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# Designing new high oxygen mobility supports to improve the stability of RU catalysts under dry reforming of methane

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The application of a novel $Ce_{0.5}Zr_{0.5}O_2$ mixed oxide prepared by the microemulsion method as a support of Ru catalysts for the reforming of $CH_4$ with $CO_2$ originates a high-activity catalytic system with excellent stability under reaction conditions. The support characteristics clearly determine the catalytic stability of Ru catalysts under $CH_4 + CO_2$ reaction conditions. The introduction of cerium as a promoter in the $ZrO_2$ structure is shown to improve the catalyst performance by increasing the oxygen mobility in the support and consequently reducing deactivation by carbon deposition during reaction.

**KEY WORDS:** oxygen exchange; $ZrO_2$; $Ce_{0.5}Zr_{0.5}O_2$; Ru catalysts; $CO_2$ reforming of methane.

## 1. Introduction

The catalytic process of conversion of methane into synthesis gas via $CO_2$ or dry reforming (DRM) has been attracting renewed interest during the last few decades because it provides a method for consuming $CO_2$, which is a recognized undesirable greenhouse gas, giving place to a chemically interesting syngas mixture ($CO + H_2$). Numerous supported catalysts have been tested, especially nickel and noble metal–based catalysts [1–3].

Many references in literature indicate that the catalyst supports can have a significant effect on the overall catalytic behavior. Both the activity and the stability of supported catalysts are affected by several factors such as the nature of the metal, the nature of the support as well as by the way and conditions for catalyst preparation and pretreatment [4]. Up to now, methane-reforming catalysts have been designed by controlling parameters such as the metallic phase using single [5,6], binary [7,8] or even ternary [9] systems, by using different types of supports ($Al_2O_3$, $SiO_2$, C, $ZrO_2$, $TiO_2$, $La_2O_3$, MgO, $Y_2O_3$, etc.) [10–12] or by controlling the metal particle size [13]. It has been already suggested that, in those cases, e.g., $Al_2O_3$, $ZrO_2$ and $TiO_2$, in which the support plays an active role in the reaction mechanism by participating in $CO_2$ activation, the metal-support interfacial zone or the metal particle perimeter is of essential importance in the reaction [7,14]. This can explain the effect of the metal particle size in a certain range on the turnover numbers and the absence of effect of the support in the case of catalysts with relatively large particle sizes.

However, little attention has been paid to the structure and characteristics of the support. Taking into account the importance of the metal carrier in the reaction kinetics, one more step towards support-designing is needed to achieve a tailor-made catalyst for this reaction. Several authors have shown that certain supports are able to provide oxygen to the metal and reduce in this way the formation of carbon deposits [10,15–17]. Thus, oxides with high oxygen exchange capacity and mobility are expected to be good candidates as supports for the DRM reaction. Our objective in this study is to prepare a high surface area support with enough thermal stability and very high oxygen mobility in order to obtain a very active and stable catalyst for the DRM process. The complex chemical properties (reducing, oxidizing, acidic and basic properties) and thermal stability of zirconia make it an attractive base material for our purpose [18]. With the aim of improving its oxygen mobility and its oxygen storage and release capacity, it has been modified with ceria [19,20]. These chemical properties of ceria make it a key component in the formulation of three-way catalysts (TWC) for automotive exhaust gas treatment. It has been firmly established that ceria contributes to the enhanced performance of TWC [19]. The catalytic properties of a ruthenium–zirconia–ceria system prepared by the microemulsion method (a reverse micellar system) in comparison with conventional ruthenium catalysts on ceria-impregnated zirconia are studied.

## 2. Experimental

A Zr-Ce mixed oxide with 1.1 Zr : Ce atomic ratio was prepared by the microemulsion method from the

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following precursor salts: zirconyl nitrate ($ZrO(NO_3)_2 \cdot H_2O$, Aldrich) and cerium nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$, Aldrich). To synthesize the support, a water-in-oil (WO) microemulsion was prepared by mixing, while stirring 50 mL of an aqueous solution containing the same concentration (0.25 M) of both Zr and Ce ions with 427 mL of heptane ($n$-$C_7H_{16}$, Aldrich), 92.8 mL of hexanol ($n$-$C_6H_{14}O$, Aldrich) and 88.8 mL of surfactant (Triton X-100, Aldrich). Another similar WO microemulsion containing tetramethylammonium hydroxide ($(CH_3)_4NOH$, Alfa) as an aqueous solution was prepared. These two microemulsions were stirred separately for 1 h, then mixed and stirred at room temperature for 24 h. The resulting suspension was centrifuged and decanted; the remaining solid was washed with methanol. After centrifuging and decanting again, the solid was first dried for a short time at room temperature, then at 110 °C for 24 h and finally it was calcined in air at 500 °C using a ramp of $2\,^\circ C\,min^{-1}$. Zirconia and ceria supports were prepared by the same method. These samples will be denoted as Zr-Ce (WO), $ZrO_2$ (WO) and $CeO_2$ (WO).

