

Ph. D. Thesis

**UNRAVELLING SYNERGISTIC EFFECTS IN
DESIGNED CATALYTIC SYSTEMS TO DRIVE
AMBIENT PRESSURE CO₂ REDUCTION**

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Introduction

Heterogeneous catalysis lies at the core of catalysis science, powering numerous vital industrial processes by effectively speeding up reaction rates at a low cost while maintaining high conversion rates and product selectivity. As estimated, 80% of chemical industry output is generated in heterogeneous catalytic processes and the global heterogeneous catalyst market is poised to increase from USD 19.5 billion in 2022 to USD 35.7 billion by 2032.

Heterogeneous catalysts drive most of industrial chemical processes, dominating in such segments as oil refining (catalytic cracking, alkylation, reforming, isomerization, hydrogenation, dehydrogenation, etc.) production of commodity goods (H_2SO_4 , NH_3 , HNO_3 , ethylene oxide, etc.), organic and inorganic fine chemicals, and polymers (for example, polymers of alpha-olefins). The latest phase of heterogeneous catalysis development is linked with efforts in environmental remediation. The breakthrough achievement in this area was the development of a catalytic converter for automobile exhaust gases, which has played a major role in preventing excessive air pollution. Nowadays, one of the research focal points of environmental protection involves reducing greenhouse gas levels (primarily CO_2) in the atmosphere to mitigate climate change and ocean acidification. The utilization of cheap, easy to transport and safe carbon dioxide as a source of carbonaceous raw materials can partially replace traditional exhaustible carbon sources such as oil and gas. Metal-based heterogeneous catalysts proved especially advantageous for this process in terms of recyclability, stability, handling, separation and also low-cost reactor construction in large-scale production¹.

The choice of the catalyst for this process remains a primary hurdle. In the past, individual catalysts were selected purely empirically. Thus, 2500 different catalysts had to be tested 6500 times to obtain a stable and working iron-based catalyst for the Haber-Bosch process which is still used to produce ammonia at an industrial scale.² Nowadays, the accumulated experience has deepened our understanding of the mechanisms of many catalytic processes, which provides the scientists with criteria for the preliminary selection of a catalyst and indicates ways to create effective catalytic systems. In order to completely shift from the trial-and-error synthesis strategy to knowledge-based catalyst design, it is imperative to investigate the aspects of the “metal-support” and “catalyst-reaction medium” interactions. The influence of the support on the catalytic properties of the supported active component is one of the fundamental problems of heterogeneous catalysis, which became the focus of my thesis.

1. Objectives

Despite having been extensively reported to play a decisive role in catalytic reactions, MSIs are usually complicated, and the possible catalytic effects with the underlying mechanisms have not been thoroughly addressed in the literature. In my doctoral thesis, I aimed at exploring the dynamics of reducible materials undergoing CO₂ hydrogenation scarcely investigated by the scholars and thus contributing to catalyst design advancements.

For these experiments, industrially relevant Co₃O₄ catalyst and combinations of Pt with Co₃O₄ and MnO₂ that were expected to be active in the CO₂ hydrogenation, were chosen as model catalysts to investigate the synergistic interactions between catalytic units and their evolution under exposed chemical environment.

In my doctoral work, I utilized controllable systems, consisting of well-defined Pt nanoparticles dispersed on 3D designed metal-oxide supports in ambient pressure CO₂ hydrogenation. With the help of ex-situ, in-situ, bulk and surface-sensitive characterization tools, I aimed to find answers to the following questions:

How does the morphology of Co₃O₄ influence its activity and the reaction route? What are the active sites and how do they change under reductive atmosphere?

What type of MSI establishes between Pt and Co₃O₄ and what is the impact of Co₃O₄ morphology on the Pt-Co₃O₄ interactions?

Is it indeed the interface that governs the activity and selectivity of Pt/MnO₂? Is there any new synergy effect that has not been previously described?

2. Experimental Methods

In my doctoral work, well-defined Pt nanoparticles dispersed on 3D-designed metal-oxide supports were utilized as catalysts. Size-controlled (~ 5 nm) Pt nanoparticles were prepared *via* the polyol method, while mesoporous metal oxides (m-Co₃O₄, m-MnO₂) were fabricated through the hard template replica method^{3,4}. The schematic representation of the synthesis steps for Pt/m-Me_xO_y is given in **Fig. 1**.

