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ScienceDirect
Catalysis Today 128 (2007) 223–229
CATALYSIS TODAY
www.elsevier.com/locate/cattod

Gold nanoparticles supported on ceria-modified mesoporous titania as highly active catalysts for low-temperature water-gas shift reaction

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Available online 11 September 2007

Abstract

New gold catalytic system prepared on ceria-modified mesoporous titania (CeMTi) used as water-gas shift (WGS) reaction catalyst is reported. Mesoporous titania (MTi) was synthesized using surfactant templating method through a neutral $[C_{13}(EO)_6–Ti(OC_3H_7)_4]$ assembly pathway. Ceria modifying additive was deposited on MTi by deposition precipitation (DP) method. Gold-based catalysts with different gold content (1–5 wt.%) were synthesized by DP of gold hydroxide on mixed metal oxide support. The supports and the catalysts were characterized by powder X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), N_2 adsorption analysis and temperature-programmed reduction (TPR). The catalytic behavior of the gold-based catalysts was evaluated in WGS reaction in a wide temperature range (140–300 °C) and at different space velocities and H_2O/CO ratios. The influence of gold content and particle size on the catalytic performance was investigated. The WGS activity of the new gold/ceria-modified mesoporous titania catalysts was compared with that of gold catalysts supported on simple oxides CeO_2 and mesoporous TiO_2, as well as gold/ceria-modified titania and reference catalyst Au/TiO_2 type A (World Gold Council). A high degree of synergistic interaction between ceria and mesoporous titania and a positive modification of structural and catalytic properties by ceria has been achieved. It is clearly revealed that the ceria-modified mesoporous titania is of much interest as potential support for gold-based catalyst. The Au/ceria-modified mesoporous titania catalytic system is found to be efficient catalyst for WGSR.

Keywords: Gold nanoparticles; Ceria additive; Mesoporous titania; Catalysis; Water-gas shift reaction; Low temperature

1. Introduction

The water-gas shift (WGS) reaction ($CO + H_2O = CO_2 + H_2$) is an important step in a number of chemical processes for the production of H_2. Although the WGS technology is well established and widely used in large scale steady-state operation, such as hydrogen or ammonia plants [1], the interest for the WGS reaction has been growing significantly in the last years, as a result of the important advance in fuel cell technology [2,3]. A critical parameter, which determines the catalytic activity, is the nature of the support. The mesoporous materials with different compositions, new pore systems and novel properties have attracted considerable attention because of their remarkably large surface areas and narrow pore size distributions, which make them ideal candidates for catalysts [4]. Other than their chemical properties, another advantage of this kind of new materials while being used as supports for metallic catalysts relies on their well-defined pore size which can limit the growth of metal or metal oxide particles [5]. These materials such as mesoporous titania and zirconia have been used for the first time for gold catalysts [5] and found to be promising supports for gold-based catalysts in WGSR [6,7]. The structure of mesoporous oxide supports facilitates the formation of well-dispersed and stable gold particles on the surface upon calcination and reduction and thus strongly improves the catalytic performances. The catalytic activity and especially the stability of gold catalysts strongly depend on both the state and

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doi:10.1016/j.cattod.2007.07.016

structure of the support and the specific interaction between gold and support. On the other hand, CeO_2-based catalysts have been reported to be very promising for the WGS reaction. Ceria is known to affect the dispersion of supported metals. The promotion by noble or transition metal enhances the ceria reducibility and facilitates the generation of very active centers at the interface between metal and support. Recently, very interesting properties for the low-temperature WGS reaction of Au–ceria catalysts have been demonstrated [8–15]. The availability of nanosized gold particles on the surface in close contact with ceria plays a decisive role for high activity and stability of these catalysts [14]. The redox properties and oxygen storage capacity of ceria is usually claimed, while the metal plays a direct role in the mechanism of the WGS reaction [16]. In this study, we try to shed some light on the relationship between textural and structural characteristics of ceria-modified mesoporous titania, the state of gold particles and catalytic activity of catalysts prepared in low-temperature WGS reaction. The WGS activity of the new catalyst was compared with that of gold catalysts supported on simple oxides such as CeO_2 and mesoporous TiO_2, as well as gold/ceria-modified titania and reference catalyst Au/TiO_2 type A (World Gold Council). We discuss the catalytic behavior of the new catalysts based on their full characterization in order to unravel the role of ceria modifying additive and possible interaction between gold nanoparticles and ceria–mesoporous titania support. The beneficial effect of CeO_2 addition to mesoporous titania is analyzed.

