Oxidation of methane over Ru/clinoptilolite catalysts[*]

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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 thath the activity of the catalysts 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 connectin with natural environment pollution increases interestings 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 Fenimoore's (radical) and Zeldowicz's (thermal) mechanisms of nitrogen oxides synthesis. Moreover, it is possbile to catalytically burn methane-air mixtures, which contain as low as several percent of methane. The best konown 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 reactin of total methane oxidation.

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[*]This article is dedicated to Professor Dobiesław Nazimek on the occasion of his 65th 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 $34.15\pm0.22 m \cdot g^{-1}$ and mean pore diameter 78.4Å. The set of four ruthenium catalysts based on this zeolite was prepared using ion exchange method (24 hours). Ruthenium red ($H_{42}Cl_6N_{14}O_2Ru_3$) 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 ± 0.0010
CL-Ru2	0.00050	0.0479 ± 0.0019
CL-Ru3	0.00100	0.0850 ± 0.0031
CL-Ru4	0.00200	0.1401 ± 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 $4000–400 cm^{-1}$ range. The spectra were measured at RT at $4 cm^{-1}$ 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 200–600ºC. Inlet mixture consisted of methane, oxygen and helium (CH_4:O_2:He ratio equal 4:20:76), its volumetric flow rate equal $6000 h^{-1}$. Experimental set included mass flow regulators (methane, oxygen, helium) connected to quartz plug-flow reactor, heated by elctric 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 detecotor and CTR–1 column. Methane conversions (X) were calculated based on CH_4 peaks surface areasusing the following equation: $X = (1 – S_{out} / S_{in}) \cdot 100\%$ (where: X – conversion of 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 $3700–1600$ cm^{-1}, in which bands corresponding to various forms of zeolitic water are observed (including –OH groups), range $1200–450$ cm^{-1}, connected with inner vibrations of Si–O(Si) and Si–O(Al) groups and, especially, subrange $800–600$ 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 cm^{-1} and difficulties in analysis, attention was focused on $800–600$ cm^{-1} range (Figure 1).

W. Mozgawa and coworkers in papers [6,7] described the interpretation of three bands within $800–600$ cm^{-1} range: c.a. 695 cm^{-1}, and c.a. 669 cm^{-1}. The both bands correspond to ring vibrations. Introduction of cations into structure of clinoptilolilte results in changes in intensity of the bands. Authors of papers [6,7] even suggest, that band 679 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, electrongativity and the radius of the ion [7].
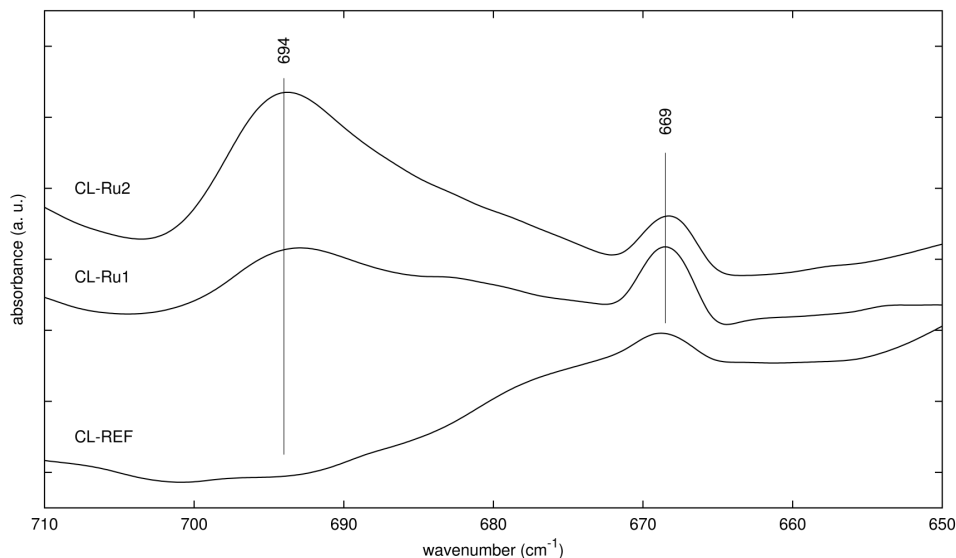
Fig. 1. IR spectra of selected materials: CL-ref (pure clinoptilolite), CL-Ru1 and Cl-Ru2.

