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Effect of the Mg/Al ratio of the hydrotalcite-type precursor on the dispersion and activity of Rh and Ru catalysts for the partial oxidation of methane

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Abstract

Active and stable catalysts for the partial oxidation of methane based on Rh and Ru nanoparticles strongly interacting with a MgO or spinel matrix have been prepared by calcination and reduction of hydrotalcite-type precursors. A Rh catalyst containing an high metal loading was used to calculate, by Rietveld analysis, the distribution of the Rh in the MgO-type and spinel-type phases obtained after calcination. The Rh particle size distribution analysed after reduction by HRTEM, has evidenced that the size of Rh particles supported on MgO is smaller than that of Rh particles supported on spinel matrix. The differences in the catalytic activity of the two type of matrix have been studied changing the Mg/Al ratio of the precursor. High Mg/Al ratio depressed the formation of the spinel and led to a narrow distribution of the particle size. The sample with the highest percentage of the MgO phase showed the highest activity. Similar tests have been carried out with Ru containing samples and in this case the increase of the MgO phase decreases the formation of RuO_2.

Keywords: Hydrotalcite-type precursors; Mixed oxide matrix; Rh particles

1. Introduction

The utilisation of natural gas as a raw material is a future goal of strategic relevance for what concern the production of chemicals and energy. Large efforts have been focused by academic and industrial research on the partial oxidation of methane that might represent an alternative to the steam reforming of methane which is energy intensive and requires high investment costs. Using the partial oxidation of methane, high methane conversion and synthesis gas selectivities can be obtained at low residence times [1–3] due to the high temperature reached during the reaction. The high production of heat and the high space velocity lead to an autothermic process carried out in small reactors. Nevertheless the temperature control and the catalyst activity and stability require further improvement due to the novel type of conditions in which the catalyst operates [4]. Aim of the contribution is to set up a strategy able to improve the catalyst activity and stability using noble metal inserted as ion in a nanocrystalline oxide structure. The metal can be extracted from the oxide by reduction forming high-dispersed nanoparticles with an enhanced interaction with the structured matrix.

2. Experimental

The samples were obtained from the HT precursors by calcination at 650 or 900 °C for 14 h. The HT precursors were prepared by precipitation of a solution containing nitrate salts of Rh^{3+} or Ru^{3+} and Mg^{2+}, Al^{3+} with a second solution containing a slight excess of Na_2CO_3. The pH was maintained at 10.0 by continuous addition of NaOH. The precipitates were kept in suspension at 60 °C for 40 min and then filtered, washed (until the sodium content, as Na_2O, was lower than 0.02% w/w), and dried overnight at 90 °C. The precursors compositions were determined after dissolution in concentrated HCl using complexometric titrations for aluminium and magnesium and spectrophotometric evaluation of the coloured complexes for the noble metals [5,6]. Using this procedure Rh/Mg/Al 5/71/24, 5/65/30, 5/80/15, 1/71/28, 1/65/34 and 1/80/19 as atomic ratio were prepared.

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The metal particle distribution of the Rh after reduction was measured using a TOPCON EM002K HRTEM operating at 200 kV. The sample was prepared by suspending a small amount of powder in an alcohol solution and depositing it on a carbon greed. The distribution was determined with a zoom of 500,000× of areas containing a number of particles close to 200.

The surface areas were determined by N_2 absorption using a Carlo Erba Sorpty model 1700.

