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# The phenol steam reforming reaction over MgO-based supported Rh catalysts

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### Abstract

The phenol steam reforming reaction toward H<sub>2</sub> formation has been investigated in the 575–730 °C range over MgO, CeO<sub>2</sub>, and ZrO<sub>2</sub> single metal oxides and various mixed metal oxides such as Mg-Ce-O, Mg-Zr-O, and Mg-Ce-Zr-O, all prepared by the sol-gel method. The same reaction has also been studied over Rh supported on these metal oxides. The effects of synthesis method of the Mg-Ce-Zr-O support (mechanical mixing versus sol-gel) and of Rh deposition (wet impregnation versus sol-gel) on the activity and H<sub>2</sub> selectivity of the reaction over the Rh/Mg-Ce-Zr-O catalyst have also been investigated. It was found that 0.5 wt% Rh/MgO and 0.1 wt% Rh/Mg-Ce-Zr-O catalysts, the supports of which were prepared by the sol-gel method, exhibit better performance when compared to a commercial Ni-based catalyst used for tar steam reforming. In particular, Rh/MgO presented the highest H<sub>2</sub> product concentrations and selectivities in the 575-730 °C range and no more than 20% drop in activity after 24 h of continuous reaction (0.5% C<sub>6</sub>H<sub>5</sub>OH/40% H<sub>2</sub>O/He). It was found that steam reforming of phenol is favored over very small Rh particles in the case of 0.1 wt% Rh/Mg-Ce-Zr-O catalyst. In particular, the specific integral reaction rate of  $H_2$  production (mmol- $H_2/(m_{Rh}^2 s)$ ) significantly increased by decreasing the Rh particle size from 2.7 to 1.2 nm. The effect of the partial pressure of water and phenol in the feed stream on catalyst activity was found to strongly depend on support chemical composition. More than one kind of carbonaceous species forming during reaction has been identified with varying compositions and reactivities toward oxygen and steam. XPS studies suggested that the  $Mg_{x}Zr_{1-x}O_{2}$  phase present in the Mg–Ce–Zr–O support is reduced by H<sub>2</sub> at 300 °C in the presence of very small Rh particles leading to the creation of oxygen vacant sites and diffusion of Zr toward the bulk of the crystal. As a result of this, the surface acidity and basicity of the Rh/Mg-Ce-Zr-O catalyst are expected to alter, thus influencing the hydrogen activity and selectivity of the reaction.

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### 1. Introduction

Nowadays, there is an increasing interest in the use of renewable energy sources in order to gradually substitute in part fossil fuels. The production of a hydrogen-rich gas (an energy carrier) is expected to play an important role toward high-purity hydrogen demands in small units for fuel cell applications [1,2]. Currently, growth in hydrogen demand is exceeding the growth in overall energy consumption. This

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growth is being driven by the needs of the refining industry to produce low-sulfur fuels and increase conversion capacity [3].

Hydrogen production is being carried out by several approaches, such as steam reforming [4], electrochemical [5], photochemical [6], biological [7] and thermochemical (thermal conversion of biomass) [8,9]. The use of biomass as an energy source leads to decreasing emissions of CO<sub>2</sub>, NO<sub>x</sub>, SO<sub>x</sub>, and particulate matter into the atmosphere [10]. The production of syngas for power generation and chemicals following gasification of biomass appears to be the main effort for meeting the goal for a biomass-based energy tech-

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nology [11–13]. Steam is one of the most commonly used gasification agents due to the high hydrogen content obtained in the product gas [14].

The formation of tar (a complex mixture of organic liquid constituents) and char (solid carbonaceous materials) is the most severe problem faced in a biomass gasification process [13,15]. Most of the efforts in biomass gasification are focused on the extensive cleanup of product gas [16]. The biomass-derived tar (contaminant in the product gas) is volatile and is known to be very harmful due to deposition on surfaces, filters, heat exchangers, and engines, thus reducing component performance and increasing maintenance requirements [17]. The product of biomass gasification contains about 5.0 wt% of phenolic compounds [18,19].

Despite the large number of research works concerning the production of hydrogen through steam reforming of aliphatic hydrocarbons [20–23], steam reforming of aromatic compounds other than benzene and toluene [24,25] has not been yet studied to a great extent. Steam reforming has been studied over supported precious metal catalysts for methane [1,26], ethane, *n*-butane and *n*-hexane [20], *n*-octane [20,22], cyclohexane, benzene, and toluene [20]. In addition, steam reforming of polycyclic aromatic compounds like naphthalene, anthracene, and pyrene has been studied over supported Ni catalysts [18], while steam reforming of industrial naptha was studied over dealuminated zeolite-based catalysts [25,27,28].

The widely used industrial catalysts for steam reforming are supported Ni catalysts. It has been reported [18,29] that for higher or aromatic hydrocarbons coke formation is a major problem on Ni-based catalysts. On the other hand, coking can be greatly suppressed by using supported noble metal catalysts. However, the high cost of noble metals necessitates the synthesis of appropriate catalytic systems with high TOFs in order to allow reduction of the metal loading used. It has been reported [30] that suppression of carbon formation is accomplished by decreasing the surface acidity of the catalyst. Also, the addition of basic oxides on the carrier increases the rate of carbon gasification due to the increased adsorption of water [30]. It has been reported [31,32] that an increase of the MgO content in support composition causes prolongation of the induction time during which practically no formation of carbon takes place. This is one of the reasons that MgO consists as part of the support chemical composition for many industrial catalysts.

The present work concerns catalytic and transient reaction studies of the steam reforming of phenol on various MgO-based supported Rh catalysts in the 575–730 °C range. The selection of phenol as a model compound of tar was based on experimental results of wood gasification by steam in a fluidized bed reactor in which phenol and toluene were the two main components of tar formation [33]. The present work is a continuation of our previous work of the phenol steam reforming over various other supported Rh catalysts [34] and provides for the first time fundamental information on the effects of (a) reaction temperature, (b) support composition, (c) Rh loading (wt%), (d) feed concentration of phenol and water, and (e) synthesis method of supported Rh catalysts on their catalytic performance toward the steam reforming of phenol to produce H<sub>2</sub>. Catalytic results on a commercial supported Ni catalyst were also obtained for a critical comparison.

# 2. Experimental

# 2.1. Catalyst preparation

Magnesia, ceria, and zirconia single metal oxides and Mg–Zr–O, Mg–Ce–O, and Mg–Ce–Zr–O mixed metal oxides, the crystal structures of which were determined by XRD and will be presented in a following section, were prepared by the sol–gel method. Mg(OEt)<sub>2</sub>, Ce(NO<sub>3</sub>)<sub>2</sub>, and ZrOCl<sub>2</sub> · 8H<sub>2</sub>O (Aldrich) were used as precursors of Mg, Ce, and Zr, respectively. For CeO<sub>2</sub> and ZrO<sub>2</sub> synthesis, appropriate amounts of cerium nitrate and zirconium oxychloride, respectively, were dissolved in distilled water and the solution pH was adjusted to the value of 9.0 by dropwise addition of ammonia solution. The solution was kept at 60 °C for 6 h until a viscous yellow and white gel, respectively, was obtained.

The preparation procedure of MgO and MgO-based mixed metal oxides was as follows. Appropriate amounts of magnesium ethoxide were dissolved in an ethanol/water (6/4 v/v) solvent mixture, while those of cerium nitrate and zirconium oxychloride were dissolved in distilled water. For the synthesis of mixed metal oxides, appropriate amounts of each solution were mixed together so as to obtain the appropriate Mg/Zr/Ce atom ratio. The resulting solution was kept at 60 °C for 6 h until viscous white (MgO, Mg–Ce–O) and yellow-like (Mg-Zr-O, Mg-Ce-Zr-O) gels were obtained. After synthesis and drying procedures (overnight at 120 °C), all solids were calcined in air at 750 °C for 4 h, cooled slowly to room temperature, and stored for further use. A reference to a support chemical composition in the rest of the text will be according to the following example. A 50Mg-25Ce-25Zr-O mixed metal oxide will be referred to that having a metal atom composition of 50% Mg, 25% Ce, and 25% Zr.

The supported Rh catalysts were prepared by the incipient wetness impregnation (IWI) method using Rh(NO<sub>3</sub>)<sub>3</sub> (Aldrich). A given amount of precursor solution corresponding to the Rh loading of interest was used to impregnate the metal oxide support in powder form at 40 °C. After impregnation and drying (T = 120 °C), the obtained solid was calcined in air at 600 °C for 2 h and stored for further use. Prior to any catalytic tests, the fresh sample was reduced in pure H<sub>2</sub> at 300 °C for 2 h.

The 0.1 wt% Rh/50Mg–25Ce–25Zr–O catalytic system was prepared by three different ways:

- (a) The support was prepared by the sol-gel method (SG), while Rh was deposited following the IWI method; coded as SG-IWI.
- (b) The support was prepared by mechanical mixing. Weighted amounts of MgO, CeO<sub>2</sub>, and ZrO<sub>2</sub> (Aldrich) corresponding to the desired composition were placed in a glass beaker containing deionized water and heated to 60 °C under continuous stirring. After drying, the solid was impregnated with Rh at 60 °C and the slurry obtained was dried at 120 °C overnight; coded as *MM-IWI*.
- (c) A weighted amount of Mg(OEt)<sub>2</sub> was added to a solvent mixture of water and ethanol (6/4 v/v), while weighted amounts of Ce(NO<sub>3</sub>)<sub>3</sub> and ZrOCl<sub>2</sub> were each dissolved in distilled water. The three solutions were then mixed together. An appropriate amount of Rh(NO<sub>3</sub>)<sub>3</sub> was dissolved in acetone at 40 °C, and the resulting Rh solution was added to the solution containing the three metals of support composition. A solution consisting of H<sub>2</sub>O and methanol (1/10 v/v) was added to the solution that contained the three support metal precursors and the Rh. The resulting mixture was then stirred at 60 °C for 10 h and the gel obtained was dried at 120 °C for 10 h. This synthesis procedure was similar to that reported [35]; coded as *SG*.

