Reforming of methane with carbon dioxide over Pt/ZrO$_2$/SiO$_2$ catalysts—Effect of zirconia to silica ratio

Gunugunuri K. Reddy$^{a,b}$, Stéphane Loridant$^a$,* Atsushi Takahashi$^a$, Pierre Delichère$^a$, Benjaram M. Reddy$^b$

$^a$ Institut de Recherches sur la Catalyse et l’Environnement de Lyon, IRCELYON, UMR5256 CNRS-Université Claude Bernard Lyon 1, 2 av. Einstein, F-69626 Villeurbanne Cedex, France
$^b$ Inorganic and Physical Chemistry Division, Indian Institute of Chemical Technology, Uppal Road, Hyderabad 500 607, India

A R T I C L E   I N F O

Article history:
Received 31 May 2010
Received in revised form 2 September 2010
Accepted 15 September 2010
Available online 22 September 2010

Keywords:
Pt supported catalysts
ZrO$_2$/SiO$_2$ support
Dry reforming
Carbon dioxide
Methane
Syngas

A B S T R A C T

ZrO$_2$/SiO$_2$ mixed oxides with different ratios (2:1 to 4:1) were prepared by a deposition–precipitation method from zirconium hydroxide and colloidal silica and used as supports for platinum nano-particles. The synthesized catalysts along with Pt/ZrO$_2$ reference materials were tested for CH$_4$ reforming with CO$_2$ at a high temperature of 1073 K and at high space velocity. Very high reforming activity was observed for the Pt/ZrO$_2$/SiO$_2$ (4:1) sample among all the prepared catalysts. The effect of zirconia to silica ratio on the physico-chemical properties that determine the catalytic activity has been investigated characterizing all the catalysts after calcination, reduction as well as after reaction with several techniques. From X-ray diffraction patterns, BET and H$_2$ chemisorption measurements, X-ray photoelectron and FTIR spectra, the better catalytic properties of the Pt/ZrO$_2$/SiO$_2$ (4:1) sample have been explained by higher Pt dispersion due to the absence of remaining free silica and the presence of amorphous ZrSiO$_4$ in higher amount. Additionally, a better thermal stability of the prepared ZrO$_2$/SiO$_2$ supports compared to ZrO$_2$ was evidenced after ageing at 1073 K for 16 h in particular for the ratio 4:1. It also underlines the interest of the preparation method.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

New reserves of natural gas have been identified and potentially represent a new source of raw material for industry being able, in many cases, to substitute the petroleum that has been steadily rising in price and whose rate of production is expected to fall in the near future. Indirect utilization of natural gas via syngas is the main route to convert methane to liquid fuels, ammonia, methanol, etc. Industrially, syngas is mainly produced by steam reforming of methane. However, the H$_2$/CO ratio of 3:1 resulting from this process is higher than what is needed for the downstream synthesis process. CO$_2$ reforming of CH$_4$ called dry reforming is an alternative to steam reforming, which gives a low H$_2$/CO ratio i.e., around 1 [1–3]. Such ratio is more suitable for obtaining sulfur free synthetic liquid fuels and valuable oxygenated chemicals than the H$_2$/CO ratio coming from the traditional steam reforming process. Another advantage of dry reforming is utilization of two greenhouse gases as resources and thereby contributing to limitation of global warming. The main drawbacks of this reaction are a high endothermicity of the reaction even if it could be used for thermochemical storage and transfer of renewable energy sources such as solar energy [4,5], the high temperature requirement to reach high conversions and the deactivation of the catalysts arising from their thermal stability and coke deposition [1,3,6,7]. Many authors agree that coke formation is the main cause of deactivation. Carbon deposition results from two reactions, Boudouard reaction (2CO → C + CO$_2$) and/or methane decomposition (CH$_4$ → C + 2H$_2$). The type and the nature of coke formed depend on the metal and in many cases on the support used.

Various metals like Ni, Ru, Rh, Pt, Ir and Pd have been investigated for the dry reforming of CH$_4$ [8–14]. Although there is some debate about the order of activity of these metals, Rh was preferred by most authors due to the good activity and stability. Ni catalysts, however, are commercially more interesting compared to noble metals but their main drawback is the high rate of coke formation. From an economic point of view (relatively low price and good availability), Pt corresponds to a reasonable compromise. In several studies, Pt/ZrO$_2$ catalysts have been shown to be very stable for the dry reforming reaction, in particular when operating at moderate temperatures i.e., 723–923 K [15–18]. However, this type of catalysts deactivate when operating at higher temperatures, in particular at 1073 K, and far from thermodynamic equilibrium [5,19–21]. Deactivation can be explained both by coking and by sintering of Pt metal particles occurring at high temperature [7,19–21].

* Corresponding author. Tel.: +33 472445334; fax: +33 472445399.
E-mail address: stephane.loridant@ircelyon.univ-lyon1.fr (S. Loridant).

DOI: 10.1016/j.apcata.2010.09.007
The sintering leads to decrease in the number of Pt active sites and could also weaken the metal–support interaction limiting the removal of carbon formed over Pt particles [20].

