

Effect of the ruthenium loading and barium addition on the activity of ruthenium/carbon catalysts in carbon monoxide methanation

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This article is dedicated to Professor Walerian Arabczyk on the occasion of his 70th birthday.

A group of supported ruthenium catalysts was prepared and tested in methanation of small CO amounts (7000 ppm) in hydrogen-rich streams. High surface area graphitized carbon (484 m²/g) was used as a support for ruthenium and RuCl₃ was used as a Ru precursor. Some of the Ru/C systems were additionally doped with barium (Ba(NO₃)₂ was barium precursor). The catalysts were characterized by the chemisorption technique using CO as an adsorbate. To determine the resistance of the catalysts to undesired carbon support methanation, the TG-MS experiments were performed. They revealed that the barium addition inhibits support losses. The studies of CO methanation (flow reactor, atmospheric pressure) have shown that some of the supported ruthenium catalysts exhibit high activities referred to the metal mass. The catalytic properties of ruthenium proved to be dependent on metal dispersion. Some of the Ru/C and Ba-Ru/C systems exhibit higher activity in CO hydrogenation than the commercial nickel-based catalyst.

Keywords: CO methanation, ruthenium catalyst, barium, carbon support.

INTRODUCTION

Methanation is widely used in industrial plants in the preparation of synthesis gas for ammonia synthesis¹. The so-called “ultramethanation” is applied in caprolactam plants, where carbon oxide concentrations must be reduced to a few ppm or less². Recently, methanation has also been proposed as an option for cleanup of reformat hydrogen fuels for low-temperature fuel cells^{2,3}. Nickel contacts supported on alumina are used in most industrial methanation plants. Consequently, the reactions of CO_x methanation on nickel are well recognized and described⁴⁻⁶. Ruthenium is believed to be more active in CO_x methanation than nickel^{2,7}. The Ru catalysts for low-temperature hydrogenation of carbon oxides to methane are offered for commercial application by Süd Chemie (METH 150) or Alvigo (RKM-3)⁸. Since the chemical formula of commercially available catalyst is a trade secret, Ru catalysts deposited on different supports are extensively studied. There are many reports concerning oxide supports, such as alumina^{3,9-12}, titania^{10,13} or silica^{11,14}. Also carbon based supports have been described in the literature^{8,15}. But information regarding carbon supported Ru catalyst is significantly modest.

The aim of this work was to establish the effect of the composition of Ru/carbon catalysts on their activity in carbon monoxide methanation. The basis of these studies was the use of a modified activated carbon as a support for ruthenium and Ba dopant in the process of obtaining active catalysts for CO methanation.

EXPERIMENTAL

The carbon material, denoted throughout the text as C, was used as a support for the catalyst preparation. It was obtained from the commercial activated carbon RO 08 (supplied by the Norit B.V. Company) via high-temperature heating (1700°C, 2 h, helium atmosphere¹⁶) and a subsequent gasification in a CO₂ stream at 855°C. After the gasification, the mass loss was 19.4%. The BET

surface area of the final carbon material equals 484 m²/g, as determined by the nitrogen physisorption studies. The carbon support was impregnated with acetone solution of ruthenium chloride (RuCl₃ · 0.5 H₂O, Aldrich), followed by solvent evaporation in a rotary evaporator. The barium nitrate – precursor of the promoter, was introduced to the Ru/C systems through impregnation from an aqueous solution at 90°C for 16 h. The detailed description of the Ru/C and Ba-Ru/C catalysts preparation can be found elsewhere¹⁷. The ruthenium content in the reduced samples differed from 1 to 25 wt.%. The catalyst symbols include information about: the Ba loading expressed in mmol Ba/g(Ru+C), the Ru loading (wt. %) and carbon support-C, for example: Ba(0.44)-Ru(25)/C.

The dispersion of the active phase in the undoped Ru/C systems was determined by means of the conventional chemisorption technique (static experiments, ASAP 2020 Micromeritics) using carbon monoxide as an adsorbate at 30°C. Prior to measurements, the sample was reduced in flowing hydrogen (80 ml/min) of high purity (>99.9999%) at 420°C for 10 h. The chemisorption data were used for calculating the ruthenium dispersion (FE) and the average sizes of the metal particles (d_{Ru}). The CO:Ru_s = 0.6:1 stoichiometry and formula proposed by Borodziński and Bonarowska were applied for calculating FE and d_{Ru}, respectively¹⁵.

