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Sonochemically prepared high dispersed Ru/TiO_2 mesoporous catalyst for partial oxidation of methane to syngas

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Highly dispersed Ru nanoparticles on mesoporous TiO_2 have been synthesized by a one-step ultrasound assisted polyol reduction procedure. The catalysts have been characterized by XRD, TEM and HR-TEM, EDX, BET and TPR methods. It has been demonstrated that the sonochemical method reduces the Ru^{+3} ions creating a narrow size distribution of metallic nanoparticles deposited on the mesoporous support without damaging its pore structure. The nanoparticles of Ru are highly dispersed and stable because of their incorporation into the mesopores, and the strong metal-support interaction. The catalytic properties of Ru/TiO_2(MSP) have been tested in the partial oxidation of methane, and high activity and selectivity towards CO and H_2 have been demonstrated.

KEY WORDS: partial methane oxidation; syngas; mesoporous support; nanoparticles; ultrasound irradiation.

1. Introduction

For the production of synthesis gas in industry, steam reforming of CH_4 is currently practiced. Recently catalytic partial oxidation of methane (POM) has attracted a great attention, since it is mildly exothermic and produces suitable H_2/CO ratios in the final synthesis gas [1]. Supported noble metals are the main catalysts used for the POM reaction, and ruthenium has been proven as one of the best catalysts in this process because of its high activity and resistance to coking [2–4]. It has been reported already in 1996 that the Ru/TiO_2 catalyst promotes the direct formation of synthesis gas without the intermediate production of CO_2 and H_2O, with high selectivity to CO and H_2 [5]. This study [5] included the elucidation of the mechanism of this reaction pathway. The unique ability of Ru/TiO_2 is attributed to the high resistance of Ru crystallites in their metallic state to oxidation under reaction conditions of (POM). It has been shown that the interaction between Ru and TiO_2, inhibited the oxidation of ruthenium in the composite, promoting the direct route of synthesis gas formation [6,7]. By XRD and TPR method it has been also demonstrated that the activity and selectivity of the Ru/Al_2O_3 catalysts (Ru nanoparticles $\sim$ 5.8 nm initial size) of high dispersion is significantly higher than with the conventionally prepared catalysts of low dispersion. The increase in the activity of the catalyst in the POM reaction is related to the shift of the equilibrium between RuO_2 and Ru towards the formation of metallic ruthenium at temperatures above 450 °C. In this reaction, metallic Ru is responsible for the selective formation of CO during methane oxidation [8,9]. Therefore, it is imperative to develop methods to prepare Ru-based catalysts with high dispersion and strong Ru-support interaction that can hinder the aggregation of Ru particles. For instance, one of the most effective techniques for the creation of metallic nanoparticles in general, and Ru in particular, is the polyol reduction method, which is employed for synthesis and stabilization of Ru nanoparticles in colloid solution [10]. The synthesis of Ru on a carbon support conducted under microwave-assisted heating accelerates the polyol reduction of the precursor, $RuCl_3$, and formation Ru particles with an average size of 2.9 nm [11].

Logically, better control of the Ru particle size and its higher dispersion should be achieved by choosing mesoporous material as a catalyst support. Recently, Ru nanoparticles have been successfully incorporated into the pores of highly ordered silica SBA-15 employing a one-step ultrasound assisted polyol method [12]. It this case the ultrasonic irradiation provides both the energy for the reduction of the Ru^{+3} ions, and the driving force for the deposition of the Ru^0 nanoparticles into the mesopores of the SBA-15. The catalyst has shown significant activity and selectivity towards CO in the POM reaction especially with a high loading of Ru. Nevertheless, the effect of particle size and metal-support interaction has been not elucidated in previous studies. We have inserted Ru nanoparticles into mesoporous

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TiO_2 – TiO_2(MSP) by a one-step ultrasound-assisted polyol reduction method. The catalyst was first briefly characterized, and tested in catalytic wet oxidation of organic acids [13]. Here we report the properties of Ru/TiO_2(MSP) with different loadings characterized by a series of physicochemical methods, and investigated for its catalytic activity in the POM reaction. This research elucidates the effect of Ru particle size, and size distribution at different loadings, on metal-support interaction and catalytic activity.