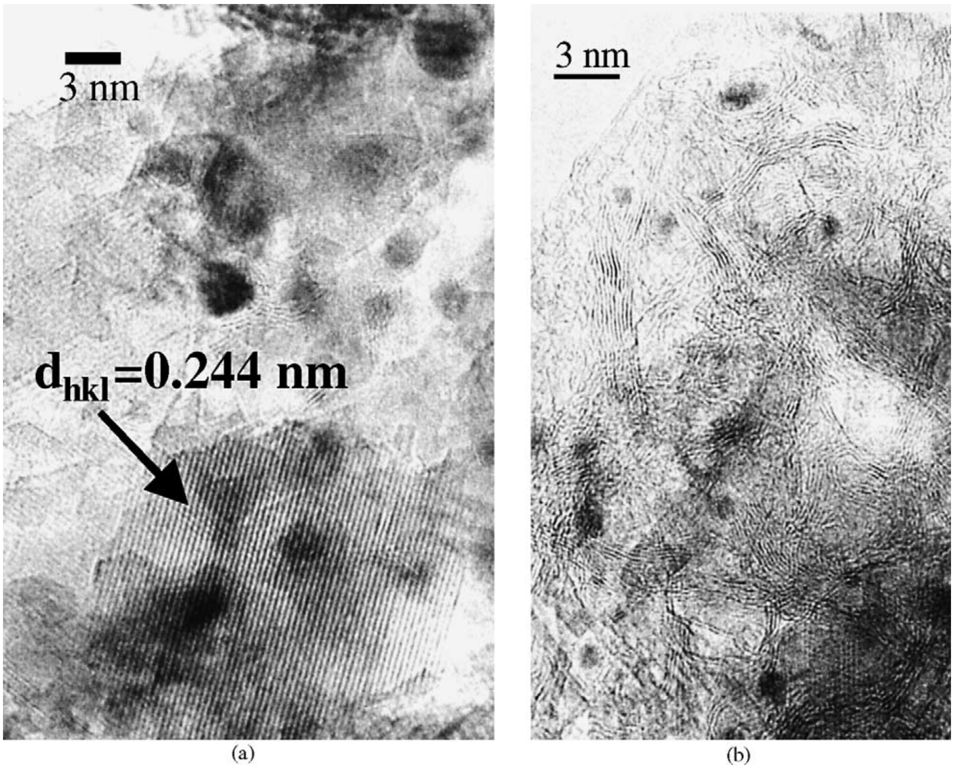
A Rh^{3+}:Mg^{2+}:Al^{3+} 5:71:24 sample has been analysed by the X-ray diffraction (XRD) and neutron diffraction. XRD powder data collection were obtained using copper radiation ($\lambda = 1.5418$ Å) and a Philips PW1050/81 diffractometer equipped with a graphite monochromator in the diffracted beam and controlled by a PW1710 unit. A 2θ range from 16° to 135° was investigated using a step size of 0.05° and a counting time of 22 s per step. After recording of the X-ray data, the samples were preserved under a nitrogen atmosphere for the neutron experiments.

Neutron diffraction experiments were carried out on the D2B diffractometer at the ILL-high flux reactor in Grenoble using a wavelength of 1.594 Å (from the Ge (3 3 5) reflection) at a resolution $\Delta d/d$ of 5×10^{-4}. An angular coverage of $5° < 2\theta < 162.5°$ for scans performed at step sizes of 0.05° were used. The scans were recorded at room temperature on samples contained in vanadium sample holders. Five scans (corresponding to a total of 750,000 neutron counts) were added to give the final profile of each sample. The two analysis have been used in a combined Rietveld analysis to define the Mg, Al and Rh position. A Rietveld refinement using only XRD analysis and carried out also on the Rh/Mg/Al 5/65/30 sample and useful to define only the Rh distribution between the phases [7].

The calcined samples have been tested in the partial oxidation of methane after activation at 750 °C for 5 h in a N_2/H_2 equimolar flow (7 l/h). The catalytic tests were carried out in a quartz reactor using an oven heated at 500 °C, feeding a gas mixture $CH_4/O_2/He = 2/1/4$ v/v using 0.075 g of catalyst and $CH_4/O_2/He = 2/1/20$ v/v using 0.150 g of catalyst in order to obtain a residence time below 10 ms. The quartz reactor has an internal diameter of 6 mm and the reaction products were analysed on-line after water condensation by two gas chromatographs equipped with HWD and carbosieve SII columns, flowing He as carrier gas for the analysis of CH_4, O_2, CO and CO_2 and N_2 as carrier gas for the H_2 analysis.