As high Pt dispersion can be favoured by high specific surface area (SSA) of ZrO₂, methods of preparation affording high surface area and good thermal stability at high temperature are required to get and maintain high number of Pt active sites. One solution is to support ZrO₂ on a thermally stable support like silica. Nanosized CeO₂ deposited over SiO₂ prepared by using a modified ammonia assisted deposition–precipitation method has already revealed improved surface area, better thermal resistance up to 1073 K [22].

In the present study, ZrO₂/SiO₂ support with different zirconia and silica ratios (2:1 to 4:1) was prepared by deposition–precipitation method and the optimum ratio was determined from catalytic testing achieved under severe conditions in particular at a temperature of 1073 K. The catalysts have been characterized after calcination, reduction as well as after reaction by using different complementary techniques, namely X-ray diffraction, IR spectroscopy, BET surface area and pore size measurements, chemical analysis, H₂ chemisorption and X-ray photoelectron spectroscopy in order to explain the effect of zirconia to silica ratio on the reforming activity. Additionally, Pt sintering and coke deposition were investigated respectively by transmission electron microscopy and both Raman spectroscopy and TGA measurements.

2. Experimental

2.1. Catalyst preparation

ZrO₂/SiO₂ supports with different zirconia to silica ratios (4:1, 3:1 and 2:1) were prepared by deposition–precipitation method [23] at a constant pH 9, by using ammonia as the precipitating agent. The precursors used were ZrO(NO₃)₂·xH₂O (Aldrich, 99%) and colloidal silica (LUDOX® AS-30, 30 wt.% respectively. In a typical procedure to prepare mixed oxides, the required quantities of Zr and Si precursors were dissolved separately in deionized water and mixed together. The mixed solution and ammonia solution (28 wt.% in water) were added in a balloon by maintaining a constant pH 9 under vigorous stirring. The obtained solids were filtered off, washed in water (acetone and HF during 24 h). After drying at 383 K for 12 h, and subsequently calcined at 773 K for 3 h under air flow leading to ZrO₂/SiO₂ supports labeled as ZrSi41, ZrSi31 and ZrSi21. For comparison, a pure ZrO₂ prepared according to the same method and commercial ZrO₂ (Saint Gobain, Norpro XZ-16075) were also used as supports and are labeled respectively as ZrO₂ and com-ZrO₂ in the following.

Platinum was deposited over various ZrO₂/SiO₂ and pure ZrO₂ supports by a standard wet impregnation method. The mass of Pt(NO₃)₂·3H₂O (Aldrich, 99.995%) required to obtain a theoretical Pt loading of 1 wt.% was dissolved in deionized water. To this clear solution, finely powdered supports were added. After evaporation of the excess water, the resulting samples were oven dried at 383 K for 12 h and calcined at 773 K for 3 h under air flow. The calcination temperature was chosen high enough to decompose (NO₃)⁻ anions and low enough to avoid Pt metal area loss as previously evidenced [24].

2.2. Catalyst characterization

X-ray powder diffraction patterns were recorded on the calcined supports, oxide precursors, reduced and spent catalysts with a Siemens D5005 diffractometer using Ni-filtered Cu Kα (0.15418 nm) radiation source and standard recording conditions. The Kα₂ contribution to the diagrams was removed with the EVA software (Bruker-AXS). The crystalline phases present in the samples were identified by comparison with reference patterns available in the JCPDS database. The average crystallite size of ZrO₂ was estimated using the Debye–Scherrer equation: \( D = K \lambda / (D \cos \theta) \) after Warren’s correction for instrumental broadening. K was taken equal to 1 and \( \lambda \) corresponded to the wavelength of the Kα₁ line (0.15406 nm). \( \beta \) was the effective line width of the X-ray reflexion calculated by means of the formula: \( \beta^2 = (\beta_{\text{mes}})^2 - (\beta_{\text{inst}})^2 \) where \( \beta_{\text{mes}} \) was the breadth of the band located around 2θ= 30.3° for the ZrO₂ tetragonal structure and of the two bands around 28.2 and 31.5° for the ZrO₂ monoclinic structure. The instrumental width \( \beta_{\text{inst}} \) was 0.07π/180°/rd.

The specific surface areas (SSAs) of calcined supports and catalysts were determined by nitrogen physisorption at 77 K using a Micromeritics ASAP 2020 instrument. The surface area was calculated according to the method of Brunauer, Emmett and Teller (BET). Adsorption–desorption isotherms have been recorded on catalysts after reduction. Their pore size distributions were determined using the BJH and t-plot methods. Before measurements, the samples were degassed under vacuum of 10⁻³ Pa for 3 h at 573 K to remove adsorbed species.

