

Detailed report of the project PD 115898

Introduction

Selective catalytic reduction of nitrogen oxides with methane ($\text{CH}_4/\text{NO}_x\text{-SCR}$) has attracted much attention and has been described as a potential method for removing NO_x from natural-gas-fueled power plants, lean-burn gas engines in combined heat and power plants [1]. Cobalt exchanged zeolites, such as Co-ZSM-5 and Co-mordenite were shown to exhibit good activity and selectivity in $\text{CH}_4/\text{NO}_x\text{-SCR}$ [2-7]; however, their thermal and hydrothermal stability seems to be still not satisfactory for long-term practical application [8-11]. Therefore, the aim of the present research project was to prepare more suitable catalysts by using thermally and hydrothermally extremely stable SSZ-13 zeolite [12-15].

Results and discussion

Catalyst preparation

Na-SSZ-13 zeolite with different Si/Al ratios was prepared using the synthesis method described by Gao et al. [16]¹. The NH_4 -form of the zeolite was obtained by Aqueous Phase Ion Exchange (APIE) using 1 M NH_4Cl at 70 °C. Cobalt was introduced into the zeolite support by (i) APIE and (ii) by Solid State Ion Exchange (SSIE) methods. Using multiple APIE procedures at 80 °C the highest achievable cobalt content was about 1.3 wt % into an SSZ-13 having Si/Al ratio of 12. Using the APIE method, the amount of introduced cobalt-ions is governed and limited by an ion-exchange equilibrium and is hindered also by the size of the aqua complex of the cobalt ion. Higher cobalt content was achievable by SSIE. This method was successfully applied in cooperation with Rania Charrad, PhD student of the Université Tunis El Manar, Faculté des Sciences.²

By SSIE method, using $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$ precursor salt, the Co/Al ratio reached 0.5 and could be varied between Co/Al ratio of 0.1 and 0.5. The application of different cobalt precursors were

¹ Thanks are to Márton Kollár for additional experimental details that were essential for the preparation of single phase SSZ-13 with high yield. Thanks are due to Sachem Zeogen for the structure directing agent (SDA) solution (Trimethyl-adamantyl ammonium hydroxide) they provided.

² Thanks to the present project (N° 115898), R. Charrad could carry out CH_4/NO -SCR tests and relating catalyst characterization in the Green Chemistry research group (RCNS HAS) during her PhD studies. Her travel costs in 2016, 2017 and 2018 were financed by the Tunisian government, and she has spent 2-3 months each year in our group. She has done the literature survey and the SSIE procedure in Tunis.

for SSIE was also studied. For the preparation of comparative catalyst samples, Pt was impregnated on SSZ-13, whereas Ni and Cu was introduced into zeolite SSZ-13 by APIE.

The successful formation of single phase, highly crystalline SSZ-13 during our zeolite synthesis was verified by X-ray powder diffraction (XRPD) measurements. We assessed the almost intact crystallinity of the samples subjected to cobalt ion exchange, and used in catalytic reaction at high temperature and in the presence of water vapor in high concentration. Formation of Co_3O_4 phase was detected in the $\text{Co}^{\text{SSIE}}(\text{acetate}, 0.4)\text{-SSZ-13}$ and $\text{Co}^{\text{SSIE}}(\text{formate}, 0.4)\text{-SSZ-13}$ samples. In the sample designation superscript SSIE refers to the method of Co introduction whereas the anion of the precursor Co salt is given in the parenthesis. The salt was used in an amount to get $\text{Co}/\text{Al} = 0.4$.

^{29}Si NMR measurements allowed us to calculate the $\text{Si}/\text{Al}_\text{F}$ ratio in the SSZ-13. ^{27}Al NMR spectra revealed the presence of only minor amount of extra-framework aluminum in the samples before and after cobalt introduction and before and after catalytic utilization.

Atomic absorption spectroscopy was applied to determine the metal content of the prepared catalysts. 9.0 - 31.0 wt.% cobalt loss was found during the SSIE process depending on the nature of the cobalt salt.

The texture of the samples was characterized by nitrogen adsorption–desorption isotherms determined at $-196\text{ }^\circ\text{C}$ using an automatic volumetric apparatus. Introduction of cobalt by SSIE or by APIE did not cause significant decrease of the specific surface area and pore volume of the zeolite. Appearance of hysteresis loop on the adsorption isotherms indicated the presence of some mesoporosity. The used catalysts showed near the same textural properties as the fresh ones.

