**Selective CO methanation with structured RuO2/Al2O3 catalysts**

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**Abstract**

Active and selective structured RuO2/Al2O3 catalysts for CO methanation using a flow simulating CO2-rich reformate gases after being treated in Water Gas Shift and Preferential oxidation of CO units (H2 excess, CO2 presence and 300 ppm CO concentration) were prepared. Both, the RuO2/Al2O3 powder and the slurry formulation prepared from it, for its structuration by washcoating of metallic micromonolithic structures, were also active and selective. Both, the slurry and micromonoliths were able to completely and selectively methanate CO at much lower temperatures than the parent RuO2/Al2O3 powder. The optimal working temperature in which the CO conversion is maximum and the CO2 conversion is minimized was determined to be 149°C-239°C for the slurried catalysts, 165°C-232°C for the structured catalyst and 217°C-226°C for the initial powder. TPR, XRD and TEM measurements confirmed that the changes in the activity and selectivity for CO methanation among the considered catalysts can be related with modifications in the surface particle size of ruthenium and its reducibility. These were ascribed to the metallic substrate, the presence of polyvinyl alcohol and colloidal alumina in the slurry preparation, the aqueous and acidic media and the thermal treatment used, resulting in a more active and selective catalysts than the parent powder.

**Key words**: RuO2/Al2O3 catalysts; metallic micromonolith; washcoating; CO methanation ; CO2 methanation

**1. Introduction**

H2 produced from the reformer stream carries significant amounts of H2O, CO and CO2. The decreasing (or elimination) of CO is mandatory if this hydrogen is used for feeding PEM fuel cells [1], since electro-catalysts as Pt and Pt-Ru are poisoned by irreversible adsorption of CO, said output must be purified to levels of CO below 10 ppm prior to admission to fuel cells. Nowadays there are different strategies to achieve the desired CO concentration levels. The typical solution consists in the use of different catalytic units after the reformate reactor. The first unit can be a water gas shift (WGS) reactor to transform CO into CO2 (Eq. 1)

CO + H2O ↔ CO2 + H2; ΔH0=-41.2 kJ/mol(Eq. 1)

WGS is a reaction limited by the equilibrium, kinetically favored at high temperature and is generally carried out in a series of adiabatic converters; typically two reactors, a high-temperature shift (HTS) to take advantage kinetically and a low-temperature one (LTS) to achieve higher CO conversion. Both reactors are working with well-established catalysts based on Fe-Cr and Cu-Zn, respectively [2]. However, when envisaged applying this reaction in one step or in mobile application for H2 purification the noble metal based catalysts gain importance [3]. In any case, even with this configuration and the best catalysts used, the minimum level of CO achieved is only ≈1 to 0.5%. In order to decrease the CO level until the ideal concentration before fuel cells, it is necessary to add other units. In that sense, preferential oxidation (PROX) (Eq.2) and CO methanation (Eq. 3) reactors can be used as solutions.

CO + ½O2→ CO2; ΔH0=-283 KJ/mol (Eq. 2)

CO + 3H2 → CH4 + H2O; ΔHo = -206 kJ/mol (Eq. 3)

Both methanation and PROX reactors have been disposed sequentially or in parallel. The final industrial selection (type, arrangement and number of processes) is related to the CO level to be abated. In that sense, as said above, a CO concentration of ≈1 to 0.5% is expected in the stream when only a WGS unit is disposed before the methanation reactor. In this case with an appropriated catalyst, the methanation reactor can convert CO until < 10 ppm [4]. On the other hand, if WGS and PROX reactors are sequentially disposed, a concentration of CO of ≈300 ppm could be expected before methanation process [5].

The catalytic hydrogenation of carbon monoxide to methane and other hydrocarbons is currently receiving a great deal of attention [6-9]. This reaction has been widely used in industry as an efficient method for the removal of carbon oxides from H2-rich feed gases for fuel cells or ammonia plants [10-12] since it could be used as the final purification step to reduce concentration of CO to extremely low levels. This reaction offers certain advantages, compared to preferential oxidation (PROX) because it does not require addition of oxygen (air) in the hydrogen-rich gas stream, which may give rise to various problems related to reduced hydrogen yield, dilution, safety and restrictions in the operating parameters. In addition, methane produced is inert to the PEM fuel cell electrodes and can be utilized in the afterburner. However, CO methanation consumes a large amount of valuable hydrogen (three moles per mol of CO abated (Eq.3)) and may run in parallel with the undesired methanation of CO2 (Eq. 4), which also consume significant quantities of hydrogen, as well as with the reverse water–gas shift (RWGS) (Eq. 1), which shifts CO2 to CO. For that reason, methanation reaction must be highly selective towards CO methanation, with CO2 methanation essentially being inhibited; otherwise the loss of H2 would become intolerable. Consequently, it is important to develop stable and selective CO methanation catalysts with sufficiently high activity at relatively low temperatures, able to suppress both CO2 methanation and RWGS reactions. In a similar way, the use of CO methanation as an H2 clean-up process is only economically viable if is applied as final step, when the CO concentration to be abated is in the 300 ppm level.

