

## Oxidation of methane over Ru/clinoptilolite catalysts\*

M. Kuśmierz

*Department of Environmental Chemistry, Faculty of Chemistry,  
Maria Curie-Skłodowska University, M. Curie-Skłodowska Sq. 3,  
20-231 Lublin, Poland.*

*tel. +48-81 537 56 92, e-mail: marcin.kusmierz@umcs.lublin.pl*

This paper describes the activity of ruthenium catalysts based on clinoptilolite, prepared by the ion exchange method, in the reaction of total methane oxidation. It has been shown that the activity of the catalysts is higher than metal oxide based ones, and is directly proportional to ruthenium loading.

### 1. INTRODUCTION

Growing natural gas share in the worldwide primary energy consumption [1] in connection with natural environment pollution increases interest in catalytic methane oxidation. Comparing to classical burning such a catalytic process is flameless: methane burns in much lower temperatures [2]. This low temperature and lack of flame with its specific combustion zones almost totally blocks Fenimore's (radical) and Zeldowicz's (thermal) mechanisms of nitrogen oxides synthesis. Moreover, it is possible to catalytically burn methane-air mixtures, which contain as low as several percent of methane. The best known catalyst for the process is palladium [3], but its high prices and low global supplies are the reasons why new, active catalysts of the process are being developed. The aim of this work was to test the behaviour of Ru/clinoptilolite catalysts, prepared by the ion exchange method, in the reaction of total methane oxidation.

---

\*This article is dedicated to Professor Dobiesław Nazimek on the occasion of his 65<sup>th</sup> birthday

## 2. METHODS

As a base material for the catalysts a natural (sodium-potassium) form of the clinoptilolite was used (supplied by PHU EREM S. C.). Prior to preparation it was converted into hydrogen form using 0.1M solution of nitric acid. Total surface area of the clinoptilolite was  $34.15 \pm 0.22 \text{ m}^2 \cdot \text{g}^{-1}$  and mean pore diameter  $78.4 \text{ \AA}$ . The set of four ruthenium catalysts based on this zeolite was prepared using ion exchange method (24 hours). Ruthenium red ( $\text{H}_4\text{Cl}_6\text{N}_{14}\text{O}_2\text{Ru}_3$ ) used as a precursor was supplied by Aldrich. The ruthenium concentrations in catalysts was measured by means of the XRF method, pure hydrogen form of the clinoptilolite was used as a reference catalyst (CL-ref). Catalysts, concentrations of ion exchange solutions and achieved ruthenium loadings in catalysts are summarized in Table 1.

Tab. 1. Catalysts, concentrations of ion exchange solutions, and achieved ruthenium loadings in catalysts.

catalyst	$C_{Ru}$ (M) (solution)	$C_{Ru}$ , wt. % (catalyst)
CL-ref	–	–
CL-Ru1	0.00025	$0.0223 \pm 0.0010$
CL-Ru2	0.00050	$0.0479 \pm 0.0019$
CL-Ru3	0.00100	$0.0850 \pm 0.0031$
CL-Ru4	0.00200	$0.1401 \pm 0.0050$

FT-IR/PAS spectra of investigated materials were recorded using transmission method by means of Bio-Rad 3000MX spectrometer equipped with DTGS detector, over the  $4000\text{--}400 \text{ cm}^{-1}$  range. The spectra were measured at RT at  $4 \text{ cm}^{-1}$  resolution and maximum source aperture. A sample of a catalyst (5 mg) was mixed and ground in an agate mortar with 400 mg of spectroscopically pure dry potassium bromide to a fine powder and then it was pressed to form a disk less than 1 mm thick. Data were collected in the transmission mode at room temperature under air. Interferograms of 256 scans were average for each spectrum.

Activity tests were carried out within temperature range  $200\text{--}600^\circ\text{C}$ . Inlet mixture consisted of methane, oxygen and helium ( $\text{CH}_4:\text{O}_2:\text{He}$  ratio equal 4:20:76), its volumetric flow rate equal  $6000 \text{ h}^{-1}$ . Experimental set included mass flow regulators (methane, oxygen, helium) connected to quartz plug-flow reactor, heated by electric oven. Sample of a catalysts was put into reactor (c. a.