The catalytic tests were carried out at atmospheric pressure in a flow–through micro reactor tube (I.D. 4 mm) made of quartz. 100 mg catalyst and $100\text{ cm}^3\text{ min}^{-1}$ flow rate was applied to have $\text{GHSV} = 30,000\text{ h}^{-1}$. The inlet gas mixture contained 1000 – 4000 ppm NO, 4000 – 9000 ppm CH_4 , 2 % O_2 in balance helium, and in some test 3-10 v/v% H_2O as well. GHSV was varied between 7500 and $40,000\text{ h}^{-1}$. The effluent gas mixture was continuously monitored by an on-line mass spectrometer (MS) (VG ProLab, Fisher Scientific), and the concentration of carbon monoxide, nitrous oxide and NO_2 was analysed by an IR gas cell (PIKE Technologies).

The catalytic tests revealed that cobalt chloride, –nitrate, and –acetyl-acetonate are adequate precursors in the SSIE to reach reasonable SCR activity, while the use of the formate or acetate salt led to poor catalytic performance in the NO-SCR reaction (Fig.1).

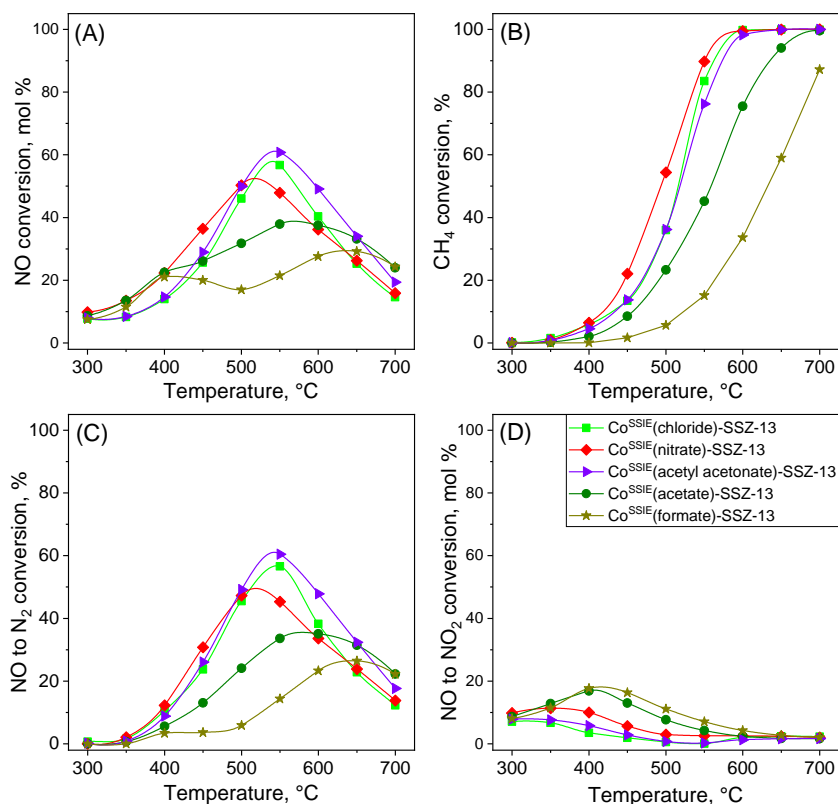


Fig. 1. The NO conversion (A), CH₄ conversion (B), NO to N₂ conversion (C), and NO to NO₂ conversion (D) in the CH₄/NO-SCR reaction over Co^{SSIE}(chloride)-SSZ-13, Co^{SSIE}(nitrate)-SSZ-13, Co^{SSIE}(acetyl acetonate)-SSZ-13, Co^{SSIE}(acetate)-SSZ-13, and (E) Co^{SSIE}(formate)-SSZ-13. The reactant flow was 4000 ppm NO/4000 ppm CH₄/2% O₂/He, the GHSV was 30,000 h⁻¹. The Co/Al ratio was about 0.4. Before reaction, the catalysts were treated in situ in He flow at 700 °C for 1 h. The catalytic test was carried out by cooling the reactor stepwise from 700 °C to 300 °C.