2. Experimental

2.1. Synthesis of mesostructured titania support

The mesoporous titania (MTi) was obtained using nonionic surfactant as templating agent. Micellar solution (50 wt.%) of $C_{13}(EO)_6$–polyoxyethylene(6) tridecylether (Aldrich) was prepared by dissolving the surfactant at room temperature in an aqueous solution during 3 h. The obtained medium was further stirred for 3 h at room temperature (RT) before adding drop by drop the inorganic source: titanium(IV) isopropoxide [$Ti(OC_3H_7)_4$] (Aldrich). The surfactant/titania molar ratio was 1.5. The obtained gel after stirring for 1 h at RT was sealed into Teflon-lined autoclaves and heated. The hydrothermal treatment was performed during 48 h at 60 °C. The template was completely removed after 48 h of ethanol extraction with the help of a Soxhlet apparatus. The mesoporous titania was dried under vacuum at 80 °C. The titania (anatase), used for the synthesis of modified by ceria comparative support, was prepared by hydrolysis of $TiCl_4$ with ammonia at pH 9.0 and at low temperature.

2.2. Synthesis of ceria-modified mesoporous titania

Ceria was loaded on mesoporous titania by deposition precipitation (DP) method. Before deposition, the mesoporous material was suspended in water by ultrasound technique. Ceria was deposited by precipitation of $Ce(NO_3)_3{\cdot}6H_2O$ with Na_2CO_3 at 60 °C and pH 9.0. ''Analytical grade'' chemicals were used in the support preparation. The precipitate was aged in a course of 1 h at the same temperature, filtered and washed carefully until absence of NO_3^- ions. The sample was dried under vacuum at 80 °C and calcined in air at 400 °C for 2 h. Ceria modifying additive is 20 wt.%. The sample was labeled as CeMTi. The comparative CeO_2–TiO_2 support was prepared by synthesis identical route. The content of ceria in the support was 20 wt.%. This support was denoted as CeTi.

2.3. Preparation of gold-containing catalysts

Different content of gold (1–5 wt.%) was loaded on MTi, CeMTi and CeTi by DP method. The gold hydroxide was supported on supports preliminary suspended in water via the chemical reaction between $HAuCl_4{\cdot}3H_2O$ and Na_2CO_3 in aqueous solution [6]. The precipitates were aged for 1 h at 60 °C, filtered and washed carefully until absence of Cl^- ions. The samples were dried under vacuum at 80 °C and calcined in air at 400 °C for 2 h. The catalysts were denoted as Au/MTi, Au/CeMTi and Au/CeTi for the samples prepared on mesoporous titania, on ceria-modified mesoporous titania and on ceria-modified titania, respectively. The measured gold loading for the catalysts Au/MTi and Au/CeMTi is shown in Table 1. The sample Au/CeTi contained 3 wt.% of gold. The samples were prepared in a ''Contralab'' laboratory reactor (Conraves AG, Switzerland) under complete control of all

Table 1
Textural properties of the supports and gold-based catalysts, and the gold content and average size of gold particles in the catalysts