For comparison purposes, another $ZrO_2$ support was used. The zirconia employed was obtained by calcination of $ZrO_2$-3.5% $SiO_2$ (Mel Chemicals) at 700 °C for 4 h ($S_{BET} = 74.2\,m^2\,g^{-1}$). Two $ZrO_2$-$CeO_2$ supports were prepared by the incipient wetness impregnation technique using $Ce(NO_3)_3 \cdot 6H_2O$ (Fluka) and commercial zirconia with $CeO_2$ contents of 1.5 and 3.5 wt%. After impregnation, the oxides were dried overnight at 110 °C and subsequently calcined at 700 °C for 4 h.

Supported catalysts with Ru loadings of 1 and 5 wt% were prepared on the diverse supports by the incipient wetness impregnation method using ruthenium nitrosylnitrate ($Ru(NO)(NO_3)_3$, Alfa) as the metal precursor compound. Another $Ru/SiO_2$ (Aerosil-Degussa, $S_{BET} = 200\,m^2\,g^{-1}$) was also synthesized as a reference catalyst for which the support effect is negligible. The catalysts thus prepared were finally calcined in air at 700 °C for 4 h using a ramp of $5\,^\circ C\,min^{-1}$. The X-ray diffraction (XRD) patterns of the calcined supports were obtained for values between 5 and 90° by using Cu K$\alpha$ radiation at 35 kV and 40 mA.

Metal dispersion of catalysts was determined by hydrogen chemisorption at 298 K in a volumetric system. An adsorption stoichiometry of one hydrogen molecule per two surface ruthenium atoms was assumed. Before the characterization test, catalysts were reduced in pure hydrogen at 550 °C for 2 h.

The oxygen exchange ability of the prepared supports was tested in a volumetric glass system by cycling at 650 °C a known amount of $^{18}O_2$ through the sample, while analyzing with a quadrupole mass spectrometer (Balzers QMS 421) the evolution with time of the gas-phase composition.

For catalytic testing, usually 40–60 mg of sample was placed between two quartz wool plugs in a tubular quartz reactor at atmospheric pressure. The amount of catalyst used for each activity test was adjusted to maintain $CH_4$ and $CO_2$ conversions far from those predicted by the thermodynamic equilibrium. The reactant gas stream ($CH_4 : CO_2 : He$) was in proportion (10 : 10 : 80) at a total flow rate of $6\,L\,h^{-1}$. The gas compositions of reactants and products were analyzed by a gas chromatograph (Varian 3400). Before each experiment, the catalyst was reduced in a flow of $H_2$ ($1.2\,L\,h^{-1}$) at 550 °C for 2 h, cleaned from residual $H_2$ with a flow of He ($6\,L\,h^{-1}$) for 1 h and then heated to 650 °C. Once this temperature was reached, the reactant gas was allowed to pass through the sample for 19 h.

## 3. Results and discussion

Table 1 summarizes the catalytic properties of the prepared Ru catalysts during the DRM reaction after 19 h at 650 °C. It can be clearly seen, especially for low metal loading catalysts, that the nature of the support establishes large differences between the several ruthenium samples. The $Ru1/SiO_2$ catalyst, which was prepared as a reference for the metal supported on an inactive carrier, demonstrated the lowest activity per surface ruthenium site and the highest $CO/H_2$ ratio, indicative of the occurrence of the secondary reverse water gas shift reaction in high proportion. In addition, a dramatic loss of activity was observed for this catalyst for the first 10 h in reaction, showing after 19 h less than half of its initial activity. In contrast, $Ru1/ZrO_2$ and especially Ru1/Ce-Zr (WO) exhibited much higher activity and good selectivity towards $H_2$. For these latter catalysts, the $CO/H_2$ ratio was closer to unity. The presence of a support such as $ZrO_2$, participating in the reaction mechanism for $CO_2$ activation, improves not only the catalytic activity as compared to the silica-supported sample but also the stability under reaction conditions, although a considerable deactivation rate is still found. However, the ruthenium catalyst prepared on the Zr-Ce (WO) support showed not only high activity but also an excellent stability. Only 3% activity was lost within the first 8 h in reaction and its performance was perfectly maintained for a further 12 h. It is important to remark on the differences found between the catalyst supported on Zr and Ce oxides prepared by the microemulsion method and those prepared by impregnation. From table 1, one can appreciate that ceria addition by impregnation of the $ZrO_2$ support does not improve the catalytic activity or the selectivity to $H_2$. Apart from the performance level, the poor stability of the $CeO_2$-impregnated catalysts in reaction must be stressed on. The observed deactivation does not seem to decrease with the amount of added $CeO_2$, as the properties of the catalysts in table 1 reflect. Additional reaction tests with catalysts with $CeO_2$ contents up to 10 wt% in the $ZrO_2$ support did not show any beneficial effect of the promoter on the catalytic stability.