H₂-TPR is a useful method to provide information about the oxidation state and reducibility of Co-species and indirectly about their location in zeolites. The H₂-TPR curves indicated that Co^{SSIE}(chloride)-, Co^{SSIE}(nitrate)-, and Co^{SSIE}(acetyl acetonate)-SSZ-13 samples contain only hard-to-reduce cobalt species, i.e. isolated cobalt ions, such as Co²⁺ and [Co-OH]⁺ cations in ion-exchange positions, while Co^{SSIE}(acetate)-SSZ-13 and Co^{SSIE}(formate)-SSZ-13 samples contain predominantly cobalt species reducible below 500 °C, which can be attributed to Co-oxide clusters on the outer surface of zeolite crystallites and to CoO_x species (including polynuclear Co-oxocations) dispersed within pores.

UV-Vis spectroscopy was applied to detect siting and distribution of Co^{2+} cations in dehydrated zeolites. It confirmed that lattice Co^{2+} and $[\text{Co-OH}]^+$ cations are only present in the $\text{Co}^{\text{SSIE}}(\text{chloride})^-$, $\text{Co}^{\text{SSIE}}(\text{nitrate})^-$, and $\text{Co}^{\text{SSIE}}(\text{acetyl acetate})^-$ -SSZ-13 samples.

The ion-exchange of H-zeolites results in weakening of the $\nu(\text{OH})$ infrared absorption bands. The drop of the band intensity is proportional to the ion-exchange level. The spectrum of H-SSZ-13 presents two overlapping $\nu(\text{OH})$ bands at 3595 and 3574 cm^{-1} attributed to OH-groups located on the 8-member and 6-member rings in the chabazite structure of zeolite SSZ-13, respectively. The lower intensity of these two bands in spectra of the $\text{Co}^{\text{SSIE}}(\text{chloride})^-$, $\text{Co}^{\text{SSIE}}(\text{nitrate})^-$, and $\text{Co}^{\text{SSIE}}(\text{acetyl acetate})^-$ -SSZ-13 samples as compared to the spectrum of zeolite H-SSZ-13 confirmed the substitution of both types of Brønsted acid sites by ionic Co species during the solid state ion exchange. The observed intensity drop suggests that the divalent cobalt cations entered with extra framework anion ligands and participate in the exchange with a net charge of +1.

The catalytic results, the H_2 -TPR, UV-vis DRS and the analysis of the FTIR spectra in the $\nu(\text{OH})$ region led to the conclusion that cobalt species present in the zeolite as lattice cations (e.g. Co^{2+} or $[\text{CoOH}]^+$), give good activity and N_2 selectivity, while catalysts hosting cobalt mainly as CoO_x species, catalyze the formation of NO_2 .

Changing the cobalt content in the zeolite between Co/Al ratio 0.1 and 0.5 (SSIE method using $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ salt), we could conclude that the NO-SCR activity is proportional to the concentration of the lattice $\text{Co}^{2+}/[\text{Co-OH}]^+$ ions.

The asymmetric internal stretching vibration modes of the zeolite framework appear red shifted in the infrared spectral range of about 980 – 880 cm^{-1} due to the perturbation by lattice cations in properly dehydrated zeolites, whereas the frequency of each shifted band is characteristic of the charge and location of the corresponding compensating cations. The analysis of these vibration bands allows to distinguish between Co^{2+} lattice cations occupying τ and d $\tau^{3\text{Si}}$ sites in the 8-member rings and σ and ω sites in the regular six member rings and hexagonal prisms in the chabazite structure. Relying on the assignment published recently for Co-SSZ-13 [17], we could conclude that the molar ratio of Co^{2+} lattice cations located in the 8 member rings and located in the 6 member rings is significantly higher for the samples prepared by SSIE than for the sample prepared by APIE.

The use of NO as probe molecule in FTIR experiments, revealed that lattice cobalt is mainly present in oxidation state 2+, and only a minor fraction is in oxidation state 3+. Using CO to probe the electrostatic fields at different Lewis acid sites, we could distinguish between four cobalt species present in the Co^{SSIE}(chloride)-SSZ-13, Co^{SSIE}(nitrate)-SSZ-13, Co^{SSIE}(acetyl acetate)-SSZ-13 both before and after catalytic utilization (i) Co-oxo-cations (e.g. [Co(II)-O-Co(II)]²⁺, [Co(III)O]⁺ and [Co_xO_y]ⁿ⁺), (ii and iii) Co²⁺ lattice cations located at two different cationic positions of the zeolite structure, namely in the 8-member rings and the 6-member rings, and (iv): a minor amount of species similar to CoAl₂O₄, which might be formed in the reaction of extra framework Al species with cobalt salts at high temperature during the SSIE process.