0.5g) with quartz grains (weight ratio 1:4) to avoid local overheating. Temperature measurements were made using chromel-alumel thermocouple. Analysis of outlet gases was carried out by means of gas chromatograph GCHF 18.3 equipped with TCD detector and CTR-1 column. Methane conversions ( $X$ ) were calculated based on  $\text{CH}_4$  peaks surface areas using the following equation:  $X = (1 - S_{out} / S_{in}) \cdot 100\%$  (where:  $X$  – conversion of  $\text{CH}_4$ ,  $S_{in}$  – area of the inlet methane peak surface,  $S_{out}$  – area of the outlet methane peak surface).

### 3. RESULTS AND DISCUSSION

According to XRF tests ruthenium loadings in catalysts were within 0.0223–0.1401 wt. % range and the amount of Ru was directly proportional to concentration of ion exchange solution (Table 1).

Infrared spectroscopy is a good tool for determining the structure of zeolitic materials and testing the process of ion exchange itself. At least three IR ranges are useful for qualitative and (to a much lesser extent) quantitative analyses [4,5], but most of the literature data focuses on mono- or divalent cations: range 3700–1600  $\text{cm}^{-1}$ , in which bands corresponding to various forms of zeolitic water are observed (including –OH groups), range 1200–450  $\text{cm}^{-1}$ , connected with inner vibrations of Si–O(Si) and Si–O(Al) groups and, especially, subrange 800–600  $\text{cm}^{-1}$ , in which bands corresponding to vibrations of clinoptilolite structural units are present. Because of small differences in IR spectra of investigated samples over 1000  $\text{cm}^{-1}$  and difficulties in analysis, attention was focused on 800–600  $\text{cm}^{-1}$  range (Figure 1).

W. Mozgawa and coworkers in papers [6,7] described the interpretation of three bands within 800–600  $\text{cm}^{-1}$  range: c.a. 695  $\text{cm}^{-1}$ , and c.a. 669  $\text{cm}^{-1}$ . The both bands correspond to ring vibrations. Introduction of cations into structure of clinoptilolite results in changes in intensity of the bands. Authors of papers [6,7] even suggest, that band 679  $\text{cm}^{-1}$  may be used as an indicator of a sorption.

In case of studied catalysts the process of ion exchange clearly increased intensities of those bands (Figure 1), but direct correlations between their intensity and the amount of ruthenium introduced into catalysts were hardly visible, which is in agreement with literature data [6,7]: too many parameters influence their intensity: atomic mass, electronegativity and the radius of the ion [7].

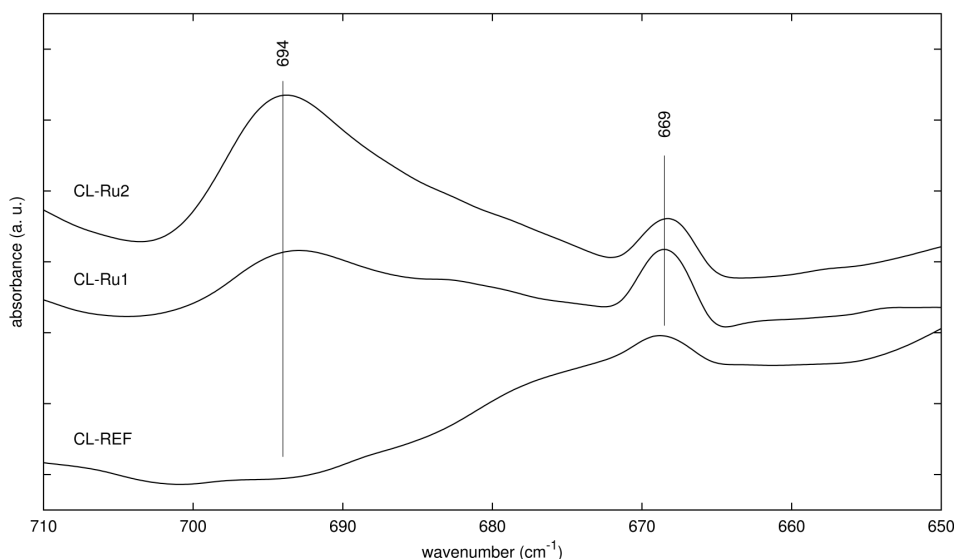


Fig. 1. IR spectra of selected materials: CL-ref (pure clinoptilolite), CL-Ru1 and CL-Ru2.

