Doctoral (PhD) Theses

PRODUCTION OF INDUSTRIAL CERAMICS AND THEIR APPLICATION IN AIR QUALITY IMPROVEMENT

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1. INTRODUCTION AND OBJECTIVES

Cordierite ceramics are very popular materials, as they can be widely used in the most diverse areas of the scientific world and the industrial sphere, thanks to their favorable physical and chemical properties. In addition, the raw materials of ceramic production are natural, thus easily and relatively cheaply available raw materials, which can be used to produce long-lasting, environmentally friendly and cost-effective products, thus contributing to better sustainability.

In the first part of my research work, I aimed to investigate the heterogeneous catalytic oxidation of carbon monoxide and I have successfully produced a cordierite-mullite type catalyst support from cost-effective and easily accessible raw materials, and then determined the optimal application method of the catalyst.

After that, I prepared a series of powder-based catalysts using non-noble metal precursors, which are more cost-effective compared to noble metals and are more easily accessible, henceforward I successfully selected the most suitable catalyst for the oxidation of carbon monoxide, and then I successfully optimized the amount of catalyst applied to the ceramic support.

After studying powder-based catalysts, it was also my goal to extend my experiments to the study of ceramic shaped bodies that can also be used for industry as catalyst supports.

To achieve this, as a first step, I made cylindrical shaped bodies with different morphologies by extrusion. Exceptionally, in this case, I have impregnated these ceramics with Pd(II)-acetate precursor and then I determined the optimal geometry in carbon monoxide oxidation reaction, and finally I made catalyst bed reactors to test their CO and NO_x reduction efficiency in exhaust gas conversion reactions.

As the last part of the first half of my experimental work, I have successfully produced ceramic bricks by extrusion with different morphologies, also for use as catalyst supports and I impregnated them with Co(II)-nitrate precursor. The aim of this work process was to reduce the emission of fireplaces manufactured by a relevant industrial participant. As a result, with the catalyst bricks we produced, the emission of harmful substances met the limit values included in the EU 2015/1185 regulation, which came into effect in 2022.

In the second half of my research work, I have also worked with cordierite-type ceramics, but I made my experimental samples using an even more cost-effective process, the casting technique. The focus of my experiments was no longer carbon monoxide, but carbon dioxide, which is also causing many headaches in today's scientific world, since at the beginning of our journey towards carbon neutrality, it is important to have applied technologies in our possession as soon as possible with which we can (for now only) compensate the carbon dioxide burden of our environment.

The main goal of the second half of my research work was to prepare a ceramic with a low density and suitable parameters from an industrial point of view, which could be used in various ways in the industrial sphere to reduce harmful emissions.
In order to achieve this, as a first step, I set the goal of producing a mass-reduced ceramic series, which I managed to achieve by replacing one of the raw materials with a modern, hollow spheric alumino-silicate in different proportions.
In addition, I wanted to prove that replacing one of the raw materials of ceramics with hollow spheric alumino-silicate plays a key role in reducing the density of the ceramics and also in keeping the mechanical parameters at an optimal level which were also important to me.
Finally, I set the goal of testing the sample with the lowest bulk density in carbon dioxide hydrogenation reactions, which we compared with an industrial quality ceramic sample.

2. EXPERIMENTAL METHODS AND PROCEDURES

Ceramic supports were produced in two ways during my work, by extrusion process and by casting. During casting, I produced ceramics with different densities where the difference between them was the different amount of hollow spheric alumino-silicate used as a pore forming agent.
During the production of the catalysts, the metal precursors were applied onto the surface of the ceramics made by extrusion by wet impregnation in each case, while the Na-Fe_3O_4 catalyst, used in the case of the ceramics made by casting was produced by the coprecipitation method.
The mineralogical properties of the powder-based samples, produced by extrusion were studied by X-ray diffractometry (XRD), while the micromorphological characteristics were studied with scanning electron microscope (SEM). The activity of the samples in catalytic carbon monoxide oxidation reactions was determined by gas chromatography (GC) using a Hewlett Packard 5890 Series II gas chromatograph. Furthermore, both before and after reaction samples

were subjected to elemental analytical tests (XPS) in order to obtain information about the oxidation state of the surface elements.
In exhaust gas conversion reactions, following the impregnation of the cylindrical shaped bodies made by extrusion, the exhaust gas source was a Honda GX390 4-stroke diesel engine and the exhaust gas analyzers used during the experiments were testo 350 type devices.
In flue gas conversion reactions, following the impregnation the impregnation of the ceramic bricks also made by extrusion, the flue gas source was a Myra 17090021 type fireplace.