3. Results and discussion

The whole series of prepared samples shows the presence of an hydrotalcite like phase in which the Rh/Mg/Al cations are inserted. The Rh insertion inside the structure of the hydrotalcite-type precursor was confirmed by the equal cation distribution calculated by chemical and XPS analysis that indicates no differences between the bulk and surface composition. After calcination at 650 °C only a mixed oxide-type phase was present while at 900 °C a $MgAl_2O_4$ spinel-type and a MgO-type phases have been detected. The combined (XRD and neutron diffraction) Rietveld analysis, carried out on the Rh^{3+}:Mg^{2+}:Al^{3+} 5:71:24 sample allowed to identify the position of Rh, Mg and Al in the calcined samples. It shows that after calcination at 650 °C the (Mg/Al)O cubic phase is a defective rock salt phase in which part of the Mg occupies tetrahedral sites [7,8]. By calcination at 900 °C this phase is less defective and closes to an ideal MgO phase nevertheless, some Al and Rh are still present. The analysis of the Rh distribution shows that, Rh was more concentrated in a spinel-type phase, even if the MgO phase was more abundant (69%), as a consequence, the Rh amount in the two phases was similar (59% in the MgO and 41% in the spinel phase). The HRTEM carried out after the reduction of the sample shows a very interconnected matrix formed by MgO-type and spinel phases in which atom columns and planes are well evidenced and highly dispersed Rh particles are present. Notwithstanding the very high Rh content of the Rh/Mg/Al 5/71/24 sample the distribution of the particle size shows a maximum close to 2–3 nm [7,9], this was possible because of the high surface area of the catalyst (close to 100 m^2/g). The HRTEM analysis carried out on the Rh/Mg/Al 1/71/28 allowed to study the different distribution of the Rh particle size supported on the two different phases. In particular, the spinel zone can be evidenced by the presence of visible oriented lattice plane with a "*d*" distance typical of the spinel phase (Fig. 1a) while the EDAX nano-analysis has evidenced a zone in which only Rh and Mg are present, i.e. a zone where Rh is supported on MgO phase (Fig. 1b). The evaluation of the particle size distribution evidences that the Rh particles supported on the MgO phase are smaller than those supported on spinel. This might be due to the different concentration of the Rh in the two phases which, being higher for the spinel, leads to a larger particle size. This observation allows to hypothesise that if a different Mg/Al ratio (modifying the amount of MgO and spinel phases) can lead to a different Rh distribution, it might be possible to affect the Rh particle size and, as a consequence, the catalytic activity and stability. To study the effect of the Mg/Al ratio in the Rh based catalysts three different $M^{2+}/M^{3+} = 65/35$, 71/19, and 80/20 as atomic ratio (a.r.) with both 5 and 1% of Rh have been used. The Rh distribution changes according to the Mg/Al ratio and the catalyst Rh/Mg/Al 5/65/30 (a.r.) analysed with the Rietveld analysis shows an higher amount of Rh in the spinel phase than that in the MgO phase (57 and 43 wt.% respectively). On the other hand the catalyst Rh/Mg/Al 5/80/15 (a.r.) shows only the MgO-type phase in which the Rh is completely soluted. Decreasing the Rh and increasing the Al amount (Rh/Mg/Al 1/65/34, 1/71/28 and 1/80/19 a.r.) the spinel phase is enhanced in all the catalysts, in fact the solubility of Al in the MgO phase is lower than that of Rh. The HRTEM and the particle size distribution calculated on the Rh/Mg/Al 5/80/15 and 1/71/28 (a.r.) show interesting changes. With



(a)

(b)

Fig. 1. HRTEM of the Rh/Mg/Al 1/71/28 (a.r.) after calcination at 900 °C and reduction at 750 °C (a) spinel zone (b) MgO zone.

increasing the Mg/Al ratio the particle size distribution become narrower with a very few Rh particles larger than 4 nm, while the maximum of the particle size distribution is between 1 and 3 nm (Fig. 2). Furthermore, using a low amount of Rh the maximum of the particle size distribution is below 2 nm even if some particles larger than 4 nm are still present.

The catalytic results confirm the high metal dispersion of the Rh, showing methane conversions and syngas selectivities comparable with the best results reported in literature. The catalytic performances were stable for 100 h in hard reaction conditions ($T_{\text{oven}} = 750\,^{\circ}\text{C}$, $CH_4/O_2/He = 2/1/4$ v/v, residence time 5 ms) notwithstanding the tests have been carried out switching off the reactor during the night. The stability of the catalyst was confirmed also by the stable surface area and the constant distribution of the Rh particle size after the catalytic tests (Fig. 2). The catalyst was stable also in terms of carbon formation since the analysis carried out before and after tests gave a C content of 0.37 and 0.35%, respectively. The small amount of carbon can be attributed to the presence of carbonates trapped in the calcined matrix [10].