The TG-MS measurements were performed using a Netzsch STA 449C thermobalance equipped with a quadrupole mass spectrometer (Netzsch QMS 403C). The experiments were conducted using samples of approximately 17 mg of catalyst powder heated up to 500°C at the constant rate of 10°C/min in a pure (>99.999 vol%) H₂:Ar = 10:40 mixture (50 ml/min). This temperature was maintained for 2 h. The mass change, temperature and selected m/e signals were monitored throughout the entire experiment. In order to avoid water condensation all the necessary apparatus parts were kept heated to 250°C.

The reaction rate measurements of carbon oxide methanation were carried out in a flow gradientless reactor¹⁵ operating under atmospheric pressure and supplied with a CO-H₂ mixture (7000 ppm CO in H₂). The concentration of methane in the outlet gas was monitored by means of a PU-4500 gas chromatograph equipped with a CO_x methanizer and a FID detector. The kinetic tests were performed under steady-state conditions at 220, 240 and 270°C. Re-reduction of the samples preceding the methanation tests was performed in flowing hydrogen (50 ml/min) at 430°C for 4 h.

RESULTS

The data collected in chemisorption experiments were used for calculating the average size of Ru crystallites in the unpromoted Ru/C samples. The obtained d_{Ru} values are summarised in Table 1.

Table 1. The average sizes of ruthenium crystallites in the unpromoted Ru/C catalysts

| Catalyst symbol | d_{Ru} , [nm] |
|-----------------|-----------------|
| Ru(1)/C | 1.38 |
| Ru(5)/C | 1.64 |
| Ru(7.5)/C | 1.78 |
| Ru(9)/C | 2.09 |
| Ru(15)/C | 3.03 |
| Ru(20)/C | 4.09 |
| Ru(25)/C | 5.44 |

There is a clear relation between the ruthenium loading in the catalyst and its dispersion. The higher the ruthenium loading, the higher d_{Ru} values (the dispersion decrease). While the Ru content varied by a factor of 25, only four-time increase of the average crystallite size was observed. It is worth noting that the Ru(25)/C sample is characterized by quite small average crystallite size, in spite of a high metal loading. The similar tendency was observed by Kowalczyk et al.¹⁵.

Since ruthenium is a good catalyst for CO methanation, it can also catalyze the undesired reaction of carbon support hydrogenation to form methane. That process may cause mechanical damage of the support material and, in consequence, the whole catalyst destruction. In order to examine the effect of ruthenium loading and barium addition on the unfavorable carbon support methanation, the TG-MS experiments were performed. Three series of catalysts were examined. In each group Ru content was constant: 7.5, 15 or 25 wt.% (Ru/Ru+C), while barium was added at two levels. The selected data, obtained for the Ru(25)/C-based series, is presented in Figure 1. The results obtained for Ru(7.5)/C and Ru(15)/C series are qualitatively similar. The first derivative of the mass change (DTG curve) observed when a sample is heated in a flowing mixture of H₂/Ar is depicted in Figure 1a. There is one peak visible on the DTG line for the Ru(25)/C catalyst. Its minimum was reached in 69th minute of the experiment (110°C). The mass loss may correspond to the emission of water adsorbed on the surface of the sample, but more probably to the reduction of RuO₂ remained on the surface of ruthenium crystallites after passivation. The addition of barium salt causes a small shift of the reduction signal towards higher temperatures (72 min, 140°C). This effect is more pronounced for larger barium amount, i.e. Ba(0.66)-Ru(25)/C. The

