

**Ph.D. thesis**

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**SELECTIVE CATALYTIC REDUCTION OF NITROGEN OXIDES BY METHANE  
OVER INDIUM CONTAINING ZEOLITES**

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2011

## INTRODUCTION AND OBJECTIVES

The abatement of the malign nitrogen oxides ( $\text{NO}_x$ ) from different emissions is a major task to protect the environment. Nitrogen oxides appearing in the atmosphere come from moving (vehicles) or stationary (chemical plants or power plants) sources and they are mostly formed during the high temperature combustion of fossil fuels. The present work is mainly related to the elimination of nitrogen oxides from the emissions of power plants.

The selective catalytic reduction of nitrogen oxides by using cheap and abundantly available methane ( $\text{CH}_4/\text{NO-SCR}$ ) is a feasible process for cleaning the emission of power plants fuelled by methane. The selective reduction of NO is however difficult since the emission contains another oxidizing component,  $\text{O}_2$  in large excess. The activation of the relatively stable methane for the reaction is also demanding. After surveying the corresponding literature we can conclude that only a few metal, such as Pt, Pd, Co, Mn, Ni, Ga, In, and the combination of these are suitable for the preparation of supported catalysts, which are active in the  $\text{CH}_4/\text{NO-SCR}$  reaction. Recently very promising results were obtained with cobalt or palladium promoted In-zeolites.

Catalyst development, which aims the design of more active and selective catalysts for the  $\text{CH}_4/\text{NO-SCR}$  reaction can be more effective if the catalytic mechanism is clarified. Although the mechanism of the reaction is more or less understood, there are number of details, which have not been clarified yet.

In the present work one of our goals was to learn about the intermediates and the unknown mechanistic details of the reductive solid state ion exchange (RSSIE) process in the  $\text{In}_2\text{O}_3/\text{H-zeolite}$  system. Because of its advantages this preparation method was used for the preparation of our In,H-zeolite catalysts for the  $\text{CH}_4/\text{NO-SCR}$  reaction.

In order to better understand the mechanism of the  $\text{CH}_4/\text{NO-SCR}$  reaction, we examined the relation between the structure and catalytic properties of In,H-zeolites applying catalytic and *operando* DRIFT spectroscopic examinations. These experiments mainly aimed the identification of the catalytically active centers and the active and inactive (spectator) surface species formed on the catalyst under reaction conditions. We also intended to clarify the promoting mechanism of palladium or cobalt on the In,H-zeolite catalysts.

The increased formation rate of  $\text{NO}_2$ , which was observed in the presence of the above mentioned promoters, was often suggested to contribute to the increased rate of the SCR reaction on In,H-zeolites. Another objective of the present work was to find out the role of the  $\text{NO}_2$  in the reaction mechanism.

## EXPERIMENTAL METHODS

In the present work different In,H-, Pd,H-, Pd,In,H-, Co,H-, and Co,In,H-zeolite catalysts were prepared from H-mordenite or H-ZSM-5 zeolites. Indium was introduced by the RSSIE method, palladium was introduced by wet impregnation, whereas cobalt was introduced either by liquid phase ion exchange or by solid state reaction.

The RSSIE process taking place in the sample and the redox properties of the metals introduced were studied by temperature-programmed reduction (H<sub>2</sub>-TPR) and oxidation (depending on the oxidizing agent, O<sub>2</sub>-TPO or NO-TPO) methods.

Catalytic experiments were carried out in a flow-trough microreactor in the temperature range of 300- 600 °C at a space velocity (GHSV) of 30 000 h<sup>-1</sup>.

The surface species formed on the surface of the catalyst under reaction conditions were studied by diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS). For these so called *operando* experiments a high temperature and pressure DRIFT spectroscopic cell was used. The concentration of the reactants and the reaction products was continuously monitored by an on line mass spectrometer.

XRD method was applied to follow the changes of the catalyst structure. Catalyst samples were pretreated *in situ* in the reactor chamber of the XRD apparatus at the desired temperature and in the preferred gas atmosphere. The samples were rendered soluble to determine the metal content by atomic absorption spectroscopy.