2. Experimental

2.1. Catalyst preparation

The mesoporous TiO_2 (MSP) has been prepared sonochemically by a method described elsewhere [14]. The insertion of Ru nanoparticles into TiO_2(MSP) has been carried out by the polyol reduction method using ultrasonic irradiation. TiO_2(MSP) has been added to 100 mL of 0.01 M $RuCl_3$ solution in ethylene glycol to form 3% and 0.5% (wt) of Ru catalyst on the support. The pH has been adjusted to 6 by the addition of NaOH to the solution. A gas mixture containing 95%Ar and 5% H_2 has been purged through the solution for 1 h. Then the sonication has been performed for 1h under the same gas flow (Ti horn, 20 kHz, 100 W/cm^2 at 60% efficiency). The product has been separated by centrifugation, washed three times with ethanol and dried in vacuum overnight. For the control experiments and comparison the 3%Ru supported on TiO_2(Degussa P25) has been prepared by the wetness impregnation method. The appropriate weight of $RuCl_3 \cdot 3H_2O$ has been dissolved in deionized water sufficient to completely wet the support. The impregnated solid has been dried and heated in air at 300 °C. This catalyst is referred to as 3%Ru/TiO_2(ICES).

2.2. Catalyst characterization

Part of the characterization process that we have carried out for the 3%Ru/TiO_2(MSP) is described in reference [13]. We will therefore omit mentioning the instruments used for XRD, TEM, HR-TEM, EDX, and BET measurements. On the other hand the TPR (Temperature Programmed Reduction) measurements are new and have been performed using a continuous-flow fixed-bed quartz micro-reactor (I.D. 4 mm) with 50 mg samples. The catalyst has been first outgased by heating at 500 °C under Ar flow for 30 min. After cooling to room temperature, the feed gas is switched to 5%H_2/Ar. The temperature is increased with a heating rate of 15 °C/min. The amount of H_2 consumed is measured by means of a thermal conductivity detector (TCD).

2.3. Catalytic experiments

The catalytic tests have been carried out in a conventional flow system at atmospheric pressure with gas hourly space velocities (GHSV) of 14400 h^{-1} in a continuous-flow fixed-bed quartz micro-reactor (I.D. 4 mm). Before testing, the catalysts have been reduced with a flow of hydrogen (40 mL/min) for 0.5 h at 500 °C. The feed gases (CH_4/O_2 = 2) are then introduced. The effluent gases CO and H_2 are measured by an on-line gas chromatography (Shimadzu GC-2010). The catalysts are evaluated for activity in terms of CH_4 conversion and of selectivity of CO and H_2 in a temperature range of 500–800 °C.

3. Results and discussion

3.1. Characterization of the catalysts

Since the incorporation of 0.5% Ru is new and has not been performed in reference [13], we will repeat some of the characterization results for the sake of comparison of the as-prepared 0.5% and 3% Ru/TiO_2(MSP) catalysts. After heating the products at 500 °C under Ar for 3 h, in both samples prepared by sonication the diffraction peaks at $2\Theta = 25.28°$, 37.80°, 48.05° and 53.89° are observed, corresponding to the anatase phase of titania (PDF: 21–1272) (figure 1). In the 3%Ru/TiO_2(MSP) sample an additional broad diffraction peak at $2\Theta = 44.37^{\circ}$ has been measured, due to

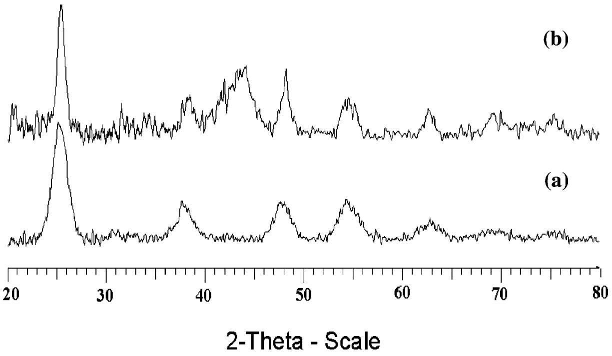

Figure 1. XRD patterns of Ru/TiO_2(MSP) calcined 3 h at 500 °C under Ar: (a) 0.5% Ru/TiO_2(MSP), (b) 3% Ru/TiO_2(MSP).

metallic Ru (PDF: 00-001-1256). The broadening is a result of the small Ru particles size. Thus, the XRD verifies the presence of metallic Ru in the catalyst. The low amount of Ru in O.5%Ru/TiO2 (MSP) does not allow the detection of the ruthenium phase.