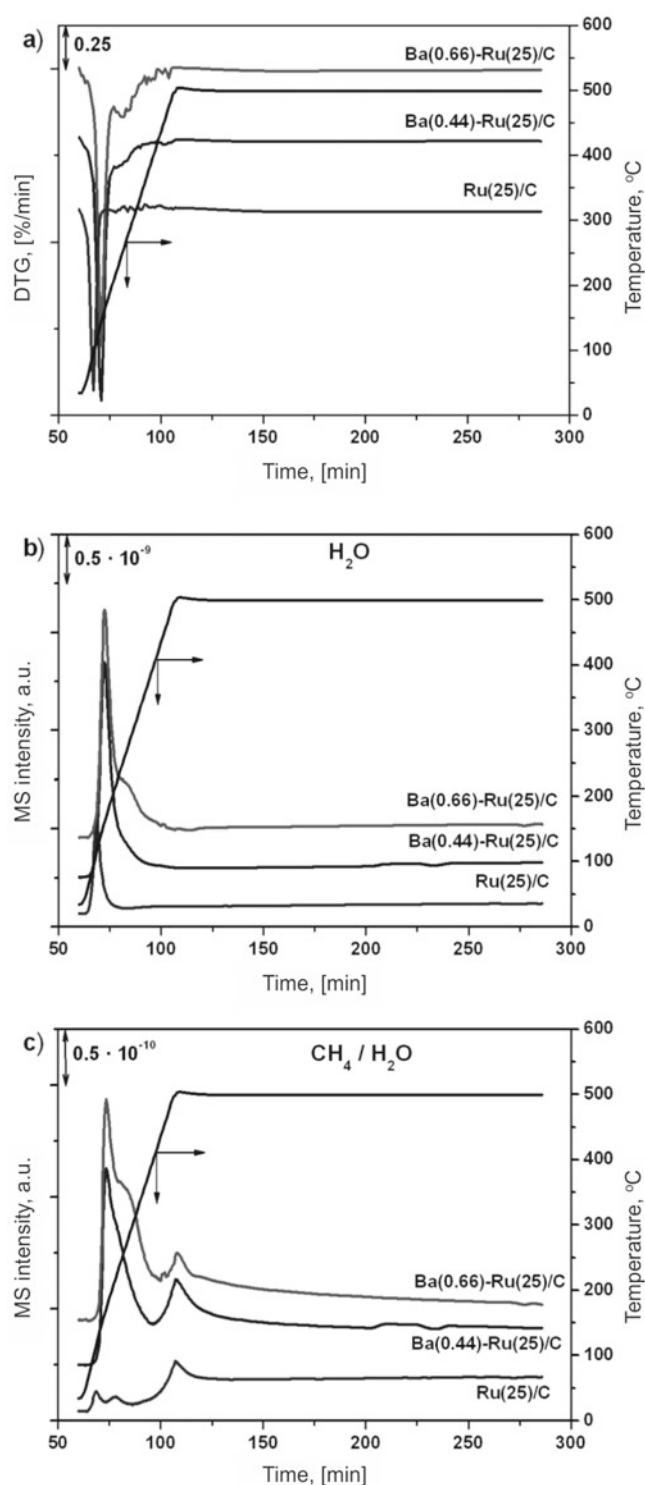


Figure 1. TG-MS measurements: a) DTG curves of the Ru(25)/C and Ba-Ru(25)/C catalysts; MS signals: b) $m/e=18$ (H₂O) vs time, c) $m/e=16$ (CH₄/H₂O) vs time

mass losses for Ba-Ru/C systems are larger than for Ru/C material. It suggests that both ruthenium- and barium compounds start to reduce since 70th minute. Additionally, for barium doped samples the second peak appears close to 80th min (230°C). The mass losses at higher temperatures may come from barium nitrate (the Ba precursor) reduction. Figure 1b shows the amount of evolved water vapour as a function of time. It is clearly visible that water is evolved at the same time as signals on DTG line appear (Fig. 1b). For the Ru(25)/C one peak was observed while two overlapping signals are visible in the case of barium doped materials. The heating of carbon supported catalyst in flowing hydrogen poses a

risk of a support methanation. The detection of $m/e = 16$ signals in the mass spectrum (Fig. 1c) are expected to give information about this undesired phenomenon. The signals corresponding to $m/e = 16$ can appear because of CH_4 presence, but also as the second line originated from H_2O . As one can note, the intensity of the spectra presented at Figure 1c is an order of magnitude lower than that for H_2O (Fig. 1b). For the Ru(25)/C sample three peaks were detected. The first one (69 min) derives from water evolution, while the signal at 78 min can be probably assigned to CH_4 emission. In the case of the Ba-Ru/C systems, the signals visible in the range 70–90 min are clearly linked with water emission. However, the one at 85 min has a significant contribution of methane. The third signal appearing on all three samples spectra at about 500°C (108 min) should be assigned to methane production. It is noteworthy that during the isothermal step ($T = 500^\circ\text{C}$) no methane signals were detected. Moreover, the $m/e = 16$ lines observed for the Ba(0.44)-Ru(25)/C and Ba(0.66)-Ru(25)/C samples tend to decrease with time of experiment.