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 200–600ºC 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_2O_3 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 between 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.
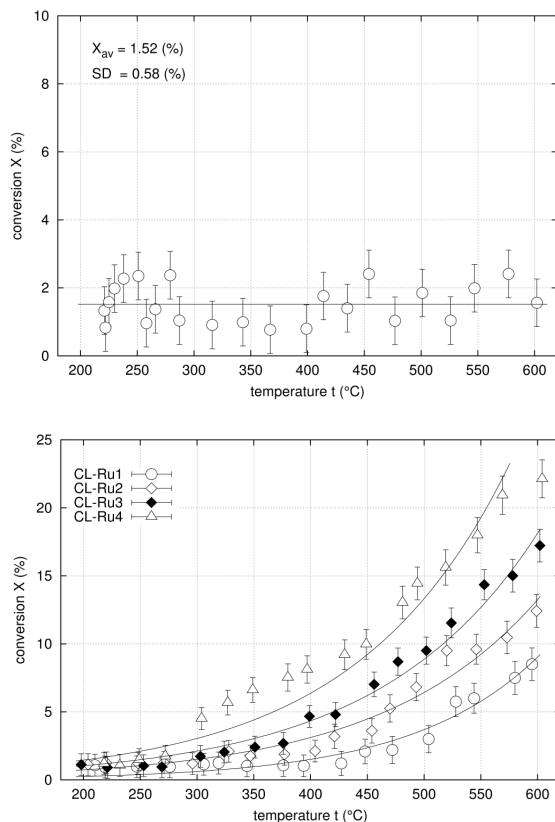

Fig. 2. Conversion of methane as a function of temperature: pure clinoptilolite CL-ref (left) and catalysts CL-Ru1, CL-Ru2, CL-Ru3, CL-Ru4 (right).
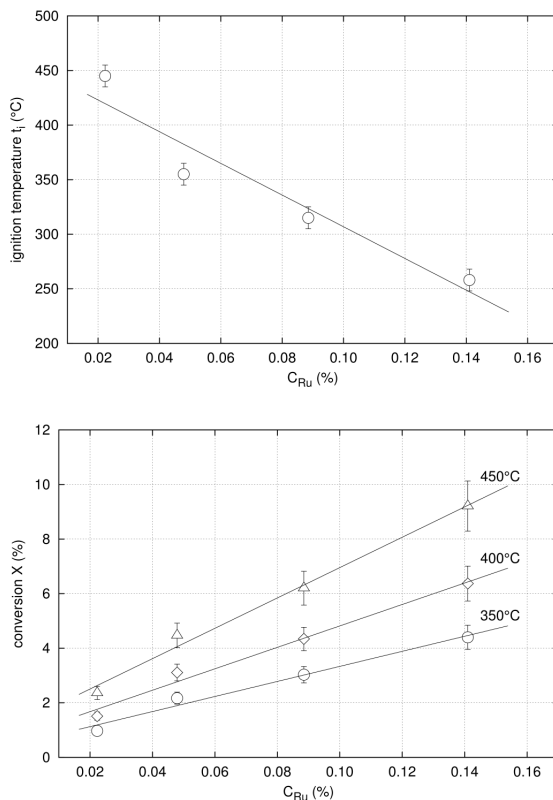
Fig. 3. Dependence between ignition temperature t_i and ruthenium loading C_{Ru} (left) and dependence between methane conversion X and ruthenium loading C_{Ru} (right).

4. CONCLUSIONS

Ruthenium loadings in catalysts are directly proportional to concentrations of ion exchange solutions – simoultaneously 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.

5. REFERENCES

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CURRICULUM VITAE

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