Pt dispersion values that correspond to the fraction of Pt surface atoms were deduced from H₂ chemisorption measurements achieved using a Micromeritics ASAP 2010C apparatus after reduction at 1073 K for 2 h under the flow of 50%H₂–50%N₂ gas mixture (100 mL min⁻¹) followed by evacuation under vacuum at 573 K and cool down at 308 K. H₂ chemisorption isotherms were measured up to 40 kPa subtracting a blank. Dispersion values were calculated using the formula:

\[ D = \frac{100 \times S \times M}{N \times \pi \times r^2} \]

where \( D \) is the dispersion, \( S \) (m² g⁻¹) the metallic surface area, \( M \) the Pt molar mass (195.084 g mol⁻¹), \( N \) the Avogadro’s number (6.023 × 10²³), \( r \) the Pt atomic radius (160 pm).

Chemical analysis of Pt, Zr and Si was obtained from ICP-OES spectra (ACTIVA/Jobin Yvon) after acidic dissolution of samples. X-ray photoelectron experiments of the oxide precursors, reduced and spent catalysts were carried out in a Kratos Axis Ultra DLD spectrometer equipped with a magnetic immersion lens, a hemispherical analyser and a delay line detector. Spectra of the O 1s, C 1s, Zr 3d, Si 2p, Pt 4f levels were recorded using Al Kα X-ray source, with pass energy of 20 eV and spot size aperture of 300 μm × 700 μm. A charge neutralizer was used to control charges effects on the samples.

Transmission FTIR spectra of supports after calcination were recorded on self-supporting disks of powder dispersed in KBr with a Bruker Vector 22 spectrometer.

Pt particle sizes were determined from High-Resolution Electron Microscopy on reduced and spent catalysts. As direct observation of metallic particles on ZrO₂ is not straightforward due to its strong electron absorption, it was necessary to prepare replicas. For that purpose, the catalysts were ground and dispersed in ethanol followed by deposition over a cleaved mica plate. This ensemble was then covered with a carbon film and placed in a solution containing water, acetone and HF during 24 h. After dissolving ZrO₂, the Pt particles stayed on the carbon film which was deposited on standard Cu grid. Pt particles were then observed with JEOL 2010 LaB₆ microscope and their average sizes were calculated from statistical treatment of TEM micrographs.

Carbon deposition was investigated from thermogravimetric measurements achieved on aged catalysts with a SETARAM TGA12 apparatus under air up to 1073 K and by Raman spectroscopy, a powerful technique to investigate coke deposition [25]. Raman spectra were recorded using a LabRam HR spectrometer (Horiba-Jobin Yvon) equipped with BXFM confocal microscope, interference
and Notch filters and CCD detector. The exciting line at 514.5 nm delivered by a 2018 RM Ar–Kr laser (Spectra-Physics) was then focused with a power of 1 mW using a 100× objective.

2.3. Activity measurements

Dry reforming of methane was performed in a down flow fixed bed differential quartz U-shaped reactor at normal atmospheric pressure. Typically 30 mg of catalyst with particles sizes lower than 80 μm were diluted in 70 mg of quartz powder to minimize heat and mass transfer limitations. The mixture was loaded into the reactor, the temperature of which was monitored by a K type thermocouple with its tip located near the catalyst bed and connected to a temperature-indicator controller. Catalytic data were measured at 1073 K with a feed composition of CO2/CH4/N2 = 0.84/1/1.80 and a total flow rate of 200 cm³ min⁻¹. This high temperature was chosen to ensure that the reaction is far from thermodynamic equilibrium, and to limit coke formation due to Boudouard equilibrium [1]. At this temperature and for such gas feed, the equilibrium CH₄ and CO₂ conversions were reported to be higher than 95% [1,26].

The space velocity was also chosen to be high (400,000 mL h⁻¹ g⁻¹cat) to limit the conversions and avoid influence of the thermodynamic equilibrium on the measurements of catalytic activities.

The Weisz–Prater criterion Nₜₚ used to estimate the influence of pore diffusion on reaction rates was found to be always lower than 0.95 showing internal mass transfer limitations can be excluded [27].

Prior to the reaction, the catalyst was reduced at 1073 K using a gas mixture N₂/H₂ = 1/1 and a flow rate of 100 mL min⁻¹. The temperature was decreased to 973 K before introduction of the reaction mixture to prevent high endothermic phenomenon and the temperature was then increased up to 1073 K. The reaction products were analyzed using an online microGC (Agilent 3000A) equipped with thermal conductivity detectors (TCD) with two columns (PLOT U and PLOT MS 5A).

3. Results

3.1. Characterization of the supports and catalysts before reaction

BET specific surface areas of supports and Pt supported catalysts after calcination are reported in Tables 1 and 2, respectively. As expected, silica containing supports exhibited much higher surface areas compared to the two pure zirconias calcined at the same temperature. Their measured values were close to that of colloidal silica calcined at 773 K indicating that zirconium oxide was over silica particles in the Zr–Si samples or if present as separated particles, owned similar surface area. A slight decrease in the surface area was observed after impregnation with platinum and subsequent calcination at 773 K. This may be due to the penetration of the dispersed Pt into the pores of supports thereby narrowing the pores diameters and blocking some of the pores. The surface areas of the Pt/ZrSi41 and Pt/ZrSi31 catalysts were respectively 188 and 170 m² g⁻¹ after reduction at 1073 K for 2 h. This very low decrease confirmed good thermal stability of the Zr–Si supports. Finally, the pore size distributions deduced from the isotherms revealed that the Zr–Si samples after reduction at 1073 K were essentially mesoporous with average size around 4 nm.