Interesting activation phenomenon was found over Co^{SSIE}(chloride)-SSZ-13: higher NO and CH₄ conversions were achieved over the catalyst tested before at temperature as high as 700 °C than over the catalyst that did not go through catalytic use before (Fig. 2). The activity enhancement was negligible if the cobalt content of the catalyst was low (Co/Al ≤ 0.2) and was more pronounced if the cobalt content was high (Co/Al > 0.2). In a third and fourth catalytic run, the catalyst maintained its higher activity. These results strongly suggest that a transformation of Co active sites may occur during a brake-in period if the density of Co species is high enough (Co/Al_F > 0.2) in the catalyst. Using H₂-TPR technique, we could ascertain that a fraction of the cobalt species was transformed to polynuclear Co-oxo species located inside the zeolite pores and to a smaller extent to Co-oxide clusters on the outer surface of the zeolite crystallites. From the area under the TPR curve below 600 °C, it was estimated that about 15 % of the cationic Co species were involved in the transformation. These observations are in agreement with the results of the UV-Vis DRS analysis indicating that a fraction of the isolated ionic Co-species was transformed to Co-oxide or oxide-like species. The UV-vis DRS spectra of the fresh and used Co^{SSIE}(chloride, 0.4)-SSZ-13 catalysts showed that the transformation affected mainly those species located in the 8-member rings. Concurrently, a small but well discernible new band appeared in the spectrum of the used catalyst, which can be assigned to charge transfer band of oxide-like cobalt species or to cobalt species with oxygen ligand. Specific catalytic test confirmed that this transformation resulted in higher catalytic activity in the oxidation of nitric oxide (NO-COX reaction).

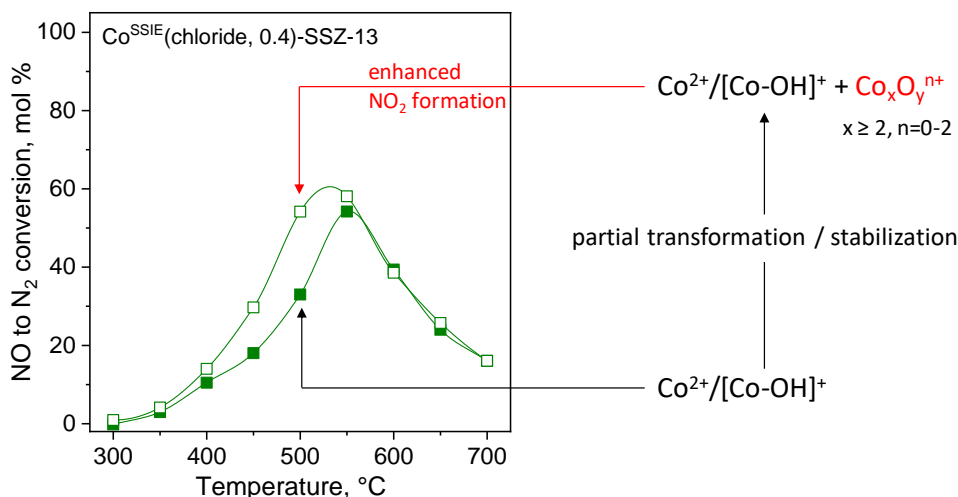


Fig. 2. NO to N₂ conversion over Co^{SSIE}(chloride, 0.4)-SSZ-13. The reactant flow was 4000 ppm NO/4000 ppm CH₄/2% O₂/He at a GHSV of 30,000 h⁻¹. The catalyst was pre-treated in He flow at 700 °C for 1 h prior the experiment. Catalytic test was carried out by heating the reactor stepwise from 300 °C to 700 °C (full symbols) and then by cooling the reactor stepwise from 700 °C to 300 °C (open symbols). The revealed transformation of the cobalt species is marked on the figure.

We aimed to find parameter settings for the catalytic use where nearly 100 % conversion and high N₂ selectivity can be reached. Applying the catalyst Co^{SSIE}(chloride, 0.4)-SSZ-13, the following parameters were varied: GHSV between 7500 and 40,000 h⁻¹, inlet NO concentration between 4000 and 1000 ppm, inlet methane concentration between 4000 and 9000 ppm. Nearly 100 % NO to N₂ conversion was obtained at GHSV 15,000 h⁻¹ using a reactant mixture that contains 1000 ppm NO, 9000 ppm CH₄ and 2 % O₂ in balance helium.

