



Review report on Doctoral dissertation

Name of student: Ing. Anna Klegova

Name of doctoral thesis: Supported shaped catalysts based on cobalt mixed oxides for N₂O decomposition

Supervisor: Prof. Ing. Lucie Obalova

Doctoral thesis focuses on the research of supported catalysts based on cobalt mixed oxides for low temperature N₂O decomposition in the tail-gas from HNO₃ production plants to reduce N₂O emission. Decreasing of N₂O emission to the atmosphere especially in nitric acid production is important goal because of its strong greenhouse effect and large emission quantity (400 kg/year only in Europe).

Main attention of this thesis is focused on investigation of cobalt mixed oxides supported on different commercial supports in the pelletized (TiO₂, Al₂O₃, and Mg-Al mixed oxides with various Mg and Al ratio) and open-cell foam (Al-Si, Zr-Mg-Al, SiC and SiC-Al) forms for their catalytic activity in N₂O decomposition. The relationship between catalysts composition, the method of catalysts preparation, physical and chemical properties (evaluated by AAS, BET, XRD, SEM, FTIR, Raman, Mercury porosimetry, H₂-TPR) and catalytic activities were also discussed.

It was found that Co₃O₄-Cs deposited on the support with a high content of Mg (70 wt. % MgO + Al₂O₃ as rings) possesses the highest catalytic activity among the all prepared pelletized supported catalysts (1); Al-Si foam is the most promising support among studied foam supports (2); impregnation method for catalyst preparation is better than suspension method (3); one Co₃O₄-Cs layer is enough for activity of foam supported catalysts (4); activity of foam supported catalysts increases with pore density (5).

Experimental data obtained for supported on different supports catalysts with the highest catalytic activity (Co₃O₄-Cs deposited on the pelletized Mg-Al mixed oxide and Co₃O₄-Cs deposited on the Al-Si ceramic foam) and for unsupported commercial catalyst (AST-4 as pellets) with the same chemical composition of active phase (Co₃O₄ with 1wt. % Cs) were used for mathematical modeling of the full scale reactor for N₂O abatement in waste gas from HNO₃ production plants to evaluate their catalytic activity in industry conditions.

In the case of supported catalysts, reactors were modeled with a bigger size in comparison to unsupported AST-4 to achieve the same N₂O conversion (80 %) at 450 °C. Despite a larger volume, the reactors with supported catalysts possess lower pressure drop in comparison to unsupported AST-4 at that foam catalyst contains less active components, that makes namely foam catalyst very attractive for industrial application.



I have several remarks to the doctoral thesis, which could be discussed during the defence of doctoral thesis:

1. Page 5. Fig 1. No SCR reactor in the scheme of nitric acid production, at that author declared very low NO content in the tail gas, hence SCR process should be. The tail gas composition strongly depends on SCR process. What type .of SCR (with hydrocarbon or with NH₃) author means? What is real tail gas composition? So data not only on tail gas temperature, but on tail gas composition and volume flow are needed in the text on the Page 5, paragraph 4.
2. Page 5, paragraph 3, 4-6 lines. There are in the literature data on secondary and tertiary solutions for N₂O decomposition in nitric acid production. Quaternary solution is alternative way, hence it would be helpful to find other arguments for quaternary solution than that (strong problems with secondary and tertiary solutions) designated in the text.
3. Fig 20, page 53. Why reduction peak at ~400 C for Co₃O₄/TiO₂ is bigger than peak for Co₃O₄ from parent solution?
4. Page 68, paragraph 2, line 5. Phase of mullite is not noticed in phase composition of Co-Cs/SiC-Al samples while according to peaks that were marked in the picture 28 it should be.
5. Page 141-142. Appendix 8. It is very interesting that catalyst Co₃O₄-Cs supported on 70Mg30Al (page 142) is more active in presence of NO in the gas flow than without NO, while supported on Al-Si_20 and unsupported (page 141) loss their activity in presence of NO. What author thinks about the reasons? What is the catalyst bed in the case of Co₃O₄-Cs/70Mg30Al. No data in the table.
6. What is the reason for lower activity of catalysts supported on SiC foam? They were prepared without alkali modification?
7. What is catalyst stability in the real gas mixture?
8. Experimental details:
Page 21. The calcination temperature after Cs impregnation for AST-2 and AST-4 catalysts was not indicated.
Page 22, paragraph 1. No data on impregnation condition in the text: solution concentration, solid and liquid ratio, duration of impregnation.
Page 23 – the same remark for foams.
Page 22, table 2. Catalysts contain Cs, Isn't it? While Cs not marked in catalyst composition? While Cs content in as prepared catalysts was not presented in Table 12, Page 46?
Fig 4, Page 28. Thermocouples positions were not marked in the fig. 4. Where the reaction temperature was controlled? The same question is for Fig 5.
9. Mistakes:
Abstract, paragraph 4, line 3. There is incorrectness in formula writing: 70%Mg+ Al₂O₃.
Fig. 28, caption, line 2. There is incorrectness in formula writing: Co₃O₄, not Co₃O₂.



Page 79, Table 24, column 5. Al-Si₄, not Al-Si₂. Isn't it?

My remarks not influence the main conclusions made in the thesis. New results presented in thesis were obtained based on modern experimental and theoretical fundamentals. Ing. Anna Klegova realised reasonable amount of experiment tests and calculations. Thesis is clearly written. The results were published at six impact international journals and presented at 13 International conferences. Ing. Anna Klegova proved her quality.

I recommend accepting the doctoral thesis of Ing. Anna Klegova.

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