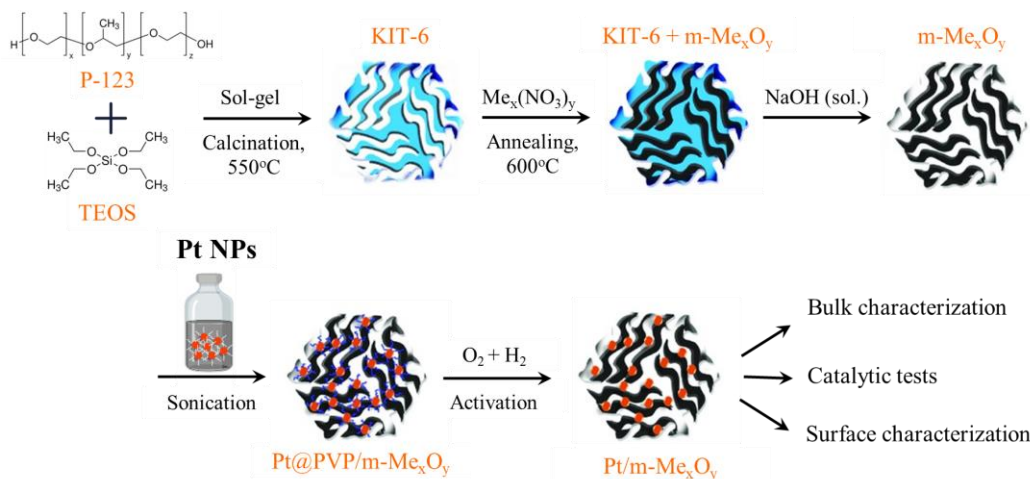


Figure 1. The schematic representation of the synthesis steps for Pt/m-Me_xO_y. Modified from ref.⁵

Various ex-situ and in-situ techniques were employed for bulk and surface characterization of Co₃O₄, MnO₂, Pt/Co₃O₄ and Pt/MnO catalytic systems.

Bulk characterization of the as-prepared catalyst was typically conducted using transmission electron microscopy (TEM) to visualize the Pt nanoparticles and probe the morphology of the supports. X-ray diffraction (XRD) and complementary electron diffraction (ED) were used to gather information about the crystal structure and composition of the samples, while the temperature-programmed reduction (TPR) was performed to investigate their reducibility.

For the samples pre-treated under O₂ at 573 K for 30 min and H₂ at various temperatures for 1 h, specific surface area was determined by the BET method. The oxidative behaviour and the basicity of the catalysts were studied with temperature-programmed techniques (O₂-TPD, CO₂-TPD). Surface characterization of pre-treated and spent samples was carried out by the means of (near ambient pressure) X-ray photoelectron spectroscopy ((NAP)-XPS) to examine the chemical species at the surface layer and their evolution under reaction conditions. Deconvolution of O 1s XPS region was performed to comparatively assess the amount of oxygen vacancies (V_o) present in the crystal lattice after the pre-treatment, while Raman spectroscopy was employed to corroborate the conclusions drawn from XPS data. In-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was primarily used to gain a molecular-level understanding of the surface layer and deduce the reaction mechanism.

The structure of the spent catalysts was studied in detail using high-resolution transmission electron microscopy (HR-TEM), high-angle annular dark-field scanning TEM (HAADF-STEM), and energy dispersive X-ray spectroscopy (EDS) mapping. For the Pt/Co₃O₄, extended X-ray absorption fine structure (EXAFS) technique was additionally employed to confirm the PtCo alloy formation.

All the catalysts were tested in the ambient pressure CO₂ hydrogenation reaction in a fixed-bed, continuous-flow quartz reactor filled with 200 mg of a pelletized catalyst. Before the catalytic experiments, the as-received catalysts were pre-treated as described above. The CO₂:H₂ mixture with 1:4 molar ratio was introduced to the reactor with a total flow rate of 40 mL·min⁻¹. Gas analysis was performed using an Agilent 5890 gas chromatograph equipped with Porapak Q and Porapak S columns, as well as thermal conductivity (TC) and flame ionization (FI) detectors. The schematic process diagram for the catalytic experiments is shown in **Fig. 2**.