In the first stage of kinetic experiments reference catalysts CL-ref (pure clinoptilolite) was tested (FER-Ref). Changes in methane conversion as a function of temperature are shown in Figure 2 (left). In temperature range 200–600°C conversion  $X$  did not exceed 0.77–2.44%, while average was 1.52% and standard deviation 0.58%. The average was treated as a bias: it was assumed that reaction started in ignition temperature  $t_i$ , in which conversion  $X$  was higher than the bias by three standard deviations.

Conversions of methane as a function of temperature for tested catalysts are presented in Figure 2 (right). Parameters of curves  $X = a \cdot e^{(b \cdot t + c)}$  were estimated using gnuplot v. 4.4 software, then on this base conversions in selected temperatures (350°C, 400°C i 450°C) and ignition temperatures  $t_i$  were calculated.

Ignition temperatures for tested catalysts were in range 258°C do 445°C. The results are comparable with literature data. For example ignition temperature estimated from data included in work [8] for Ru/Al<sub>2</sub>O<sub>3</sub> catalyst was c. a. 230°C, but it should be noted that authors of [8] used a different type of reactor and in this case metal loading was much higher. Authors of paper [9] report ignition temperatures within range 430–450°C. Correlation between ignition temperature  $t_i$  and ruthenium loadings in catalysts is presented in Figure 3 (left). The function  $t_i = f(C_{Ru})$  is linear, what suggests that activity depends on amount of ruthenium in catalysts.

Catalytic activity may be also expressed as degree of conversion  $X$  at given temperature  $t$ . Correlations estimated from curves  $X = a \cdot e^{(b \cdot t + c)}$  degrees of conversions at selected temperatures (350°C, 400°C and 450°C) and ruthenium loadings are presented in Figure 3 (right). Their linear characteristic clearly suggest that ruthenium ions introduced into clinoptilolite play a special role in the reaction of methane oxidation.

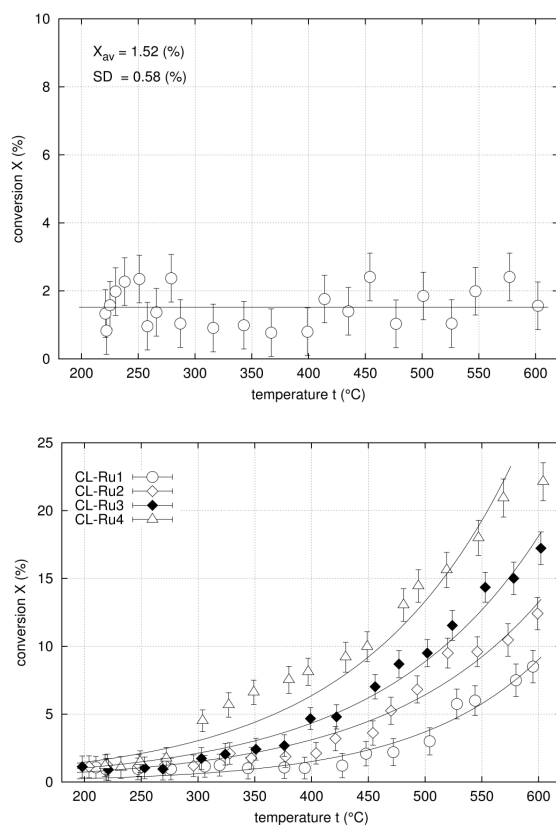


Fig. 2. Conversion of methane as a function of temperature: pure clinoptilolite CL-ref (left) and catalysts CL-Ru1, CL-Ru2, CL-Ru3, CL-Ru4 (right).