Table 1
$CH_4$ and $CO_2$ specific activity, $CH_4$ conversion, $H_2$ selectivity, $CO/H_2$ ratio and deactivation over various catalysts after 19 h on stream. (Reaction conditions: T = 650 °C, reactant mixture: ($CH_4:CO_2:He$) (10 : 10 : 80), flow rate: 6 L/h)

| Catalyst | H/Ru | Specific activity ($s^{-1}$) | | $X_{CH_4}$ (%) | $S_{H_2}$ (%) | $CO/H_2$ | Deactivation |
|---|---|---|---|---|---|---|---|
| | | $CH_4$ | $CO_2$ | | | | |
| $Ru1/SiO_2$ | 0.13 | 1.1 | 1.7 | 13 | 74 | 1.6 | 54 |
| $Ru1/ZrO_2$ | 0.17 | 2.6 | 3.1 | 39 | 88 | 1.1 | 12 |
| Ru1/Ce-Zr (WO) | 0.19 | 3.0 | 3.7 | 51 | 85 | 1.1 | 3 |
| $Ru1/ZrO_2$-$CeO_2$ (1.5%) | 0.15 | 0.8 | 1.2 | 11 | 76 | 1.5 | 35 |
| $Ru1/ZrO_2$-$CeO_2$ (3.5%) | 0.14 | 0.3 | 0.7 | 4 | 48 | 2.9 | 41 |
| $Ru5/ZrO_2$ | 0.08 | 1.5 | 1.9 | 35 | 87 | 1.1 | 22 |
| Ru5/Ce-Zr (WO) | 0.09 | 1.6 | 1.9 | 53 | 87 | 1.1 | 5 |
| $Ru5/ZrO_2$-$CeO_2$ (1.5%) | 0.07 | 1.8 | 2.1 | 36 | 85 | 1.1 | 20 |
| $Ru5/ZrO_2$-$CeO_2$ (3.5%) | 0.07 | 1.7 | 2.2 | 35 | 84 | 1.1 | 20 |

For samples with higher metal loading (larger metal particles), differences between catalysts due to the support modification are less important because of a more predominant role of the metal. A certain decrease in the $Ru5/ZrO_2$ specific activity as compared to the 1 wt% metal loading catalyst is observed. In this case, $CeO_2$ addition by impregnation did not show any significant effect on the catalytic performance (table 1). The largest difference was found again for the Ru5/Ce-Zr (WO) sample, for which deactivation with time was strongly reduced.

From data in table 1, it is seen that under reaction conditions deactivation for $CeO_2$-impregnated $ZrO_2$ catalysts is similar to (5 wt% Ru loading) or even faster (1 wt% Ru loading) than that for the respective unpromoted catalysts. The stability with time of the different samples with 1 wt% metal loading is compared in figure 1. As previously mentioned, the role of the support becomes more relevant in the case of low metal loadings. The utilization of supports able to activate $CO_2$ by reducing it to CO through carbonate-, bicarbonate- and/or formate-type intermediates opens an alternative pathway for the reaction enabling a bifunctional mechanism [14–16,21,22]. This reaction pathway is favored as long as the metal-support perimeter is enlarged. Thus, according to this and in agreement with the obtained results, smaller particle sizes obtained at lower metal loadings favor this bifunctional mechanism in the catalysts for $CO_2$ activation, showing a more pronounced effect of the support. In the case of these low metal loading samples, addition of $CeO_2$ to the $ZrO_2$ by impregnation led to an initial activity increase related to the $CeO_2$ loading. However, this effect disappeared with time, leading to a faster deactivation. This behavior is typical in $CeO_2$-supported catalysts [23,24], for which a strong decay of the initial activity in the DRM reaction is usually observed. The redox properties of ceria and the high mobility of lattice oxygen are probably the factors that initially promote catalytic activity in the DRM reaction, but its easier reducibility under the reaction conditions probably leads to decreased $CO_2$ adsorption on the support surface.