Sample	Calcination temperature (°C)	Specific surface area (m^2/g)	Pore diameter (nm)	Pore volume (cm^3/g)[a]	Au content (wt.%)	Au particle size (nm)[b]
MTi	80	204.0	7.0	0.4765	–	–
	400	124.7	11.0	0.4452	–	–
CeMTi	80	164.9	7.2	0.3858	–	–
	400	102.8	10.5	0.3260	–	–
2.5Au/MTi	400	133.0	9.0	0.4475	1.63	4.0–4.5
5Au/MTi	400	134.0	8.0	0.3100	4.73	6.0–6.5
2Au/CeMTi	400	108.9	11.4	0.3343	1.36	6.0–7.0
5Au/CeMTi	400	105.8	11.4	0.3288	3.15	6.0–7.0

[a] Total pore volumes at $p/p_0 = 0.99$.
[b] Determined by XRD and HRTEM methods.

parameters: temperature, pH, stirrer speed and reactant feed flow rates. All chemicals used were ''analytical grade''.

2.4. Sample characterization

The XRD patterns were obtained with a Philips PW 170 diffractometer, using Cu Kα (1.54178 Å) radiation. High-resolution transmission electron microscopy (HRTEM) analysis was performed on a JEOL JEM-3010 microscope at 300 kV. Nitrogen adsorption-desorption isotherms and specific surface areas were measured at −196 °C over a wide relative pressure range from 0.01 to 0.995 with a volumetric adsorption analyzer TRISTAR 3000 manufactured by Micromeritics. The pore diameter and the pore size distribution were determined by the Barret–Joyner–Halenda (BJH) method using the adsorption branch of isotherms [17]. The gold content in catalysts was analyzed by atomic absorption method and made by the Analytical Center of the CNRS, Lyon, France.

Temperature-programmed reduction (TPR) of the samples was carried out in the measurement cell of a differential scanning calorimeter (DSC) model DSC-111 (SETARAM) directly connected to a gas chromatograph (GC). A quartz reactor was loaded with 0.17 g of the samples. The measurements were performed in the range of 20–700 °C at 15 °C/min heating rate in flow of 10% H_2/Ar, the total flow rate being 25 ml/min. A cooling trap between DSC and GC removed the water obtained during the reduction. The samples were calcined in synthetic air (20% O_2 in Ar) for 30 min before the TPR measurements.

2.5. Catalytic activity measurement

Catalytic activity test was performed in a fixed-bed flow reactor at atmospheric pressure and temperature range from 140 to 300 °C. The following conditions were applied: catalyst bed volume 0.5 cm^3, space velocity 4000 h^{-1}, partial pressure of water vapor 31.1 kPa and the reactant gas mixture contained 4.494 vol.% CO in argon. The CO and CO_2 content was analyzed on ''URAS-3G'' and ''URAS-2T'' (Hartmann & Braun AG) gas analyzers and the catalytic activity was expressed by degree of CO conversion. The stability of the catalysts was studied under different space velocities and different water vapor partial pressures.

3. Results and discussion

3.1. Structural and textural characterization

3.1.1. XRD and TEM analysis

The XRD patterns of the samples are shown in Fig. 1. The initial mesoporous material shows normal anatase lines (MTi). There are significant differences in the XRD patterns after deposition of ceria additive. The addition of ceria leads to formation of a highly defective anatase crystal structure (CeMTi). The typical diffraction patterns of anatase are broader and less intensive. No shift of the peak positions (2θ = 25.28, 37.79, 48.04 and 53.88) can be seen, indicating that no changes

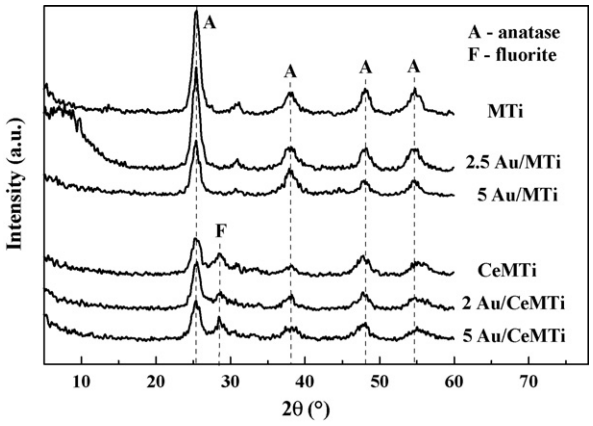

Fig. 1. X-ray diffraction patterns of the supports and gold-based catalysts with different gold content.