### 2.2. Catalyst characterization

# 2.2.1. Surface area and Rh metal dispersion measurements

The specific surface area  $(m^2 g^{-1})$  of the fresh and some used supported Rh catalysts, the supports of which were prepared by the sol-gel method, was checked by N<sub>2</sub> adsorption at 77 K (BET method) using a multipoint Fisons Sorpty 1900 System. Before any measurements were taken, the samples were outgassed at 400 °C under vacuum ( $P \sim 1.3 \times 10^{-3}$  mbar) overnight.

The dispersion of Rh metal was determined by  $H_2$  chemisorption followed by TPD in He flow according to the following procedure. The catalyst was first calcined in 20% O<sub>2</sub>/He at 600 °C for 2 h and then reduced in 20% H<sub>2</sub>/He at 300 °C for 2 h. Following reduction, the catalyst was heated to 500 °C in He flow to desorb any H<sub>2</sub> that might had been spilled over the support. The catalyst was then cooled in He to 200 °C. The feed was then switched to a 2% H<sub>2</sub>/He gas mixture for 30 min. After this adsorption step, the catalyst was cooled in 2% H<sub>2</sub>/He to room temperature and left for 15 min. The feed was then switched to He for 15 min, after which no H<sub>2</sub> signal in the mass spectrometer was observed, and the temperature of the catalyst was increased to 700 °C to carry out a temperature-programmed desorption (TPD) experiment.

### 2.2.2. XRD analyses

The crystal structures of the fresh single metal oxides (CeO<sub>2</sub>, ZrO<sub>2</sub>, MgO) and of the mixed metal oxides (Mg–Ce– O, Mg–Zr–O, and Mg–Ce–Zr–O) prepared by the sol–gel method were checked by XRD (Shimadzu 6000 series) after employing Cu $K\alpha$  radiation ( $\lambda = 1.5418$  Å).

#### 2.2.3. SEM studies

The particle size and surface morphology of supports of some of the supported Rh catalysts were examined using a JEOL JSM 5200 scanning electron microscope (25 kV). Powdered specimens were spread on the SEM slabs and were sputtered with gold.

### 2.2.4. TEM and HRTEM studies

TEM studies were performed on the Rh/CeO<sub>2</sub>, Rh/ZrO<sub>2</sub>, Rh/50Mg–50Ce–O, and Rh/50Mg–50Zr–O fresh catalysts (0.5 wt% Rh). All fresh catalysts were calcined in air at 600 °C for 2 h and then reduced in H<sub>2</sub> at 300 °C for 2 h before TEM measurements were performed. A 5-mg powder sample was dispersed in 1 ml of ethanol/water mixture (1/1 v/v) and kept in an ultrasonic bath for 3 h. The sample was then deposited onto a carbon-covered copper grid and dried at 25 °C. The instrument used was a JEOL 1010 electron microscope operated at an acceleration voltage of 80 kV.

The specimens for high-resolution transmission electron microscopy (HRTEM) analyses were prepared from powders of samples following conventional crushing in an agate mortar and dispersing the powder in acetone. They were then placed on holey carbon microgrids. Micrographs were taken using a JEOL-JEM-300F field emission electron microscope operated at 200 kV.

#### 2.2.5. X-ray photoelectron spectroscopy studies

X-ray photoelectron spectroscopy (XPS) experiments were conducted on a VG Escalab 200 R spectrometer equipped with a hemispherical electron analyzer and an Mg*K* $\alpha$  (1253.6 eV) X-ray source. The XPS spectrometer was equipped with a chamber for sample treatments under controlled gas atmospheres and at temperatures lower than 700 °C. A certain region of the XPS spectrum was scanned a number of times in order to obtain a good signal-to-noise ratio. The binding energies (BE) were referenced to the C 1s peak (103.4 eV) as internal standard to take into account charging effects.

### 2.3. Catalytic studies

The experimental apparatus used for evaluating the catalytic performance of supported Rh solids and their supports alone for the phenol steam reforming has been described in detail elsewhere [34]. A 0.3-g catalyst sample in particle form (d = 0.2-0.3 mm) was loaded into the reactor. The total gas flow rate used was 200 N mL/min (GHSV ~ 80,000 h<sup>-1</sup>). The following reaction scheme can be considered to describe the steam reforming of phenol reaction [13,18,36]:

$$C_6H_5OH + 5H_2O \to 6CO + 8H_2,$$
 (1)

$$CO + H_2O \leftrightarrow CO_2 + H_2.$$
 (2)

The conversions  $X_1$  and  $X_{WGS}$  associated with reactions (1) and (2), respectively, can be estimated according to our recent publication [34]. Hydrogen selectivity parameters are defined according to the following two relationships:

$$S_{\rm H_2}^{\rm I} = \frac{y_{\rm H_2}}{y_{\rm H_2}^{\rm th}},$$
 (3)

$$S_{\rm H_2}^{\rm II} = \left[\frac{F_{\rm T} y_{\rm H_2}}{6(F_{\rm T}^{\rm f} \times y_{\rm C_6H_5OH}^{\rm f})}\right] \frac{1}{2.33},\tag{4}$$

$$y_{\rm H_2}^{\rm th} = \frac{8}{6}y_{\rm CO} + \frac{14}{6}y_{\rm CO_2}.$$
 (5)

In Eqs. (3)–(5),  $y_{H_2}$  is the measured mole fraction of hydrogen at the exit of the reactor,  $y_{C_6H_5OH}^{f}$  is the mole fraction of phenol in the feed,  $F_{\rm T}^{\rm f}$  is the total feed molar flow rate (mol/min),  $F_{\rm T}$  is the total molar flow rate at the exit of the reactor (mol/min),  $y_{H_2}^{th}$  is the theoretical mole fraction of H<sub>2</sub> produced exclusively by reactions (1) and (2), and  $y_i$  is the mole fraction of component *i* in the exit gas product stream of reactor. In Eq. (4), the value of 2.33 represents the maximum ratio of moles of H<sub>2</sub> per mole of C in phenol obtained via the network of reactions (1) and (2) when all phenol in the feed is converted to  $CO_2$  and  $H_2$ . Thus,  $S_{H_2}^{II}$  is a selectivity parameter relative to the maximum theoretical production of hydrogen that could be obtained. In Eq. (5), the coefficients 8/6 and 14/6 represent the correspondence of 1 mol of hydrogen to that of CO and CO<sub>2</sub> produced, respectively, based on the network of reactions (1) and (2). The  $S_{\text{H}_2}^{\text{I}}$  selectivity parameter allows identification of whether reactions other than those described by Eqs. (1) and (2) are present in the reaction network. For example, hydrogenation of phenol to form benzene would make  $S_{H_2}^{I}$  to take values lower than unity.

The carbon mass balance was checked in several experimental runs and it was found to be close within 5%. However, it was not possible to perform a reliable hydrogen mass balance due to the high  $H_2O$  content used in the feed and the fact that water was removed by condensation before analysis of the reactor effluent stream [34].

# 2.4. Characterization of carbonaceous deposits by transient experiments

The amount and reactivity toward oxygen and steam of carbon-containing intermediate species that had been accumulated on the surface of x wt% Rh/50Mg–25Ce–25Zr–O (x = 0.1, 0.5) catalysts after used in phenol steam reforming were studied by two different transient experiments. In the first experiment, following reaction (0.5% C<sub>6</sub>H<sub>5</sub>OH/40% H<sub>2</sub>O/He) at 655 °C for 3 h, the catalyst was heated to 800 °C in He flow to remove adsorbed water, CO<sub>2</sub>, and/or carbonaceous deposits that could thermally be decomposed in He flow. The reactor was then cooled quickly in He flow to room

temperature and the gas flow was switched to a 2% O<sub>2</sub>/He gas mixture for a temperature-programmed oxidation (TPO) experiment ( $\beta = 30 \text{ °C/min}$ ).

In the second transient experiment, the reactivity of accumulated carbonaceous species toward steam was studied isothermally. After reaction at 655 °C for 3 h, the feed was changed to He until H<sub>2</sub>, CO, and CO<sub>2</sub> mass spectrometer signals reached practically their respective baseline value. The feed was then switched to a 40% H<sub>2</sub>O/2% Ar/He gas mixture and the H<sub>2</sub> (m/z = 2), CO (m/z = 28), and CO<sub>2</sub> (m/z = 44) signals were recorded continuously by on-line mass spectrometer. Quantification of the CO and CO<sub>2</sub> signals was made after accounting for the contribution of CO<sub>2</sub> to the 28 signal and using standard calibration gas mixtures in He diluent gas for the CO and CO<sub>2</sub>. Transient experiments were conducted in a specially designed gas-flow system that has been described elsewhere [37].