CO2 +H2 ↔ CO + H2O; ΔH0= -165 kJ/mol (Eq. 4)

Hydrogenation of carbon oxides toward methane and higher hydrocarbons can be catalyzed by several metal catalysts, including Ni [13-17], Ru [18-23], Rh [22,24] and mixed of them [12] among others [25]. Ru is believed to be the most active methanation catalysts [26-27]. It has been usually supported on a number of oxide materials such as Al2O3, TiO2, SiO2, MgO, MgAl2O4 and CeO2 [27-45]. The supported Ru catalysts have been found to exhibit high activity for the solo-methanation of CO [12,20] or CO2 [17,28-32] and selective CO-methanation in CO/CO2 mixtures [20,22,30,33-34]. For CO methanation, Nawdali *et. al* [46] demonstrated that the CO species are directly adsorbed on Ru sites and then the hydrogenation to CH4 can occur in the temperature range 170-205 °C. In the presence of adsorbed CO on the surface, hydrogen is adsorbed on other sites aside from those involved in the absence of CO. Then CO is dissociated, leading to active and inactive, carbon species, where the former are stepwise methanated to CHx species and finally to CH4 [47-48].

According to literature [26], methane production rates for noble metals decrease in the order Ru > Rh > Ir ≈ Pd ≈ Pt ≈ Re. For base metals, the activity ranking is Ni > Co > Fe, with Ni more active to methanation and Fe highly selective to WGS. It has been reported [27] that the specific activity of Ru/Al2O3 for CO hydrogenation is about one order of magnitude higher, compared to that of Al2O3- supported Rh, Pd or Pt which catalyze the RWGS reaction [14]. Utaka *et. al* [19] used Pt-catalysts in methanation of CO. At temperatures from 100 to 250oC high CO conversion were reached, but the contribution of RWGS was observed. They found that the highest CO conversion was reached with SiO2 and Al2O3 supports impregnated with ruthenium. Rehmat and Randhava [36] compared some commercial catalysts such as Ru/γ-Al2O3, Raney nickel and alumina-supported Ni catalysts and found that Ru was the most effective, followed by the Raney nickel-type catalyst. Inui *et. al* [40] prepared Ru-Ni-La2O3 catalyst for CO and CO2 methanation, and found that CO2 methanation was completely retarded until CO has been converted to methane. This behavior could not be observed by the use of less active catalysts, i.e., both CO and CO2 were converted into methane at higher temperatures [41]. Choudhury *et. al* [12] demonstrated that the complete conversion of CO to methane preferentially occurred on Ru-Rh-Ni-La2O3 at 230oC. As long as CO remained in the syngas, methanation of CO2 is completely retarded. La2O3 increases Ni dispersion, and Rh and Ru enhance H2 adsorption, and induce the reduction of NiOx at low temperatures by hydrogen spillover.

The activity and selectivity of Ru catalysts to CH4 have been claimed to be largely dependent on the dispersion, concentration and particle size of the metallic phase. Panagiotopoulou *et. al* [20] used supported ruthenium catalysts from 0.5 to 5.0 wt.% for the selective methanation of CO in the presence of excess CO2. Conversion of CO2 was completely suppressed until conversion of CO reached its maximum value. Increasing metal loading resulted in a significant shift of the CO conversion curves towards lower temperatures with a lower participation of RWGS. Optimal results were obtained with 5%Ru/TiO2 catalyst with a mean crystallite size of 13.6 nm against 1.3 nm for 0.5%Ru/TiO2. 5%Ru/TiO2 was able to completely and selectively convert CO at temperatures around 230oC. Takenaka *et. al*. [37] found an opposite trend. They proposed Ni/ZrO2 and Ru/TiO2 as promising catalysts based on the screening experiment and concluded that the larger Ni and the smaller Ru were plausible for the high catalytic activity.

The activity of Ru base catalysts in selective CO methanation has been also related with the support selected and the addition of modifiers/promoters that can chemically interact with the metal [24]. The nature of the support affects the mechanism for CO/CO2 hydrogenation reactions, since the metal support interaction modifies the adsorption of the intermediates as well as desorption of the products [21]. Lin *et. al* [35] found that the activation energy of H2 adsorption was affected by the modification of the ruthenium due to the interactions between metal and support. In this case the activation energy decreases in the order of Ru/TiO2 > Ru/Al2O3 > Ru/SiO2.

Despite the high activity reported with Ru catalysts in CO methanation and their influence on the adsorption capacity of CO, there are some obstacles to be overcome in these systems: (i) The temperature window showing high CO conversion is very narrow even in the lab-scale experiments. This can cause severe problems in the scale-up process because this reaction is highly exothermic. (ii) The reaction temperature, which is still relatively high, allowing for the RWGS reaction to occur, which can cause the unacceptable CO concentration at low space velocities frequently encountered in the cyclic operation. (iii) The rapid consumption of hydrogen can be carried out via the CO2 methanation in the absence of the fine temperature control, adequate CO/CO2 ratio and active and selective catalysts. (iv) The inlet CO concentration should be low enough to reduce CO concentration satisfactorily with an acceptable H2 loss.

