



Preliminary communication / Communication

Efficient hydrogen production by ethanol reforming over Rh catalysts. Effect of addition of Zr on CeO₂ for the oxidation of CO to CO₂

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Received 1 August 2003; accepted after revision 2 March 2004

Abstract

Reforming of ethanol in excess of water (1 to 8 molar ratio) has been investigated on Rh/CeO₂, Rh/ZrO₂ and a series of Rh/CeO₂-ZrO₂ (with Ce/Zr = 4, 2, and 1). XPS results indicate that the presence of Rh has resulted in partial reduction not only of CeO₂ but also of ZrO₂ (where the presence of XPS Zr²⁺ lines were seen at 180.8 ± 0.15 eV). At the temperature range of 400–500 °C, all catalysts showed complete conversion of ethanol with high selectivity towards hydrogen production (approaching the theoretical value of 6 mol of H₂ per mole of ethanol inlet). The effect of the support was mainly noticed on the CO₂/CO ratios. At 400 °C and above, this ratio was thermodynamically limited for the most active catalysts. For the series Rh/CeO₂-ZrO₂, there appears to be a relationship between the total surface oxygen atoms (as determined by XPS) and the extent of water gas shift reaction (WGSR): the higher the surface oxygen concentration, the higher the WGSR. *To cite this article: C. Diagne et al., C. R. Chimie 7 (2004).*

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Résumé

Le vaporéformage de l'éthanol a été étudié avec un grand excès d'eau (rapport molaire 1/8) pour des catalyseurs Rh/CeO₂, Rh/ZrO₂ et Rh/CeO₂-ZrO₂ (rapport Ce/Zr = 4, 2 et 1). Tous les catalyseurs conduisent à une conversion complète de l'éthanol entre 400 et 500 °C et à une forte sélectivité en hydrogène, approchant la valeur de 6 moles d'hydrogène par mole d'éthanol introduit. L'effet du support sur la formation de CO₂ et de CO est particulièrement remarquable. À partir de 400 °C, le rapport CO₂/CO approche l'équilibre thermodynamique de la réaction de conversion de gaz à l'eau pour le catalyseur le plus actif (Ce/Zr = 1). Pour la série Rh/CeO₂-ZrO₂, une relation entre la quantité d'atomes d'oxygène de surface déterminé par XPS et la réaction de conversion de gaz à l'eau a été mise en évidence, expliquant la formation sélective de CO₂ aux dépens de CO pour les catalyseurs présentant une concentration d'oxygène importante en surface. *Pour citer cet article : C. Diagne et al., C. R. Chimie 7 (2004).*

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Keywords: Rh/CeO₂; Rh/ZrO₂; Rh/CeO₂-ZrO₂; H₂ production; Ethanol reforming; Methane reforming; Water-gas shift reaction (WGSR)

Mots clés : Rh/CeO₂ ; Rh/ZrO₂ ; Rh/CeO₂-ZrO₂ ; Production d'hydrogène ; Réformage d'éthanol ; Réformage du méthane ; Conversion du gaz à l'eau

1. Introduction

Hydrogen, as a source of energy for stationary power plants and moving vehicles, will almost certainly be widely used in a decade or so and is now in trials in several cities world-wide [1,2]. Several sources for hydrogen are now considered. Methanol, ethanol, and natural gas are the most important candidates for an efficient production of hydrogen. Ethanol has a major advantage when compared to the other two candidates: it can be easily made from renewable sources. Ethanol can be produced either by hydrolysis of cellulosic materials followed by fermentation or by direct fermentation of sugar containing corps. In both processes a mixture of ethanol-water with a ratio close to 1 ethanol for 10 water molecules is formed. It is thus highly desirable to find efficient catalytic materials for the production of hydrogen in a high water to ethanol ratios. We have previously investigated the hydrogen production from ethanol by direct oxidation (Rh-Pt/CeO₂ [3] and Au/CeO₂ [4]) or via reforming with water (Rh/CeO₂-ZrO₂ [5]). An important requirement for the catalytic hydrogen production from any of the carbon-containing source is the absence of CO. In order to power, with hydrogen, moving or stationary plants, fuel cells are used. The irreversible adsorption of CO on the Pt anode of the fuel cells at the operating temperature (about 80 °C) degrades their performance and ends by totally poisoning them. Thus, the working catalyst is required to be both very efficient for abstracting hydrogen atoms from the carbon containing reactant and fully oxidising the carbon atoms to CO₂.