#### 3. Results and discussion

# 3.1. Catalyst characterization

# 3.1.1. BET surface area measurements

The specific surface areas (BET,  $m^2 g^{-1}$ ) of the fresh Rh/MgO, Rh/CeO<sub>2</sub>, Rh/ZrO<sub>2</sub>, and Rh/MgO-based catalysts, the supports of which were prepared by the sol-gel method, are listed in Table 1. The fresh catalysts (calcined at 750°C for 4 h after synthesis) had been recalcined in air at 200 °C for 2 h before BET measurements were taken. In the case of Rh/50Mg-50Ce-O, a relatively high surface area was obtained (79.8  $m^2 g^{-1}$ ), a result that is in harmony with SEM studies performed (a fine microcrystal structure is obtained (see Section 3.1.3). Settu [38] has reported the synthesis of a 93 mol% MgO-7 mol% ZrO2 mixed oxide with a BET area of 22 and 6 m<sup>2</sup> g<sup>-1</sup> after calcination at 600 and 850 °C, respectively. Also, Burch and Loader [39] have synthesized by the sol-gel method a 1 wt% Rh/ZrO2 catalyst with a BET area of  $12 \text{ m}^2 \text{ g}^{-1}$  after calcination at 700 °C. In the case of Rh/50Mg-50Ce-O and Rh/50Mg-25Ce-25Zr-O solids, after phenol steam reforming in the 575–730 °C range for 3 h, the former solid showed a significant decrease in its BET area, while the latter showed practically a constant value (Table 1). In our previous study [34] it was reported that the 50Ce-50Zr-O solid (Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> the main crystal phase) after treatment with 40% H<sub>2</sub>O/He at 655  $^{\circ}$ C for either 3 h or 24 h did not show any BET surface area loss and changes in its crystal structure. The same result is obtained with the 50Mg-25Ce-25Zr-O solid but not with the 50Mg-50Ce-O one. The presence of  $Ce_x Zr_{1-x}O_2$  solid solution (see Section 3.1.3) as one of the main crystal phases in the 50Mg-25Ce-25Zr-O solid seems to be the reason for this behavior. On the contrary, Choudhary and co-workers [40,41] have observed an increase of the BET area of LaCoO<sub>3</sub> by a factor of 2.5 and reduction of its crystal size by a factor of 2.7 after steam treatment at 800 °C.

Table 1					
Textural and	structural	properties	of	suppoted-Rh	catalyst

•		
BET (fresh) <sup>a</sup> $(m^2 g^{-1})$	BET (used) <sup>b</sup> $(m^2 g^{-1})$	SEM d (um) of support
( 8 /	( 8 )	
79.8	43.8	9–30
11.1	_	9–45
30.5	29.1	9–15
27.7	-	_
22.1	_	_
23.0	_	_
	BET (fresh) <sup>a</sup> (m <sup>2</sup> g <sup>-1</sup> ) 79.8 11.1 30.5 27.7 22.1 23.0	BET (fresh) <sup>a</sup> BET (used) <sup>b</sup> $(m^2 g^{-1})$ $(m^2 g^{-1})$ 79.8     43.8       11.1     -       30.5     29.1       27.7     -       22.1     -       23.0     -

The supports were prepared by the sol-gel method.

<sup>a</sup> After synthesis the solid was calcined in air at 750 °C for 4 h.

<sup>b</sup> After phenol steam reforming reaction in the 575–730 °C range for 3 h.



Fig. 1. X-ray diffraction patterns of (a) 50Mg–25Ce–25Zr–O (fresh); ZrO<sub>2</sub> (fresh); CeO<sub>2</sub> (fresh); (b) and (c) 0.1 wt% Rh/50Mg–25Ce–25Zr–O fresh and used (after 24 h in phenol steam reforming reaction at 700 °C) catalysts. All support materials were prepared by the sol–gel method.

# 3.1.2. X-ray diffraction studies

Fig. 1a presents XRD patterns of 50Mg-25Ce-25Zr-O mixed metal oxide and  $ZrO_2$  and  $CeO_2$  single metal oxides, all prepared by the sol-gel method. At the applied synthesis conditions of 50Mg-25Ce-25Zr-O, introduction of  $Zr^{4+}$  cations within the ceria crystal lattice was favored, which led to a  $Ce_xZr_{1-x}O_2$  solid solution according to ASTM data (peaks marked as 1 in Fig. 1a). The peaks appear broader and slightly shifted when compared to those observed in pure CeO<sub>2</sub>. These features are in harmony with previous publications [42–44]. In addition, diffraction peaks corresponding to a  $Mg_xZr_{1-x}O_2$  solid solution (marked as 3 in Fig. 1a) were also observed after deconvolution of the double peak (marked as 1, 3) shown in Fig. 1a. XRD peaks corresponding to MgO (marked as 2) but not to  $ZrO_2$  have been observed.

Figs. 1b and c present XRD patterns of the fresh and used 0.1 wt% Rh/50Mg-25Ce-25Zr-O catalysts, the latter corresponding to a 24-h run of the phenol steam reforming reaction at 700 °C. The appearance of slightly narrower peaks (by  $0.2^{\circ} 2\theta$ ) in the fresh than the used catalyst indicates that there was a small decrease in the particle size of  $Ce_xZr_{1-x}O_2$  and  $Mg_xZr_{1-x}O_2$  (Fig. 1b) and MgO (Fig. 1c) supports after 24 h of continuous reaction. A similar result was also seen in the 45–65°  $2\theta$  range in the X-ray diffractogram (not shown here). The change in support crystal size is suggested to be due to the presence of a large concentration of water in the feed, in agreement with previous studies reported in the literature [34,40,41]. The X-ray diffraction profiles of 50Mg-50Zr-O and 50Mg-50Ce-O solids obtained but not presented here revealed the following. In the case of the former solid, an  $Mg_xZr_{1-x}O_2$  solid solution was obtained (broader and slightly shifted peaks compared to pure ZrO<sub>2</sub>). Also, main diffraction peaks corresponding to pure MgO but not to ZrO<sub>2</sub> were observed. In the case of 50Mg-50Ce-O solid, main diffraction peaks corresponding to single MgO had been observed (lower intensities compared to those appeared in the XRD pattern of pure MgO). In addition, diffraction peaks slightly shifted from those corresponding to pure CeO<sub>2</sub> had also been observed. Introduction of Mg<sup>2+</sup> into CeO<sub>2</sub> would result in the formation of oxygen vacancies since Mg<sup>2+</sup> is of lower valence than  $Ce^{4+}$  [45]. However,  $Mg_x-Ce_{1-x}O_2$  solid solution is not thermodynamically stable [46] but the presence of  $Mg^{2+}$  at interstitial positions in the ceria lattice under nonequilibrium conditions cannot be excluded [46].

# 3.1.3. SEM-EDX studies

Fig. 2a presents a scanning electron microscopy (SEM) photograph obtained on the fresh 0.5 wt% Rh/50Mg–25Ce–25Zr–O catalyst. The particle size of the 50Mg–25Ce–25Zr–O support crystals was found to be between 9 and 15  $\mu$ m with mainly a rod-like morphology, while larger particle sizes (9 < *d* < 30  $\mu$ m) with a spherical-like morphology were observed for the 50Mg–50Ce–O support crystals. EDX microanalyses had indicated no significant changes in chemical composition. The particle size of the 50Mg–50Zr–O support crystals (not presented here) was found to be between 9 and 45  $\mu$ m. Table 1 summarizes the SEM results obtained.

# 3.1.4. Rh metal dispersion and particle-size measurements

Based on the amount of adsorbed hydrogen ( $\mu$ mol-H/g<sub>cat</sub>) estimated from the H<sub>2</sub> TPD experiments (see Section 2.2.1) and the metal loading (0.5 wt% Rh) used, the dispersion and particle size of Rh can be calculated [47]. Results obtained on six supported Rh catalysts before being exposed to the reforming reaction mixture (fresh) are reported in Table 2. Summarizing, Rh dispersion (0.5 wt% Rh) ranges between 23 and 90% depending on support chemical composition. The estimated Rh dispersions of Rh/CeO<sub>2</sub> and Rh/ZrO<sub>2</sub> catalysts find good agreement with those reported [48,49]. In the case of MgO-based supported Rh catalysts, the estimated Rh dispersion values are somehow higher than those obtained on similar catalysts [50,51].

Figs. 2b and c show HRTEM micrographs obtained on the 0.5 wt% Rh/50Mg-25Ce-25Zr-O catalyst as fresh (Fig. 2b) and after used in phenol steam reforming at 700 °C for 10 h (Fig. 2c). The excellent quality of micrographs obtained allows illustration of a highly dispersed supported Rh catalyst prepared with a mean Rh particle size of 0.5 nm and a narrow particle-size distribution. However, after phenol steam reforming the mean Rh particle size was increased to 2.7 nm. The mean Rh particle size calculated from the HRTEM photographs confirmed the correctness of the H<sub>2</sub> chemisorption results (Table 2). The dispersion of Rh/MgO and Rh/50Mg-25Ce-25Zr-O catalysts used in phenol steam reforming was also checked by H<sub>2</sub> chemisorption. The catalyst was first exposed to a 20% O2/He gas mixture (a temperatureprogrammed oxidation run to 750 °C was applied) in order to remove the carbonaceous deposits accumulated on the catalyst surface. In the case of 0.5 wt% Rh/MgO and 0.5 wt% Rh/50Mg-25Ce-25Zr-O catalysts, after 10 h of reaction at 700 °C the Rh dispersion was found to be 35 and 50%, respectively (Table 2).