## NEW SCIENTIFIC RESULTS

### 1. Preparation of In,H-zeolites by reductive solid state ion-exchange:

1.1. It was shown that the reaction between H-zeolites and In<sub>2</sub>O<sub>3</sub> in the presence of hydrogen (reductive solid state ion exchange, RSSIE), in contrast to the mechanism suggested in the literature, proceeds via volatile InOH intermediate formed by the reduction of In<sub>2</sub>O<sub>3</sub>. The InOH intermediate reacts with the Brønsted acid site (proton) within the zeolite pores in an acid-base reaction, in which In<sup>+</sup> cation, replacing the proton, is formed together with a water molecule.

(Published in publication No.4.)

1.2. It was demonstrated that the In-ion exchange could take place by the reaction of metallic In and the H-zeolite, via, so called, oxidative solid state ion exchange (OSSIE). The ion-exchange reaction also proceeds through the formation of InOH

intermediate. The formation of InOH intermediate requires the presence of water (steam). The metallic In is oxidized by water in the reaction resulting in the formation of H<sub>2</sub> and volatile InOH. The ion-exchange then takes place in the reaction between the Brønsted acid site and InOH intermediate as disclosed in thesis 1.1. (Published in publication No.4.)

1.3. It was shown that without hydrogen in the system only a low ion-exchange level could be reached even at high temperatures (>500 °C) in the solid state reaction between H-zeolites and In<sub>2</sub>O<sub>3</sub>, that is by the so called auto reductive solid state ion exchange (ARSSIE), which reaction most probably also proceeded via InOH intermediate. In the process In<sub>2</sub>O<sub>3</sub> reacts with water formed in the high temperature dehydroxylation of zeolite resulting in the formation of InOH intermediate and O<sub>2</sub>. The oxygen formation in the reaction can be detected by mass spectrometry, whereas InOH intermediate reacts with the Brønsted acid sites and thereby evidently forms In<sup>+</sup> cations in the zeolite. (Published in publication No.4.)

1.4. It was confirmed that In<sup>+</sup> centers formed in the solid state ion-exchange process could be oxidized to [InO]<sup>+</sup> centers with molecular oxygen. It was found that the oxidation temperature was strongly dependent on the density of the In<sup>+</sup> sites determined by Si/Al ratio of the zeolite and the ion-exchange level. The oxidation with molecular oxygen requires the transfer of 4 electrons and therefore proceeds more easily on nearby In<sup>+</sup> centers in the zeolite lattice, which explains the very different oxidation temperatures (differing by 200 – 300 °C) of the In-zeolites, having different Si/Al ratio. (Published in publication No.3.)

2. Catalytic effect of In,H-zeolites in the selective catalytic oxidation of NO with methane in the presence of excess oxygen (CH<sub>4</sub>/NO-SCR):

2.1. It was shown that when In,H-zeolites prepared with RSSIE method were contacted with NO/O<sub>2</sub> gas mixture at reaction temperature (300 – 500 °C), zeolite bound nitrosonium (NO<sup>+</sup>) and nitrate (NO<sub>3</sub><sup>-</sup>) ions were formed. The NO<sup>+</sup> ions are formed in two well separable processes. One of the processes takes place on the Brønsted acid sites according to the mechanism known from the literature. In the second process NO<sup>+</sup> and NO<sub>3</sub><sup>-</sup> ions are formed simultaneously on [InO]<sup>+</sup>Z<sup>-</sup> active sites (where Z<sup>-</sup> represents a segment of the zeolite lattice with one negative charge).

(Published in publication No. 3.)

2.2. It was evidenced that from the  $\text{NO}^+$  and  $\text{NO}_3^-$  ions formed simultaneously on  $[\text{InO}]^+\text{Z}$  active sites only the nitrate ions were able to activate (oxidize) methane, in which reaction the active intermediate of the reaction (according to the corresponding literature  $\text{CH}_3\text{NO}_2$  can be substantiated) was formed.

(Published in publication No.3.)

2.3. It was shown that the active intermediate ( $\text{CH}_3\text{NO}_2$ ) formed in the reaction of surface nitrate and methane or the products of fast transformation thereof (nitrite, isocyanate, or amine groups) react most probably with  $\text{NO}^+$  ions. Nitrogen formation takes place in this reaction. This finding is based on the observation that  $\text{NO}^+$  ions are consumed in the reaction together with  $\text{NO}_3^-$  ions, whereas  $\text{NO}^+$  ions alone can not react with methane. Our suggestion is in line with earlier findings that the formation of nitrogen requires the reaction of two intermediates, in which the formal oxidation state of the nitrogen atom is +3 and -3.

(Published in publication No. 3.)