In the case of samples produced by casting, in order to check the success of the synthesis, I examined the mineralogical properties and the oxide composition of the ceramic samples using X-ray diffraction (XRD) and X-ray fluorescence spectrometry (XRF).
After that, I have measured the coefficient of linear thermal expansion (CLTE) of the ceramics using a Linseis L-75 type dilatometer with a heating rate of 5 K/minute and then I determined their bending strength in each case by an IGV AS-102 type three-point bending strength measuring machine, where during the measurement the support distance was 100 mm. In all cases, the density of the ceramic specimens was measure using the Archimedes method, during which tap water was used as the immersion medium.
The thermal stability of the samples was experimentally determined with water immersion test, for which I used 12 mm thick, 20 mm wide and 120 mm long ceramic rods. I studied the micromorphological feature with a scanning microscope (SEM), while the internal structure of the ceramic samples was studied by computerized tomography (μ-CT) device, during which I gained insight into the porosity (full and open) and connection density (cross-linking) of the samples.
Finally, I determined their activity in catalytic carbon dehydrogenation reactions using an Agilent 7820A gas chromatograph.

3. SUMMARY OF NEW SCIENTIFIC RESULTS

T. 1. During the synthesis of ceramic supported catalysts containing non noble metals, the order of impregnation and heat treatment, as well as the concentration and quality of the used transition metal, equally responsible for the activity of the catalyst during carbon monoxide oxidation.

1.1. The sequence of impregnation and heat treatment has an important effect on the heterogeneous catalytic activity of the catalyst during the synthesis. I proved by gas chromatography tests, that the activity of the catalyst heat treated at 1473 K after the impregnation process can perform a maximum conversion of 52% and shows a further decrease in conversion at permanently high temperatures. The conversion of the catalyst made from the precursor applied subsequently onto the ceramic support fired at 1473 K was already 92% even at 473 K, moreover, this sample retained its catalytic activity even at permanently high temperature.

1.2. During the carbon monoxide oxidation reaction, the material quality of the transition metal was crucial from the point of view of the activity of the ceramic-supported noble metal-free catalysts. I verified with gas chromatography tests that cobalt nitrate proved to be the most effective one of the six noble metal-free precursors.

1.3. I was the first, who optimized the amount of Co(II)-nitrate precursor, applied onto a ceramic support. Based on the gas chromatography tests I found that 0.5 w% Co(II) is the most appropriate amount based on the weight of the catalyst support.

T. 2. The ceramics I developed is suitable for the production of shaped bodies as catalyst supports, where impregnating the appropriate metal precursor onto its surface we can obtain an inexpensive and easily applicable catalyst for the industry.

2.1. After their impregnation with the Pd(II) precursor, the cylindrical shaped bodies with different morphologies were mechanically and chemically stable in carbon monoxide oxidation and flue gas conversion reactions as catalyst beds. I showed by gas chromatography measurements that the cylindrical bodies with 4 holes were capable of similar catalytic activity as the heavier bodies without holes, so it is more cost-effective solution due to the smaller material consumption.

2.2. After their impregnation with the Co(II) precursor, the ceramic bricks remained mechanically and chemically stable in the flue gas conversion reaction during their use as catalytic fireplace inserts. I have shown with accredited laboratory measurements that the catalysts made of ceramic bricks are able to reduce the concentration of CO (≤ 1500 mg/Nm^3) and NO_x (≤ 200 mg/Nm^3) in the flue gas below the limit values included in the EU 2015/1185 regulation, which came into effect in 2022.

T. 3. The low-density ceramics produced by me has excellent mechanical and thermal parameters and works well as a catalyst support in carbon dioxide hydrogenation reactions.

3.1. I have successfully developed a process in which I produced a cordierite-type ceramics with high porosity and low density, which did not lose its mechanical strength even after the lightening process. With micro-CT tests, as well as three-point bending strength measurement and density measurement based on the Archimedes principle, I proved that while the bending strength of a ceramics with a density of 2,00 g/cm^3 used in industry is 23,69 MPa on average, the bending strength of the ceramics I created with a density of 1,40 g/cm^3 is 20,17 MPa on average. So, I managed to reduce the density by 30%, while the mechanical strength only decreased by 14,85%.

3.2. The thermal parameters of the low-density ceramic I have developed are better than the properties of its industrial counterpart. With a 10-cycle, 500 K sudden temperature shock resistance test, flexural strength measurements and dilatometric tests, I proved that while the mechanical strength degradation of the reference ceramics with a density of 2,00 g/cm^3 due to the thermal shocks was 54,70% , for the low-density ceramics the same value was 48,90%. Furthermore, the linear thermal expansion coefficient of $2{,}26 \cdot 10^{-6}\ K^{-1}$, measured at 873 K for the low-density ceramics is also 8,50% lower than the same parameter of the reference ceramics measured at the same temperature of $2{,}47 \cdot 10^{-6}\ K^{-1}$, which also proves the better thermal shock resistance of low-density one.