# 3.2. Catalytic performance of supported Rh catalysts

### 3.2.1. Effect of support chemical composition

Fig. 3 presents results of the specific integral rate of hydrogen production (mmol- $H_2/(m^2 min)$ ) obtained in the



8 µm





Fig. 2. (a) SEM photograph of 0.5 wt% Rh/50Mg-25Ce-25Zr-O catalyst; (b) HRTEM photograph of fresh 0.5 wt% Rh/50Mg-25Ce-25Zr-O catalyst; (c) HRTEM photograph of used 0.5 wt% Rh/50Mg-25Ce-25Zr-O catalyst.

575-730 °C range over four supported Rh catalysts (0.5 wt% Rh) the supports of which were prepared by the sol-gel method. In Fig. 3, the activity behavior of the corresponding supports alone is also presented. Rh/MgO and Rh/CeO<sub>2</sub> catalysts exhibit the highest specific activity compared to the other catalysts examined. On the other hand, in terms of H<sub>2</sub>

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Catalyst (0.5 wt% Rh)	Rh dispersion (%) H <sub>2</sub> chemisorption	Mean Rh particle size, d (nm) H <sub>2</sub> chemisorption	Rh dispersion (%) TEM/HRTEM	Mean Rh particle size, $d$ (nm) TEM/HRTEM
Rh/MgO	60.0 (35) <sup>b</sup>	1.5 (2.6) <sup>b</sup>	_	_
Rh/CeO <sub>2</sub>	28.0	3.1	25.0	3.4
Rh/ZrO <sub>2</sub>	23.0	3.8	26.0	3.5
Rh/50Mg-50Ce-O	26.0	3.4	23.0	4.0
Rh/50Mg-50Zr-O	45.0	2.0	38.0	2.4
Rh/50MgO-25Ce-25Zr-O	90.0 (50) <sup>b</sup>	$1.2(2.2)^{b}$	41.0 <sup>b</sup>	$0.5(2.7)^{b}$

Table 2 Metal dispersion of fresh<sup>a</sup> supported Rh catalysts measured by H<sub>2</sub> chemisorption, TEM, and HRTEM techniques

<sup>a</sup> After synthesis the solids were calcined in air at 750 °C for 4 h.

<sup>b</sup> After phenol steam reforming reaction at 700 °C for 10 h.

product concentration the Rh/MgO exhibited higher values (e.g., 11.5 versus 9.1 mol% H<sub>2</sub> at 735 °C) than the Rh/CeO<sub>2</sub> catalyst; the maximum theoretical value of H<sub>2</sub> concentration that would be expected via the network of reactions (1)–(2) for the present feed composition and complete conversion of phenol is 11.6 mol%. This result could be explained by considering that a partial coverage of rhodium surface by species generated via reduction of ceria support might have occurred, thus decreasing the number of active Rh sites. This is in harmony with the large difference in reducibility of the present CeO<sub>2</sub> and MgO solids as confirmed by H<sub>2</sub> TPR experiments.

By comparing the catalytic activity of the single metal oxides and of the corresponding supported Rh catalysts (Fig. 3), it appears that the activity of supported Rh is largely due to the presence of Rh metal. In addition, it is clearly illustrated that this specific activity strongly depends on support chemical composition. Fig. 3b shows that 0.5 wt% Rh supported on 50Mg-25Ce-25Zr-O mixed metal oxide presents much higher specific integral rates of hydrogen production compared to Rh supported on 50Mg-50Ce-O. This catalytic activity was found to be the best among the other mixed metal oxides investigated. In terms of H<sub>2</sub> production, 0.5 wt% Rh/50Mg-25Ce-25Zr-O ranks second after the 0.5 wt% Rh/MgO catalyst. Rh supported on MgO, CeO2 and Mg-Ce-Zr-O presents specific integral rates in the 575-730 °C range that do not differ by more than 15% (Fig. 3). This is a significant result from a practical point of view and demonstrates the wide temperature window of operation of these catalytic systems that are able to convert about 65-80% of the hydrogen content of phenol into H<sub>2</sub> gas according to mass balance estimations.

Table 3 reports specific integral hydrogen production rates (mmol-H<sub>2</sub>/(m<sup>2</sup> min)) obtained in the 575–730 °C range over (a) MgO, ZrO<sub>2</sub>, and CeO<sub>2</sub> commercial metal oxides, (b) ZrO<sub>2</sub> and 50Mg–50Zr–O solids prepared by the sol–gel method, and (c) two additional supported Rh catalysts (Rh/ZrO<sub>2</sub> and Rh/50Mg–50Zr–O). The BET areas of the commercial MgO, CeO<sub>2</sub>, and ZrO<sub>2</sub> metal oxides were found to be 150.0, 5.0, and 3.2 m<sup>2</sup> g<sup>-1</sup>, respectively. Ceria prepared by the sol–gel method presents by far the highest activity compared to MgO and ZrO<sub>2</sub> metal oxides, either commercial or lab-synthesized by the sol–gel method. These



Fig. 3. Dependence of specific reaction rate of hydrogen formation (mmol- $H_2/(m^2 min)$ ) on reaction temperature over (a) 0.5 wt% Rh/MgO, 0.5 wt% Rh/CeO<sub>2</sub>, MgO and CeO<sub>2</sub>, and (b) 0.5 wt% Rh/50Mg-50Ce-O, 0.5 wt% Rh/50Mg-25Ce-25Zr-O, 50Mg-50Ce-O, and 50Mg-25Ce-25Zr-O solids. Feed: 0.5% C<sub>6</sub>H<sub>5</sub>OH/40% H<sub>2</sub>O/He; W = 0.3 g;  $F_T = 200$  N mL/min; GHSV  $\approx$  80,000 h<sup>-1</sup>.

results may be related to the enhanced redox properties of  $CeO_2$  to be compared to those of MgO and  $ZrO_2$  [52]. Ceriasupported noble metals have also shown exceptionally high water–gas shift activity due to the redox properties of  $CeO_2$  [53]. In addition, Asadullah et al. [52] have reported that after gasification of cellulose at 823 K in the presence of several metal oxides,  $CeO_2$  was found to exhibit the highest activity toward hydrogen formation.

By comparing the specific activities of all metal oxides reported in Fig. 3 and Table 3, it is more than clear that the reaction rate is not specific to the BET surface area but rather to the intrinsic reactivity of the active sites. This result points

Table 3						
ruble 5		2				
Specific integral H	2 production rates (mmo)	$1/(m^2 min))$ obtained	l on various metal	oxides after phenol s	steam reforming rea	action

Support chemical composition	$R_{\rm H_2} \ (\rm mmol/(m^2 n Temperature (^{\circ}C))$	nin))			
	575	615	655	700	730
MgO, commercial	$1 \times 10^{-5}$	$3 \times 10^{-5}$	$1 \times 10^{-4}$	$1.2 \times 10^{-3}$	$3.5 \times 10^{-3}$
CeO <sub>2</sub> , commercial	$2.8 \times 10^{-3}$	0.014	0.039	0.081	0.138
ZrO <sub>2</sub> , commercial	$2.1 \times 10^{-3}$	0.011	0.028	0.073	0.132
$ZrO_2$ , SG (×10 <sup>2</sup> )	0.014	0.27	0.73	1.33	1.52
50Mg-50Zr-O, SG	$5 \times 10^{-4}$	$1.3 \times 10^{-3}$	0.011	0.037	0.058
$Rh/ZrO_2$ (×10 <sup>2</sup> )	6.45	6.46	6.48	6.5	6.53
Rh/50Mg-50Zr-O (×10 <sup>2</sup> )	12.00	11.90	11.67	12.07	12.26

Feed gas composition: 0.5% C<sub>6</sub>H<sub>5</sub>OH/40% H<sub>2</sub>O/He; GHSV =  $80,000 \text{ h}^{-1}$ .

out that the catalytic activity of solids prepared by the solgel method strongly depends on the individual site reactivity, the latter determined by the surface physicochemical properties of each metal oxide (e.g., acidity, basicity, reducibility of lattice oxygen species). The catalytic activity of the solgel-prepared CeO<sub>2</sub> and ZrO<sub>2</sub> is in harmony with the high reducibility of CeO<sub>2</sub> (672  $\mu$ mol-H<sub>2</sub>/g) compared to ZrO<sub>2</sub>  $(3.0 \,\mu\text{mol}-\text{H}_2/\text{g})$  according to H<sub>2</sub> TPR experiments (not presented here), a result that correlates with the positive role of labile oxygen species toward the combustion of adsorbed hydrocarbon fragments to produce CO, CO<sub>2</sub>, and H<sub>2</sub>, which is discussed below. Among the mixed metal oxides investigated, 50Mg-50Zr-O appears to be the best (Fig. 3, Table 3). Of interest is the fact that the hydrogen specific integral reaction rates obtained over the commercial metal oxides appear to be significantly lower compared to those obtained over the corresponding sol-gel prepared metal oxides.