2.4. It was substantiated that in the reaction of surface nitrate species and methane  $\text{In}^+\text{OH}^-$  was formed, which further reacted with a nearby acidic hydroxyl group to give  $\text{In}^+$  compensating cation. This latter reaction is the same as observed in the final reaction step of the RSSIE process. It was shown that  $\text{In}^+$  was quickly oxidized to  $[\text{InO}]^+$ , closing thereby the catalytic cycle.

(Published in publication No.3.)

2.5. It was revealed that correlation exists between the activity in the methane combustion side reaction and the oxidability of the  $\text{In}^+$  species with molecular oxygen. The catalyst sample, in which the  $\text{In}^+$  centers can be oxidized into  $[\text{InO}]^+$  species at relatively low temperatures (<200 °C), becomes active in the methane combustion reaction at lower temperature (the “light off” temperature is lower). Both indium and methane oxidation are redox reactions requiring multiple electron transfer and therefore proceed more easily, if the density of the active sites is higher, that is the indium centers are located relatively close to each other in the catalyst.

(Published in publication No.3.)

### 3. Promoting effect of palladium and cobalt in the $\text{CH}_4/\text{NO}$ -SCR reaction over In,H-zeolites

3.1. It was demonstrated that the catalytic properties (activity and selectivity) of In,H-zeolites could be significantly improved by introduction of small amount (0.5 wt%)

of Pd, which was attributed to the concerted action of  $[\text{InO}]^+$  and  $\text{Pd}^{n+}$  sites. It was shown that, on one hand, in the presence of Pd the concentration of In-bound nitrate species, which are highly reactive towards methane, were increased. On the other hand, during reaction the  $\text{In}^+/\text{[InO]}^+$  redox centers prevent the transformation of Pd-bound nitrosyl species ( $\text{Pd}^{n+}\text{-NO}$ ) into less reactive isocyanate ( $\text{-NCO}$ ) and nitril ( $\text{-CN}$ ) species. (Published in publication No.3.)

3.2. It was shown that  $\text{Co}^{2+}$  and/or  $[\text{Co-OH}]^+$  sites in ion-exchange positions do not provide any promoting effect, whereas Co-oxide clusters formed on the outer surface of the zeolite crystallites show significant promoting effect. The reason is that the ionic centers are inactive in the oxidation of NO with oxygen to  $\text{NO}_2$  (NO-COX), whereas Co-oxide clusters, especially those containing  $\text{Co}_3\text{O}_4$ , significantly increase the rate of the NO-COX reaction.

(Published in publication No.1. and in an upcoming publication.)

3.3. It was confirmed that the reaction requires two different active sites. One type of active sites is responsible for the oxidation of NO with molecular oxygen to  $\text{NO}_2$  (NO-COX reaction), whereas the other type of active sites catalyze the reaction leading to the formation of  $\text{N}_2$  (NO-SCR reaction). It was proved that the NO-COX reaction is catalyzed by the Brønsted acid sites, however, the Co-oxide clusters, introduced as promoters, are significantly more active in this reaction. The  $\text{N}_2$  forming reaction takes place on  $\text{Co}^{2+}/[\text{CoOH}]^+$  or  $[\text{InO}]^+/\text{[InOH]}^{2+}$  centers occupying ion-exchange positions in the zeolite.

(Published in publication No.1. and in an upcoming publication.)

3.4. It was substantiated that the presence of  $\text{NO}_2$  intermediate formed in the NO-COX reaction is prerequisite for the formation of  $\text{NO}_3^-/\text{NO}^+$  active surface species on the  $\text{Co}^{2+}/[\text{CoOH}]^+$  or  $[\text{InO}]^+/\text{[InOH]}^{2+}$  centers. It was shown that In-bound nitrate species can react with methane much faster than Co-bound nitrate species, which is clearly reflected by the significantly higher activity of the In-zeolite catalyst.

(Published in publication No.1. and in an upcoming publication.)

3.5. It was revealed that due to the higher rate of the NO-COX reaction in the presence of Co-oxide promoter, the formation rate of In-bound nitrate is also increased, and thus the rate of the NO-SCR reaction became also higher. This relation reveals how the NO-COX and the NO-SCR reactions are connected to each other.

(Published in publication No.1.)

3.6. It was substantiated that over a given catalyst the NO-COX and NO-SCR reactions should proceed in a concerted manner, so that the ratio of their rates should be suitable in order to reach the maximal reaction rate in the overall reaction and avoid the appearance of NO<sub>2</sub> in the product mixture. (In an upcoming publication.)