Among the good supports for oxidising CO to CO₂, cerium oxide has been shown as one of the most efficient [6,7], and the addition of ZrO₂ to CeO₂ has resulted in enhancing the ceria activity for oxidation reactions [8,9]. This enhancement has been reported as due to increasing oxygen mobility and the formation of a solid solution.

In the case of making hydrogen from ethanol, a noble metal capable of breaking the carbon-carbon bond is needed. Rh/CeO₂ [10,11] and Rh/Al₂O₃

[12,13] (alone or in presence of a second metal: Pd or Pt) catalysts have shown interesting activity for ethanol decomposition in presence of oxygen or water.

In this work we show that total conversion of ethanol can be achieved at reasonable temperatures with a hydrogen selectivity of 70 mol% over Rh catalysts. Moreover, catalysts composed of both Ce and Zr oxides gave the highest CO₂/CO ratios.

2. Experimental

The method for making the catalysts has been reported previously and only a brief description is given here. CeO₂, ZrO₂, and CeO₂-ZrO₂ supports were prepared by precipitation with an ammonia solution of cerium and/or zirconium nitrates (Strem). Rh (2 wt%) was added by impregnation of an aqueous solution containing RhCl₃·3 H₂O under stirring at room temperature followed by drying (120 °C) and calcination at 680 °C. BET surface area was conducted using a Coulter SA 3100 apparatus. XRD spectra were collected using a D5000 Siemens with a Cu radiation (Cu K α = 1.5406 Å) at a 2 θ interval of 20–60° with a step size of 0.05° and a count time of 35 s per step. Temperature-programmed reduction (TPR) experiments were conducted using a 50 mg of catalyst (in a fixed-bed quartz reactor) under 10% H₂ in Ar (2 l h⁻¹) with a ramping rate of 15 °C min⁻¹ from 25 to 950 °C.

Catalytic reactions of ethanol reforming were conducted in a fixed-bed reactor (containing 100 mg of catalyst) with a molar ratio H₂O/ethanol = 8, a flow rate of 0.77 l h⁻¹ and an Ar flow rate of 3 l h⁻¹ (Ar/H₂O/ethanol = 35/8/1). Prior to the catalytic reaction, all catalysts were reduced in a H₂ flow (10% in Ar) at 320 °C (1 h). Reaction products were analysed as a function of time at different temperatures. The results reported here are those taken after 90-min reaction (a steady-state condition was usually obtained after ca. 30 min). Products were analysed using three GC apparatus, equipped with FID and TCD.

X-ray photoelectron spectroscopy (XPS) was conducted in a UHV chamber, using a double pass CMA

Phi 20-805 analyser and a Phi 32-095 X-ray source at the following conditions: Mg K α for X-rays at 300 W, 50 eV pass energy for all elements, 0.1 eV/step and 300 ms/step.

3. Results and discussion

BET surface area of ZrO₂, CeO₂-ZrO₂ (Ce/Zr = 4, 2, 1) and CeO₂ were 55.7, 49.5, 50.8, 36.6 and 22.7 m² g⁻¹, respectively. Surface area of ZrO₂ is more than twice higher than that of CeO₂. Interestingly the addition of small amounts of ZrO₂ to CeO₂ (about 20%) increases considerably the surface area of the catalyst. No dramatic change in the surface area of these catalysts is seen upon impregnation with 2 wt% Rh. These surface areas were found equal to 46.7, 42.8, 43.6, 28.5 and 17.6 m² g⁻¹ for Rh/ZrO₂, Rh/CeO₂-ZrO₂ (Ce/Zr = 4, 2, 1) and Rh/CeO₂, respectively.