Fig. 4 presents the effect of reaction temperature and support chemical composition on the CO/CO<sub>2</sub> product ratio obtained over the supported Rh catalysts presented in Fig. 3. According to the main network of reactions (1) and (2), the  $CO/CO_2$  product ratio is determined by the relative rates of these reactions, considering that the WGS reaction is not at true equilibrium. According to the results of Fig. 4, Rh/MgO, Rh/CeO<sub>2</sub>, and Rh/50Mg-25Ce-25Zr-O catalysts largely promote the WGS reaction at low temperatures. The increase of CO/CO2 ratio with increasing reaction temperature is consistent with the fact that the equilibrium conversion of CO associated with the WGS reaction decreases with increasing reaction temperature. On the other hand, the  $CO/CO_2$  ratio is found to decrease significantly with increasing temperature for the Rh/50Mg-50Ce-O catalyst (Fig. 4b). This could be explained by considering that either the WGS reaction is kinetically controlled (the CO/CO2 ratio is controlled by the relative rates of reactions (1)-(2)) or a decrease in the number of active sites responsible for the formation of CO (reaction (1)) occurs in the 575–735 °C range. The latter could be likely the result of deposition of carbonaceous material as evidenced at least at 655 and 700 °C (see Section 3.3).

Table 4 presents the product gas composition (dry basis), phenol conversion  $(X_1)$ , water–gas shift reaction conversion



Fig. 4. Dependence of CO/CO<sub>2</sub> product ratio on reaction temperature for (a) single metal oxide-supported Rh and (b) MgO-based-mixed metal oxide-supported Rh catalysts. Feed gas composition: 0.5% C<sub>6</sub>H<sub>5</sub>OH/40% H<sub>2</sub>O/He; W = 0.3 g;  $F_T = 200$  N mL/min; GHSV  $\approx 80,000$  h<sup>-1</sup>.

( $X_{WGS}$ ), CO/CO<sub>2</sub> product ratio, and H<sub>2</sub> selectivities obtained at 700 °C over six supported Rh catalysts, the supports of which were prepared by the sol–gel method. It is illustrated that Rh/50Mg–50Ce–O and Rh/50Mg–50Zr–O catalysts exhibit the lowest efficiency for hydrogen production (lowest value of  $S_{H_2}^{II}$ ) and at the same time the highest CO concentration in the product gas stream. On the other hand, Rh/MgO exhibits the highest efficiency of hydrogen production ( $S_{H_2}^{II} = 91.9$ ), indications that favor the phenol steam reforming network of reactions (1)–(2) and utilizes the highest percentage of hydrogen content in phenol compared to the other catalysts. It is reported that Rh/MgO produces about 1.2 times more hydrogen than Rh/50Mg–50Ce–O at 700 °C,

Table 4 Catalytic performance of various supported Rh catalysts toward phenol steam reforming

Catalyst (0.5 wt% Rh)	Catalytic performance								
	$H_2 \pmod{3}$	CO (mol%)	CO <sub>2</sub> (mol%)	$X_1(\%)$	$X_{WGS}$ (%)	$CO/CO_2$	$S_{\mathrm{H_2}}^{\mathrm{I}}$	$S_{\mathrm{H_2}}^{\mathrm{II}}$ (%)	
Rh/MgO	11.6	0.5	4.0	88.5	89.6	0.125	1.09	91.9	
Rh/CeO <sub>2</sub>	9.1	0.4	4.0	88.3	91.1	0.100	0.92	78.2	
Rh/ZrO <sub>2</sub>	9.1	0.4	4.1	90.3	91.2	0.097	0.90	78.2	
Rh/50Mg-50Ce-O	6.4	0.5	3.0	70.7	85.4	0.167	0.84	55.6	
Rh/50Mg-50Zr-O	8.2	0.5	3.0	71.2	86.4	0.167	1.06	71.3	
Rh/50Mg-25Ce-25Zr-O	9.4	0.4	4.3	97.0	92.0	0.093	0.90	84.2	

Feed gas composition: 0.5% C<sub>6</sub>H<sub>5</sub>OH/40% H<sub>2</sub>O/He; T = 700 °C; GHSV = 80,000 h<sup>-1</sup>; Gas product composition in dry-basis (mol%).

where the latter shows the lowest value of  $S_{H_2}^{II}$  (55.6%). Rh/MgO exhibits the highest value of  $S_{H_2}^{II}$  (1.09), while Rh/50Mg–50Ce–O the lowest one ( $S_{H_2}^{II} = 0.84$ ). Most of the catalysts present  $S_{H_2}^{II}$  values different than unity, namely in the 0.84–1.09 range. The lower than unity value of  $S_{H_2}^{II}$  suggests that in addition to the main reactions (1)–(2) other side reactions that consume hydrogen must be considered (e.g., hydrogenation of phenol). Indeed, higher benzene concentrations were found in the condensed product stream for the catalysts with low  $S_{H_2}^{II}$  values. No methane was observed, indicating that the CO/H<sub>2</sub> reaction does not occur for the present catalytic systems.

It has been postulated [54,55] that the reaction mechanism of steam reforming of toluene over supported Rh, Pd, and Pt catalysts consists of two important reaction pathways. In the first one, toluene is primarily dissociated on the noble metal leading to adsorbed hydrocarbon fragments. In the second pathway, water adsorption and dissociation occur mainly on the support surface. The resulting -OH groups migrate onto the metal particles through the metal/support interface. Once on the metal, they react rapidly with hydrocarbon fragments to give CO, CO<sub>2</sub>, and H<sub>2</sub>. The abovedescribed reaction pathways have also been adopted to explain the steam reforming of other aromatic compounds [30, 56]. The spillover of -OH species from the metal oxide support surface to the metal of a supported metal catalyst has recently found strong support in the partial oxidation of CH<sub>4</sub> over  $Ru/\gamma$ -Al<sub>2</sub>O<sub>3</sub> [57] and the steam reforming of ethane [58]. In fact, this spillover process was found to be of kinetic significance and the rate of spilt-over OH species was of the same order of magnitude as the rate of oxidation steps of  $CH_x$  [57]. For oxygenated molecules, like phenol, it has been reported [59,60] that the predominant reaction is the decomposition of the adsorbed reactant into  $H_2$  and CO. Assafi and Duprez [60] proposed a mechanism in which the -OH group attached to the aromatic ring participates in the overall reaction in a similar manner as the -OH group derived from the dissociation of water. The efficiency of the catalyst to keep the metal surface clean through O and -OH spillover processes seems to be an important step toward catalyst activity.

The above-offered discussion on the mechanism of steam reforming of aromatic compounds should be considered

when trying to understand why the catalytic performance of Rh/MgO and Rh/50Mg-25Ce-25Zr-O catalysts appears to be significantly better than that shown by the other catalysts investigated. The following is aimed at addressing this important fundamental question.

(a) The XRD pattern obtained on the Rh/50Mg–25Ce– 25Zr–O catalyst (Fig. 1) shows the presence of  $Ce_xZr_{1-x}O_2$ as one of the main crystal phases of support composition. According to the literature [61],  $Ce_xZr_{1-x}O_2$  presents much higher oxygen storage capacity (µmol-O/g) than pure CeO<sub>2</sub> and ZrO<sub>2</sub>. In addition, water is able to fill in oxygen vacancies in the 300–900 °C range [62]. From the fact that O and –OH back spillover processes appear to be of great importance for the phenol steam reforming reaction, as previously discussed, it is expected that Rh/50Mg–25Ce– 25Zr–O will have higher steam reforming activity than the other catalysts investigated.

(b) It is well known that enhancement of support basicity can lead to the promotion of carbon gasification through increased water chemisorption [30], and thus –OH concentration. It was found that the present 50Mg–25Ce–25Zr–O support exhibits the largest specific number of basic sites  $(0.95 \,\mu mol/m^2)$  among the other mixed metal oxides investigated  $(0.8 \,\mu mol/m^2, 50Mg-50Ce–O; 0.7 \,\mu mol/m^2, 50Mg-$ 50Zr–O). Considering the mechanism of steam reforming of aromatics over supported metal catalysts as previously discussed, higher spillover rates of –OH are expected for the Rh/50Mg–25Ce–25Zr–O compared to the other catalysts. Therefore, Rh/50Mg–25Ce–25Zr–O is expected to lead to an improved catalytic performance.

(c) It has been reported that  $\operatorname{Ce}_x \operatorname{Zr}_{1-x} O_2$  is more stable toward sintering compared to  $\operatorname{CeO}_2$  and  $\operatorname{ZrO}_2$  [61]. This is of great importance in the present work where high concentrations of water in the feed are considered. In fact, the WGS reaction over  $\operatorname{TiO}_2$ -based supported noble metals was found to strongly depend on the morphology of  $\operatorname{TiO}_2$  [63]. In particular, a drastic decrease in the  $\operatorname{TOF}_{CO}$  with increasing crystallite size of titania was reported.