A completely different behavior is observed for the catalysts prepared by the microemulsion method as compared to those supported on the Ce-promoted $ZrO_2$ supports. This diverging trend cannot be ascribed to the Ce ceria content in the catalyst, which is much higher for the Zr-Ce (WO) sample, but more probably to the structure and properties of these oxides. XRD patterns for the diverse supports are presented in figure 2. The commercial $ZrO_2$ and the microemulsion-prepared $ZrO_2$ have tetragonal structure, although the latter showed a

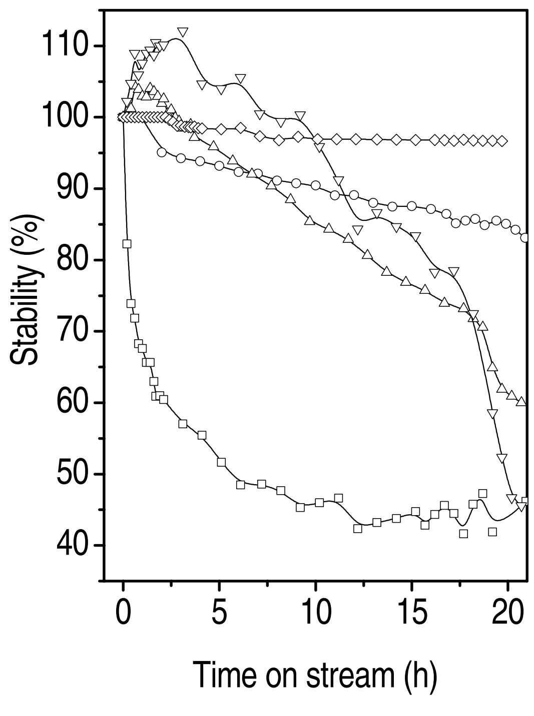

Figure 1. Stability with time during the $CH_4 + CO_2$ reaction for the 1 wt% Ru loaded catalysts. Reaction temperature: 650 °C, flow rate: 6 L $h^{-1}$. (–□–)$Ru1/SiO_2$, (–○–)$Ru1/ZrO_2$, (–△–)$Ru1/ZrO_2$-$CeO_2$ (1.5%), (–▽–)$Ru1/ZrO_2$-$CeO_2$ (3.5%), (–◇–)Ru1ZrCe (WO).

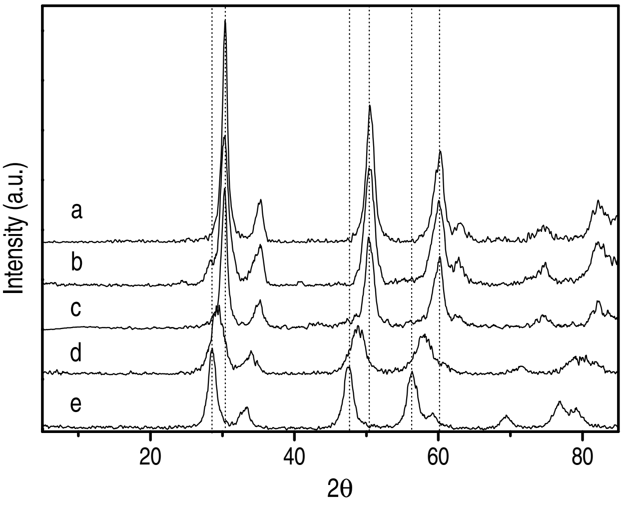

Figure 2. XRD patterns of the supports: (a) $ZrO_2$, (b) $ZrO_2$ (WO), (c) $ZrO_2$-$CeO_2$ (10%), (d) Zr-Ce (WO) ($Zr_{0.5}Ce_{0.5}O_2$) and (e) $CeO_2$ (WO).