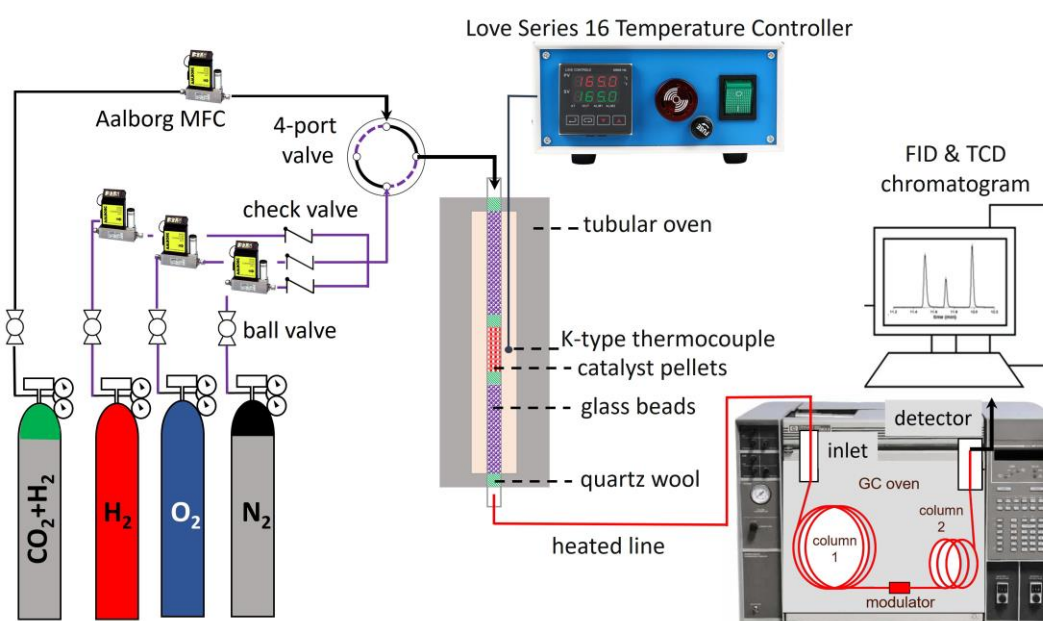


Figure 2. Schematic process diagram for the ambient pressure CO₂ hydrogenation.

4. Perspective Novel Findings

T1: I prepared a novel mesoporous Co₃O₄ (m-Co₃O₄) as a cheap noble metal-free catalyst for the CO₂ methanation which surpasses the activity and stability of the commercial Co₃O₄ (c-Co₃O₄).

T1.1 The m-Co₃O₄ was prepared by the hard template method which is aimed at producing an ordered mesoporous structure. The applied reaction conditions initiated the generation of hydroxyl surface moieties enhancing the basicity of the catalyst. Apart from carboxylate species, the formate intermediate, that arises as the result of the interaction between CO₂ and weak basic sites, additionally appears in the case of m-Co₃O₄. Superior activity and methane selectivity of the m-Co₃O₄ compared to the c-Co₃O₄ are attributed to the morphology-induced surface basicity which opens a new reaction route and limits the coke formation.

T1.2 The c-Co₃O₄ apart from Co₃O₄, contains CoO phase as well, which facilitates its reduction. Abundant oxygen vacancies prevailing in the c-Co₃O₄ lattice due to its disordered structure serve as the sites for CO₂ adsorption to produce carboxylate species. However, due to facilitated reduction, the c-Co₃O₄ is deactivated promptly as the cobalt oxide phase becomes unavailable for the CO₂ activation.

T1.3 Both metallic cobalt and cobalt oxide phases are participating in the activating of the reactants and stabilizing the intermediates. Metallic Co activates the hydrogen molecules while activation of CO₂ takes place on the cobalt oxide phase. The carbon dioxide activation may also occur on metallic Co in the case of dissociative CO₂ adsorption. For both studied types of Co₃O₄, the 573 K reduction temperature led to the formation of optimal Co/cobalt oxides ratios since at this reduction temperature, the highest catalytic activity and methane selectivity were observed.