in the phase composition occurred. Additionally, no extra lines due to compounds of mixed phases between titania and ceria are registered. Only a weak line at 2θ = 28.5 due to most intense fluorite oxide-type diffraction pattern of CeO_2 is visible. The other diffraction lines characteristic of cubic structure of ceria (2θ = 47.48 and 56.33) are not discernible because of their location very close to the respective patterns of titania. The mean particle size of MTi and CeMTi was determinated from XRD line broadening by the Scherrer's equation. The average size of MTi was calculated to be equal to 9.7 nm, while modification by ceria led to its decrease to 6.1 nm. The results revealed the beneficial role of ceria additive in decreasing the degree of crystallinity of MTi and decreasing its particle size.

No significant differences after deposition of gold can be detected. The typical lines of gold at 2θ = 38.2 and 44.4° in the gold-containing samples calcined at 400 °C (2Au/CeMTi and 5Au/CeMTi) are very hardly observable due to the very fine dispersion of gold nanoparticles on the surface of mesoporous titania and ceria-modified mesoporous titania.

TEM observation (Fig. 2) revealed that the gold nanoparticles are homogeneously dispersed on both metal oxide supports. The gold loading and particle size are given in Table 1. The TEM micrographs of the mesoporous titania support and the corresponding gold catalysts [6] have a disordered structure with a large number of wormhole-like channels lacking a long range packing order as previously reported [18–20]. Ceria-modified mesoporous titania support has a disordered structure with an aggregation of the nanoparticles. These results are being consistent with that estimated by XRD analysis (Fig. 1).

3.1.2. Nitrogen adsorption analysis

Fig. 3 depicts the N_2 adsorption–desorption isotherms (A) and pore size distribution (B) of the supports (MTi and CeMTi) and the gold-based catalyst with different gold contents calcined at 400 °C. The textural properties of the supports and catalyst samples are listed in Table 1. The isotherms of all above samples are of type IV, characteristic for mesoporous materials according to the classification of BDDT [21]. A sharp increase in adsorption volume of N_2 is observed in the p/p_0

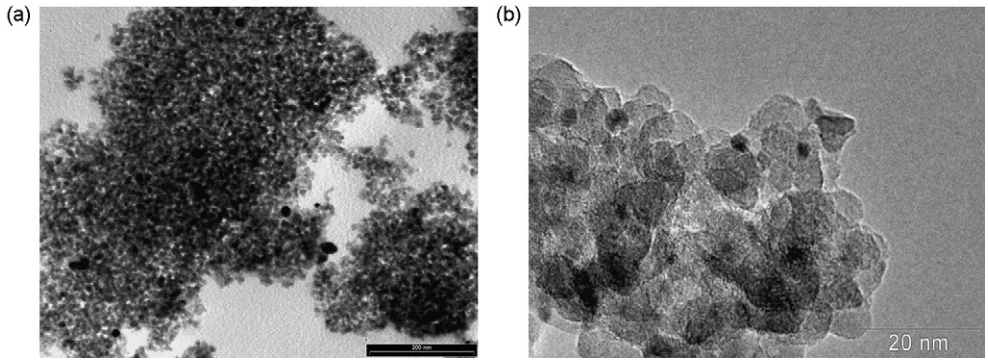

Fig. 2. TEM micrographs of the gold-based catalyst supported on MTi and CeMTi calcined at 400 °C: (a) Au/MTi, scale bar 200 nm and (b) Au/CeMTi, scale bar 20 nm.

range of 0.60–0.90, corresponding to the capillary condensation and indicating the good homogeneity of the samples and large pore size since the p/p_0 position of the inflection point is related to the pore size. The pore size distribution obtained with BJH method is quite narrow confirming good quality of our samples. For pure mesoporous titania, the surface area decreases from 204 to 125 m^2/g, while the surface area of ceria-modified mesoporous titania decreases from 165 to 103 m^2/g with increasing calcination temperature from 80 to 400 °C. After ceria deposition on mesoporous titania, the surface area significantly decrease, as well as the pore volume (Table 1) due very probably to some insertion of the ceria additive into the pores. The decrease of the surface area upon calcination is related to the crystallization of the walls separating mesopores as previously reported [22]. The high temperature treatments are responsible for the crystallization of the walls and grain coarsening.