Fig. 1 shows TPR results of the different catalysts (supports and Rh-supported) as a function of hydrogen consumption per surface BET. ZrO₂ incorporation into CeO₂ has resulted in a higher reduction yield (per m²). Although some deviations occurred for the Rh-supported series, such a characteristic was qualitatively preserved for the supported Rh catalysts.

Table 1 shows XPS results for all catalysts and compared to those of CeO₂ and ZrO₂ supports. In

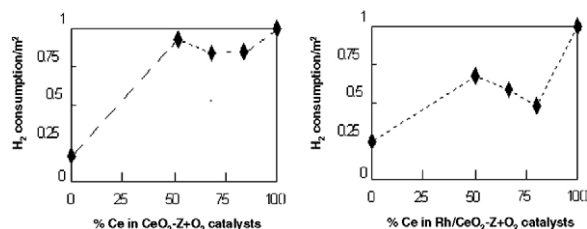


Fig. 1. Hydrogen consumption per catalyst specific surface as a function of Ce content for: (a) Supports and (b) Rh catalyst.

Table 1

Atomic% of the surface and near surface elements of Rh catalysts and supports as determined by XPS.

Catalyst	2 wt% Rh/CeO ₂	2 wt% Rh/ZrO ₂	2 wt% Rh/CeO ₂ -ZrO ₂ , Ce/Zr ^a =			CeO ₂	ZrO ₂
			4	2	1		
Ce	26.8	–	26.5	34.1	19.6	23.5	–
Zr	–	30.9	8.9	12.2	6.2	–	23.7
O	70.2	66.4	62.1	50.2	71.8	76.5	76.3
Rh	3.0 (3.3)	2.7 (2.4)	2.5 (3.2)	3.5 (3.1)	2.4 (2.8)	–	–
Ce/Zr			3.0	2.8	3.2		
O/(Ce+Zr)	2.6	2.2	1.78	1.1	2.8	3.3	3.2

Numbers in parentheses are those of the expected theoretical atomic% from the equivalent of 2 wt% impregnation of the Rh salts.

^a atomic ratios.

general there is no major deviation from the expected Rh atomic% on the surface when compared to the bulk (with the exception of the 2 wt% Rh/4 CeO₂ – 1 ZrO₂ catalyst). Some traces of Cl atoms (left from the preparation) are also found. For all catalysts, XPS Rh 3d lines were in an oxidised form (Rh3d_{5/2} at 309 eV (\pm 0.2 eV depending on the catalyst). Although the difference in the binding energy between Rh³⁺ (Rh₂O₃) and Rh⁴⁺ (RhO₂) is almost 1 eV, the small amount of Rh and the potential presence of ligand effect (due to proximity of Cl atoms) make the exact assignment rather difficult and not directly relevant for this study. XPS Ce 3d lines for all catalysts showed the presence of a small% of Ce³⁺ (except for CeO₂ alone, where all Ce atoms were Ce⁴⁺). The spectra of XPS Ce 3d for oxidized and reduced surfaces have been published by us and other workers and can be found elsewhere [14–16]. Similar observation was seen for Zr 3d lines, where Zr²⁺ in addition to Zr⁴⁺ were also seen. The XPS Zr 3d lines of Rh/ZrO₂ are very similar to those reported for ZrO₂ containing materials that have been subject to particle bombardment [17,18]. When compared to CeO₂ less efforts have been devoted to investigate the XPS Zr 3d lines for ZrO_{2-x} (x < 1) in its reduced form. A representative spectrum for XPS Zr 3d lines for Rh/ZrO₂ is given in Fig. 2 (and compared to that of stoichiometric ZrO₂). We can also notice that the ratio Ce/Zr given for Rh/CeO₂-ZrO₂ catalyst is different from that expected from the bulk. If the ratio Ce/Zr is almost the same for CeO₂-ZrO₂ alone [19], literature shows that segregation occurs when a transition metal is present [20,21].