(d) Fig. 5 presents H<sub>2</sub>-TPR profiles obtained on the Rh/50Mg–25Ce–25Zr–O, Rh/50Mg–50Ce–O, Rh/50Mg–50Zr–O, and Rh/MgO catalysts following calcination in 20% O<sub>2</sub>/He at 750 °C for 2 h. The 50Mg–25Ce–25Zr–O support exhibits the largest amount (127  $\mu$ mol-O/m<sup>2</sup>) of reducible oxygen species in the 100–800 °C range com-



Fig. 5. Temperature-programmed reduction (TPR) profiles in terms of rate of hydrogen consumption ( $\mu$ mol-H<sub>2</sub>/(g min)) versus temperature obtained on 0.5 wt% Rh supported on 50Mg-25Ce-25Zr-O, 50Mg-50Ce-O, 50Mg-50Zr-O, and MgO metal oxides prepared by the sol-gel method.

pared to 50Mg-50Zr-O (105 µmol-O/m<sup>2</sup>), 50Mg-50Ce-O (22.5 µmol-O/m<sup>2</sup>), and MgO (0.8 µmol-O/m<sup>2</sup>) solid supports. It is noted that these quantities were estimated after subtracting the amount of oxygen corresponding to Rh<sub>2</sub>O<sub>3</sub>. From the fact that Rh/MgO exhibited higher specific reaction rates than the Rh/50Mg-25Ce-25Zr-O catalyst but a lower concentration per square meter of reducible oxygen species, it could be argued that labile oxygen may not be the only important parameter for the enhancement of phenol steam reforming activity.

# 3.2.2. Effect of synthesis method on catalyst performance

The effect of synthesis method of the 0.1 wt% Rh/50Mg– 25Ce–25Zr–O solid on its catalytic performance toward steam reforming of phenol was studied by making use of sol–gel (SG), mechanical mixing (MM), and the combination of sol–gel with the incipient wetness impregnation method (SG-IWI, see Section 2.1). As shown in Fig. 6a, the catalyst coded SG-IWI appears to be superior to the other catalysts in terms of H<sub>2</sub> production. A remarkable result is the fact that at the lowest temperature of 575 °C, the SG-IWI catalyst shows 20 and 12 times larger H<sub>2</sub> concentrations compared to the ones prepared by the MM and SG methods, respectively. On the other hand, at temperatures higher than 700 °C the effect of synthesis method appears to become less but still significant.

It is suggested that the different morphological characteristics and surface physicochemical properties of 50Mg– 25Ce–25Zr–O support crystal phases established by the different preparation methods largely determine the performance of the present supported Rh catalysts. In the case of SG-IWI and SG catalysts, the support phases of MgO,  $Mg_xZr_{1-x}O_2$ , and  $Ce_xZr_{1-x}O_2$  (Fig. 6b) influence the catalytic activity. The marked XRD peaks in Fig. 6b correspond to the following crystal phases: (1)  $Ce_xZr_{1-x}O_2$ ; (2) MgO;



Fig. 6. (a) Effect of preparation method of the 0.1 wt% Rh/50Mg–25Ce–25Zr–O catalyst on the H<sub>2</sub> product concentration obtained in the 575–730 °C range after steam reforming of phenol. (b) X-ray diffraction patterns of 0.1 wt% Rh/50Mg–25Ce–25Zr–O catalyst prepared by three different methods (see Section 2.1). Peaks 1,  $Ce_xZr_{1-x}O_2$ ; peaks 2, MgO; peaks 3,  $Mg_xZr_{1-x}O_2$ ; peaks 4, ZrO<sub>2</sub>; peaks 5, CeO<sub>2</sub>.

(3)  $Mg_x Zr_{1-x}O_2$ ; (4)  $ZrO_2$ ; and (5)  $CeO_2$ . After careful examination, the X-ray diffraction peaks of the MgO phase present in the SG catalyst are slightly shifted toward lower  $2\theta$  values compared to the SG-IWI catalyst. This result could be explained by considering that some interactions of MgO lattice with Rh had occurred which resulted in a significant decrease of Rh surface concentration and site reactivity. The spinel structure of MgRh<sub>2</sub>O<sub>4</sub> has been reported [64], even though this phase was not detected by XRD in the present work.

Based on H<sub>2</sub> TPR results (not presented here), the SG-IWI catalyst exhibited the largest amount of reducible oxygen species ( $305 \mu$ mol-O/g) compared to the SG ( $235 \mu$ mol-O/g) and MM ( $59 \mu$ mol-O/g) catalysts, results that could partly contribute to an increased rate of phenol steam reforming over the SG-IWI catalyst (oxygen spillover) as previously discussed.

### 3.2.3. Effect of rhodium loading

Fig. 7 shows the effect of Rh loading on the hydrogen specific integral production rate (per m<sup>2</sup> of Rh) (Fig. 7a), the hydrogen selectivity,  $S_{H_2}^{II}$  (%) (Fig. 7b), and the CO/CO<sub>2</sub> product ratio (Fig. 7c) obtained over the *x* wt% Rh/50Mg–25Ce–25Zr–O catalysts in the 575–730 °C range. As shown in Fig. 7a, by increasing the Rh loading from 0.1 to 0.5 wt%

results in a significant decrease of the specific activity of reaction. It is noted that the specific reaction rates given in Fig. 7a were estimated by considering the mean Rh particle size determined by HRTEM studies (Fig. 2). It was found that the mean Rh particle sizes of the used supported Rh catalysts were 2.7, 1.7, and 1.2 nm for the 0.5, 0.3, and 0.1 wt% Rh loadings, respectively. Based on the results of Fig. 7a, it can be said that steam reforming of phenol is significantly favored over small Rh particles. However, it is not excluded that metal-support electronic interactions that become significant for small metal particles (d < 2.0 nm) [65,66] may operate synergistically, thus increasing further the activity of the catalyst toward H<sub>2</sub> formation. Duprez [24] has also reported that the TOF dependence of steam reforming of toluene over supported Rh catalysts on the product  $D_0^2 X_m$ was of the 0.7 power ( $D_0$  is the percentage of Rh dispersion and  $X_{\rm m}$  is the metal loading).

Fig. 7b illustrates that the use of 0.1 wt% Rh results in the highest hydrogen selectivity  $S_{H_2}^{II}$  values obtained in the 615-730 °C range, a result that is in harmony with the effect of Rh loading on the specific integral rate of H<sub>2</sub> formation (Fig. 7a). The effect of Rh particle size on the  $CO/CO_2$ product ratio is illustrated in Fig. 7c. Except at 730°C, the 0.1 wt% Rh/50Mg-25Ce-25Zr-O exhibits significantly higher CO/CO<sub>2</sub> ratio values in the 575-700 °C range compared to the other catalysts. It has been reported [63] that the WGS reaction is not Pt- or Ru-structure sensitive but depends strongly on the structure and morphology of TiO<sub>2</sub> support. What is not yet clear in the present catalytic system is whether the reaction of phenol with steam to produce CO and  $H_2$  (reaction (1)), the WGS (reaction (2)), or both could be considered Rh structure sensitive. Of interest is the profile of CO/CO<sub>2</sub> product ratio with reaction temperature in the case of 0.1 wt% supported Rh catalyst that shows a nonmonotonic behavior as opposed to that obtained on the catalysts with higher Rh loadings (Fig. 7c).

# *3.2.4. Effect of water and phenol composition in the feed stream*

The effect of H<sub>2</sub>O feed concentration on the hydrogen production over the 0.1 wt% Rh/50Mg-25Ce-25Zr-O catalyst was studied in the 575-730 °C range at phenol conversions higher than 40%. The phenol concentration was kept constant at 0.3 mol%, while the water concentration was varied in the 20-40 mol% range. It was found that hydrogen production increases significantly with increasing concentration of water in the feed in the whole 575-730 °C range. In particular, at 575 °C hydrogen production increases by approximately 40% by increasing the H<sub>2</sub>O feed concentration from 20 to 40 mol%. This result is in harmony with the fact that steam reforming of oxygenated aromatic compounds requires high steam to carbon ratios in order to minimize coke formation [36]. On the other hand, the effect of reaction temperature on the hydrogen production was found to be small. This result may suggest that the size of the steady state -OH reservoir formed on the support surface is little affected by



Fig. 7. Dependence of (a) specific hydrogen integral production rate (mmol-H<sub>2</sub>/(m<sup>2</sup>-Rh s)), (b) hydrogen reaction selectivity  $S_{H_2}^{II}$  (%), and (c) CO/CO<sub>2</sub> product ratio on reaction temperature and Rh loading (wt% Rh) for the *x* wt% Rh/50Mg–25Ce–25Zr–O catalysts. Feed: 0.5% C<sub>6</sub>H<sub>5</sub>OH/40% H<sub>2</sub>O/He; W = 0.3 g;  $F_T = 200$  N mL/min; GHSV  $\approx 80,000$  h<sup>-1</sup>.

the reaction temperature but is largely affected by the feed water concentration.

The dependence of hydrogen production on phenol concentration in the feed (0.3–0.5 mol%, 40% H<sub>2</sub>O, He as balance) and in the 575–730 °C range is described as follows. There was a significant increase (at least by a factor of 2) of H<sub>2</sub> production in the whole 575–730 °C range by increasing the phenol concentration from 0.3 to 0.5 mol%. It is sug-



Fig. 8. Comparison of the hydrogen product concentration obtained in the 575–730 °C range on the 0.1 wt% Rh/50Mg–25Ce–25Zr–O, 0.5 wt% Rh/MgO, and a commercial Ni-based catalyst (code: C11-PR, Süd-Chemie). Feed gas composition: 0.5% C<sub>6</sub>H<sub>5</sub>OH/40% H<sub>2</sub>O/He; W = 0.3 g;  $F_T = 200$  N mL/min; GHSV  $\approx$  80,000 h<sup>-1</sup>.

gested that this could be related to the increase of the surface coverage of hydrocarbon fragments deposited on Rh without blocking necessary sites for the reaction to proceed.