Hydrothermal stability of deNO_x catalysts is important because combustion exhaust gas contains steam in high concentrations. Additional catalytic tests were carried out to investigate the effect of water on the catalytic activity and hydrothermal stability of catalysts showing favorable catalytic properties in the NO-SCR reaction.

The test of the hydrothermal stability of the Co^{SSIE}(chloride,0.4)-SSZ-13 catalyst in the presence of 3,5 – 10 v/v % water vapor in the inlet reactant mixture, was tested at 550 °C and is presented in Fig. 3. The test was carried out by alternating addition and removal of the water vapor to / from the reactant mixture in 1-h time intervals during 10-12 h at each investigated parameter setting. Fig. 3 (A) shows the NO and CH₄ conversions when 5.5 v/v % H₂O was mixed to the 4000 ppm NO, 4000 ppm CH₄, 2% O₂ / He mixture at 30,000 h⁻¹ space velocity. The addition of water

vapor decreased both the NO and CH₄ conversions, but the decrease in the CH₄ conversion was stronger. At this temperature the NO to NO₂ conversion was below 1%. We can conclude that the presence of water vapor suppressed the consumption of CH₄ in the side reaction (CH₄ + O₂ = CO₂ + 2 H₂O) to higher extent, and in the main reaction (2 NO + O₂ + CH₄ = N₂ + CO₂ + 2 H₂O) to lower extent. After the removal of the water vapor from the inlet mixture, the higher NO and CH₄ conversions were retrieved. It means, that the effect of water vapor on the catalyst activity is reversible at 550 °C. The NO and CH₄ conversions under wet conditions did not show further decrease in the 3rd, 4th and 5th cycles, which means that the catalyst has lower but stable activity in the presence of 5.5% H₂O vapor. The extent of the decrease in the CH₄ conversions due to the presence of water vapor in the inlet reactant mixture, changes linearly with the water concentration (Fig. 3 (C)). At each water concentration the decrease of CH₄ conversion is higher than the decrease of NO conversion, which infers the beneficial change of the methane selectivity index (α , Eq.1) under wet conditions.

$$\alpha (\%) = \frac{0.5 \times [NO]^0 \times X_{NO \rightarrow N_2}}{[CH_4]^0 \times X_{CH_4}} \times 100 \quad (1),$$

where [NO]⁰ and [CH₄]⁰ are the concentrations of NO and CH₄ at the reactor inlet, whereas X_{NO→N₂} and X_{CH₄} are the NO to N₂ conversion and methane conversion, respectively.

When 5.5% water vapor was added to a reactant mixture containing NO in lower concentration (2000 ppm NO, 4000 ppm CH₄, 2 % O₂/He), decrease of methane conversion was observed, but the NO conversion did not change or slightly increased (Fig. 3 (B)). The addition of 5.5% water suppressed the side reaction, and the higher concentration of unreacted methane compensated the suppressing effect of water vapor on the main reaction. As shown in Fig. 3 (D), both in the absence of water and in the presence of 5.5% water vapor in the reactant mixture, the methane conversion is decreasing and the selectivity index (α) is increasing in the function of NO concentration. It is established by several studies [10, 18], that oxide-like cobalt species catalyze both the formation of NO to NO₂ and the combustion of methane by O₂. The competitive reaction of NO and CH₄ on these sites might account for the higher methane combustion when the reactant mixture contains NO in lower concentration.