It is very interesting to note that the values of S_{BET} after calcination of the samples at 400 °C for gold-containing catalysts in comparison with mesoporous titania and ceria-modified mesoporous titania are higher. It can be concluded that the deposition of gold enhances the thermal stability of the supports. The differences in the surface areas and pore volumes of support and catalysts with different gold loadings are insignificant. The pore diameter of gold-loaded catalysts on MTi support remains lower after calcinations compared to pure mesoporous titania, while the gold catalysts supported on CeMTi have practically equal pore diameter (Table 1). The shape of the isotherms and the pore sizes did not change significantly, meaning that material kept its mesoporous structure after introduction of the ceria.

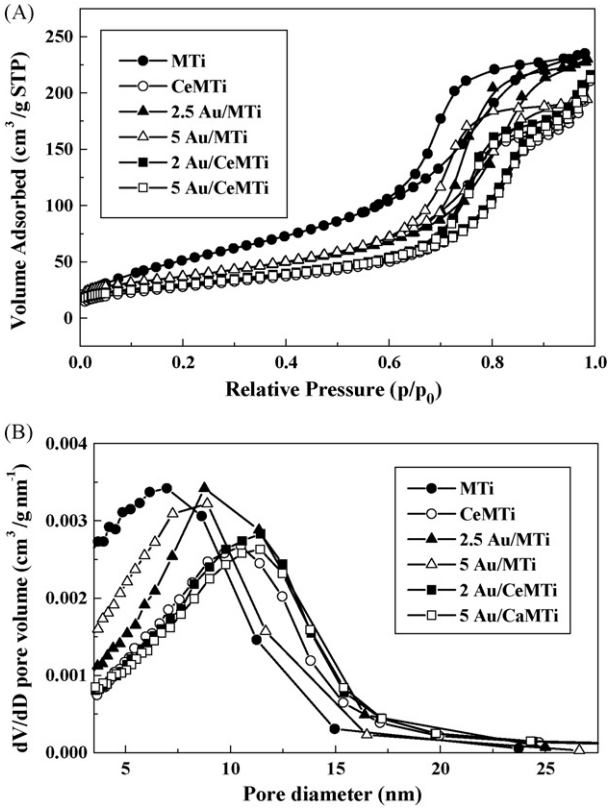

Fig. 3. Nitrogen adsorption isotherms (A) and pore size distribution (B) of the supports (MTi and CeMTi) and the gold-based catalysts supported on MTi and CeMTi with different gold content, calcined at 400 °C.

3.1.3. TPR measurements

In Fig. 4 are shown the TPR profiles of the supports (MTi and CeMTi) and the gold-based catalyst (5Au/CeMTi) as well as that of ceria for comparison. In the profile of mesoporous titania (MTi) only a peak at above 500 °C due to the titania reduction is observed. The modification with ceria causes

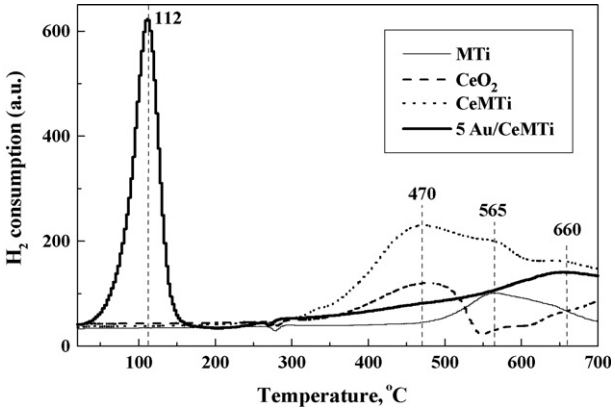

Fig. 4. TPR profiles of the calcined at 400 °C supports ($MTiO_2$, CeO_2, and CeMTi), and gold-based catalyst (5Au/CeMTi).

