Chemistry, 113* (2016), 1-Ch, pp. 3-10

[41] Berkowicz, G., *et al*. Oxidative Decomposition of Methanol in a Vibroacoustic Fluidized Bed of Ag-coated Cenosphere Core-shell Catalyst, *Polish Journal of Chemical Technology, 18* (2016), 4, pp. 70-74

[42] Wang, P., *et al*., Deposition of Iron on Graphite Felts by Thermal Decomposition of $Fe(CO)_5$ for Anodic Modification of Microbial Fuel Cells, *International Journal of Electrochemical Science, 8* (2013), 4, pp. 4712-4722

[43] Bowker, M., *et al*., Methanol Oxidation on Fe_2O_3 Catalysts and the Effects of Surface Mo, *Faraday Discussions, 188* (2016), July, pp. 387-398

[44] ***,National Toxicology Program, Department of Health and Human Services, Report on Carcinogens, Thirteenth Edition, Formaldehyde, https://ntp.niehs.nih.gov/ntp/roc/content/profiles/formaldehyde.pdf

[45] Wachs, I. E., *et al*., The Oxidation of Methanol on a Silver (110) Catalyst, *Catalyst Surface Science, 76* (1978), 2, pp. 531-558

[46] Schwaner, A. L., *et al*., The Thermal and Electron-Induced Chemistry of N20/Ag(111), *Surface Science, 351* (1996), 1-3, pp. 228-232