Furthermore, the important point is not only to develop a catalyst having the ability of effectively transforming CO, but also to rapidly eliminate the exothermic energy from the active zone, because the methanation is a relatively high exothermic reaction. So, development of an innovative reaction system that provides the CO methanation zone having a superior heat transfer property and a mass processing ability of the material is definitely required. A structured reaction system, which integrates a reactive zone and a heat-transferring zone, would be a candidate reaction system that provides advantages for heat exchange and material processing [44]. It has been acknowledged that microchannels reactors have unique features of process intensification. They present excellent temperature control and improve mass transfer especially in the application of highly exothermic and endothermic reactions. That way, the existence of hotspots can be minimized, increasing the selectivity of the process. Thus a metallic structured support with its inherent high thermal conductivity is an appropriate substrate for CO methanation reaction, favouring the selectivity and diminishing the occurrence of the CO2 methanation and WGS reactions.

As for the development of the catalyst for the structured-type CO methanation system, little research has been reported concerning to Ru catalysts [11,39,49]. Mostly are devoted to Ni catalysts [45,49-50]. In both cases there are issues that are not completely solved yet, e.g. [11,39,45,49-51] the high temperatures of operation, the high amount of the active phase required and the low selectivity towards CO methanation against CO2 methanation. In some cases, the addition of O2 has been necessary to complete the conversion of CO. Görke *et. al* [11] used a microchannel reactor to reduce the CO content by methanation in a model gas mixture containing CO, CO2, O2 and H2. Microchannels were coated with Ru/SiO2 and Ru/Al2O3. The selective CO methanation was effective at 300oC using Ru/SiO2. Men *et. al* [49] deposited on microchannel sheets Ru and Ni-based supported metal catalysts. All the prepared Ru-based catalysts showed insufficient activity under current reaction conditions, being the highest CO conversion only 44% at 350oC. Galleti *et. al* [39] reported a complete removal or CO in H2-rich gas stream through CO methanation over 3%Ru-based catalysts supported on γ- Al2O3 and CeO2. In this case Ru/γ-Al2O3 showed the best performance. Consequently, it was deposited on microchannel metal plates reactor but the performance was poor and complete CO conversion was not reached and also CO2 methanation was present, thus reducing catalysts selectivity.

The use of micromonoliths is presented as alternative to the powder catalysts and reported structured systems for selective CO methanation. The heat and mass transport properties are strongly enhanced offering high precision in catalysis at all relevant scales of the catalytic processes. Moreover the micromonoliths present low energy input, high catalytic performance per mass unit of active phase, safer operating conditions, lower pressure drop and easiest catalysts separation, making them the structure of choice for different catalytic reactions [52]. Metallic micromonoliths offer a better mechanical strength and higher thermal conductance than ceramic ones, which can be also advantageous. However, the adhesion of the catalytic layer to the metallic substrate is an important limitation. A suitable pretreatment of the micromonolith surface and the carefully control of the parameters of the catalysts deposition are mandatory [53]. Among the metallic substrates used in the literature for preparing micromonoliths, ferritic stainless steel (for instance fecralloy) is one of the most interesting due to adequate chemical and thermal stability at the temperature normally used in catalytic reactions and chemical compatibility with the catalytic layer.

In the present study the catalytic performances of powder and micromonolithic RuO2/Al2O3 catalysts were investigated in selective methanation reaction of CO, using a methanation flow simulating CO2-rich reformate gases from WGS and PROX units (H2 excess, CO2 presence and 300 ppm CO concentration).

**2. Experimental**

**2.1 Micromonolith manufacture**

Commercial Fecralloy stainless steel sheets 50 μm thick (Goodfellow, typical analysis Cr 22%, Al 4.8%, Si 0.3%, Y 0.3%, C 0.03%, Fe balance) were used as raw material. The foils were washed with water and soap, rinsed with acetone under sonication (30 min) and finally dried at room temperature. The micromonoliths were prepared by rolling together around an axis a flat and a corrugate sheet leading to a cylindrical-shaped body (L= 3 cm, Ø= 1.6 cm, 540 cm2 total surface area) resulting in parallel longitudinal channels (2063 cells per square inch). The micromonoliths were thermally pretreated in an oven at 900oC during 22 h in order to grow a rough, homogeneous and well adhered oxide scale layer, mainly composed by α-Al2O3, on the metallic surface. This layer easies the catalyst anchoring on the surface by improving the physical adhesion and the chemical compatibility [54-55].

**2.2 Catalysts preparation**

**2.2.1 Powder catalyst**

Wet impregnation was selected as synthesis method. A commercial γ- Al2O3 support (Sasol, Puralox Scca 30/100) was impregnated with the adequate amount of Ruthenium (III) nitrosyl nitrate solution (Johnson Matthey) diluted in water (200 ml per gram of support) in order to obtain a nominal Ru loading of 10 wt. % (that corresponds to RuO2 loading of 13 wt.%) . After 15 min of stirring at room temperature the solvent was removed on rotavapor and the obtained solid was dried at 130oC for 24h and finally calcined at 400oC for 2h with a heating ramp of 10oC.min-1.