#### 3.2.5. Comparison with a commercial catalyst

Fig. 8 compares the performance toward phenol steam reforming in the 575-730 °C range of the 0.1 wt% Rh/50Mg-25Ce-25Zr-O (SG-IWI), 0.5 wt% Rh/MgO, and commercial Ni-based (Sud-Chemie, code C11-PR) catalysts. The latter catalyst is used for tar steam reforming. The H<sub>2</sub> product concentrations obtained on Rh/MgO are larger than on the commercial catalyst. In particular, at the highest temperature of 730 °C the amount of H<sub>2</sub> produced is higher by 30%. Similarly, the commercial catalyst presents lower H<sub>2</sub> reaction selectivity  $(S_{\text{H}_2}^{\text{II}})$  values compared to the Rh/MgO. In particular, values of 89.3 and 99.0 were obtained at 575 and 730 °C, respectively, in the case of Rh/MgO compared to 76.2 and 73.8 in the case of commercial catalyst. The 0.1 wt% Rh/50Mg-25Ce-25Zr-O catalyst also competes favorably with the industrial catalyst at 700 and 730 °C. It is very important to point out that the commercial catalyst has a Ni loading of 44 wt% to be compared to 0.1-0.5 wt% of Rh used in the present supported Rh catalysts.

# 3.3. Characterization of carbonaceous species formed in steam reforming of phenol

Temperature-programmed surface reaction (TPSR) and oxidation (TPO) experiments were conducted following reaction of phenol with steam (655 °C, 3 h) over the 0.1 wt% Rh/50Mg–25Ce–25Zr–O (SG-IWI) catalyst. After reaction and a 15-min He purge, the temperature of the catalyst was increased to 800 °C. H<sub>2</sub> and CO evolved simultaneously in the 650–800 °C range (similar shape and peak maximum positions). On the other hand, CO<sub>2</sub> evolved at higher temperatures (680–800 °C) and in larger concentrations. The amounts of CO, CO<sub>2</sub>, and H<sub>2</sub> formed were found to be 69.0, 77.0, and 51 µmol/g<sub>cat</sub>, respectively. The amounts



Fig. 9. Characterization of the accumulated carbonaceous species on the 0.1 wt% Rh/50Mg–25Ce–25Zr–O catalyst after phenol steam reforming by isothermal transient reaction with steam. Gas delivery sequence: 0.5% C<sub>6</sub>H<sub>5</sub>OH/40% H<sub>2</sub>O/He (655 °C, 3 h)  $\rightarrow$  He (655 °C, 15 min)  $\rightarrow$  40% H<sub>2</sub>O/2% Ar/He (655 °C, t). *W* = 0.3 g; *F*<sub>T</sub> = 200 N mL/min.

of H<sub>2</sub> and CO far exceed the equivalent amount of surface Rh (6.8  $\mu$ mol/g<sub>cat</sub>). Hydrogen evolution arises from the thermal decomposition of hydrogen-containing carbonaceous species, some of which must reside on the support. The fact that before the start of the He TPSR run the H<sub>2</sub>O signal reached the baseline, and no molecularly adsorbed  $H_2O$  is expected at  $T > 650 \degree C$ , the route of  $H_2$  production through H<sub>2</sub>O dissociation or reaction with the deposited carbonaceous species must be excluded. It is suggested that CO and CO<sub>2</sub> originate from the reaction of carbonaceous species formed during reforming with the O and -OH species, the latter accumulated mainly on the support and which spilled over to the Rh surface during the He TPSR run. The route of formate decomposition to CO, CO<sub>2</sub>, and H<sub>2</sub> cannot be excluded [67]. However, formate decomposition starts at much lower temperatures [67], and since no  $H_2$  signal was found at 650 °C in He flow (before the TPSR run) this route must be excluded.

At the end of the He TPSR run, the reactor was cooled quickly in He flow to 300 °C and the feed was switched to a 20% O<sub>2</sub>/He gas mixture (TPO run,  $\beta = 18$  °C/min). Two CO<sub>2</sub> peaks (41.7 µmol/g,  $T_{\rm M} = 430$  and 560 °C) and a smaller CO peak (9.8 µmol/g,  $T_{\rm M} = 430$  °C) were observed. The equivalent amount of carbon was found to be 51.5 µmol-C/g (compared to 146 µmol-C/g measured after the He TPSR run), where part of it must reside on the support and may not be of the same nature and chemical composition as that associated with the He TPSR run. The same TPO experiment performed over the 0.5 wt% Rh/50Mg-25Ce-25Zr-O catalyst showed only the formation of CO<sub>2</sub> (94.8 µmol/g<sub>cat</sub>). This result probes for the effects of Rh particle size on the amount and reactivity toward oxygen of carbonaceous deposits formed during phenol steam reforming.

Fig. 9 shows the evolution of transient isothermal response curves of CO, CO<sub>2</sub>, and H<sub>2</sub> obtained following the switch 0.5% C<sub>6</sub>H<sub>5</sub>OH/40% H<sub>2</sub>O/He (3 h)  $\rightarrow$  He (15 min)  $\rightarrow$ 40% H<sub>2</sub>O/He/2% Ar (t) at 655 °C on the 0.1 wt% Rh/50Mg-25Ce-25Zr-O catalyst. Integration of the transient isothermal response curves of CO and CO<sub>2</sub> provided the equivalent amount of carbon deposits reacted off with steam. This was found to be 5.6 mmol-C/g, compared with 0.32 mmol-C/g estimated from the TPO run. Also, an amount of 13.5 mmol- $H_2/g$  was estimated. A similar experiment performed on the 0.5 wt% Rh/50Mg-25Ce-25Zr-O catalyst provided 3.55 mmol-C/g and 14.7 mmol-H<sub>2</sub>/g. From these results, an approximate H/C compositional ratio of carbonaceous deposits could be estimated. This is found to be 4.8 and 8.3 for the 0.1 and 0.5 wt% Rh/50Mg-25Ce-25Zr-O catalysts, respectively. It appears that Rh particle size determines the chemical composition of adsorbed carbonaceous deposits formed during steam reforming of phenol at 655 °C.

The results of Fig. 9 illustrate the beneficiary effect of steam compared to oxygen in removing higher amounts of carbonaceous material accumulated during phenol steam reforming over the present supported Rh catalysts. It is suggested that this might be the result of the capability of steam for a continuous supply of active "oxygen-containing" species formed on the support or the metal–support interface via water dissociation that is absent in the case of oxygen. The significant reactivity of steam is in harmony with the observed increase of the rate of hydrogen production by increasing the water concentration in the feed from 20 to 40 mol%.

### 3.4. Catalyst stability studies

Fig. 10a presents results of the stability (in terms of H<sub>2</sub> production) with time on stream at 700 °C of one of the best catalysts developed (0.5 wt% Rh/MgO) for phenol steam reforming at both low (less than 20% for 2 h on stream) and high (more than 70% for 2 h on stream) phenol conversions. There is about 12-15% drop in hydrogen production after 2 h on stream for both catalytic runs. The initial partial deactivation of the catalyst is likely due to carbon accumulation on the catalyst surface. As reaction proceeds, labile O and -OH species accumulate on the support and migrate toward the Rh metal-support interface. There will be a critical time for an enhanced rate of combustion of the accumulated carbonaceous species due to the establishment of a critical concentration of such oxygen-containing species. The free Rh surface is, therefore, expected to increase and this could explain the small increase of H<sub>2</sub> production in the time interval of 2-6 h. On the other hand, due to the decrease of Rh dispersion noticed for this catalyst (Table 2), some decrease of H<sub>2</sub> production is seen from 6- to 24-h time period.

Fig. 10b presents stability profiles for the 0.1 wt% Rh/50Mg-25Ce-25Zr-O catalyst. In this case, different profiles are observed at low or high phenol conversions. This particular catalyst composition is more susceptible to a sig-



Fig. 10. Stability tests performed on the (a) 0.5 wt% Rh/MgO and (b) 0.1 wt% Rh/50Mg–25Ce–25Zr–O catalysts at 700 °C. Experiments were conducted under low (less than 20%) and high (more than 70%) phenol conversions. Feed gas composition: 0.5% C<sub>6</sub>H<sub>5</sub>OH/40% H<sub>2</sub>O/He;  $F_{\rm T} = 200$  N mL/min.

nificant deactivation during the first 2 h of reaction at low phenol conversions and to a lesser extent at high conversions. In addition, at low conversions a rather stable activity is obtained after 2 h on stream, while at high conversions local minima and maxima in the activity profile are obtained.

# 3.5. X-ray photoelectron spectroscopy studies

Fig. 11a presents the Rh (3d) photoelectron spectrum obtained on the 0.5 wt% Rh/50Mg–25Ce–25Zr–O catalyst (fresh) after calcined at 600 °C in 20% O<sub>2</sub>/He for 2 h and reduced at 300 °C in 20% H<sub>2</sub>/He for 2 h. Fig. 11b presents the Rh (3d) XP spectrum obtained on the catalyst after being used for 24 h in phenol steam reforming at 655 °C. For pure Rh metal foil, Rh(3d<sub>5/2</sub>) and Rh(3d<sub>3/2</sub>) peaks occur at 307.0 and 311.8 eV, respectively, with 1.6 eV FWHM [68]. The binding energy of the most intense Rh(3d<sub>5/2</sub>) peak at 307.4 eV is attributed to Rh<sup>0</sup>, while that at 309.7 eV (Fig. 11a) to oxidized Rh particles (Rh<sup>3+</sup> oxidation state) [69]. The appearance of incomplete reduction of Rh at the applied conditions may be due to the inherent oxidation of Rh<sup>0</sup> by surface hydroxyl groups of the support. Incomplete reduction of Rh (Rh/MgO) by hydrogen at



Fig. 11. X-ray photoelectron spectra of Rd (3d) core level obtained on the fresh 0.5 wt% Rh/50Mg–25Ce–25Zr–O catalyst. (a) after oxidation at 600 °C for 2 h followed by H<sub>2</sub> reduction at 300 °C for 2 h; (b) after steam reforming of phenol at 655 °C for 24 h.