T2: The deposition of 5 nm Pt nanoparticles in 1% improves the catalytic activity of Co₃O₄ catalysts to a different extent: 1.9 for c-Co₃O₄ vs 1.3 for m-Co₃O₄ due to the complex metal-support interactions.

T2.1 In both cases after the pre-treatment, a formation of Co-Pt alloy particles partially covered by the Co_xO_y overlayer occurs. This structure reconstruction process is responsible for the generation of new basic centers. Thus, Pt/c-Co₃O₄ with abundant weak basic sites demonstrates great CO₂ capture capacity far exceeding that of the c-Co₃O₄, which resulted in the larger catalytic activity enhancement effect.

T2.2 The incorporation of Pt slightly compromises methane selectivity. However, due to the Co_xO_y overlayer formation, the overreduction of the catalysts is prevented and thus stability of the catalysts is improved at higher temperatures, which is especially pronounced in the case of Pt/c-Co₃O₄.

T2.3 While RWGS pathway is the only reaction route which operates in the case of Pt/c-Co₃O₄, for Pt/m-Co₃O₄, formate intermediate additionally contributes to the CO₂ conversion, thus, the activity of Pt/m-Co₃O₄ is the best. Unlike the free-standing supports, carboxylate route was not established for Pt-loaded catalysts, presumably due to the fact that oxygen vacancies stabilizing the carboxylate species are favourable sites for Pt nanoparticles.

T3: I revealed a new type of metal-support interaction between Pt nanoparticles and MnO to produce a single crystal type structure with distortions based on the lattice parameter differences.

T3.1 At the Pt/MnO interface edge dislocations are generated, which is manifested in the decrease of the linearly adsorbed CO frequency (2024 cm^{-1}). The adsorbed CO on defect-free Pt is also observed at a regular wavenumber – 2077 cm^{-1} , however, independently on the location, the adsorbed CO species, formed as the result of formate species decomposition, are greatly destabilized on the Pt surface and desorb at very low temperatures (373 K). The destabilization is assigned to the weakening of the Pt-CO bond due to the Pt lattice expansion in the course of mismatched-row structure formation.

T3.2 Alleviated Pt-CO bond strength allows excellent CO-poisoning resistance and results in ~10 times higher RWGS activity of Pt/MnO compared to the reference Pt/SBA-15 catalyst with >99% CO selectivity.

T3.3 At the same time, MnO species impose a geometric impact on Pt nanoparticles as the result of strong metal-support interaction. Thus, the number of available Pt metal sites is considerably reduced compared to the reference Pt/SBA-15 catalyst. The greatly diminished number of exposed metal sites is considered as the primary hurdle for the Pt/MnO system to demonstrate superior catalytic activity compared to the most efficient catalysts in the RWGS.

5. Scientific Activities

Hungarian Scientific Bibliography (MTMT) identifier: 10076687

Research Articles – related to the dissertation

1. Szent Imre; **Efremova Anastasiia**; Kiss János; Sági András; Óvári László; Halasi Gyula; Haselmann Ulrich; Zhang Zaoli; Morales-Vidal Jordi; Baán Kornélia; Kukovecz Ákos; López Núria; Kónya Zoltán.

Pt/MnO Interface Induced Defects for High Reverse Water Gas Shift Activity
ANGEWANDTE CHEMIE INTERNATIONAL EDITION, 63 (8), 2023

doi: 10.1002/anie.202317343

SJR indicator: **D1**

Impact factor₂₀₂₃: 16.1

Independent citations: 3

2. Efremova Anastasiia*; Szent Imre*; Kiss János; Szamosvölgyi Ákos; Sápi András; Baán Kornélia; Olivi Luca; Varga Gábor; Fogarassy Zsolt; Pécz Béla; Kukovecz Ákos; Kónya Zoltán. **these authors contributed equally*

Nature of the Pt-Cobalt-Oxide Surface Interaction and its Role in the CO₂ Methanation
JOURNAL OF APPLIED SURFACE SCIENCE, 571, **2022**

doi: 10.1016/j.apsusc.2021.151326

SJR indicator: **Q1**

Impact factor₂₀₂₂: 6.7

Independent citations: 26

3. Efremova Anastasiia; Rajkumar T.; Szamosvölgyi Ákos; Sápi András; Baán Kornélia; Szent Imre; Gómez-Pérez Juan; Varga Gábor; Kiss János; Halasi Gyula; Kukovecz Ákos; Kónya Zoltán.