**2.2.2 Micromonolithic catalysts**

Washcoating was the selected method for the catalysts deposition on the micromonoliths. The pretreated micromonolithic structures were immersed in a slurry of RuO2/Al2O3 catalyst with the adequate composition and rheological properties (particle size, viscosity and pH). These properties were properly adjusted in order to ensure a layered homogeneous deposition and to avoid cracking effects of the layer.

First, the RuO2/Al2O3 catalyst was milled in a zirconia jar on a Retsch® PM100 equipment until obtaining a 5μm < ø < 10 μm particle size. Then, the adequate amount of solid was dispersed in deionised water and the mixture was sonicated using an ultrasonic disperser (Sonicator Misonix) working at 50 W. After that PVA (polyvinyl alcohol), previously dissolved in hot water, was added as tensioactive and colloidal alumina (Nyacol Al20) was also added to improve the stability. The mixture was kept under vigorous stirring for 24 h. The optimized composition of the suspension was 18.2 wt. % catalyst, 11 wt. % PVA, 6.28 wt. % colloidal alumina and distilled water as balance. The viscosity of the final slurry was 7.5 cps and the pH was 6.18. This pH value assures the stability of the slurry, avoiding catalyst particle agglomeration since the measured isoelectric point of the RuO2/Al2O3 solid was 9.5.

The coating procedure consists in the immersion of the micromonolith in the prepared slurry for 1 min and then withdrawn at a constant speed of 3 cm/min. To avoid obstruction of the micromonolith channels, the excess of colloid was removed by centrifugation at 600 rpm for 10 min. Then, the micromonolith was dried at 130oC for 30 min. The deposition process was repeated three times until 150-160 mg of catalyst was supported. Finally, the structured catalyst was calcined at the same temperature than the bare powder catalyst (400oC, 2h) but employing 2oC/min heating rate to avoid cracking phenomena. Two micromonithic catalysts were prepared in order to verify the reproducibility of the results. The weight gain was additive in both micromonoliths, increasing about 53-56 mg after each washcoating procedure (Fig. 1). After calcination, the final weight gain was 138.3 and 147.3 mg. Taking into account the amount of colloidal Nyacol used as additive (6.1 wt.%), and its relative content of alumina (20 wt.%), the real amount of the bare RuO2/Al2O3 catalysts deposited was 129.6 and 138 mg, respectively. For comparative purposes, fresh prepared slurry was dried and calcined in the same way, obtaining a powder representative of the washcoated catalysts (slurried catalyst).

The bare calcined powder catalyst, the calcined slurried catalyst and the micromonolithic systems were denoted as RuAl, S-RuAl and M-RuAl respectively.

**2.4 Characterization techniques**

- The chemical composition of the samples was measured by X-Ray fluorescence (XRF) spectrometry carried out in an X Panalytical AXIOS PW4400 with Rh tube as a source.

-The instrument used for the X-ray diffraction (XRD) analysis was the X`Pert Pro PANalytical. Diffraction patterns were performed using Cu Kα radiation (40 mA, 45kV) in a 2ϴ-range of 10 to 80o and a position-sensitive detector using a step size of 0.05o and a step time of 80 s.

-TEM analysis was performed in a Philips CM 200 working at 200 kV with EDS analysis and CCD camera. The average particle size, dav, was estimated from equation 5 considering the relative contribution of the particles of different sizes:

$d\_{av}=\frac{\sum\_{}^{}n\_{i}d\_{i}^{3}}{\sum\_{}^{}n\_{i}d\_{i}^{2}} $(Eq. 5)

-The textural properties were analyzed by N2 adsorption-desorption measurements at liquid nitrogen temperature. The experiments were carried out on a Micrometrics ASAP 2010 instruments. Previously the system was degassed during 2 h at 250oC in vacuum. For the micromonolithic samples, a homemade cell that allows analyzing the complete micromonolith was used. Pore size distribution was calculated using the BJH method on the desorption branch.

-Temperature-programmed reduction (TPR) experiments were carried out in a conventional quartz reactor connected to a TCD detector. The reactive gas stream (5% H2 in Ar) was flowed at 50 mL/min over 50 mg of sample, and the temperature raised at 10°C/min from room temperature to 700°C. A CO2-acetone trap was used to condense the gaseous products evolved, mostly water. Quantitative analyses were done by integration of the reduction signal and comparison with hydrogen consumption of a CuO reference sample. To obtain the reducibility percentage, the loading of RuO2 was taken from XRF results and a theoretical molar ratio RuO2:H2 1:2 was considered (Eq. 6).

RuO2 +2H2 → Ru + 2H2O (Eq.6)

-Before the cross sections analysis, the micromonoliths were cut, embedded in a polymeric resin matrix and polished. The line analysis and the mapping micrographs were obtained in a Hitachi S4800 SEM-FEG high-resolution microscope (1–3 nm) coupled to EDX Bruker X Flash Detector 4010 (133 eV resolution).