The catalysts have been compared at an oven temperature of 500 °C, a residence time of 7.5 ms, and in two reaction conditions, $CH_4/O_2/He = 2/1/4$ and 2/1/20 v/v, the latter being far from the thermodynamic equilibrium [11]. The comparison shows a change of the catalytic performances as a function of the amount and the position of the Rh in the oxide matrix (Figs. 3 and 4). In particular the methane conversion and syngas selectivity of the samples with an M^{2+}/M^{3+} ratio of 80/20 was higher than those

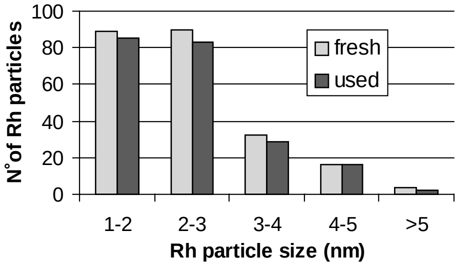


Fig. 2. Rh particle size distribution of the Rh/Mg/Al 5/80/15 (a.r.) sample after reduction (fresh) and after catalytic tests (used).

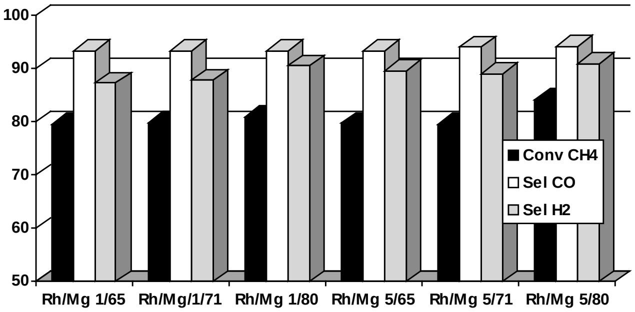


Fig. 3. Partial oxidation of methane with Rh catalysts carried out at 5 ms, $T_{\text{oven}} = 500\,^{\circ}\text{C}$, $CH_4/O_2/He$ 2/1/4 v/v, 0.075 g of catalyst (in the figure the Al content is complementary to 100).

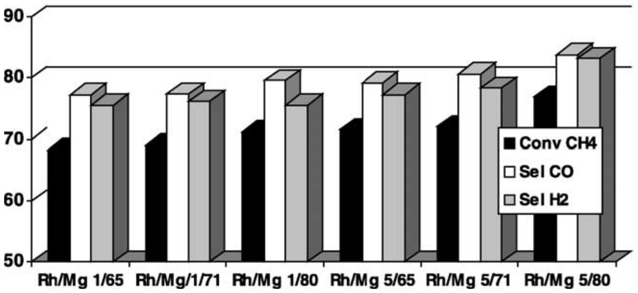


Fig. 4. Partial oxidation of methane with Rh catalysts carried out at 7.5 ms, $T_{oven} = 500\,°C$, $CH_4/O_2/He$ 2/1/20 v/v, 0.15 g of catalyst (in the figure the Al content is complementary to 100).