300 °C has also been reported by Baltanas et al. [70]. Kawai et al. [68] reported single Rh  $(3d_{5/2})$  peaks in the XP spectra obtained on Rh/ZnO and Rh/MgO catalysts following hydrogen reduction at 200 °C, but the spectra also exhibited large FWHM values (> 3.5 eV) which were attributed to a mixture of two Rh oxidation states.

Table 5 reports binding energies of core electrons of Mg, Zr, Ce, and Rh observed on the 0.1 and 0.5 wt% Rh supported on 50Mg–25Ce–25Zr–O after being exposed to different gas atmospheres. After calcination of fresh catalysts, BE values that correspond to Mg(1s), Ce(3d), and Zr(3d) XP peaks fit with the values expected for their respective metal oxides. Rhodium is also fully oxidized (Rh<sup>3+</sup>) in all fresh catalyst samples. When the oxidized sample was reduced in H<sub>2</sub> at 300 °C, reduction of Rh appears not to be complete (Fig. 11a, Table 5). For instance, only 37% of Rh is reduced in the case of 0.5 wt% Rh/50Mg–25Ce–25Zr–O catalyst. On the other hand, the used catalyst (only treated in He after re-

Table 5 Binding energies (eV) of core electrons in Rh/50Mg-25Ce-25Zr-O samples

1				
Sample	Mg 1s	Zr 3d <sub>5/2</sub>	Ce 3d <sub>5/2</sub>	Rh 3d <sub>5/2</sub>
0.1 wt% Rh/Mg-Ce-Zr-C	)			
oxidized <sup>a</sup>	49.5	182.2	882.8	309.7 (100)
0.1 wt% Rh/Mg-Ce-Zr-C	)			307.4 (39)
reduced <sup>b</sup>	49.5	182.2	882.8	309.6 (61)
0.5 wt% Rh/Mg-Ce-Zr-C	)			
oxidized <sup>a</sup>	49.4	182.2	882.8	309.9 (100)
0.5 wt% Rh/Mg-Ce-Zr-C	)			307.4 (37)
reduced <sup>b</sup>	49.5	182.2	882.7	309.7 (63)
0. 5 wt% Rh/Mg-Ce-Zr-C	С			
used <sup>c</sup>	49.5	182.3	882.7	308.2 (100)

<sup>a</sup> Use of 20% O<sub>2</sub>/He at 600  $^{\circ}$ C for 2 h.

<sup>b</sup> Use of 20%  $H_2$ /He at 300 °C for 2 h in the oxidized sample (see footnote a).

 $^{\rm c}$  After the catalyst sample was used in phenol steam reforming for 10 h at 700 °C.

Table 6	
Surface at% composition derived from the 2	XPS analyses

Catalyst	at% Mg	at% Zr	at% Ce	at% O	at% Rh
0.1 wt% Rh/Mg-Ce-Zr-O					
oxidized <sup>a</sup>	19.6	10.8	6.6	61.3	1.7
0.1 wt% Rh/Mg-Ce-Zr-O					
reduced <sup>b</sup>	28	5.5	8.3	56.5	1.7
0.5 wt% Rh/Mg-Ce-Zr-O					
oxidized <sup>a</sup>	32.5	7.0	3.2	56.2	1.1
0.5 wt% Rh/Mg-Ce-Zr-O					
reduced <sup>b</sup>	34.2	6.8	3.1	55.0	0.9
0.5 wt% Rh/Mg-Ce-Zr-O					
used <sup>c</sup>	32.6	6.9	3.9	55.9	0.7

<sup>a</sup> Use of 20%  $O_2$ /He at 600 °C for 2 h.

<sup>b</sup> Use of 20% H<sub>2</sub>/He at 300 °C for 2 h in the oxidized sample (see footnote a).

 $^{\rm c}$  After the catalyst sample was used in phenol steam reforming for 10 h at 700  $^{\circ}{\rm C}.$ 

action) shows Rh (3d) BE corresponding to oxidation states between Rh<sup>3+</sup> and Rh<sup>0</sup> (308.2 eV), characteristic of Rh<sup>+</sup> species [71]. This result suggests that small rhodium clusters become oxidized to Rh<sup>+</sup> by –OH groups, the latter present along the metal–support interface.

Table 6 reports the surface atom percentage composition of the catalysts after treatment with a respective gas composition (Table 5). Reduction in H<sub>2</sub> at 300 °C of the preoxidized surface of 0.1 wt% Rh/50Mg–25Ce–25Zr–O resulted in significant changes of Mg and Zr at% surface compositions. There is an increase by 42.8% in Mg and 49% reduction in Zr surface composition. As evidenced by XRD (Fig. 1, Section 3.1.2), the Mg<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> phase is present in the 50Mg–25Ce–25Zr–O solid. It appears that reduction of this phase and, therefore, creation of oxygen vacant sites promote diffusion of Zr atoms deeper to the crystal. Note that Mg and Zr consist of about 80% of the surface metal atoms in the oxidized state of the solid surface. The significance of this important information lies in the fact that the acid–base character of the support surface is expected to change with reaction conditions, since more than 5% H<sub>2</sub> is produced, under which reduction of CeO<sub>2</sub>, Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub>, and Mg<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> is expected. On the other hand, the presence of water under reaction conditions reoxidizes the support surface. It is, therefore, the net rate of oxygen depletion and supply that will determine the surface concentration of oxygen vacant sites, and thus the surface metal at% composition. The latter will determine the surface acid–base character of the support that influences the rate of steam reforming reaction.

In the case of 0.5 wt% Rh/50Mg–25Ce–25Zr–O, H<sub>2</sub> reduction resulted practically in the same metal at% composition, a result opposite to that observed on the 0.1 wt% Rh50/Mg–25Ce–25Zr–O catalyst. The increase of Rh particle size seems to have hindered significantly the reduction of support. It is suggested that atomic hydrogen species formed on the Rh surface spill over onto the support and react with lattice oxygen. The rate of this H spillover process seems to be controlled by the Rh particle size. The higher at% surface Rh composition observed in the 0.1 wt% Rh compared to 0.5 wt% Rh-supported catalyst and the reduction of surface Rh composition in the used compared to the fresh 0.5 wt% Rh-supported catalyst (see Table 6) are in agreement with the Rh dispersions estimated (Table 2).

# 4. Conclusions

The following conclusions can be derived from the results of the present work:

- (a) The support chemical composition was found to significantly influence the catalytic activity and H<sub>2</sub> selectivity of the steam reforming of phenol over MgO-based-supported Rh catalysts in the 575–730 °C range.
- (b) The use of 0.1 wt% Rh resulted in a significantly better catalytic performance in terms of specific (per m<sup>2</sup> of Rh) integral H<sub>2</sub> production rate than the use of 0.3 and 0.5 wt% Rh supported on 50Mg-25Ce-25Zr-O. It is concluded that steam reforming of phenol is favored over very small Rh particles.
- (c) The synthesis of the 50Mg-25Ce-25Zr-O mixed metal oxide support by the sol-gel method, and the Rh deposition (0.1 wt%) by the incipient wetness impregnation method led to a significantly more active catalytic system compared to the one for which the same support composition was prepared by mechanical mixing of MgO, CeO<sub>2</sub>, and ZrO<sub>2</sub> or by the cohydrolysis and condensation of Rh, Mg, Ce, and Zr precursors (sol-gel method).
- (d) The effect of water feed concentration on the steam reforming of phenol activity of supported Rh catalysts does not seem to depend on reaction temperature. A significant increase in the H<sub>2</sub> production is obtained by increasing the water concentration in the 20–40 mol% range. The effect of phenol concentration in the feed on

the steam reforming activity also appears to be largely positive, while the effect of temperature appears to be less significant.

- (e) Steam was found to remove in a more efficient way than oxygen the accumulated carbonaceous species formed during phenol steam reforming over the 0.1 and 0.5 wt% Rh/50Mg-25Ce-25Zr-O catalysts.
- (f) More than one kind of carbonaceous species was found to accumulate on the 0.1 and 0.5 wt% Rh/50Mg-25Ce-25Zr-O catalysts. The H/C atomic compositional ratio of these carbonaceous species seems to depend on Rh particle size.
- (g) XPS studies revealed that the reducibility of  $Mg_xZr_{1-x}$ O<sub>2</sub> crystal phase present in the 50Mg-25Ce-25Zr-O support by H species, the latter spilled over from the Rh surface to the support, results in a large change of Mg and Zr surface atomic composition due to Zr diffusion deeper into the crystal. This effect is expected to influence the acid-base character of the support surface during reaction conditions, and in turn the steam reforming activity of the supported Rh catalyst.

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