-The adherence of the catalytic layer to the substrate was evaluated using an ultrasonic method previously described [54-55]. It consists in the measurement of the weight loss caused by the exposition of the sample to ultrasound. The micromonoliths immersed in acetone were submitted to an ultrasonic treatment in a Cole Parmer ultrasonic bath (47 kHz and 130W) for 60 min at room temperature. After that, the samples were dried, calcined and the weight loss determined by the difference in the mass of the coating before and after the ultrasonic test. The adherence is defined as the quantity of catalysts retained on the micromonolith expressed in percentage.

-Roughness of the micromonolith after thermal treatment was measured with a Mitutoyo SJ-201P surface roughness tester.

-The isoelectric point (IEP) of the powder catalyst before slurry preparation was determined in a Malvern ZETAMASTER equipment, using a 10-1 M HCl solution as an acidity buffer and a 10-1 M NaOH as a basicity buffer for the pH adjustment. For the measurements, 5 mg of the sample was dissolved in 100 mL of NaCl 10-2 M. Measurements were made from pH 3 to pH 12. The IEP value was determined as the pH at which the zeta potential value is zero

-Brokfield DV-III equipment coupled with a Unitronic 22 Selecta bath was used to determine the viscosity of the slurried catalyst. An initial cutting speed of 250 rpm was used. The system was left under stirring until a constant viscosity value was obtained.

**2.5 Catalytic activity**

Selective CO methanation measurements were carried out in a Microactivity PID Eng&Tech equipment using a 9 mm internal diameter tubular AISI316 stainless steel reactor (Autoclave Engineers). The powder samples (140 mg sieved in the 100-200 µm range), were diluted in a volume of glass particles sieved in the same diameter range (100-200 µm) equal to that occupied by the micromonolithic devices (6 cm3). The feed gas simulating an output stream from PROX unit consists of 0.03% CO, 15 % CO2, 50% H2, 15% H2O and N2 as balance. The WHSV (Weight Hourly Space Velocity) was fixed at 80000 ml.g-1.min-1. For micromonoliths a tubular reactor (16 mm inner diameter) was employed and the total flows for methanation reaction were adjusted to achieve the same WHSV as for the powder tests. In all cases the temperature was controlled by using two thermocouples before and after the catalytic bed. Before reaction the samples were *in-situ* pre-activated at 300oC for 2 h in 60 ml/min pure H2 flow, purged with N2, and then conditioned at 105oC for 1 h within the reaction mixture. The methanation activity was evaluated from 105oC to 270oC. After water removal at the reactor exit, the reactant and products were analyzed by on-line gas chromatography (GC) using a Varian micro GC 4900 instrument with two channels, one with a Porapaq-Q and the other with a Molecular Sieve 5A column, and thermal conductivity detectors (TCD). The CO2 was analyzed by a Vaisala detector CARBOCAP GMT220. CO and CO2 conversions (XCO, XCO2), and selectivity to CO methanation (SCO/CO2) was defined as (Eq. 7 to 9):

|  |  |
| --- | --- |
| $$X\_{CO }\left(\%\right)=\frac{\left(F\_{COin}-F\_{COout}\right)}{F\_{COin}}\*100$$ | (Eq. 7) |
| $$X\_{CO\_{2}}\left(\%\right)=\frac{\left(F\_{CO\_{2 in}}-F\_{CO\_{2 out}}\right)}{F\_{CO\_{2 in}}}\*100$$ | (Eq. 8) |
| $$S\frac{CO}{CO\_{2}}\left(\%\right)=\left(\frac{X\_{CO}\*F\_{COin}}{F\_{CH\_{4} out}}\right)\*100 $$ | (Eq. 9) |

Being$ F\_{CO}$, $F\_{CO\_{2 }} and F\_{CH\_{4}}$ the flows in ml/min of CO, CO2 and methane respectively, the subscripts *in* or *out* correspond to the inlet or the outlet flow.

In all cases, the methane selectivity, defined as Eq. 10, was always higher than 99.98% and only small traces of ethane and ethene were detected.

$S\_{tw CH\_{4}}\left(\%\right)=\left(\frac{^{C\_{CH\_{4}, out}}/\_{υ\_{CH\_{4}}}}{\sum\_{i}^{}^{C\_{i, out}}/\_{υ\_{i}}}\right)\*100$ (Eq. 10)

$C\_{i, out}$ is the product *i* concentration in the outlet and $ν\_{i}$ is the carbon numbers according to its chemical formula.

In all cases, the carbon balance resulted to be better than 95%.

**3. Results and discussion**

**3.1 Characterization**

XRF measurements on reduced samples at 300oC revealed that the real Ru content of the RuAl powder catalysts was 8.64 wt.% (11.38 wt.% of RuO2). This value decreased to 8.10 wt.% (10.66 wt.% RuO2) in the slurried sample S-RuAl due to the additional amount of alumina incorporated to the formulation because of using Nyacol colloidal alumina as binder.