The X-ray diffraction patterns of the various Zr–Si supports and pure zirconias are plotted in Fig. 1. Only diffraction peaks pertaining to tetragonal ZrO₂ were observed in the case of ZrO₂. The average crystallite size deduced from its pattern was 8.8 nm which is close to the d theoretical value obtained assuming that not-agglomerated spherical particles were present. Indeed, in that assumption, d is given by 6/(ρ × SSA) where ρ is the mass volume of ZrO₂ (5.89 g cm⁻³) and SSA is the specific surface of ZrO₂ (98 m² g⁻¹) and is equal to 10 nm. The com-ZrO₂ was a mixture of mainly monoclinic ZrO₂ and also small amount of tetragonal ZrO₂. No bands due to crystalline SiO₂ or zircon ZrSiO₄ compounds were observed in the XRD patterns of Zr–Si samples. They contained mainly broad bands suggesting that both silica and zirconia were present as amorphous phases. However, additional weak band at 30.3° (2θ) indicated the presence of small amount of crystalline tetragonal ZrO₂, the quantity of which was the highest for the ZrSi41 support.

Finally, no diffraction peaks of PtO were observed for the Pt catalysts after calcination which is due to the very low noble metal loading over high surface area supports.

Fig. 2 shows FTIR spectra of Zr–Si supports from 400 to 1800 cm⁻¹. The bands observed between 800 and 1800 cm⁻¹ cannot be due to any allotropic form of ZrO₂ since all the optical modes of these phases are below 750 cm⁻¹ [28,29]. The ones near 1065, 1123 and 1225 cm⁻¹ were attributed to νasym(Si–O–Si) stretching vibrations [30–32] and that around 1635 cm⁻¹ was due to δ(H–O–H) bending vibration of water molecules [32]. The band located at 988 cm⁻¹ in the Zr21 support with weak intensity could correspond to ν(Si–OH) vibrations [30,31,33]. It was much more

### Table 1

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Specific surface area (SSA) values, crystallite sizes, and crystalline phases present in the supports after calcination at 773 K.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Support</td>
<td>After calcination at 773 K</td>
</tr>
<tr>
<td></td>
<td>SSA (m² g⁻¹)</td>
</tr>
<tr>
<td>com-ZrO₂</td>
<td>200</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>98</td>
</tr>
<tr>
<td>ZrSi41</td>
<td>208</td>
</tr>
<tr>
<td>ZrSi31</td>
<td>212</td>
</tr>
<tr>
<td>ZrSi21</td>
<td>215</td>
</tr>
<tr>
<td>SiO₂</td>
<td>205</td>
</tr>
</tbody>
</table>

m: monoclinic, t: tetragonal, a: amorphous, n.d.: not determined.

### Table 2

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Chemical compositions, specific surface area (SSA) values, XPS ratios and hydrogen chemisorption results for the different Pt supported catalysts.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst</td>
<td>Pt loading (wt.%)</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt/com-ZrO₂</td>
<td>0.65</td>
</tr>
<tr>
<td>Pt/ZrO₂</td>
<td>0.74</td>
</tr>
<tr>
<td>Pt/ZrSi41</td>
<td>0.88</td>
</tr>
<tr>
<td>Pt/ZrSi31</td>
<td>0.80</td>
</tr>
<tr>
<td>Pt/ZrSi21</td>
<td>0.80</td>
</tr>
</tbody>
</table>

m: monoclinic, t: tetragonal.

a: Derived from H₂ chemisorption results.
Fig. 1. XRD patterns of (a) ZrSi21, (b) ZrSi31, (c) ZrSi41 (d) ZrO2 and (e) com-ZrO2 after calcination at 773 K.

Fig. 2. FTIR spectra between 400 and 1800 cm$^{-1}$ of (a) ZrSi21, (b) ZrSi31, (c) ZrSi41 supports after calcination at 773 K.

Fig. 3. FTIR spectra between 3700 and 3800 cm$^{-1}$ of (a) ZrSi41, (b) ZrSi31, (c) ZrSi21 supports and (d) colloidal SiO2 after calcination at 773 K.

intense and shifted to 980 cm$^{-1}$ in the ZrSi41 sample revealing an additional band that could arise from Si–O–Zr linkages between silica and zirconia [30,34].

The FTIR spectra of the Zr–Si mixed oxide supports are zoomed between 3700 and 3800 cm$^{-1}$ and compared to that of colloidal SiO2 calcined at 773 K in Fig. 3. This last one contained bands near 3736 and 3744 cm$^{-1}$ attributed to $\nu$(SiO–H) stretching modes of isolated silanol groups [31,33]. The relative absorbance of these bands were strongly reduced for the ZrSi21 and Zr31 samples indicating consumption of silanol groups during deposition of zirconium hydroxide over colloidal silica. Interestingly, no bands were evidenced for ZrSi41 that means no free silica remained in this mixed support contrary to the two others [35].