We have previously investigated by XRD the bulk structure of the above catalysts [5]. CeO₂ shows the expected diffraction of the fluorite structure while the monoclinic + tetragonal diffraction lines are shown for

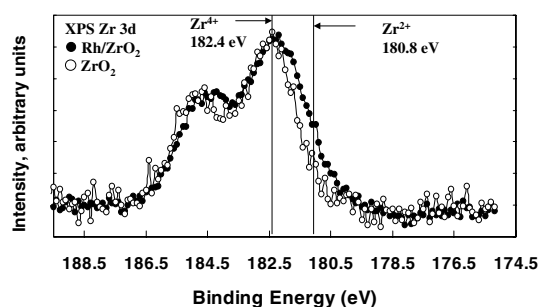


Fig. 2. XPS Zr 3d lines for the as prepared Rh/ZrO₂ and ZrO₂.

ZrO₂. The absence of ZrO₂ diffraction lines at low loading of ZrO₂ into CeO₂ (Ce/Zr = 4 and 2) indicates the presence of a solid solution. The shift of the diffraction lines to higher degrees is attributed to shrinking of the lattice due to the replacement of Ce ions (1.09 Å) by Zr ions (0.86 Å) [5,22]. At a higher loading of ZrO₂ (Ce/Zr = 1), an additional tetragonal phase was also seen [5].

Table 2 (A and B) shows results from the catalytic reactions of the Rh catalysts as a function of temperatures. Both the conversion and product distributions are reported in Table 2A, while the yield of each product per mole of ethanol is given in Table 2B. With the exception of Rh/CeO₂, all catalysts showed a 100% conversion at and above 300 °C. H₂ production increases with increasing temperature, while that of CH₄ declined. This may indicate that an additional formation of hydrogen occurs due to reforming of methane; methane is produced via the decomposition of acetaldehyde (see below Equations (4) and (5)). By 450 °C, all catalysts are virtually identical, reaching about 70 mol% production of H₂ in selectivity at total conversion, while CH₄ formation is below 5%. This composition is within experimental errors very close thermodynamic equilibrium: (H₂ (70.64%); CH₄ (3.4%); CO₂ (22.1%); CO (53.8%)). This composition changes with the water/ethanol ratio [23].

Contrary to hydrogen production, the CO₂ to CO ratio changes dramatically from catalyst to catalyst. The lowest CO₂/CO was seen for Rh/CeO₂, while the most active catalysts are those containing both Zr and Ce oxides (Fig. 3).

If we consider that at high temperatures reforming of methane by water is taking place followed by WGSR:

Table 2A
Conversion (%) and product yield (%) at different temperatures for the Rh catalysts

Rh/CeO ₂ /Temperature (°C)	300	350	400	450
Conversion, %	58.5	82.3	100	100
Product Yield, %				
H ₂	59.7	64.7	66.3	69.1
CH ₄	15.6	12.3	11.4	8.2
CO	18.2	5.4	3.7	3.5
CO ₂	6.5	17.0	18.7	19.2
CO ₂ /CO	0.4	3.1	5.1	5.5

Rh/ZrO ₂	300	350	400	450
Conversion, %	100	100	100	100
Product Yield, %				
H ₂	59.6	63.5	68.1	71.7
CH ₄	15.9	13.8	9.8	6.0
CO	13.1	4.3	1.6	2.1
CO ₂	11.4	18.4	20.5	20.3
CO ₂ /CO	0.9	4.3	12.8	9.4

Rh/4 CeO ₂ -1 ZrO ₂	300	350	400	450
Conversion, %	100	100	100	100
Product Yield, %				
H ₂	57.4	62.0	65.8	70.3
CH ₄	18.2	15.4	12.1	7.2
CO	11.6	2.8	0.8	1.6
CO ₂	12.7	19.7	21.3	20.8
CO ₂ /CO	1.1	6.9	27.7	13.2

Rh/2 CeO ₂ -1 ZrO ₂	300	350	400	450
Conversion, %	100	100	100	100
Product Yield, %				
H ₂	56.9	58.7	64.2	69.2
CH ₄	17.8	18.5	13.6	8.5
CO	16.9	4.7	1.8	1.6
CO ₂	8.4	18.2	20.3	20.7
CO ₂ /CO	0.5	3.9	11.1	13.1