3.3. The ceramic catalyst support with a density of 1,40 g/cm^3 at a pressure of 50 bar, a temperature of 613 K and a content of 10 w% Na-Fe_3O_4 has a similar catalytic activity as its industrial counterpart with a density of 2,00 g/cm^3. I verified by gas chromatography tests that under the same reaction conditions with the ceramic support with a density of 2,00 g/cm^3, the CO_2 conversion of the catalyst is 56% and the consumption rate of CO_2 per the amount of iron is 1363 nmol/$g_{[Na\text{-}Fe3O4]}\cdot s$. On the other hand, the CO_2 conversion of the catalyst used with the low-density ceramic support is 53% and the consumption rate of CO_2 per the amount of iron is 1302 nmol/$g_{[Na\text{-}Fe3O4]}\cdot s$, but its density is 30% lower than the other one.

4. APPLICABILITY OF THE SCIENTIFIC RESULTS

During my doctoral research, I dealt with the production of cost-effective industrial quality ceramics that can help to improve air quality and their optimization for application areas that meet the needs of our time. With the results presented here and the suggestions for their usability, I hope that I can contribute to the further development of this field, marking the way for myself and, of course, for future researchers who are interested in the topic.

Based on the results of my work in the first part of my research, we have successfully developed a catalyst containing non-noble metals that can be produced from easily accessible raw materials, moreover we were the first in the literature to experimentally proof the optimal metal content in relation to the weight of the catalyst support.

There is a good chance that the cylindrical shaped ceramic bodies produced by extrusion process can be used as catalyst supports in the future as catalyst beds for internal combustion engines, thanks to their good catalytic activity, which they provided during the carbon monoxide oxidation and NO_x reduction reactions during our tests.

There is a good chance that the ceramic bricks produced by extrusion process can be used as a catalyst support in the future in mixed fuel heaters as a catalytic fireplace insert or as a smoke deflector. Based on our tests carried out by relevant industrial participants in their own thermal and combustion technology laboratories, these shaped bodies coated with a noble metal-free catalyst layer performed extremely well during the catalytic transformation of the CO and NO_x content of the flue gas of mixed fuel stoves. Another advantage of these bricks is that, when used as a smoke deflector or fireplace insert, their size, shape and position can be easily optimized for all types of mixed fuel equipment, without the equipment's construction having to be seriously modified. Last but not least, since the optimal position of the catalytic ceramic inserts is in the firebox due to the temperature conditions and the generated flue gas, they can be replaced easily, and in addition, the ceramic inserts can be regenerated in case of replacement, so they do not have to be permanently thrown away, which increases their life cycle, thus reducing the carbon footprint.

The results of our measurements carried out in accredited laboratories so far have been so promising that after further optimization of these ceramic bricks and a thorough market research, even their serial production may be realized in the future, so experiments with these materials are currently ongoing at our department.

Based on the results of my work in the second part of my research, the low-density ceramic I developed functioned well in carbon dioxide hydrogenation reactions as a catalyst support. That is why it can be used as a lightweight but mechanically durable catalyst support, which can be used in places where, in addition to low weight, relatively high mechanical strength is also important. Such an alternative target of use could be, for example, the market for various cordierite rotating packed bed reactors using Fischer-Tropsch synthesis.
Thanks to the low-density ceramic I developed, its excellent mechanical strength, good thermal shock resistance and relatively low coefficient of linear thermal expansion could be used very well in the ceramics industry, including for factories producing refractory ceramics and kiln furniture. In terms of their function, kiln furniture are fire-resistant ceramics that mainly help other participants in the ceramic industry, such as roof tile factories, to anneal their own products. For this reason, the ideal kiln furniture must meet a number of requirements. For example, the appropriate mechanical strength, which is necessary so that the automated stacking machines operating in the tile factories cannot break the apparatus. Thermal shock resistance is also an important criterion, which provides protection against cracking/fracture as a result of the thermal stress caused by the relatively rapid and cyclical heating and cooling processed during the firing of the tiles. Nowadays, these market participants also have to deal with constantly increasing energy prices and constantly decreasing CO_2 emission quotas.
The ceramic I have developed has a good chance of meeting all the criteria mentioned above, as its mechanical strength is almost the same as that of an industrial ceramic, while its thermal shock resistance is better and its coefficient of linear thermal expansion is lower. In addition, its density (volumetric weight) is almost 30% lower, which means that it requires less energy to heat it (which is actually only a dead load as an auxiliary device), which directly results in lower CO_2 emissions. Furthermore, since its thermal shock resistance is better than its industrial counterpart, a faster heat treatment (heating-cooling) cycle could be developed during their eventual use, which would allow for even more economical and faster firing process.

Through my research results, we were able to learn more about the possibilities of using cordierite-mullite type ceramics, which presupposes the possibility of more economical and at the same time more environmentally friendly catalyst supports and kiln furniture. I hope that these technological innovations will be able to play a role in improving our air quality in the future at the beginning of our journey towards carbon neutrality.