3.7. It was demonstrated that the active sites responsible for the NO-COX and NO-SCR reaction, respectively, can be physically separated from each other, but – especially over 400 °C, where the formation of NO<sub>2</sub> is thermodynamically limited – the catalyst works more effectively, if the two types of the active centers are in close proximity. When these active sites are close to each other the transport rate of NO<sub>2</sub> between the active sites of NO-COX and NO-SCR activity, will not become the process, determining the reaction rate. (In an upcoming publication.)

## PUBLICATIONS RELATED TO THE THESIS

### \* Publications used in the thesis

#### *Articles in journals:*

1.\* *Journal of Molecular Catalysis A: Chemical*, (2011) *accepted*,  
doi:10.1016/j.molcata.2011.05.021

The activation of NO and CH<sub>4</sub> for NO-SCR reaction over In- and Co-containing H-ZSM-5 catalysts, F. Lónyi, **H.E. Solt**, J. Valyon, A. Boix, and L.B. Gutierrez

IF<sub>2010</sub>: 2,872

2. *Catalysis Today*, (2011), *accepted*, doi:10.1016/j.cattod.2011.02.033

The role of Pd–In interactions on the performance of PdIn-Hmordenite in the SCR of NO<sub>x</sub> with CH<sub>4</sub>, H. Decolatti, **H. Solt**, F. Lónyi, J. Valyon, E. Miró, L. Gutierrez

IF<sub>2010</sub>: 2,993

3.\* *Applied Catalysis B: Environmental* **100** (2011) 133–142

An operando DRIFTS study of the active sites and the active intermediates of the NO-SCR reaction by methane over In,H- and In,Pd,H-zeolite catalysts, F. Lónyi, **H.E. Solt**, J. Valyon, H. Decolatti, L.B. Gutierrez, E. Miró

IF<sub>2010</sub>: 4,749

4.\* *J.Phys.Chem. C*, **112** (2008) 19423-19430

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IF<sub>2008</sub>: 3,396

*Articles in conference proceedings:*

**5.\*** 10<sup>th</sup> Pannonian International Symposium on Catalysis, 29 August – 2 September, 2010, Krakow, Poland, ISBN: 978-83-929430-4-4, p 60-67

Catalytic activity of In-containing zeolite catalysts in the NO<sub>x</sub>-SCR reaction by methane, **H.E. Solt**, F. Lónyi, J. Valyon

**6.\*** 9<sup>th</sup> Pannonian International Symposium on Catalysis, 8-12 September 2008, Strbske pleso, Slovakia, ISBN 978-80-227-2923-9, p 250-256

Preparation of In,H-Zeolite Catalysts and their Activity in the NO-SCR Reaction by Methane, **H. Solt**, F. Lónyi, J. Valyon

*Abstracts of posters:*

16<sup>th</sup> International Zeolite Conference joint with the 7<sup>th</sup> International Mesostructured Materials Symposium, July 4-9, 2010, Sorrento, Italy, Book of Abstracts, p 1187-1188, In,H-, In,Pd,H-, and In,Co,H-zeolite catalysts for the SCR of NO<sub>x</sub> by methane, **H. Solt**, F. Lónyi, J. Valyon

16<sup>th</sup> International Zeolite Conference joint with the 7<sup>th</sup> International Mesostructured Materials Symposium, July 4-9, 2010, Sorrento, Italy, Book of Abstracts, p 1347-1348, The effect of Pd-In interactions in a mordenite framework upon NO<sub>x</sub> SCR with methane, H. Decolatti, F. Lónyi, **H. Solt**, E. Miró, L. Guiterrez

Third International Congress on Operando Spectroscopy, April 19-23, 2009, Rostock-Warnemünde, Germany, Book of Abstracts, P3-04, Catalytic activity of In,H- and In,Pd,H-zeolite catalysts in the NO<sub>x</sub>-SCR reaction by methane, **H. Solt**, F. Lónyi, J. Valyon

**OTHER PUBLICATIONS**

*Articles in journals:*

*CrystEngComm* **13** (2011), 1946-1952,  
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IF<sub>2010</sub>: 4,006

*Journal of Molecular Catalysis A: Chemical*, **333** (2010) 37-45  
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IF<sub>2010</sub>: 3,383