The percentage mass losses calculated for the examined samples at isothermal stage are summarised in Table 2. The presented values were calculated on the basis of the TG line level for all barium containing samples and for comparison for respective Ru/C materials.

The higher the ruthenium loading in the unpromoted Ru/C system, the higher the mass loss at isothermal step (500°C) – Table 2. Ruthenium itself, without additives, catalyzes readily the methanation reaction of carbon support¹⁸. The effect increases with increasing ruthenium content in the material. The introduction of barium inhibits this process. For each group of catalysts with the same Ru loading, the mass losses assigned to carbon support methanation decrease with increasing barium content. These results are in good agreement with those published by Kowalczyk et al.¹⁸. In conclusion, the TG-MS studies revealed that barium has an inhibiting effect on unwanted carbon support methanation in Ru/C systems.

The most relevant results of carbon monoxide methanation studies are presented in Figures 2 and 3. Figure 2 presents the changes in activity of the catalysts with increasing ruthenium loading. The reaction rate constants were calculated on the basis of data collected under steady-state conditions of pressure (0.1 MPa) and CO content in the gas phase (7000 ppm) in the temperature range of $220\text{--}270^\circ\text{C}$.

The relation $\ln k = f(1/T)$ demonstrates (Fig. 2), that the activity of the unpromoted Ru/C catalysts increases with increasing temperature and Ru content in the sample. This is in accordance with the literature data^{8, 9, 15}.

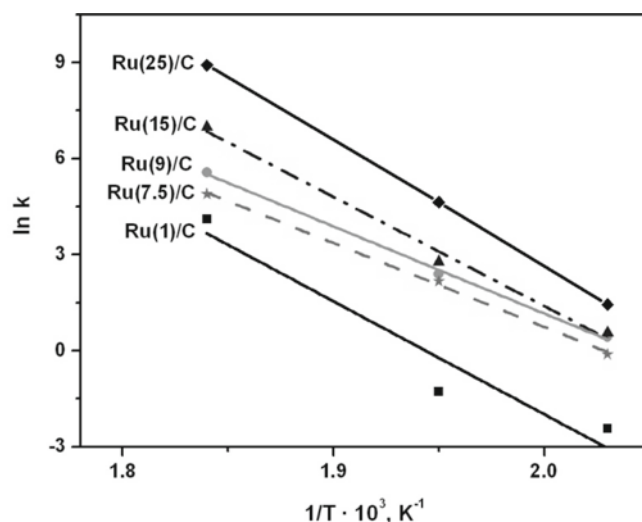


Figure 2. The activity of the Ru/C catalysts in carbon monoxide methanation

These results correlate well with the d_{Ru} values obtained from the chemisorption experiments (Table 1). The increasing activity of Ru/carbon systems with increasing average size of the active phase crystallites suggests that carbon oxide methanation reaction is “structure sensitive”. The phenomenon has already been mentioned in the literature¹⁵. Further studies are necessary to determine the optimum size of ruthenium crystallites in Ru/carbon systems, which exhibit the highest activity in CO methanation.

The representative results of methanation studies over barium doped Ru/C systems are shown in Figure 3. The data obtained for the commercial Ni-based catalyst (RANG-19) have also been included in Figure 3. The reported rate constants (k) are referred to metal mass (ruthenium for Ru/carbon systems or nickel for the industrial catalyst RANG-19) and correspond to fixed CO concentration (7000 ppm) in the gas mixture at 270°C and $p = 0.1$ MPa.

As can be seen in Figure 3, the introduction of Ba decreases catalytic activity of ruthenium supported on carbon, in general. For Ru(25)/C series both barium containing catalysts are less active than the Ru/C system. The same effect was observed for Ru(7.5)/C series (data not presented). In the case of the Ru(15)/C catalyst, a small amount of barium decreases the activity in CO methanation. Whereas Ba(0.59)-Ru(15)/C system is more active than barium free system.