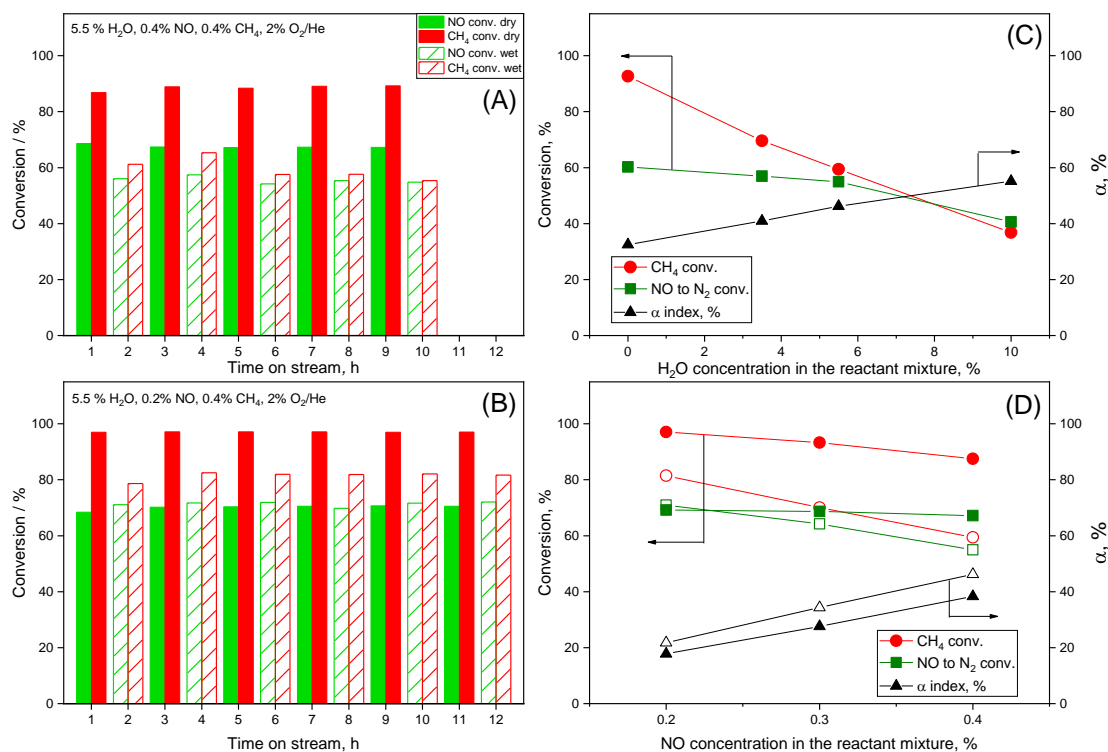


Fig. 3. Effect of water on the CH₄/NO-SCR reaction over Co^{SSIE}(chloride,0.4)-SSZ-13. Reaction was carried out at 550 °C and GHSV of 30,000 h⁻¹. (A-B) conversion of NO and CH₄ in the function of time on stream using alternating dry (full bars) or wet (grafted bars) reactant mixture containing 5.5% water vapor. The inlet NO concentration was 4000 ppm (A) or 2000 ppm (B). (C-D) conversion of NO to N₂ and CH₄ and the α selectivity index in the function of the H₂O concentration (C) and in the function of the NO concentration (D) in the inlet gas stream; reaction was carried out as for (A-B) and conversion values shown were obtained by averaging data points during 10-12 h time on stream. In (D) full symbols refer to dry reaction stream, open symbols refer to wet reaction stream.

Operando DRIFTS experiments carried out over Co^{SSIE}(chloride,0.4)-SSZ-13 confirmed the reaction mechanism suggested earlier for the CH₄/NO-SCR reaction over Co-mordenite and Co-ZSM-5 catalysts [4].

The introduction of rare earth metals to Co-SSZ-13 samples did not result in the improvement of the catalytic activity, selectivity neither under dry nor under wet reaction conditions.

Publications

- 1) H.E. Solt, R. Charrad, M. Mhamdi, F. Lónyi, J. Valyon: Chabazite type zeolites in the selective catalytic reduction of NO by methane, Book of Abstracts, 13th Pannonian International Symposium on Catalysis, 19-23 September 2016 - Siófok, Hungary, Hungarian Chemical Society, ISBN 978-963-9970-56-4, 2016
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- 3) H.E. Solt, R. Charrad, M. Mhamdi, c, F. Lónyi, J. Valyon: Reaction enhanced CH₄/NO-SCR activity of Co-SSZ-13 zeolite catalysts, Book of Abstracts, 14th Pannonian International Symposium on Catalysis, High Tatras, September 3-7, 2018, Ed.: A. Kaszonyi, M. Stolcová, L. Lépesová, ISBN 978-80-89597-94-9, 2018
- 4) H.E. Solt, R. Charrad, M. Mhamdi, F. Lónyi, J. Valyon: Activity enhancement of Co-SSZ-13 catalysts during CH₄/NO-SCR reaction, Book of Abstracts, 1st International Conference on Reaction Kinetics, Mechanisms and Catalysis June 6-9, 2018, Budapest, Hungary, p268, ISBN 978 963 05 9913 9, 2018
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- 7) R. Charrad, F. Ayari, H.E. Solt*, F. Lónyi, J. Valyon, M. Mhamdi and Z. Ksibi, Preparation of Co-SSZ-13 zeolite catalysts via solid-state reaction with different Co-compounds for CH₄/NO-SCR reaction, manuscript prepared for publication.

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