Rh/1 CeO ₂ -1 ZrO ₂	300	350	400	450
Conversion, %	100	100	100	100
Product Yield, %				
H ₂	57.1	59.6	64.4	70.3
CH ₄	18.1	18.4	13.5	7.3
CO	13.5	0.8	0.7	1.5
CO ₂	11.3	21.3	21.5	20.9
CO ₂ /CO	0.8	28.0	32.6	14.0

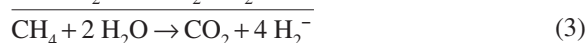


Table 2B
Production in mole per mole of ethanol at different temperatures for the Rh catalysts

Mole/mole of ethanol/Temperature (°C)	300	350	400	450
Rh/CeO₂				
H ₂	1.2	2.7	3.5	5.0
CH ₄	0.3	0.5	0.6	0.6
CO	0.4	0.24	0.2	0.2
CO ₂	0.1	0.7	1.0	1.4
Rh/ZrO₂				
H ₂	2.9	3.8	4.9	5.7
CH ₄	0.8	0.8	0.7	0.5
CO	0.6	0.3	0.1	0.2
CO ₂	0.5	1.1	1.5	1.6
Rh/4 CeO₂-1 ZrO₂				
H ₂	2.5	3.7	4.3	5.5
CH ₄	0.8	0.9	0.8	0.6
CO	0.5	0.2	0.1	0.1
CO ₂	0.5	1.2	1.4	1.6
Rh/2 CeO₂-1 ZrO₂				
H ₂	2.8	3.5	4.1	5.3
CH ₄	0.9	1.1	0.9	0.7
CO	0.7	0.1	0.1	0.1
CO ₂	0.6	1.3	1.3	1.6
Rh/1 CeO₂-1 ZrO₂				
H ₂	2.6	3.2	4.4	5.8
CH ₄	0.8	1.0	0.9	0.6
CO	0.6	0.2	0.1	0.1
CO ₂	0.7.0	1.0	1.5	1.7

If we add to Equation (3) the following two equations:



Equation (2) is repeated twice because one CO is formed by Equation (5) and another by Equation (1).

Then, the total number of molecules of H₂ per molecule of ethanol is equal to 6 (accompanied by two molecules of CO₂). The inset in Fig. 3 shows the molar% of H₂ and CO₂ as a function of temperature for three representative catalysts (Rh/CeO₂, Rh/ZrO₂, and Rh/1 CeO₂-1 ZrO₂). The H₂/CO₂ molar ratio is very close to 3 at 450 °C and slightly over 3 at 500 °C (this falls within experimental uncertainties). In all cases,

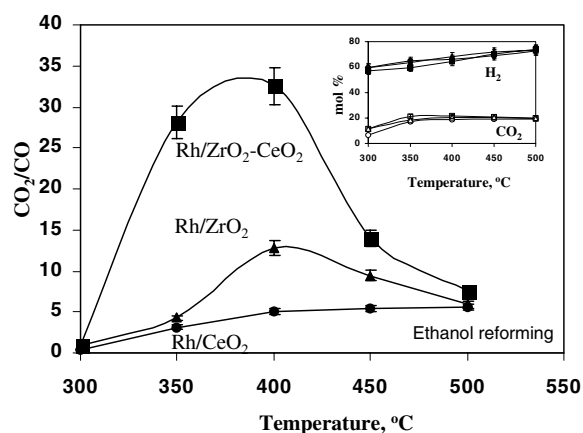


Fig. 3. CO₂/CO molar ratios for Rh/CeO₂, Rh/ZrO₂ and Rh/1 ZrO₂-1 CeO₂ catalysts as a function of reaction temperature; the inset shows both CO₂ and H₂ molar% for the same catalysts.

this shows that all catalysts are similarly active for the reforming of ethanol.