5. SCIENTIFIC PUBLICATIONS

Hungarian Scientific bibliography (MTMT) identifier: 10089373

Publications related to the scientific topic of the dissertation:

[1] **T. Boldizsár**, R. Mucsi, Á. Szamosvölgyi, I. Szenti, Gy. Halasi, A. Sápi, Á. Kukovecz, Z. Kónya, *Optimalization of ceramic-based noble metal-free catalysts for CO oxidation reactions*, Reaction Kinetics, Mechanisms and Catalysis, 135, 575-587 **(2022)**
DOI: 10.1007/s11144-022-02166-1

Citations: 2 (2) **I.F. 2022: 1,843**

[2] O. Al-Aqtash, F. Farkas, A. Sápi, I. Szenti, **T. Boldizsár**, K. B. Ábrahámné, Á. Kukovecz, Z. Kónya, *Differently shaped Al_2O_3-based Pd catalysts loaded catalytic converter for novel non-road mobile machinery exhaust systems*, Reaction Kinetics, Mechanisms and Catalysis, 136, 149-161 **(2023)**
DOI: 10.1007/s11144-023-02363-6

Citations: 2 (1) **I.F. 2023: 1,843**

[3] **T. Boldizsár**, H. Bali, I. Szenti, I. Sebők-Papp, Zs. Bán, S. Herczeg, G. Barna, A. Sápi, Á. Kukovecz, Z. Kónya, *Environmental-friendly economical cordierite-mullite-based ceramics for kiln furniture production and supports for CO_2 hydrogenation towards C_{5+} fuels*, Journal of the European Ceramic Society, 43, 13, 5596-5605 **(2023)**
DOI: 10.1016/j.jeurceramsoc.2023.04.057

Citations: 2 (2) **I.F. 2023: 6,364**

Σ I.F.: 10,050

Other international publication:

[4] B. Réti, **T. Boldizsár**, D. Szarka, Z. Major, E. Horváth, A. Magrez, L. Forró, A. Dombi, K. Hernádi, *Influence of TiO_2 phase composition on the photocatalytic activity of TiO_2/MWCNT composites prepared by combined sol–gel/hydrothermal method*, Journal of Molecular Catalysis A: Chemical, 414, 140-147 **(2016)**
DOI: 10.1016/j.molcata.2016.01.016

Citations: 44 (34) **I.F. 2016: 4,211**

[5] B. Buchholcz, H. Haspel, **T. Boldizsár**, Á. Kukovecz, Z. Kónya, *pH-regulated antimony oxychloride nanoparticle formation on titanium oxide nanostructures: a photocatalytically active heterojunction*, CrystEngComm, 19, 1408-1416 **(2017)**
DOI: 10.1039/C6CE02340A

Citations: 4 (3) **I.F.** $_{2017}$**: 3,367**

Σ I.F.: 7,578

Σ Σ I.F.: 17,628

6. PRESENTATIONS, POSTER, CONFERENCE PARTICIPITATIONS

1. **T. Boldizsár**: Friends2 Workshop, Advanced coating and characterization techniques, Dresden, Germany **(2016)**

2. **T. Boldizsár, B. Buchholcz, H. Haspel, Z. Kónya, Ákos Kukovecz:** *Synthesis of photoactive antimony oxyiodide hierarchical nanostructures*, SIWAN7 - 7th Szeged International Workshop on Advances in Nanosciences, Szeged, Hungary **(2016)**

3. **Tamás Boldizsár:** *Electrical and stability investigations of layered* $HfTe_2$ *semimetal***,** CYSC 2017 - 12th Conference for Young Scientists in Ceramics, Novi Sad, Serbia **(2017)**

7. CO-AUTHOR CONFERENCE PARTICIPATIONS

4. B. Réti, **T. Boldizsár**, A. Dombi, K. Hernádi, *Photocatalytic activity of* TiO_2*/MWCNT nanocomposites with different* TiO_2 *phase compositions*, NT13: Fourteenth International Conference on the Science and Application of Nanotubes, Espoo, Finnország **(2013)**

5. B. Réti, **T. Boldizsár**, D. Szarka, Z. Major, A. Dombi, K. Hernádi, TiO_2 */MWCNT nanocomposites with different anatase/rutile ratio: preparation and photocatalytic activity*, IEEE-NANO 2015 - 15th International Conference on Nanotechnology, Róma, Olaszország **(2015)**

6. B. Buchholcz, H. Haspel, **T. Boldizsár**, Á. Kukovecz, Z. Kónya**:** *pH-regulated antimony oxychloride nanoparticle formation on titanium oxide nanostructures: a photocatalytically active heterojunction*, 21st Topical Meeting of the International Society of Electrochemistry, Szeged, Magyarország **(2017)**