

HYDROGENATION OF CO₂ ON IRON BASED CATALYSTS

Martina Kubíková, Libor Kvítek, Aleš Panáček, Robert Prucek

Palacký University Olomouc, Faculty of Science, 17. listopadu 1192/12, 771 46 Olomouc, Czech Republic

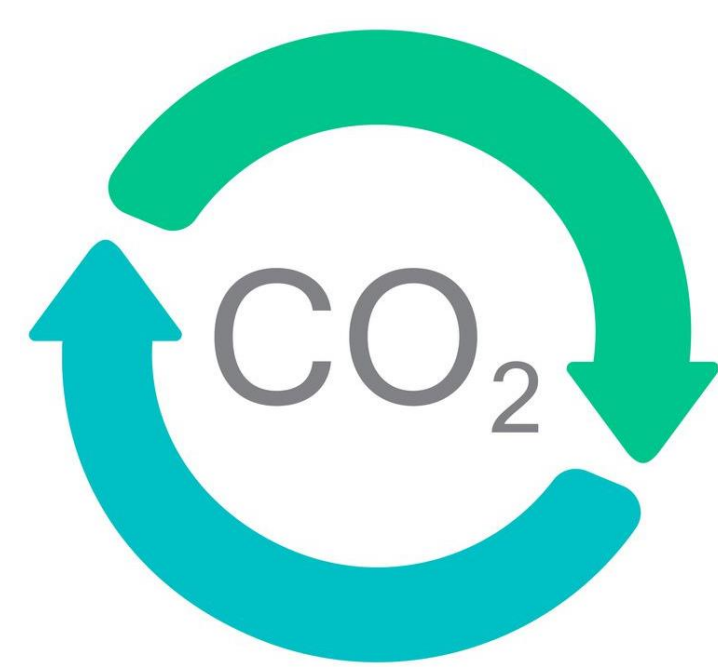


Palacký University
Olomouc



Regional Centre
of Advanced Technologies
and Materials

INTRODUCTION

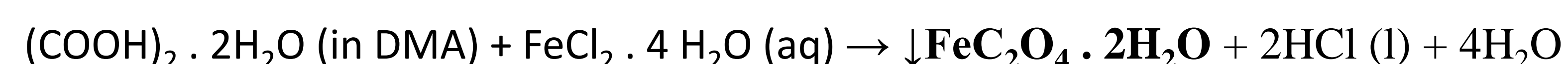


Nowadays, global warming represents significant ecological problem. The crucial aspect is the increasing concentration of greenhouse gases (especially CO₂) in the atmosphere. [1] Possible solution could be assigned to the lowering concentration of CO₂ by conversion into more valuable compounds. [2] For this purposes, iron-based materials demonstrate one of the most effective catalytic material for CO₂ hydrogenation to methane, methanol and another simple hydrocarbons. [3] This study focuses on the catalytic hydrogenation of CO₂ in the gas phase. Catalysts based on iron oxides are prepared by thermal decomposition of iron(II) oxalate at relatively low temperature of 175 °C. Catalytic reactions proceed at the pressure of only 1 bar and the temperature of 325 °C in the microreactor Microactivity Effi connected with GC/MS for product analysis.

CATALYST PREPARATION

Catalysts were prepared by a two-step synthesis in four different forms.

1st step: Preparation of iron(II) oxalate (FeC₂O₄ · 2H₂O)

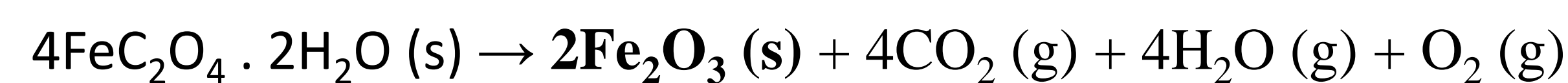


- 4 different setups of an addition of reactants



Fig. 1 Iron(II) oxalate samples.

2nd step: Preparation of mesoporous iron(III) oxide (Fe₂O₃)/ iron oxides (FeO_x) by thermal decomposition of iron(II) oxalate



- 175 °C in air



Fig. 2 Iron(III) oxide samples.