Complexity of a Co₃O₄ System under Ambient-Pressure CO₂ Methanation: Influence of Bulk and Surface Properties on the Catalytic Performance

JOURNAL OF PHYSICAL CHEMISTRY C, 125 (13), **2021**

doi: 10.1021/acs.jpcc.0c09717

SJR indicator: **Q1**

Impact factor₂₀₂₁: 4.2

Independent citations: 39

Research Articles – unrelated to dissertation

1. Szamosvölgyi Ákos; Pitó Ádám; **Efremova Anastasiia**; Baán Kornélia; Kutus Bence; Suresh Mutyala; Sápi András; Szent Imre; Kiss János; Kolonits Tamás; Fogarassy Zsolt; Pécz Béla; Kukovecz Ákos; Kónya Zoltán.

Optimized Pt–Co Alloy Nanoparticles for Reverse Water–Gas Shift Activation of CO₂
APPLIED NANOMATERIALS, **2024**

doi: 10.1021/acsanm.4c00111

SJR indicator: **Q1**

Impact factor₂₀₂₃: 5.3

Independent citations: 0

2. Najari Sara; Saedi Samrand; Sápi András; Szamosvölgyi Ákos; Papp Ádám; **Efremova Anastasiia**; Bali Henrik; Kónya Zoltán.

Synergistic Enhancement of CO₂ Hydrogenation to C₅+ Hydrocarbons Using Mixed Fe₅C₂ and Na-Fe₃O₄ Catalysts: Effects of Oxide/Carbide Ratio, Proximity, and Reduction

CHEMICAL ENGINEERING JOURNAL, 485, **2024**

doi: 10.1016/j.cej.2024.149787

SJR indicator: **D1**

Impact factor₂₀₂₃: 13.3

Independent citations: 1

3. Yadav Mohit; Gyulavári Tamás; Kiss Janos; B. Ábrahámné Kornélia; **Efremova Anastasiia**; Szamosvölgyi Ákos; Pap Zsolt; Sápi András; Kukovecz Ákos; Kónya Zoltán.

Noble Metal Nanoparticles and Nanodiamond Modified Strontium Titanate Photocatalysts for Room Temperature CO Production from Direct Hydrogenation of CO₂

JOURNAL OF CO₂ UTILIZATION, 78, 2023

doi: 10.1016/j.jcou.2023.102621

SJR indicator: **Q1**

Impact factor₂₀₂₂: 7.7

Independent citations: 1

4. Khoshroo Ghazaleh; Sápi András; Szent Imre; **Efremova Anastasiia**; Bali Henrik; Baán Kornélia; Erdőhelyi András; Kukovecz Ákos; Kónya Zoltán.

Pure Ni-Based and Trimetallic Ni-Co-Fe Catalysts for the Dry Reforming of Methane: Effect of K Promoter and the Calcination Temperature

CATALYSIS LETTERS, 153, 2022

doi: 10.1007/s10562-022-04203-z

SJR indicator: **Q3**

Impact factor₂₀₂₂: 2.8

Independent citations: 0

5. Malik Shan Ali; Bali Henrik; Czirik Fanni; Szamosvölgyi Ákos; Halasi Gyula; **Efremova Anastasiia**; Šmíd Břetislav; Sápi András; Kukovecz Ákos; Kónya Zoltán.