of the samples with lower M^{2+}/M^{3+} ratio. Among all the catalysts the Rh/Mg/Al 5/80/15 (a.r.) was particularly active and selective confirming the importance to make maximum the amount of the MgO phase and to decrease the number of large Rh particles. Furthermore, the catalyst Rh/Mg/Al 1/80/19 (a.r.) shows catalytic results equal or higher than those of the catalyst containing a much higher Rh amount (5% as a.r.) but lower Mg/Al ratio. The differences among the catalysts with 1% (a.r.) of Rh can be evidenced also by comparing the two catalysts with M^{2+}/M^{3+} ratio 80/20 and 71/28 as a function of the residence time ($T_{oven} = 500\,°C$, $CH_4/O_2/He = 2/1/20$ v/v). The results show the higher activity of Rh/Mg/Al 1/80/29 (a.r.) and point out an increasing difference in terms of methane conversion and syngas selectivity with decreasing the residence time (Fig. 5). The increase of differences is due to the prevalence of the kinetic regime that is established in diluted conditions where the heat produced is limited [11]. The main change of the catalyst structure occurring with increasing the M^{2+}/M^{3+} ratio is the narrow distribution of the Rh particle size and the increase of the basic properties of the support. The low amount of large Rh particles present in the sample with high Mg/Al ratio, besides increasing the metal dispersion can decrease the intensity of hot spot due to the distribution on a large area of the oxidation reaction occurring in the first zone of the reactor. On the other hand the hot spot due to the large particle size favours the fast consumption of the oxygen and produces very sharp peak of temperature [9,10], so decreasing the temperature of the last part of the bed where reforming reactions occur. Beside these aspects, also the presence of a more basic support can have a strong effect on the syngas selectivity by increasing the electron density of the Rh and its interaction with the support and/or by affecting the CO_2 absorption/desorption equilibrium [7,12,13]. The same considerations about M^{2+}/M^{3+} ratio can be extended with an analogous effect on Ru catalysts. The sample calcined at 900 °C gives rise to a partial segregation of Ru as RuO_2 while the rest of Ru is soluted in the MgO phase. The increase of Mg/Al ratio increases the amount of Ru in the MgO structure. In particular the Ru/Mg/Al 1/80/19 showed only traces of RuO_2 while the amount of RuO_2 in the Ru/Mg/Al 1/71/28 was close to the 50%. Also in this case, the sample with higher Mg/Al ratio gives higher catalytic activity (using the conditions of Fig. 4, CH_4 conversion 64.6 and 46.2% for Ru/Mg/Al 1/80/19 and 1/71/28, respectively). The yield in synthesis gas are not comparable with those obtained with Rh samples because of the presence of the RuO_2 and of the lower specific activity of Ru in this reaction [7].

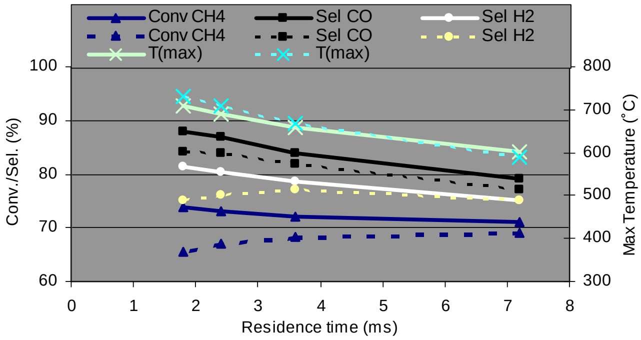


Fig. 5. Partial oxidation of methane carried out at $T_{oven} = 500\,°C$, $CH_4/O_2/He$ 2/1/20 v/v, 0.15 g of catalysts as a function of the residence time with Rh/Mg/Al 1/80/19 (a.r.) (solid line) and 1/71/28 (a.r.) (dashed line).

4. Conclusion

The preparation of stable and active catalyst is necessary to the industrial application of the partial oxidation reaction. Active and stable Rh and Ru nanoparticles strongly interacting with a MgO or spinel matrix have been prepared by calcination and reduction of M/Mg/Al hydrotalcite precursors. The $MgAl_2O_4$ spinel-type and MgO-type phases obtained by calcination of the Rh/Mg/Al 5/71/24 (a.r.) sample were studied. Rh was more concentrated in the spinel phase but the larger amount of MgO phase leads to a similar amount of Rh in the two phases. The reduction of the sample leads to Rh disperse particles with a maximum of the particle-size distribution between 2 and 3 nm, in particular the Rh^0 particle size supported on the spinel was larger than that supported on the MgO phase.

The change of the M^{2+}/M^{3+} ratio changes the amount of the phases and the Rh distribution. In the catalysts with the $M^{2+}/M^{3+} = 80/20$ the amount of spinel phase was low or absent (depending on the Al/Rh concentration) and the Rh was completely soluted in the MgO phase. These phenomena lead to a narrow distribution of the Rh particle size and to an high methane conversion and syngas selectivity. The catalyst and the particle size distribution were stable for 100 h in hard reaction conditions. The increase of the M^{2+}/M^{3+} ratio applied to the Ru catalysts, increases the amount of Ru in the MgO structure decreasing the segregation of RuO_2 and as a consequence, the catalytic activity increases.

Therefore, the properties and the dispersion of the active metal sums depend on the type of oxide in which the metal is inserted and this parameter can be taylored by the M^{2+}/M^{3+} ratio.

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