CATALYTIC ACTIVITY MEASUREMENT

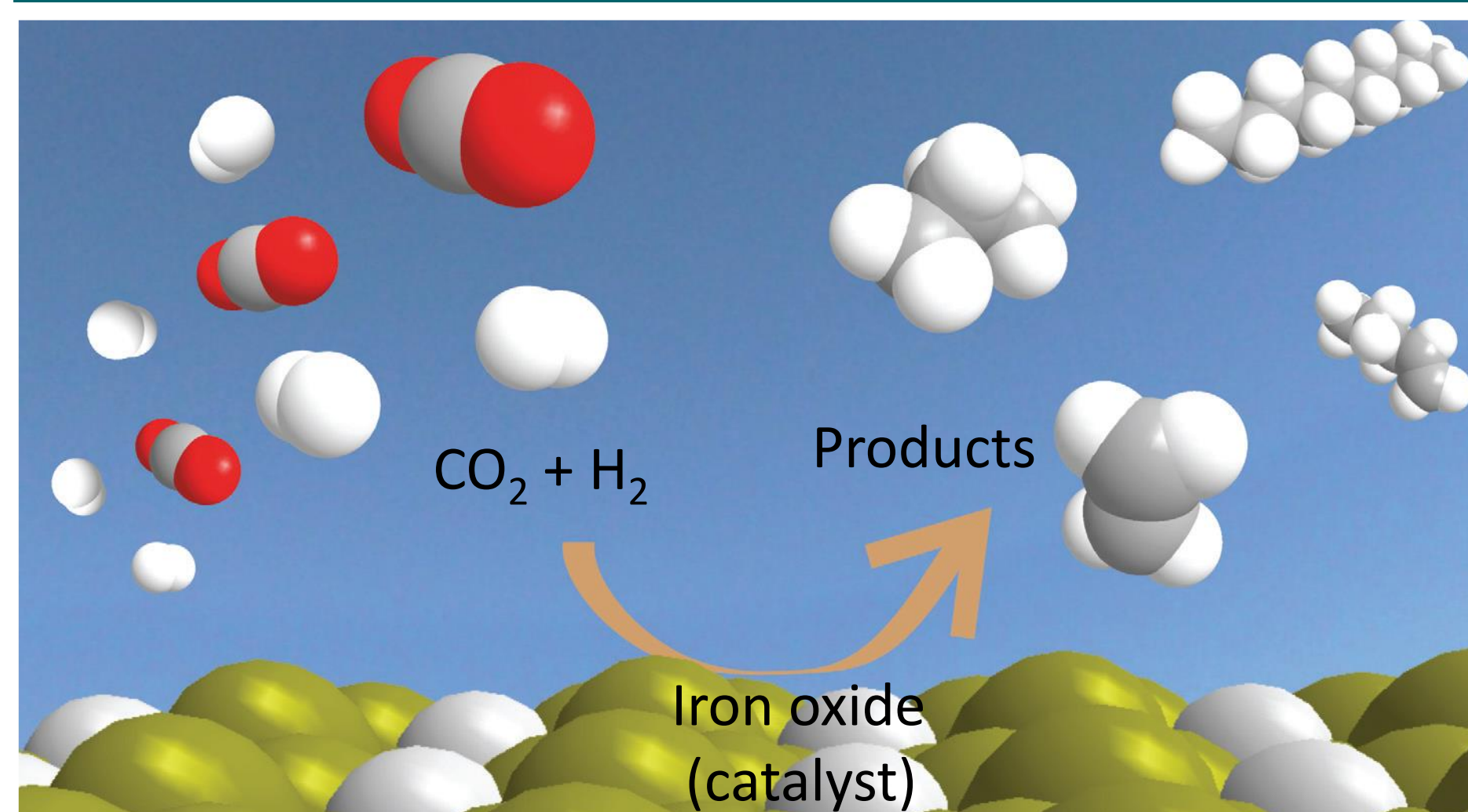


Fig. 3 Scheme of catalytic hydrogenation of CO₂.



Fig. 4 Microreactor Microactivity Effi (inside) and scheme of the experiment.