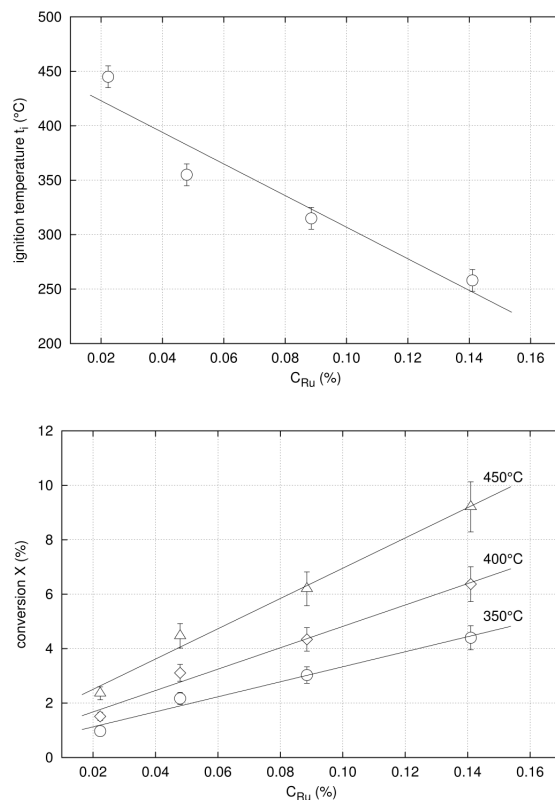


Fig. 3. Dependence between ignition temperature  $t_i$  and ruthenium loading  $C_{Ru}$  (left) and dependence between methane conversion  $X$  and ruthenium loading  $C_{Ru}$  (right).

#### 4. CONCLUSIONS

Ruthenium loadings in catalysts are directly proportional to concentrations of ion exchange solutions – simultaneously IR spectroscopy tests clearly shows that ruthenium ions were introduced into structure of clinoptilolite.

Ignition temperature of the process  $t_i$  is reverse proportional to ruthenium loading in catalyst, and degrees of methane conversion ( $X$ ) at given temperatures increase with  $C_{Ru}$ . This results clearly indicates that ruthenium ions play a special role in the process of methane oxidation. Comparison with literature data [8-10] shows that catalysts based on oxide supports like  $Al_2O_3$ ,  $SiO_2$  or  $Y_2O_3$  are less active than Ru/clinoptilolite.

**Acknowledgements.** The author wish to express his gratitude to dr Sylwia Pasieczna-Patkowska for FT-IR experiments.

## 5. REFERENCES

- [1] R. A. Hefner, *Int. J. Hydrogen Energy*, 27 823 (1999).
- [2] B. Stasińska, A. Machocki, *Pol. J. Chem. Tech.*, 9 29 (1997).
- [3] D. Roth, P. Gelin, A. Kaddouri, E. Garbowski, M. Primet, E. Tena, *Catal. Tod.*, 112 134 (2006).
- [4] J. C. Vedrine, Y. S. Yin, A. Aurox, *Appl. Catal.*, 37 1 (1988).
- [5] J. Datka, M. Kawalek, K. Góra-Marek, *Appl. Catal. A: General*, 243 293 (2003).
- [6] W. Mozgawa, T. Bajda, *Journal of Molecular Structure*, 170 792 (2006).
- [7] W. Mozgawa, Z. Fojud, M. Handke, S. Jurga, *Journal of Molecular Structure*, 614 281 (2002).
- [8] L. Paturzo, F. Gallucci, A. Basile, P. Pertucci, N. Scalera, G. Vitulli, *Ind. Eng. Chem. Res.*, 42 2968 (2003).
- [9] S. Rabe, M. Nachtegaal, F. Vogel, *Phys. Chem.*, 9 1461 (2007).
- [10] Nishimoto H. et al., *Catalysis Letters*, 82 (2002) 161.

## CURRICULUM VITAE



**Marcin Kuśmierz.** Born in Lublin (1971). Graduated from Maria Curie-Skłodowska University in Lublin (1997). Received his Ph. D. degree in 2005 from the Maria Curie-Skłodowska University. His main field of interest is preparation of metallic and bimetallic catalysts, hydrogenation of carbon dioxide, total and selective oxygenation of methane and catalytic conversion of alcohols into hydrocarbons.