The high dispersion of the Ru nanoparticles in the sonochemically-prepared Ru/TiO_2(MSP) catalysts is also observed by TEM and HR-TEM measurements. The TEM images illustrate the spherical particles of mesoporous TiO_2(MSP), which are homogeneously decorated with the Ru nanoparticles (figure 2a, c). HR-TEM measurements reveal the difference between the low and high loaded catalysts (figure 2b, d). In the 0.5%Ru/TiO_2(MSP) the particles are smaller (average size ~1.6 nm), and have a narrow size distribution (see the histograms in figure 3a). According to the histograms, almost 40% of Ru particles in 0.5%Ru/TiO_2(MSP) catalyst are of the same diameter, 1.6 nm. On the other hand the average size of the Ru in the 3%Ru/TiO_2(MSP) sample is about 2.6 nm. These larger

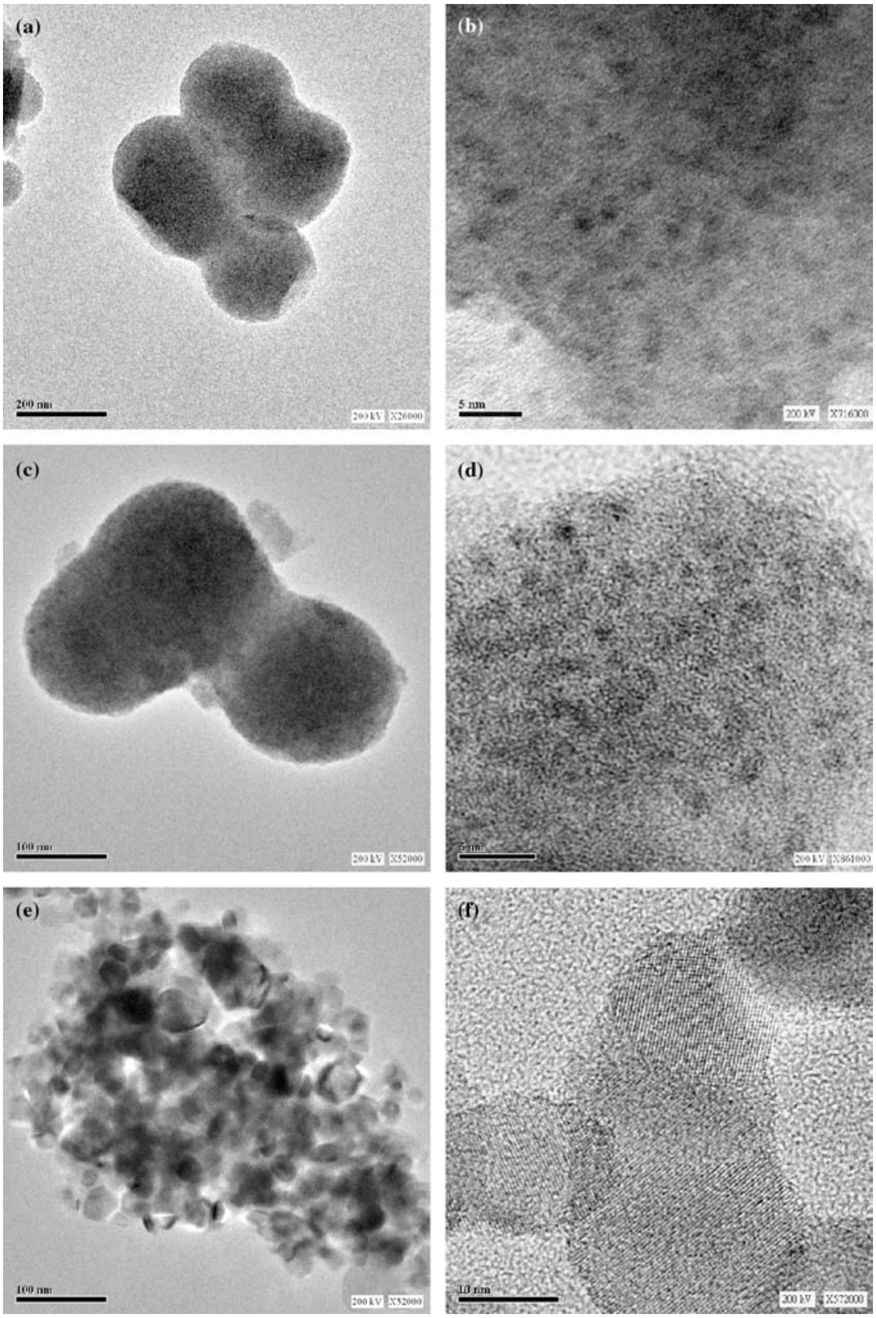

Figure 2. TEM images (a, c, e) and HR TEM images (b, d, f) of Ru/TiO_2 catalysts: (a, b) 0.5%Ru/TiO_2(MSP); (c, d) 3%Ru/TiO_2(MSP), (e, f) – 3%Ru/TiO_2(ICES).