strong effect on the reducibility of mesoporous titania. Differences are observed both in the intensity and the shape of the TPR peaks. The H_2–TPR profile of ceria contains two major peaks, one at lower temperature (around 500 °C), attributed to the reduction of surface oxygen, and another at higher temperature (around 800 °C), and attributed to the removal of bulk oxygen from the ceria structure as reported by Yao and Yu Yao [23]. A significant increase of the intensity of the peak at 470 °C assigned to ceria surface oxygen reduction is registered in the TPR profile of ceria-modified mesoporous titania. This higher hydrogen consumption could be related to the synergistic interaction of ceria and mesoporous titania in agreement with results from the other characterization methods used.

Clear evidence that gold facilitates the reducibility of the surface oxygen of ceria-modified mesoporous titania is found by H_2–TPR. An intense and sharp low-temperature (LT) peak with $T_{max} = 112$ °C is observed in the TPR profile of 5Au/CeMTi. A recent TPR study of Au/ceria catalysts prepared by DP method has shown that the hydrogen consumption at low-temperature is due to two processes, namely, the reduction of oxygen species on nanosize gold particles and the surface reduction of ceria [8]. This is in agreement with other studies that the presence of noble metals can increase the oxygen storage capacity of CeO_2 due to noble metal–CeO_2 interaction. Two reduction peaks have been observed in the profile of gold-supported mesoporous titania [6]. The low-temperature (LT) peak has been assigned to the reduction of oxygen species on the nanosize gold particles and to the $Ti^{4+} \rightarrow Ti^{3+}$ reduction on the border with gold particles. It was also observed that the addition of gold promotes the formation of superoxide O_2^- bound to Ti^{4+} and proposed that the presence of Au species make easy the formation of oxygen defects on titania surface at the boundary of gold particles. We can conclude (i) the ceria additive interacts with the mesoporous titania and induces strong effect on the reducibility of the support; (ii) the gold loading promotes the reducibility of the surface oxygen of ceria-modified mesoporous titania; (iii) the presence of gold and ceria species makes easy the formation of oxygen defects at the boundary of titania surface. The sample with lower gold content (2Au/CeMTi) has shown similar TPR profile, only the LT peak is shifted toward high temperature with 5–10 °C.

3.2. Catalytic activity

The catalytic activity of the gold-based catalysts was evaluated in the water-gas shift reaction at wide temperature range of 140–300 °C. Fig. 5 shows the WGS activity of the ceria-modified mesoporous titania gold catalyst (Au/CeMTi), compared with that of the gold catalysts supported on simple oxides such as CeO_2 (Au/Ce) and mesoporous TiO_2 (Au/MTi), as well as that of a reference catalysts Au/TiO_2 type A commercially available from World Gold Council (Au/Ti Ref.). The activity of the pure mesoporous titania, ceria-modified mesoporous titania and ceria in this temperature region in WGS reaction is imperceptible. It is seen that the addition of gold significantly increases the catalytic activity of the samples. The