Pt loadings and atomic Zr to Si ratios are listed in Table 2 for all the prepared catalysts. The bulk ratios determined from chemical analyses were slightly lower than the theoretical values. It could arise from higher hydration degree of the ZrO(NO3)$_2$·xH$_2$O precursor than expected. The Zr to Si ratios determined from XPS measurements afforded surface compositions since the mean free path of emitted electrons is ca 3.5 nm. All the values after calcination reported in Table 2 were lower than the bulk ratios. Additionally, two components were evidenced by XPS in the Si 2p signals of Pt/ZrSi catalysts after calcination at 773 K (Fig. 4). The first one centered at 103.2 eV was due to SiO$_2$ whereas the second one near 101.7 eV was ascribed to amorphous ZrSiO$_4$ [36,37]. This last band represented only 22 and 24% for the Pt/ZrSi31 and Pt/ZrSi21 catalysts respectively but reached 40% for Pt/ZrSi41 evidencing a stronger solid state reaction between ZrO2 and SiO2 for this compound. Furthermore, the highest Si(ZrSiO$_4$)/Zr ratio was measured for this sample in spite of the lowest Si/Zr ratio (Table 2).

The presence of ZrSiO$_4$ phase was confirmed from the O 1s signals that showed a third band at 531.1 eV in addition to two bands at 530.1 eV and 532.4 eV due to oxygen anions in ZrO2 and SiO2 respectively [36,37]. However, all the Zr 3d spectra of the Pt/ZrSi catalysts contained only two bands at 182.2 eV (Zr 3d$_{5/2}$)
Fig. 4. X-ray photoelectron Si 2p spectra of (a) Pt/ZrSi41, (b) Pt/ZrSi31, (c) Pt/ZrSi21 catalysts after calcination at 773 K and of (d) Pt/ZrSi41, (e) Pt/ZrSi31 and (f) Pt/ZrSi21 after reduction at 1073 K.

and 184.6 eV (Zr 3d3/2) the positions of which were close to those of ZrO2 [35–37]. Nevertheless, the small shift of 0.4 eV by comparison with the Pt/ZrO2 catalyst after calcination (Fig. 5) is probably due to the presence of ZrSiO4 as previously reported [36].

After reduction of the catalysts at 1073 K for 2 h, all the Zr–Si samples remained amorphous for X-ray diffraction. Additionally, only small decrease in specific surface areas was noticed. For instance, SSA values of 188 and 170 m2 g−1 were measured for the Pt/ZrSi41 and Pt/ZrSi31 catalysts respectively instead of 202 m2 g−1 after calcination for the two samples. It confirms that the precipitation–deposition method used in the present study allows preparation of catalysts with good thermal stability. For ZrO2, a mixture of tetragonal and monoclinic zirconia was observed at this step of the preparation whereas only tetragonal was evidenced after calcination. This structural evolution was related to the crystalline growth of ZrO2 crystallites. Indeed, tetragonal zirconia can be stabilized at room temperature for small crystals because of difference in the surface energy between the tetragonal and monoclinic phases [38–40]. This metastability is lost during thermal treatment when the crystallite size becomes higher than critical size. In the same way, only monoclinic zirconia was evidenced in the com-ZrO2 after reduction indicating transformation of tetragonal crystallites present after calcination to monoclinic ones.

After reduction, the contribution of the Si 2p band due to ZrSiO4 to the overall Si 2p signal remained high for Pt/ZrSi41 (Fig. 4) and as after calcination, its corresponding Si(ZrSiO4)/Zr ratio was the highest (Table 2).

Fig. 5. X-ray photoelectron Zr 3d spectra of Pt/ZrO2 (a) after calcination, (b) after reaction and of Pt/ZrSi41 (c) after calcination and (d) after reaction.

X-ray photoelectron Pt 4f spectra of the catalysts after reduction are presented in Fig. 6. The main bands Pt 4f7/2 and Pt 4f5/2 were located near 71.1 eV and 74.1 eV which are characteristic of platinum metal [41,42]. The asymmetric character of the doublet is related to the density of states on the constituent atoms at the Fermi level [43]. The presence of Pt4+ cations stabilized by strong metal–support interaction (SMSI) can increase this asymmetry and induce a broadening of the Pt 4f doublet [42,44]. However, no significant difference from one sample to the other was evidenced in the present study.