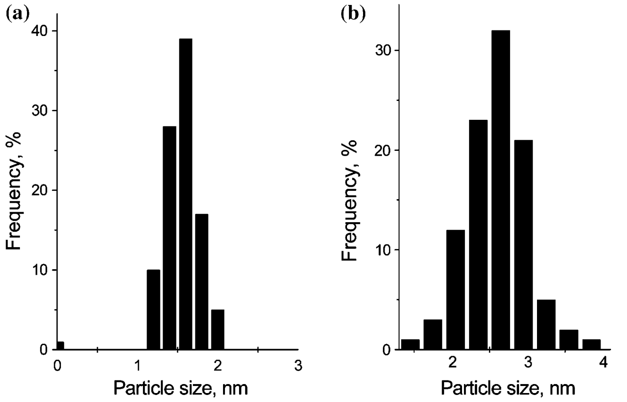

Figure 3. Histograms of Ru/TiO_2(MSP) catalysts: (a) 0.5%Ru/TiO_2(MSP); (b) 3%Ru/TiO_2(MSP).

particles are also homogeneously distributed on the surface of support, but the histogram is not as narrow as that of the lower loaded sample (figure 3b).

The Ru catalyst prepared by traditional incipient wetness impregnation method with TiO_2 commercial support is not of a regular shape, and most of the deposited nanoparticles observed by HR TEM are of 15–20 nm and highly aggregated (figure 2e, f). By the interplanar distance calculation it has been determined that the supported phase is the ruthenium oxide.

One of the advantages of the sonochemical method for the synthesis of supported catalysts is demonstrated in this research. The ultrasound irradiation results in producing highly dispersed nanoparticles having a narrow size distribution. It is well-known that bubbles formed by the ultrasonic waves tend to collapse preferentially near solid surfaces [15]. Moreover, they don't collapse in a symmetric form but rather as an elongated structure directed towards the solid surface. The after effects of the collapse are microjets and shock waves directed towards the solid. The nanoparticles formed during the collapse of the ultrasonic bubbles near solids are thrown at their surfaces and into the mesopores by these microjets. In a previous publication we have discussed the comparison between the sonochemistry and other methods such as thermal spreading and impregnation in insertion of nanoparticles into mesostructures [16, 17].

The surface area of the supported catalysts measured by the BET method is represented in the table 1. The decrease in the specific surface area and in the pore volume after insertion of Ru nanoparticles into the support is not drastic. This reduction is attributed to incorporation of the metallic particles into the mesopores as analyzed before [12]. In the low loaded catalysts the decrease of surface area is less. For instance, for 0.5%Ru/TiO_2(MSP) surface area has changed from 750 m^2/g of TiO_2(MSP) to 600 m^2/g, and for the 3%Ru/TiO_2(MSP) – to 517 m^2/g. At the same time, the pore volume and pore size has not changed significantly, showing that material keeps its mesoporous structure after introduction of the metal nanoparticles.

Table 1
BET measurements

Catalyst	Surface area, m^2/g	Pore volume, mL/g	Pore size, Å
TiO_2(MSP)	750	0.36	25
0.5%Ru/TiO_2(MSP)	600	0.30	24
3%Ru/TiO_2(MSP)	517	0.24	20
3%Ru/TiO2(ICES)	50	0.02	16

According to the TEM measurements, the average particles size of Ru in 0.5%Ru/TiO_2(MSP) catalyst is 1.6 nm that is smaller than the pore diameter of the support (2.5 nm). It opens a better possibility to insert the Ru nanoparticles into the mesopores of TiO_2. In the case of 3%Ru/TiO_2(MSP), the average particles size of Ru is comparable with the diameter of the TiO_2 support mesopores that makes it more difficult for the incorporation of Ru nanoparticles into the support. It means that in the high loaded catalyst only the small nanoparticles of Ru (< 2.5 nm) are inserted into the mesopores, and the larger ones are deposited on the outer surface of the TiO_2(MSP) support.