Turning CO₂ to CH₄ and CO over CeO₂ and MCF-17 Supported Pt, Ru and Rh Nanoclusters – Influence of Nanostructure Morphology, Supporting Materials and Operating Conditions

FUEL, 326, 2022

doi: 10.1016/j.fuel.2022.124994

SJR indicator: **Q1**

Impact factor₂₀₂₂: 7.4

Independent citations: 7

6. Chawla Harshita; Garg Seema; Rohilla Jyoti; Szamosvölgyi Ákos; **Efremova Anastasiia**; Szent Imre; Ingole Popinand Pravin; Sápi András; Kónya Zoltán; Chandra Amrish

Visible LED-light Driven Photocatalytic Degradation of Organochlorine Pesticides (2,4-D & 2,4-DP) by Curcuma Longa Mediated Bismuth Vanadate

JOURNAL OF CLEANER PRODUCTION, 367 (20), 2022

doi: 10.1016/j.jclepro.2022.132923

SJR indicator: **D1**

Impact factor₂₀₂₂: 11.1

Independent citations: 17

7. Bali Henrik; Mutyala Suresh; **Efremova Anastasiia**; Xie Shaohua; Collier Samantha; Ábel Marietta; Sáp András; Kukovecz Ákos; Kónya Zoltán.

Role of Active Metals Cu, Co, and Ni on Ceria Towards CO₂ Thermo-Catalytic Hydrogenation.

REACTION KINETICS, MECHANISMS AND CATALYSIS, 133, 2021

doi: 10.1007/s11144-021-02007-7

SJR indicator: **Q3**

Impact factor₂₀₂₁: 1.85

Independent citations: 3

8. Sápi András; Rajkumar T.; Ábel Marietta; **Efremova Anastasiia**; Grósz András; Gyuris Anett; Ábrahám Kornélia B.; Szent Imre; Kiss János; Varga Tamás; Kukovecz Ákos; Kónya Zoltán.

Noble-Metal-Free and Pt Nanoparticles-Loaded, Mesoporous Oxides as Efficient Catalysts for CO₂ Hydrogenation and Dry Reforming with Methane

JOURNAL OF CO₂ UTILIZATION, 32, 2019

doi: 10.1016/j.jcou.2019.04.004

SJR indicator: **Q1**

Impact factor₂₀₁₉: 6.3

Independent citations: 33

Summary

Total publications: **11**

Of which related to Dissertation: **3**

Total independent citations: **130**

Of which related to Dissertation: **68**

Total impact factor: **82.8**

Of which related to Dissertation: **27**

Conference Participation – related to dissertation

1. **Efremova A.**; Szenti I.; Kiss J.; Sápi A.; Kónya Z. (**poster** presentation)

Origin of the Pt/Me_xO_y synergy effect for driving activity and selectivity in the CO₂ hydrogenation

18th ICC - International Congress on Catalysis. Lyon (France), July 13-19, 2024.

#A member of Young Scientists Committee (ICC organizational committee).

2. **Efremova A.**; Szenti I.; Kiss J.; Sápi A.; Kukovecz Á.; Kónya Z. (**oral** presentation)

Unraveling Synergistic Effects in Designed Catalytic Systems to Drive Ambient Pressure CO₂ Reduction

Katalízis Munkabizottság. Szeged (Hungary), May 9, 2024.

#Dr. Paál Zoltán Award – 2023.

3. **Efremova A.**; Szenti I.; Kiss J.; Sápi A.; Óvári L.; Halasi Gy.; Zhang Z.; Kukovecz Á.; Kónya Z. (**oral** presentation)

Structure-catalytic activity correlations of Pt/m-MnO₂ system in RWGS

ECOSS 35: The 35th European Conference on Surface Science. Luxembourg (Luxemburg), August 29-September 02, 2022.

4. **Efremova A.**; Sápi A.; Szenti I.; Kiss J.; Kukovecz Á.; Kónya Z. (**pitch** presentation)

„3D” designed catalysts towards high activity and tunable selectivity in CO₂ hydrogenation

YOURHETCAT - 1st Forum of Young Researchers on Heterogeneous Catalysis. Szeged (Hungary), July 11-13, 2022.

#Best pitch presentation award.

5. **Efremova A.**; Szenti I.; Kiss J.; Sápi A.; Kukovecz Á.; Kónya Z. (**oral** presentation)

Pt-mesoporous-metal-oxide surface interactions during CO₂ methanation

14th CYSC - 14th Conference for Young Scientists in Ceramics. Novi Sad (Serbia), October 20-23, 2021.