The high yield of CO₂ on the series containing Zr might be tracked to the amount of available oxygen on the surface initially. Fig. 4 shows XPS O(1s) for the three Zr-containing catalysts and the CO₂/CO molar ratio. The higher the surface oxygen the higher is the CO₂/CO molar ratio. WGS may operate in two ways [24]: (i) via a CO reaction with surface hydroxyls to make formate species that decompose to CO₂ leaving water to dissociate on the oxygen vacancy (regeneration); (ii) CO is directly oxidised by surface oxygen to CO₂ (Eley-Rideal mechanism) and again water dissociation regenerates the surface vacancy. Over CeO₂ surfaces several workers have reported that regeneration of oxygen vacancies formed upon CO oxidation is due to water dissociation [25]. Both mechanisms involve an active surface oxygen transfer to oxidise CO to CO₂. It is thus highly likely that for a similar material the higher the surface oxygen concentration, the higher is the possibility of CO oxidation.

The decrease of CO₂/CO molar ratio at high temperature (above 400 °C) is attributed to thermodynamic limitations. WGS is exothermic and is thus not favoured at very high temperature, while steam reforming is endothermic. The shape of the curves in Fig. 4 translates both reactions and the maximum is a compromise between them. Fig. 5 shows the computed $\frac{p_{\text{CO}_2} \times p_{\text{H}_2}}{p_{\text{CO}}}$ as a function of reaction temperature; also shown are $K_{\text{wp}} \times p_{\text{H}_2\text{O}}$ and $1/K_{\text{mp}}$, where K_{wp} is the

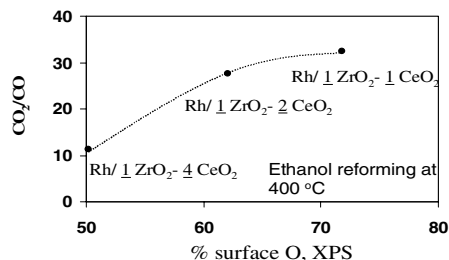


Fig. 4. CO_2/CO molar ratios as a function of surface percentage of O (1s) evaluated by XPS for Rh/1 ZrO_2 -1 CeO_2 , Rh/1 ZrO_2 -2 CeO_2 and Rh/1 ZrO_2 -4 CeO_2 . Ethanol reforming at 400 °C.

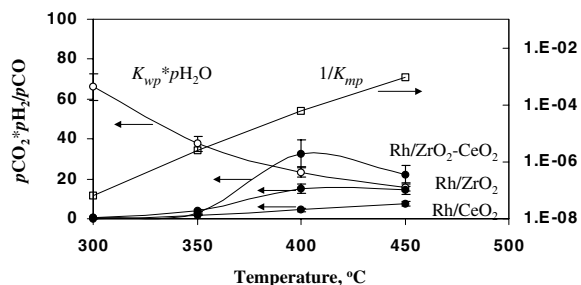


Fig. 5. Experimental $\frac{p_{\text{CO}_2} \times p_{\text{H}_2}}{p_{\text{CO}}}$ product as a function of reaction temperature for Rh/CeO₂, Rh/ZrO₂ and Rh/1 ZrO_2 -1 CeO_2 catalysts; also shown $K_{\text{wp}} \times p_{\text{H}_2\text{O}}$ and $1/K_{\text{mp}}$. Equilibrium constants for WGS (K_{wp}) and methane reforming ($1/K_{\text{mp}}$) are obtained from [23].

equilibrium constant for WGS and $1/K_{\text{mp}}$ that of methane reforming [26].

As can be seen, within experimental errors at 400 °C and above, the formation of both H_2 and CO_2 is governed by the equilibrium constant for WGS over the catalyst containing both Zr and Ce oxides (the most active catalyst). At higher temperatures, all catalysts behave similarly, because methane reforming has become very efficient, but the limitation is due to WGS.

In summary, results of this work indicate the following two points: (1) the best catalyst for making hydrogen and CO_2 is Rh supported over CeO_2 - ZrO_2 and (2) the CO_2/CO is sensitive to the Ce/Zr in the Rh/ CeO_2 - ZrO_2 series investigated and the production at high temperature reaches the thermodynamic equilibrium of WGS.

Acknowledgements

The authors thank Peter Buchanan for his assistance during XPS data collection and Suzanne Libs for her help in gas-phase analyses of the catalytic reactions.

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