Temperature programmed reduction (TPR) results of the three supported ruthenium samples are reported in figure 4. The TPR profile of 3%Ru/TiO_2 (ICES) contain three main peaks in the range 100–200 °C. These peaks are assigned to the reduction of ruthenium oxide. The 0.5% Ru and 3%Ru catalysts on mesoporous TiO_2 support exhibit a similar behaviour in this range, except that the peaks are much less intense than those measured for 3%Ru/TiO_2 (ICES). The low intensity is explained as a result of an efficient sonochemical reduction process leaving only a small part of the Ru unreduced.

It is therefore necessary to interpret the high temperature reduction peak. The 0.5% sample exhibits a strong peak near 480 °C, indicating that some of the Ru below this temperature is still oxidised and undergoes a reduction at this temperature. We argue that some of Ru atoms that are thrown at the walls of the titania form Ru–O–Ti bonds. These Ru atoms are susceptible to the further reduction which happens at higher temperatures. For the 3% Ru samples the corresponding peak shifts to about 370°C. The Ru-support interaction is stronger for the 0.5% sample where the particles are smaller and better dispersed on the TiO_2 walls. The higher the reduction temperature, the stronger is the interaction between the Ru and TiO_2 and the more difficult for Ru particles to aggregate or sinter. It is more noticeable for the 0.5%Ru/TiO_2(MSP) sample, in which most of Ru particles are located in the pores of the TiO_2(MSP) support. Another explanation of the peaks observed at 370 and 480 °C is that they could be ascribed to a partial reduction of the titania surface, and may be associated

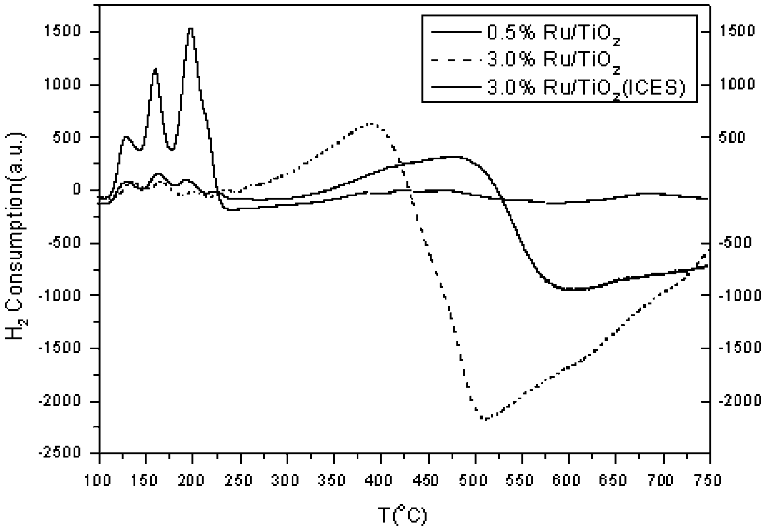

Figure 4. TPR patterns of Ru supported on TiO_2 catalysts.

with the appearance of the SMSI effect. The TPR studies of the high dispersed Ru/TiO_2 catalysts obtained by a spray reduction method (SPR) have also demonstrated that the reduction peaks are broad and moved to higher temperatures (305–670 °C) indicating that Ru–O–Ti bond is really strengthened in SPR fine particles [18].

The negative peaks observed for the 3.0% Ru/TiO_2(MSP) and the 0.5% Ru/TiO_2(MSP) at 510 and 570 °C, respectively, are probably, due to the release of H_2 accumulated in the mesopores. To check whether the negative peaks are due to water molecules formed as a result of the condensation of hydroxide ions, TPR and TPD coupled to GC-MS measurements (instrument-HIDEN-200) at high temperatures were conducted. Hydrogen was detected in the outlet gases in both modes, with no evidence for H_2O formation within the instrumentation detection limits. The tendency of hydrogen to adsorb on the supported Ru catalysts has been recently studied by TPD method, and the increase of the H_2 desorption temperature is attributed to the hydrogen spillover from Ru metal to the support [19]. The increase of temperature causes the hydrogen atoms on the support to migrate back to the metal, recombine to hydrogen molecules and desorb. This process is related to the metal support interaction. The higher dispersion in the low loading sample of 0.5% Ru/TiO_2(MSP) is manifested in the higher temperature of the negative peak. In other words the highly dispersed Ru is more stronger bonded to the support and to the hydrogen as well.