Fig. 6. X-ray photoelectron Pt 4f spectra of (a) Pt/ZrSi41, (b) Pt/ZrSi31 and (c) Pt/ZrSi21 catalysts after reduction at 1073 K.
Table 3
Pt loadings, \( X_i \), initial conversions, \( V_i \), initial rates of transformation, \( \Delta X/X_i \), relative losses in conversion during 16 h catalytic testing and CO/H\(_2\) initial ratios measured at 1073 K for the different Pt supported catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pt loading (wt.%)</th>
<th>( X_{i(CH_4)} ) (%)</th>
<th>( V_{i(CH_4)} ) (mmol g(Pt)(^{-1}) s(^{-1}))</th>
<th>( \Delta X_{CH_4}/X_{i(CH_4)} ) (%)</th>
<th>( X_{i(CO_2)} ) (%)</th>
<th>( V_{i(CO_2)} ) (mmol g(cat)(^{-1}) s(^{-1}))</th>
<th>( \Delta X_{CO_2}/X_{i(CO_2)} ) (%)</th>
<th>CO/H(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/com-ZrO(_2)</td>
<td>0.65</td>
<td>30.3</td>
<td>57.8</td>
<td>62.4</td>
<td>51.8</td>
<td>0.64</td>
<td>51.7</td>
<td>1.4</td>
</tr>
<tr>
<td>Pt/ZrO(_2)</td>
<td>0.74</td>
<td>44.4</td>
<td>74.4</td>
<td>62.8</td>
<td>60.5</td>
<td>0.75</td>
<td>56.5</td>
<td>1.3</td>
</tr>
<tr>
<td>Pt/ZrSi(_4)</td>
<td>0.88</td>
<td>73.5</td>
<td>103.6</td>
<td>29.8</td>
<td>96.4</td>
<td>1.20</td>
<td>25.3</td>
<td>1.2</td>
</tr>
<tr>
<td>Pt/ZrSi(_3)</td>
<td>0.80</td>
<td>46.0</td>
<td>71.3</td>
<td>60.2</td>
<td>63.0</td>
<td>0.78</td>
<td>56.0</td>
<td>1.2</td>
</tr>
<tr>
<td>Pt/ZrSi(_2)</td>
<td>0.80</td>
<td>41.8</td>
<td>64.8</td>
<td>70.3</td>
<td>57.1</td>
<td>0.71</td>
<td>68.9</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Pt surface areas and dispersion values deduced from H\(_2\) chemisorption are given in Table 2. All the catalysts owned rather good dispersion values after reduction at 1073 K except Pt/com-ZrO\(_2\). An interesting observation in the present study is that Pt/ZrSi\(_4\) exhibited significantly better Pt dispersion than Pt/ZrSi\(_3\) and Pt/ZrSi\(_2\) in spite of similar surface areas.

3.2. Catalytic activity for dry reforming of methane

Among the tested Pt/ZrO\(_2\) and Pt/ZrSi catalysts, Pt/ZrSi\(_4\) showed much better CH\(_4\) and CO\(_2\) conversions, rates of CH\(_4\) and CO\(_2\) consumption (Table 3). Interestingly, the rate of CH\(_4\) transformation expressed per gram of Pt (Table 3) was directly linked to the Pt dispersion (Table 2) except for Pt/com-ZrO\(_2\). It indicates that CH\(_4\) conversion is determined by the number of Pt atoms at the surface.

Figs. 7 and 8 present the evolution of CH\(_4\) and CO\(_2\) conversions versus time at a reaction temperature of 1073 K. As it was previously reported for Pt/ZrO\(_2\) catalysts in similar reaction conditions [7,19–21], all the samples suffered from continuous deactivation which was more limited for Pt/ZrSi\(_4\) (see the relative \( \Delta X/X_i \) parameters in Table 3).

However, the \( X_{CO_2}/X_{CH_4} \) ratios were found to be higher than 1.19 the value expected for a feed with a CO\(_2\) to CH\(_4\) ratio of 0.84 considering that only the dry reforming reaction was involved. These higher ratios can be explained by the reverse water-gas shift (RWGS) reaction occurring simultaneously with CO\(_2\) reforming of CH\(_4\) [1,19] according to:

\[
CO_2 + H_2 \leftrightarrow CO + H_2O, \quad \Delta H_{298K} = 41 \text{kJ mol}^{-1} \tag{1}
\]

The existence of the RWGS reaction was clearly confirmed by the detection of H\(_2\)O in the products. It also leads to CO/H\(_2\) ratios significantly higher than unity (Table 3). Nevertheless, high \( X_{CO_2}/X_{CH_4} \) and CO/H\(_2\) ratios can also be explained by contribution of the reverse Boudouard’ equilibrium consecutive to coke deposition leading to higher CO formation:

\[
CO_2 + C \leftrightarrow 2CO, \quad \Delta H_{298K} = 171 \text{kJ mol}^{-1} \tag{2}
\]

CO/H\(_2\) ratios increased versus time on stream (Fig. 9) suggesting higher contribution of one of these reactions what could arise from the increase in the CO\(_2\) partial pressure consecutive to deactivation.