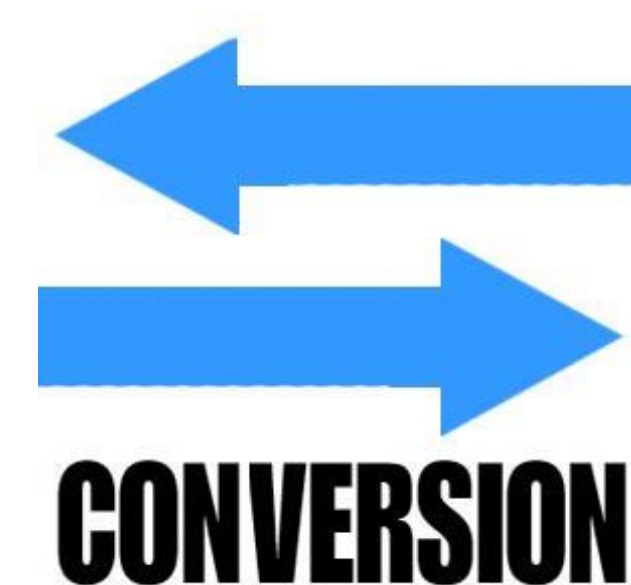
Catalytic activity in CO₂ hydrogenation process was measured for all prepared samples of iron(III) oxide and reference (commercial Fe₂O₃ from Sigma-Aldrich). The experiment proceeded in the microreactor Microactivity Effi (Fig. 4). The catalyst were activated at the temperature of 400 °C for 3 h before the reaction. Active forms were created by the transformation of iron(III) oxide. All catalysts were tested at the temperature of 325 °C and the pressure of only 1 bar for 20 h. 350 mg of catalysts were mixed 1:1 (w/w) with silica and loaded into the steal capillary with waxtrap (diameter - 9,1 mm). Molar H₂/CO₂ ratio was 3:1, inert gas was He (76 %). The flow of CO₂ was 46 mmol/h.g_{cat}.

RESULTS

CO₂ conversion and selectivity of the main product (methane) are defined as follows:

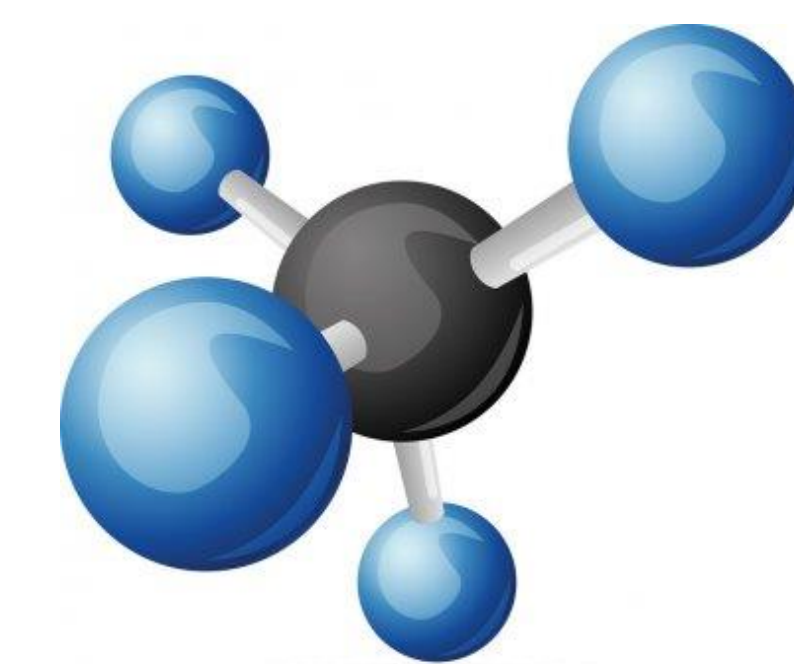
$$x_{\text{CO}_2} (\%) = \left(1 - \frac{[\text{CO}_2]}{[\text{CO}_2] + [\text{CO}] + [\text{CH}_4]} \right) \times 100,$$

$$s_{\text{CH}_4} (\%) = \frac{[\text{CH}_4]}{[\text{CH}_4] + [\text{CO}]} \times 100$$



CONCLUSION

- Four different catalysts were prepared by two-step synthesis – mesoporous iron oxides with surface area higher than 300 m²/g.
- The high-temperature XRD proved that hematite crystallized at higher temperatures as well as different behavior of the samples in the reducing atmosphere of H₂. It is in accordance with the different catalytic activity of each sample in reduction reaction of CO₂ with H₂.
- Activation before reaction has produced active forms for the CO₂ hydrogenation, which were magnetite (Fe₃O₄) and especially cementite (Fe₃C).
- The reaction was carried out at 325 °C for 20 h. The catalytic activities of the samples were compared with commercial Fe₂O₃. In the case of prepared mesoporous samples, methane was also produced which is essential for further use. By-products were CO and H₂O which were the only products on the commercial catalyst.
- The most active for the formation of CH₄ was the sample 3.



ACKNOWLEDGEMENT

The authors gratefully acknowledge the support provided by the Internal Grant of Palacký University in Olomouc – IGA_Prff_2020_34.