6. **Efremova A.**; Szenti I.; Kiss J.; Sápi A.; Kukovecz Á.; Kónya Z. (**oral presentation/virtual**)

Nature of mesoporous metal oxide support in the ambient pressure CO₂ methanation
Euromat 2021. Austria, September 13-17, 2021.

7. **Efremova A.**; Szenti I.; Kiss J.; Sápi A.; Kukovecz Á.; Kónya Z. (**oral presentation/virtual**)

Nature of the Pt-Cobalt-Oxide surface interaction and its role in the CO₂ methanation
Katalízis Munkabizottság Hungary, June 25, 2021.
#A member of Katalízis Munkabizottság since 2021

8. **Efremova A.**; Szenti I.; Kiss J.; Sápi A.; Kukovecz Á.; Kónya Z. (**oral presentation/virtual**)

Investigation of the complexity of Co₃O₄ system under CO₂ hydrogenation reaction
Magyar Tudományos Akadémia, Felületkémiái és Nanoszerkezeti Munkabizottság,
Budapest (Hungary), September 8, 2020.

9. **Efremova A.**; Sápi A.; Szenti I.; Kukovecz Á.; Kónya Z. (**poster presentation/virtual**)

Oxidation state drives CO₂ hydrogenation over Co₃O₄ catalyst: molecular level understanding
9th Virtual Nanotechnology Poster Conference NANOPOSTER-2020. April 20-26, 2020.

10. **Efremova A.**; Szenti I.; Sápi A.; Kukovecz Á.; Kónya Z. (**oral presentation**)

Optimizing noble metal free catalysts for CO₂ activation towards high activity and selectivity
XLII. Kémiai Előadói Napok. Szeged (Hungary), October 28, 2019.
#Nívódíj.

11. **Efremova A.**; Szenti I.; Sápi A.; Kukovecz Á.; Kónya Z. (**oral presentation**)

Pt nanoparticles-supported and pristine mesoporous metal oxides as efficient catalysts for CO₂ activation
13th CYSC - 13th Conference for Young Scientists in Ceramics. Novi Sad (Serbia), October 16-19, 2019.
#Best student presentation award.

12. **Efremova A.**; Sápi A.; Kukovecz Á.; Kónya Z. (**oral presentation**)

Catalytic activity studies of Pt nanoparticles-supported and pristine mesoporous metal oxides for chemical utilization of CO₂
8. Környezetkémiai Szimpózium. Siófok (Hungary), October 10-11, 2019.

6. References

1. Wang, W., Wang, S., Ma, X. & Gong, J. Recent advances in catalytic hydrogenation of carbon dioxide. *Chem. Soc. Rev.* **40**, 3703–3727 (2011).
2. Chen, S., Perathoner, S., Ampelli, C. & Centi, G. Electrochemical Dinitrogen Activation: To Find a Sustainable Way to Produce Ammonia. in *Studies in Surface Science and Catalysis* vol. 178 31–46 (Elsevier B.V., 2019).
3. Sápi, A. *et al.* In Situ DRIFTS and NAP-XPS Exploration of the Complexity of CO₂ Hydrogenation over Size-Controlled Pt Nanoparticles Supported on Mesoporous NiO. *J. Phys. Chem. C* **122**, 5553–5565 (2018).

4. Sápi, A. *et al.* Noble-metal-free and Pt nanoparticles-loaded, mesoporous oxides as efficient catalysts for CO₂ hydrogenation and dry reforming with methane. *J. CO₂ Util.* **32**, 106–118 (2019).
5. Lyu, X. *et al.* Towards Low Temperature Operation of Catalytic Gas Sensors: Mesoporous Co₃O₄-Supported Au–Pd Nanoparticles as Functional Material. *Nanomaterials* **13**, (2023).

DECLARATION

I declare that the contribution of Anastasiia Efremova was significant in the publication: “Pt/MnO Interface Induced Defects for High Reverse Water Gas Shift Activity” which appeared in the Angewandte Chemie International Edition journal in December 2023. The results reported in this article and in the Ph.D. dissertation of Anastasiia Efremova have not been used to acquire any PhD degree previously and will not be used in the future for the purpose of acquiring an academic degree or title.

Szeged, 10.18.2024

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