X-ray diffraction of both calcined samples RuAl and S-RuAl (Fig. 2A) confirms that the crystalline structure of the bare catalyst remains unchanged after the preparation of the slurry, being composed by RuO2 (JCPDS 40-1290) and γ-Al2O3 (JCPDS 46-1215). From the broadening of the reflection peak of the (110) plane at 28° 2θ, and applying the Scherrer equation, the crystalline domain size of RuO2 crystallites were calculated to be 11 and 10 nm for RuAl and S-RuAl, respectively. After the reduction procedure needed to activate the catalysts (300°C, 2h in H2), RuO2 is fully reduced to metallic Ru (JCPDS 06-0663, Fig 2A) and the estimated crystallites sizes of Ru from the (101) (102) (103) planes at 44.01°, 58° and 78° 2θ,resulted to be 7.2 and 6.5 nm for RuAl and S-RuAl respectively. The determination of the crystallite sizes from XRD was carried out after subtraction of the support contribution, previously stablished by an appropriate deconvolution process with the X'Pert High Score software, assuring the meaning and accuracy of the measure.

Although small, the changes in the average crystalline domain are significant. They suggest that the slurry preparation drives to an alteration of the size of supported ruthenium. The previous milling of the powder catalyst and the concurrence of the presence of the additive PVA (with reductant character), an aqueous and acidic media, the stirring and the final thermal treatment (drying and calcination) could result in dissolution-reprecipitation or any other processes of modification of the ruthenium species. Those change the average and distribution of sizes of the metallic particles of S-RuAl from the original powder RuAl. These assumptions are confirmed by TEM analyses (Fig. 3). In this case representative TEM micrographs of the reduced powder samples as well as the ruthenium particle size distribution histograms are shown. RuAl sample presents an average Ru size of 6.8 nm, while that of S-RuAl results to be 7 nm. The values are very similar to those calculated from XRD, although the mean size determined by TEM for S-RuAl is higher than that of RuAl, the opposite trend that XRD one. This must be related with the differences in the particle evaluation method in each technique. However, despite the higher calculated average size, S-RuAl sample has a higher proportion of smaller metallic particles (lower than 4 nm).

Fig. 2B shows the XRD results for the structured catalyst (M-RuAl). For comparative purposes, those of bare and pretreated metallic substrate before catalyst deposition are also shown. Un-treated Fecralloy micromonolith shows the characteristic peaks of the martensitic structure (JCPDS 34-0396). After thermal pre-treatment, diffractions due to corundum α-Al2O3 (JCPDS 34-0306) and YAlO3 (JCPDS 10-0425) phases appear. This thermal treatment generated α-alumina layer that is the responsible of the increment of the surface roughness (from 0.9 μm to 2.7 μm), which helps the physical anchoring of the catalyst. Obviously, its chemical compatibility with the RuAl catalyst also favors the deposition. Previous studies have demonstrated that this oxide layer is formed by randomly oriented alumina whiskers with a thickness of about ≈ 3 μm and is generally accepted to be an excellent substrate to adhere catalysts [54,56].

The diffraction pattern of the micromonolithic catalysts (Fig. 2B) confirms the successful deposition of the catalyst, showing the characteristic peaks of the S-RuAl sample simultaneously with those of the pretreated metallic substrate. After reduction treatment, the RuO2 is also reduced to metallic ruthenium (not shown). The estimated crystalline domain size of RuO2 and Ru were 10.5 nm and 7.0 nm, respectively, intermediate values between those obtained for RuAl and S-RuAl powder catalysts. Again, the small differences points to a different degree of modification of ruthenium sizes because of the influence of the metallic substrate in the washcoating procedure and from the slurry preparation.

The N2 adsorption–desorption isotherms of the powders and micromonolith catalysts are shown in (Fig. 4). Table 1 summarizes the textural properties of the samples. All of them show similar isotherms characteristics of mesoporous materials (type IV with H2 hysteresis loop) with complex and heterogeneous size structures having average pore radius of 6.0, 7.5 and 7.0 nm for RuAl, S-RuAl and M-RuAl respectively. A small increment in the textural properties of the S-RuAl and M-RuAl catalysts with respect to those of the parent RuAl was noticed, which is assigned to the presence of the additional alumina Nyacol. In fact, the increment matches the theoretical one calculated assuming the additional amount of alumina added (6.28 wt.%) and its textural properties (see table 1).

The homogeneity of the S-RuAl coating onto the metallic substrate was confirmed by SEM observations (Fig. 5), where crack and spalling phenomena are not visible. The adherence of the catalyst was excellent. In this case 96 wt.% of the layer was preserved after adherence test. The mapping and in-line cross section in-depth compositional EDX analyses (Fig 6 and Fig. 7) confirm the presence of the α-alumina layer below the RuAl coating. The RuAl layer penetrates deep in the α-alumina layer reaching the oxide–alloy interface. Thereby, EDX analysis confirms that deposited RuAl is not confined at the more external surface, penetrating through the oxide scale of the substrate. Similar results have been described for CeO2 and Au/CeO2 catalysts deposited on fecralloy micromonoliths [54]. This observation impedes the correct evaluation of the coating thickness from the direct measurement of the cross section SEM micrographs. Despite this, an estimative value in the 4-to-7 μm range could be obtained. A second approach to calculate the average catalytic thickness is taking into account the estimated volume of the layer [56]. This can be estimated from the amount of coating (138.3 or 147.3 mg in our case), the total surface of the metal sheet (540 cm2), the density of the coating calculated from the pore volume (M-RuAl, 0.37 cm3/g) and the apparent density of the deposited solid (4.3 g/cm3). The average thickness obtained was ≅ 1.6 μm, a bit far of that calculated from SEM. Probably, an intermediate value is the more representative one of the average thickness of the coating. In any case, the catalytic layer thickness of the micromonoliths is small and we can discard, in principle, any mass transfer limitations produced during reaction [56-57].