3.2. *Catalytic properties*

The catalytic properties of the Ru/TiO_2(MSP) catalysts with different Ru loading have been studied in the reaction of partial oxidation of methane. Table 2 shows the CH_4 conversion, and the selectivity towards CO and H_2 at different temperatures. Conversion and selectivity increased with increasing temperature.

The sonochemically prepared catalysts exhibit a better catalytic activity and selectivity to synthesis gas than the catalyst prepared by the impregnation method. For example, at 600 °C the CH_4conversion with 0.5%Ru/TiO2(MSP) is 1.4 times higher and the selectivity towards CO is 1.2 times higher than with 3.0%Ru/

Table 2
Catalytic activities of Ru/TiO_2 catalysts for the POM to syngas[a]

Ru (wt%)	CH_4 Conversion (mol%)				CO Selectivity (mol%)				H_2 Selectivity (mol%)			
	T, °C											
	500	600	700	800	500	600	700	800	500	600	700	800
0.5[b]	52.0	57.1	61.9	65.2	69.7	75.2	80.1	83.4	69.0	74.8	79.2	81.4
3.0[b]	67.7	73.9	82.5	88.5	82.4	87.4	92.3	95.5	84.9	88.7	93.3	95.8
3.0[c]	36.6	39.6	43.6	44.9	60.1	60.5	62.7	65.6	32.9	43.1	50.7	54.7

[a] Reaction conditions: pressure 1 bar, $CH_4/O_2=2$, GHSV = 14400h^{-1}.

[b] on TiO_2(MSP) prepared by sonication method.

[c] on TiO_2 (ICES) prepared by incipient wetness impregnation; reduced 500 °C/30 min.

TiO2(ICES) at the same ratio of CH_4:O_2 flow rate, although the later has higher Ru loading. The 3%Ru/TiO_2(MSP) catalyst, is more active in the whole temperature range than the catalyst with low Ru loading 0.5%Ru/TiO_2(MSP), but the difference is not as large as could be expected for a 6-fold increase in the active metal loading. As discussed previously, this difference can be attributed to some structural difference of the catalysts. In the 3%Ru/TiO_2(MSP) catalyst, part of the pores are blocked due to the larger Ru particle size (average size of Ru is 2.6 and average support pore size is 2.5 nm). On the other hand, in the 0.5% catalyst the Ru nanoparticles (average pore size 1.6 nm) are inserted into the inner pores of the catalysts and available to the reagents during the catalytic activation of methane. Because in the catalyst with 0.5% loading most of the Ru particles are located in the mesopores of TiO_2, it might affect the results in two different ways. First, the pore walls will inhibit the aggregation of Ru particles effectively, even at high temperatures, and second, the stronger interaction with the support will cause a better contact of the Ru nanoparticles with the support. The strongest metal-support interaction for the 0.5%Ru/TiO_2(MSP) sample has been also revealed by the TPR results as indicated by the highest reduction temperature for this catalyst. In the 3%Ru/TiO_2(MSP) the Ru particles are larger, and the support interaction is less. However, both of the catalysts supported on mesoporous TiO_2 demonstrate a much stronger metal support interaction and higher thermal stability than the 3%Ru/TiO_2 (ICES) catalyst prepared by traditional method.

4. Conclusions

The Ru catalysts on mesoporous TiO_2 have been prepared by a one-step ultrasound-assisted polyol reduction process. The product was characterized by a variety of physicochemical methods. The XRD studies have shown the presence of metallic Ru in the catalyst. The high dispersion of Ru nanoparticles and their narrow size distribution has been demonstrated by TEM and HR-TEM. According to BET results, the specific surface area of the mesoporous TiO_2 and its pore structure does not change drastically. It means that the support keeps its pore structure after the incorporation of the active metal phase The TPR measurements indicate a strong metal-support interaction in the sonochemically prepared catalyst that prevents the agglomeration of Ru nanoparticles at high temperatures. The evaluation of catalytic activity of these Ru/TiO_2 catalysts, differently prepared, for the partial oxidation of methane to syngas has been reported. Compared with the traditional Ru/TiO_2 catalysts the low concentrated Ru catalysts on the mesoporous support with Ru–O–Ti interactions demonstrate higher activity in the partial oxidation of methane, with higher selectivity towards the target products.

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