3.3. Thermal stability and coke formation

The thermal stability of zirconia-based supports after 16 h of ageing under reaction feed at 1073 K was investigated by XRD. The patterns of catalysts revealed that crystallization of ZrO\(_2\) occurred in all the supports. For instance, the crystallite size increased from 11.4 to 19.7 nm for the com-ZrO\(_2\) support (Table 4). The ZrO\(_2\) support that owned only tetragonal structure after calcination consisted of mixture of monoclinic and tetragonal phases after reduction at 1073 K and after reaction at the same temperature. As already said, the transition of crystallites from tetragonal to monoclinic structure is explained by the crystalline growth rendering unstable the tetragonal structure. This crystalline growth was
clearly evidenced from the evolution of the crystallite size (Table 4). It was also observed for the Zr–Si supports that were amorphous after calcination and reduction but became crystalline with tetragonal structure after reaction. Nevertheless, this evolution was more limited than for the pure ZrO₂ supports showing better thermal stability. Furthermore, ZrSi₄1 owned the best thermal stability with a crystallite size of only 7.9 nm after reaction among all the supports (Table 4). No mixed crystalline phase such as ZrSiO₄ zircon was evidenced by XRD after reaction.

The good thermal stability of Zr–Si supports was confirmed from the X-ray photoelectron Si 2p spectra of the Pt/ZrSi catalysts after reduction at 1073 K that were similar to those after calcination with two components due to SiO₂ and amorphous ZrSiO₄ (Fig. 4). The Zr 3d signal of the activated Pt/ZrSi catalysts did not change after reduction but was shifted to higher energy after reaction as illustrated for Pt/ZrSi41 in Fig. 5d. It suggests the presence of higher amount of ZrSiO₄. It was not possible to confirm this assumption from the Si 2p signal because of the presence of quartz used for dilution of catalysts.

The sintering of Pt particles was investigated measuring the average size before and after reaction for the Pt/ZrO₂ catalyst (Fig. 10a and b). HREM images revealed growth of Pt particles but rather limited. Indeed, statistical analysis for this sample showed an increase of Pt diameter from 3.9 to 4.7 nm. As the dispersions corresponding to these sizes are respectively 24 and 20%, the sintering of Pt particles cannot explain the significant loss of activity of the Pt supported catalysts.

Thermogravimetric measurements achieved during heating under air flow up to 1073 K did not reveal coke deposition on aged catalysts. It revealed that the amount of deposited coke was below the detection limit of TGA. However, as shown for Pt/ZrSi41 after reaction in Fig. 11, the presence of disordered graphite was clearly evidenced in the Raman spectra of all the tested catalysts through observation of two bands near 1380 cm⁻¹ and 1570 cm⁻¹ typical of disordered graphite [45]. The thin band at 471 cm⁻¹ was due to quartz powder used for catalyst dilution. The XPS C 1s signal mainly revealed one band located at 284.6 eV attributed to graphitic carbon [46] and by the high C/Pt ratios measured for the catalysts after reaction (Table 4).

4. Discussion

4.1. Structure of the ZrSi supports

In this paper, a deposition–precipitation method was used to prepare mixed ZrO₂/SiO₂ supports with high specific surface area (200 m² g⁻¹). The consumption of the main part of silanol groups revealed by FTIR indicated that at least a part of zirconium oxide

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Crystalline phase</th>
<th>ZrO₂ crystallite size (nm)</th>
<th>XPS ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pt/Zr</td>
</tr>
<tr>
<td>Pt/com-ZrO₂</td>
<td>m</td>
<td>19.7</td>
<td>-</td>
</tr>
<tr>
<td>Pt/ZrO₂</td>
<td>t + m</td>
<td>22.0 + 21.0</td>
<td>0.008</td>
</tr>
<tr>
<td>Pt/ZrSi41</td>
<td>t</td>
<td>7.9</td>
<td>0.005</td>
</tr>
<tr>
<td>Pt/ZrSi31</td>
<td>t</td>
<td>10.0</td>
<td>0.007</td>
</tr>
<tr>
<td>Pt/ZrSi21</td>
<td>t</td>
<td>10.0</td>
<td>0.007</td>
</tr>
</tbody>
</table>

m: monoclinic, t: tetragonal.
was present as an amorphous thick layer over SiO2. FTIR and XPS revealed interaction between ZrO2 and SiO2 to form amorphous ZrSiO4 the proportion of which was higher for ZrSi41. This phase was formed at much lower temperature than that of crystalline ZrSiO4 which was reported to be higher than 1473 K [47,48].

An interesting parameter was the Zr/Si ratio deduced from XPS measurements that was lower than the bulk ratio for all the Zr–Si compounds (Table 2). As such difference cannot be explained by a difference of mean free path between Si 2p and Zr 3d electrons, it revealed that SiO2 or ZrSiO4 was preferentially probed by XPS compared to ZrO2. The presence of uncovered SiO2 particles seems to be rejected since the amount of silanol groups remaining at the surface of silica was very low. A possible explanation is agglomeration of amorphous ZrO2 particles deposited over SiO2. Such agglomerates would be then less probed by XPS than ZrSiO4 particles.

After 16 h of ageing at 1073 K under reaction mixture, tetragonal ZrO2 was nucleated in the Zr–Si supports. However, their crystalline growth was limited compared to pure ZrO2 in particular for ZrSi41 which owned a crystallite size of only 7.9 nm. This result confirmed that the deposition–precipitation method used in this study leads to oxides with better thermal stability as previously reported [22].