Finally, no Fe and Cr diffusion from the stainless steel substrate to the catalytic layer was detected by EDX, even in the reacted micromomoliths, only the migration of aluminium oxide to the catalytic layer could be considered. In some cases, and specially under demanding reaction conditions, the migration of chromium and other metal cations from the fecralloy substrate to the catalytic coating have been reported in micromonolithic catalysts [54-55], resulting in a modification of the composition and catalytic performances of the bare catalyst.

The H2-TPR profiles of the RuAl , S-RuAl and M-RuAl are presented in Fig. 8. In both cases a single peak of H2 consumption is observed, directly ascribed to the RuO2 reduction to Ruo. The total reduction of RuO2 species to Ru0 was confirmed by the TPR quantification. The H2 consumptions expressed as mmol of H2 per mg of catalysts were 1.709x10-3 for Ru-Al and 1.703x10-3 for S-RuAl. Those values correspond to ≈ 99% of reducibility of RuO2 species. From Fig. 8 the temperature at which the reduction process proceed is lower for S-RuAl than for RuAl (207 oC vs 225oC). According to the literature, the reduction of RuO2/Al2O3 occurs at temperatures in the 100-230oC range, and varied with the RuO2 crystallite size, in such a way that higher the size, higher the reduction temperature [58-61]. According to these there are two reduction peaks normally described in the literature one at ≈190oC ascribed to well-dispersed ruthenium oxide phase, and the other at ≈223oC, due to bulk RuO2 reduction. Thus, the observed decrease in the reduction temperature of the RuO2 in the slurry compared to the initial powder catalyst agrees with the lower crystallite size of RuO2 determined from XRD, and reinforces the idea of the existence of changes in the ruthenium particle size of the catalysts during the washcoating procedure.

**3.2 Catalytic Activity**

In the conditions of catalytic activity (0.03% CO, 15 % CO2, 50% H2, 15% H2O and N2 as balance, atmospheric pressure) and in the range of temperatures studied (105-270oC), the thermodynamics equilibrium reported the full conversion of CO towards CH4 (Figure not shown). With respect to CO2, its methanation was completed till 195oC. Then, CO2 conversion decreased exponentially with temperature.

Fig. 9A shows the CO (XCO) and CO2 (XCO2) conversions as function of reaction temperature. At the lowest temperature studied (105oC) all catalytic systems have a certain CO methanation activity, being XCO of around 10%. Increasing the temperature drives to an increment in the XCO until arriving a maximum in the 160 - 220 oC temperature range. Further increase of temperature results in a drastic decrease of XCO due to the concurrence of the reverse Water Gas Shift reaction (Eq. 1), thermodynamically and kinetically favored at high temperatures [20].

Powder RuAl catalyst does not achieve total CO conversion, a maximum XCO of 94% was obtained at around 220oC. The slurried catalyst (S-RuAl) is able to completely abate the CO molecules of the reactive stream (XCO=100%) at a lower temperature (160oC). These catalytic activities are comparable to those reported previously for Ru/Al2O3 systems [62] and at much lower temperatures that other similar Ru catalysts [39, 49, 51]. The structured catalysts present a catalytic behavior similar to that of the S-RuAl powder, although showing the appearance of the consequences of the R-WGS reaction (decay of the XCO) at a bit higher temperatures.

For all solids, CO2 methanation is practically zero at temperatures up to ca. 180oC. Then, it progressively increases with the temperature (Fig. 9A). The CO2 conversion starts when, at least, a 70% of CO is methanated. This behavior reflects that CO interacts more strongly with the catalyst surface at low temperatures, compared to CO2. Similar results have been also observed for similar catalysts [43]. As long as CO remained in the syngas, methanation of CO2 is completely retarded.

The selectivity of the CO methanation against CO2 methanation is shown in Fig. 9B. It is clear that S-RuAl presents the best selectivity. Powder RuAl sample is the less selective, meanwhile the micromonolithic systems present an intermediate behavior, although more similar to that of S-RuAl. This selectivity can be also evaluated considering the temperature range in which the CO concentration in the outstream is less than 20 ppm (more than 93.3% of CO conversion) and the total consumption of H2 is under 4% (implying a CO2 conversion lower than 3.2%), see figure 9A. This optimal range of working temperatures is 149-239°C for S-RuAl, 165-232 °C for the micromonoliths and 217-226°C for the powder RuAl. Further increase in temperature favors the reverse Water Gas Shift reaction, thermodynamically and kinetically favored at higher temperatures. Due to CO2 methanation activity, the temperature window was shifted toward higher temperatures, simultaneously with a decreasing of the width of the temperature window of selectivity. Tada *et. al* [65] observed a similar behavior with similar Ru supported Al2O3 and TiO2. In this case CO concentration and CO2 conversion were less than 500 ppm and 1%, respectively for the optimal range of working temperatures. Echigo and Tabata [38] reported that the CO concentration below 10 ppm could be obtained only by multi-stage CO methanation over Ru/γ-Al2O3.