certain proportion of monoclinic phase revealed by the shoulder at $2\theta = 28.3^\circ$ corresponding to a *d*-spacing of 3.15 Å. Although cubic and tetragonal structures in zirconia are difficult to differentiate, the splitting of the diffraction lines at $2\theta$ values close to 50.5 and 60.0°, which would correspond to single diffraction lines for the cubic structure [25], suggests the formation of the tetragonal phase. Cerium oxide prepared by the microemulsion method corresponded to $CeO_2$ with cubic structure. The ceria-impregnated $ZrO_2$ samples presented the same diffraction pattern as the *t*-$ZrO_2$ support alone, but only for the support with 10 wt% $CeO_2$ content (figure 1(c)) very weak diffraction peaks corresponding to $CeO_2$ were detected. On the contrary, the Zr-Ce (WO) sample revealed the structure of a mixed oxide $Zr_{0.5}Ce_{0.5}O_2$ with cubic structure according to the stoichiometry of its preparation. No other peaks due to single phases of ceria or zirconia were detected.

In order to characterize the supports in more detail, isotopic exchange experiments of oxygen between gas-phase $^{18}O_2$ and $^{16}O$ in the structure of the oxides were carried out at the reaction temperature (650 °C). The rate of exchange between $^{16}O$ in the oxide and $^{18}O$ in the gas phase can give a good parameter for comparison related to the oxygen mobility in the oxide and the ability of each catalyst to oxidize the carbonaceous deposits generated on the metal during the reactants' activation under reaction conditions.

Table 2 summarizes the oxygen exchange rate for the different oxides and their specific surface areas as determined by $N_2$ adsorption at 77 K according to the Brunnauer–Emmett–Teller equation. In good correlation with the experimental results obtained in the DMR reaction, the Zr-Ce (WO) ($Zr_{0.5}Ce_{0.5}O_2$) support exhibits the highest oxygen exchange rate, even higher than that of the $CeO_2$ (WO) oxide. The obtained results indicate that, even when the XRD patterns show similar structures for the $ZrO_2$-3.5%$SiO_2$ support and the $ZrO_2$ (WO) prepared by the microemulsion method, their oxygen exchange ability is completely different. By considering that the specific surface area of the silica-stabilized zirconia is even higher than that of the sample prepared by the WO microemulsion method, the large difference between the oxygen exchange rate in both samples reveals that the preparation of the oxide support has a major effect on their oxygen exchange capacity. On the other hand, the excellent stability under DRM conditions of the catalysts prepared on this new $Ce_{0.5}Zr_{0.5}O_2$ support can be explained by the synergy between the metal and the mixed oxide for reactants' activation and removal of carbonaceous species by oxidation. Studies by computer-simulation techniques using atomistic models on surfaces of cubic $CeO_2$-$ZrO_2$ solid solutions have suggested that the increase in the oxygen storage capacity experimentally observed in these systems relative to pure ceria can be explained by the introduction of zirconia into the ceria lattice, a fact that decreases the $Ce^{4+}/Ce^{3+}$ reduction energy on stable surfaces and increases the oxygen vacancies' tendency to segregate to these surfaces [26]. Especially for low metal loading catalysts, in which the bifunctional mechanisms are favored by increasing the metal-support interfacial zone [12,15,27–29], the catalytic stability of ruthenium catalysts is largely improved by using a high oxygen exchange capacity support.

In summary, a novel Ru/$Ce_{0.5}Zr_{0.5}O_2$ catalyst prepared by the impregnation with $Ru^{3+}$ of a mixed Ce-Zr oxide obtained by the water-to-oil microemulsion method has shown excellent catalytic properties for the $CH_4/CO_2$ reaction. Its high activity as well as its good stability in the reforming of methane with dioxide of

Table 2
Rate of oxygen exchange of the different oxide supports. $T_{\text{exchange}} = 650\,^\circ C$

| Oxide | $r_{\text{exchange}}$ ($^{18}O$) (mmol $g^{-1}$ $s^{-1}$) | $S_{\text{BET}}$ ($m^2$ $g^{-1}$) |
|---|---|---|
| $SiO_2$ | $8.91 \times 10^{-8}$ | 189 |
| $ZrO_2$-3.5%$SiO_2$ | $1.92 \times 10^{-7}$ | 74 |
| $ZrO_2$ (WO) | $1.04 \times 10^{-6}$ | 58 |
| $ZrO_2$-10% $CeO_2$ | $3.65 \times 10^{-6}$ | – |
| Zr-Ce (WO) $Zr_{0.5}Ce_{0.5}O_2$) | $5.69 \times 10^{-6}$ | 62 |
| $CeO_2$ (WO) | $4.98 \times 10^{-6}$ | 72 |

carbon opens an unexplored way for the designing of new catalysts for this reaction.

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