4.2. Role of the ZrSi support on Pt dispersion and catalytic activity

In this study, the rate of CH4 transformation was significantly higher for the Pt/ZrSi41 catalyst than for the other ones. This improvement cannot be explained by higher surface area since it was close to that of Pt/ZrSi21 and Pt/ZrSi31. Additionally, these two catalysts owned Pt dispersions and catalytic activities similar to those of Pt/ZrO2 in spite of a two times higher SSA value. The lower properties of Pt/ZrSi21 and Pt/ZrSi31 could arise from the presence after calcination of remaining free silica in the corresponding supports contrary to ZrSi41 as evidenced by FTIR spectroscopy (Fig. 3). Indeed, the Pt2+(NH3)4 cations should adsorb stronger on free silica than on zirconia surface because of a much smaller isoelectric point. Hence, for ZrSi31 and ZrSi21 supports, a part of Pt particles would be formed on free silica. As the interaction between Pt and SiO2 is weak [49,50], the Pt sintering would be higher for these supports during reduction at 1073 K than for ZrSi41 leading to lower dispersions (Table 2) and catalytic activities (Table 3). A Zr/Si ratio of 4 would lead to supports with complete coverage of SiO2 by amorphous ZrO2 or ZrSiO4 phases.

Another explanation for the better dispersion and catalytic activity of Pt/ZrSi41 is the higher proportion, at the surface, of ZrSiO4 compared to SiO2 and ZrO2 as evidenced by XPS data (Fig. 4 and Table 3). This phase already formed after calcination of the support would afford better dispersions.

4.3. Stability with time on stream

Among simple oxides supports, ZrO2 was reported to lead to a better catalytic stability [18]. This stability can be explained from the bifunctional pathway occurring on Pt/ZrO2 catalysts [1,24,51]. Indeed, the first path involves the decomposition of CH4 on the Pt particle, resulting in the formation of H2. Carbon formed during the decomposition of CH4 can partially reduce the oxide support near the metal particle or, in the absence of a reducible oxide, form carbon deposits on the metal. The second path is the dissociation of CO2. The CO2 adsorbs on the support and, when near the metal particles, dissociates to form CO and O. The oxygen formed during the dissociation can then reoxidize the support providing a redox mechanism for continuous cleaning. Hence, the balance between the rate of decomposition and the rate of cleaning determines the overall stability of the catalyst [21]. The higher stability of Pt/ZrO2 catalysts has been related to strong Pt–Zr+ interactions [19] and their coking resistivity due to the ability of ZrO2 for CO2 dissociation [24].

However, Pt/ZrO2 catalysts slowly deactivate at high reaction temperature when operating far from thermodynamic equilibrium [7,19–21]. This feature was confirmed in the present study both for platinum supported on pure ZrO2 and ZrSi mixed oxide supports. The deactivation of catalysts seems to arise mainly from the platinum coverage by coke and in lesser extent from Pt sintering in agreement with the literature [7,18–21]. The presence of coke was clearly evidenced for the catalysts characterized after reaction by Raman spectroscopy and XPS. The absence of coke detection by TGA during thermal treatment under air flow indicated that the quantity of coke is low but enough to deactivate the catalysts by covering the Pt particles present in small number and size. Deactivation rate was more limited for Pt/ZrSi41 but it could arise from conversions closer to those of the thermodynamic equilibrium [7].

5. Conclusions

ZrO2/SiO2 mixed oxides with different ratios (2:1 to 4:1) were prepared by a deposition–precipitation method of zirconium hydroxide over colloidal silica and used after calcination as supports for platinum nano-particles. After calcination, these catalysts contained amorphous ZrSiO4 and amorphous ZrO2 covering SiO2.

The corresponding catalysts and Pt/ZrO2 references were tested for CH4 reforming with CO2 under severe conditions (high temperature and space velocity). Excellent reforming activity was observed for Pt/ZrO2/SiO2 (4:1) sample among the various tested catalysts and has been explained by higher Pt dispersion due to the absence of remaining free silica and the presence of amorphous ZrSiO4 in higher amount.

Additionally, a better thermal stability of the prepared ZrO2/SiO2 supports compared to pure ZrO2 was evidenced after ageing at 1073 K for 16 h in particular for the ratio 4:1. It also underlines the interest of the preparation method.

However, in the chosen reaction conditions, the Pt/ZrO2/SiO2 suffered from deactivation mainly due to coking in similar way than Pt/ZrO2 catalysts. Therefore, addition of promoters with the ability to further enhance the dissociation of CO2, oxygen exchange and removal of carbon from the metal should result in improved catalytic performance.

Acknowledgements

S. Prakash and B. Phung Ngoc are acknowledged for helping G.K. Reddy to use the FTIR spectrometer and testing apparatus respectively. The authors also acknowledged P. Mascunan for H2 chemisorption measurements and L. Burel for TEM. A. Takahashi training stay was supported by the ECSAW program (CNRS–France–AIST/Japan). G.K. Reddy was supported during his stay in France by the Ambassade de France in India (Sandwich Ph.D. program).

References