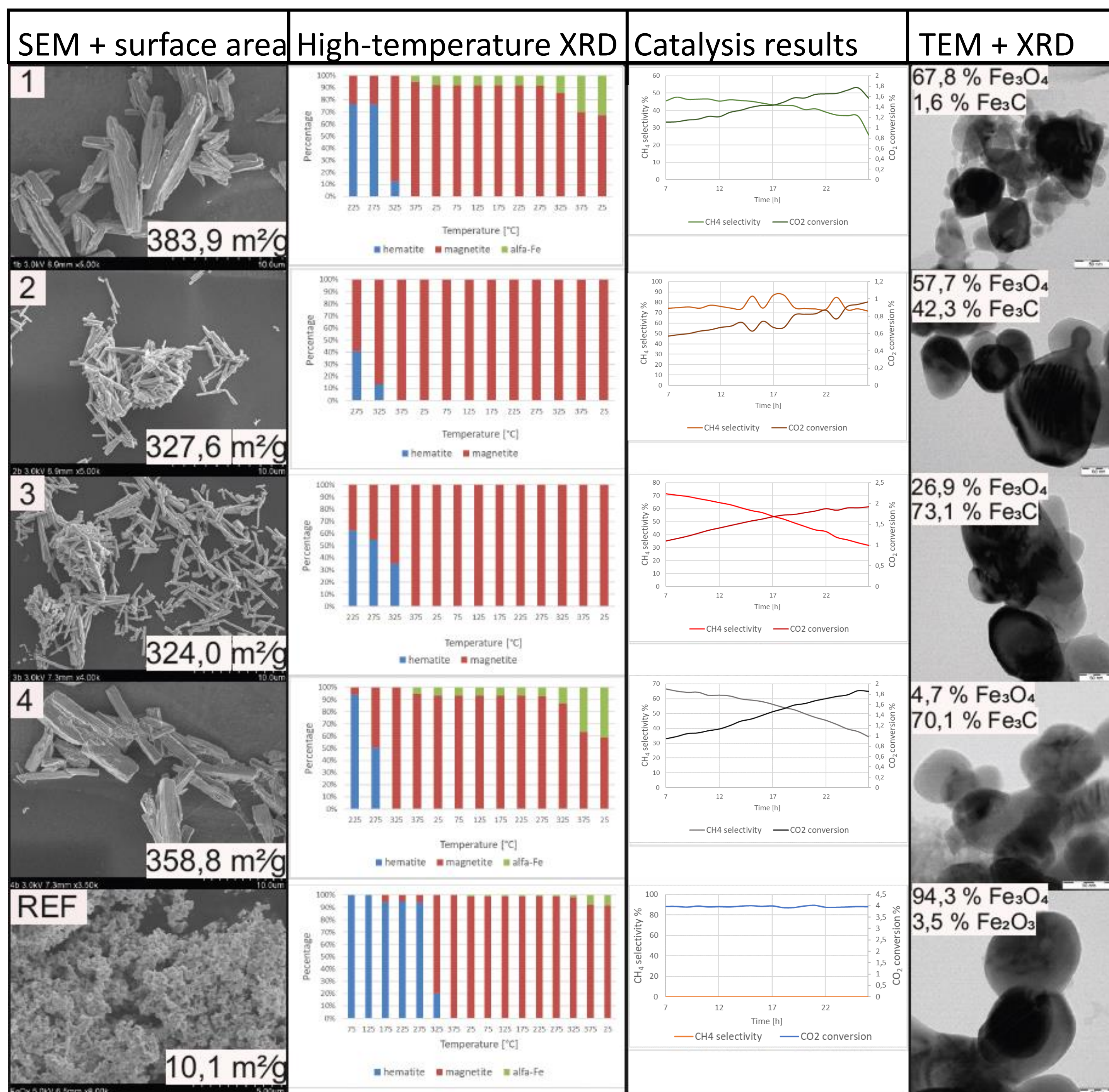


Fig. 5 SEM images and surface area, high temperature XRD of catalysts, conversion and selectivities and TEM images of spent catalysts.

CONTACT PERSON

Martina Kubíková
Palacký university Olomouc
martina.kubikova01@upol.cz

REFERENCES

- [1] M. Áresta, A. Dibenedetto, Dalton Trans, 28 (2007) 2975.
- [2] A. Rafiee, R. Khalilpour, D. Milani, M. Panahi, J. Environ. Chem. Eng., 6 (2018) 5771.
- [3] C.-S.T. Chih-Hung Huang, T. Chung-Sung, Aerosol Air Qual. Res., 14 (2014) 480.