To favor the selective CO methanation in Ru catalysts Fujita *et. al* [63] studied the competitive methanation in a mixed 10 vol% CO and 10 vol% CO2 in balance H2 with Ru/SiO2 catalyst. They observed that CO2 methanation rate at 200oC is 4.6 times faster than the CO methanation rate. Over *et. al* [64] pointed out that changing the CO/CO2 ratio in the gas feed to higher values than 2:1 will deteriorate the overall activity due to blocking the surface by CO molecules. These facts have strongly indicated that when more highly active catalysts are used the preferential methanation of CO could be achieved prior to CO2 methanation at lower temperature range, and also that the ratio CO/CO2 must be carefully adjusted. Even though most previous works were conducted with rather low inlet CO concentration below 0.5 vol%, the acceptable CO concentration below 10 ppm was not be obtained.

In the current study the changes in the activity and selectivity of the CO methanation reaction observed among the considered catalysts can be related with the observed changes in the ruthenium particle size, as evidenced by TPR, XRD and TEM results, that modify the metal-support interaction. In this sense, it is well reported that methanation reactions are size-dependent ones. Despite works that state that CO methanation is enhanced by increasing crystallite size of the metal [20,45,49-50], some studies find the opposite [37,65]. Takenaka *et. al.* [37] proposed Ru/TiO2 as promising catalysts based and concluded that smaller Ru particles were plausible for the high catalytic activity. In our case, we observe that both, the CO conversion and the selective operating temperature range, increase with the lower ruthenium particle size of Ru. As proposed above, the modification of the ruthenium dispersion is probably produced during the washcoating process, caused by the presence of additives (PVA and colloidal alumina), the acidic aqueous media and the subsequent additional thermal treatment. All of this can drive to a surface structural reorganization of the metal. However, the change in the ruthenium dispersion and metal-support interaction is not probably the only responsible of the changes in the catalytic activity, and the presence of additional hydroxyl groups in the slurry, coming from the colloidal alumina added, could also play a determinant role, making the slurry more active and selective than the parent powder. A detailed *in-situ/in-operando* FTIR study is currently under realization in order to gain insights in the mechanistic aspects of our results. The presence of the metallic substrate also alters the final ruthenium dispersion, the structured systems presenting intermediates values of activity between those of the S-RuAl and the raw RuAl. From here, the structuration of the RuAl powder sample on stainless steel micromonoliths not only is possible but also drives to more active and selective systems. Thus, it would be promising and practical to explore the application of Ru catalyst in micromonoliths reactors to realize methanation reaction. This might open more opportunities for the reliable engineering applications of microchannel systems.

**4. Conclusions**

The results of the present study show that the deposition of RuO2/Al2O3 powder catalysts on stainless steel micromonoliths is possible. Active and selective systems for CO methanation using a flow simulating CO2-rich reformate gases from WGS and PROX units (H2 excess, CO2 presence and 300 ppm CO concentration) were obtained. The slurried RuO2/Al2O3 was active and selective for CO methanation as well. The changes in the activity and selectivity observed have been related to the observed changes in the ruthenium dispersion and its reducibility as was confirmed by TPR, XRD and TEM characterization.

The metallic substrate in the washcoating procedure and the slurry preparation affected the ruthenium particle size. Thereby, the presence of PVA and colloidal alumina, the acidic aqueous media and the thermal treatment favored the surface structural reorganization of the metal towards more active catalysts. This was confirmed when the optimal range of working temperatures in which the CO concentration in the outstream is less than 20 ppm (more than 93.3% of CO conversion) and the total consumption of H2 is under 4% (implying a CO2 conversion lower than 3.2%) was compared. Thus, it was shifted to lower temperatures when S-RuAl and M-RuAl were used. In those cases the optimal ranges of working temperatures were from 149°C to 239°C for slurried catalysts and from 165°C to 232 °C for the micromonoliths, whilst it was from 217°C to 226°C for the RuAl powder. Further increase in temperature resulted in a drastic decrease of CO conversion due to the concurrence of the reverse Water Gas Shift reaction, thermodynamically and kinetically favored at higher temperatures.

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**Fig. 1.** Weight gain comparison between two micromonoliths before calcination

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**Fig. 9** (A) CO (solid lines) and CO2 (dash lines) conversions during selective CO methanation with powders and micromonolithic catalysts. The selective temperature range, where less than 20 ppm CO is emitted with a total H2 consumption lower than 4% is also shown. (B) Selectivity towards CO methanation vs CO conversions. Feed composition: 0.03%CO, 15% CO2, 50%H2 (balance N2); WHSV: 80000 ml.g-1.min-1

**List of Table**

**Table 1:** Textural properties of studied samples

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