The influence of barium addition is ambiguous. The role of Ba seems to depend on its loading in the sample and also on ruthenium content. When barium is present

Table 2. Chemical composition of the promoted Ba-Ru/C catalysts; the effect of the presence of barium on the undesired carbon support methanation

| Catalyst symbol | Ru loading, [wt. %] | Ba loading, [mmol _{Ba} /g _{C+Ru}] | Mass loss at isothermal stage, [wt. %] |
|--------------------|---------------------|--|--|
| Ru(7.5)/C | 7.5 | 0 | 1.34 |
| Ba(0.37)-Ru(7.5)/C | 7.5 | 0.37 | 0.91 |
| Ba(0.55)-Ru(7.5)/C | 7.5 | 0.55 | 0.44 |
| Ru(15)/C | 15 | 0 | 3.16 |
| Ba(0.42)-Ru(15)/C | 15 | 0.42 | 2.18 |
| Ba(0.59)-Ru(15)/C | 15 | 0.59 | 1.59 |
| Ru(25)/C | 25 | 0 | 4.67 |
| Ba(0.44)-Ru(25)/C | 25 | 0.44 | 3.63 |
| Ba(0.66)-Ru(25)/C | 25 | 0.66 | 2.17 |

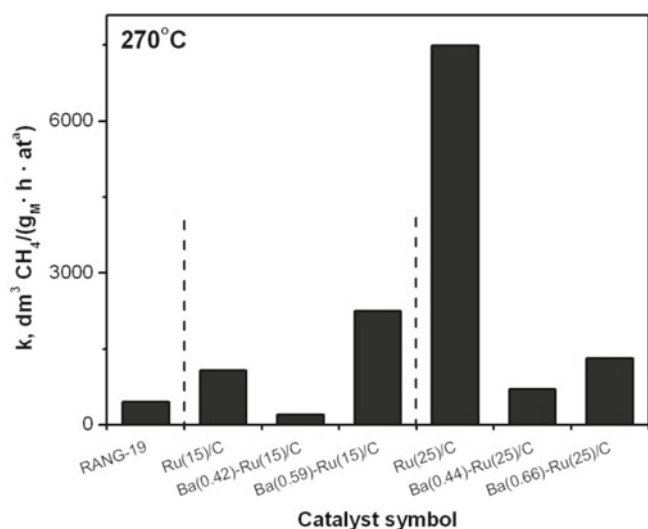


Figure 3. The activity of carbon supported ruthenium catalysts in CO methanation (7000 ppm CO in the gas mixture, 270°C, 0.1 MPa)

in small amounts, the only positive influence observed was the inhibition of support methanation (see Table 2). But when barium content increases the promoting effect on ruthenium can also appear (see Fig. 3: Ba(0.59)-Ru(15)/C). Such a trend has already been reported in the literature for the caesium promoted Ru/Al₂O₃ catalysts for CO methanation¹². The analysis is complicated because of the methodology of the catalytic measurements. In this system methane can be produced in two ways: during desired CO methanation reaction and unwanted carbon support losses. Further studies are necessary to explain the role of barium in the Ru/C materials. It is noteworthy that some of the obtained Ru/carbon catalysts are more active than the nickel-based industrial system (RANG-19). However, a thermal stability of the above mentioned systems is essential for their practical application. Further experimental work, including stability tests, is necessary for the implementation of the promoted Ru/C catalyst to the industrial practice in the future.

CONCLUSIONS

The activity of Ru/C samples increases with increasing Ru crystallites size. It suggests that CO methanation on carbon-supported ruthenium catalyst is structure sensitive. On the basis of TG-MS experiments it was revealed that barium inhibits unwanted carbon methanation during interaction with hydrogen. The role of barium in the studied systems is ambiguous. On the one hand, the presence of Ba decreases the catalytic activity of Ru(7.5)/C and Ru(25)/C materials. On the other hand, for Ru(15)/C contact the promoting effect of barium was observed. Some of the obtained Ru/carbon and Ba-Ru/carbon catalysts are more active than the nickel-based industrial system (RANG-19). Further studies are necessary to resolve an issue of the barium influence on the catalytic properties of Ru/C materials and to improve the application potential of ruthenium/carbon systems.

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