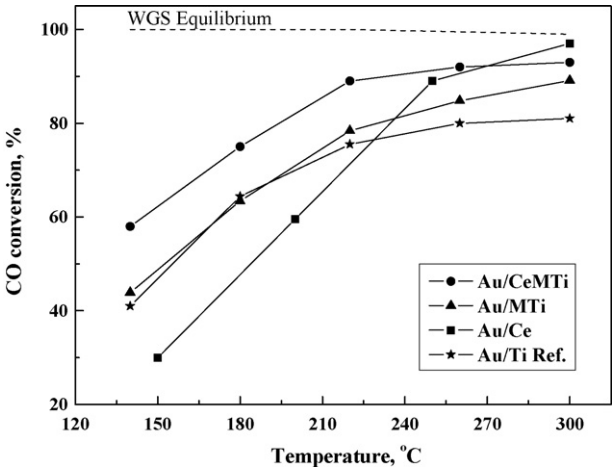

Fig. 5. The WGS activity of the new catalyst (Au/CeMTi, Au content-3.15 wt.%), compared with that of gold catalysts supported on simple oxides, CeO_2 (Au/Ce) and mesoporous TiO_2 (Au/MTi), and reference catalyst Au/TiO_2 type A commercially available from World Gold Council (Au/Ti Ref.). The equilibrium conversion is shown for comparison.

WGS activity of the catalyst Au/CeMTi is significantly higher than that of the gold catalysts supported on simple oxides, mesoporous TiO_2 (Au/MTi) and CeO_2 (Au/Ce) [6,8,14]. The comparison in CO conversion of the new gold catalyst with the reference catalyst Au/TiO_2 type A indicates that the catalyst supported on the ceria-modified titania exhibited significantly higher catalytic activity. A high degree of synergistic interaction between ceria additive and mesoporous titania was observed. Fig. 6 confirms this beneficial effect of ceria modification showing its strong influence on the activity. The WGS activity of the gold ceria-modified mesoporous titania catalyst (Au/CeMTi), compared with that of the gold catalyst prepared on ceria-modified anatase is significantly higher. The different catalytic behavior of Au/CeMTi and Au/CeTi catalysts indicate that the processes occurring on the catalyst surface depend on the nature of support.

It is also observed that the degree of CO conversion increases with the gold loading on ceria-modified mesoporous titania. Fig. 7 depicts the effect of gold loading of the gold catalysts on

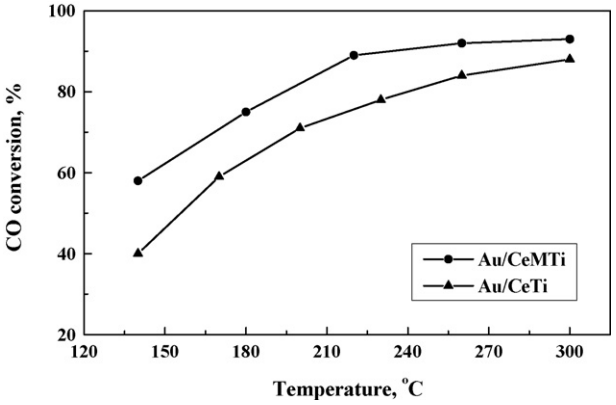

Fig. 6. The WGS activity of the gold ceria-modified mesoporous titania catalyst (Au/CeMTi), compared with that related to gold catalyst prepared on ceria-modified anatase.

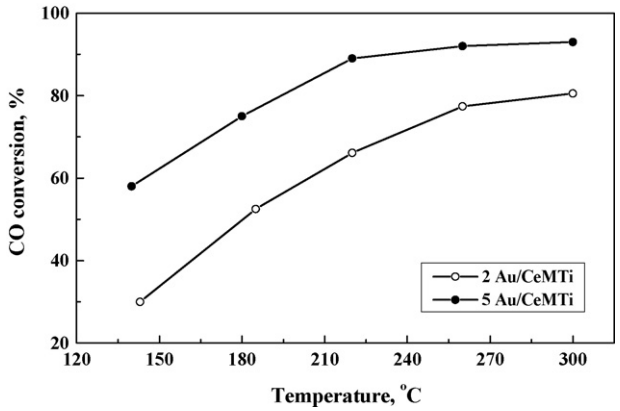

Fig. 7. Effect of gold loading of the gold ceria-modified mesoporous titania catalysts on the WGS activity (2Au/CeMTi, Au-1.36 wt.%; 5Au/CeMTi, Au-3.15 wt.%).

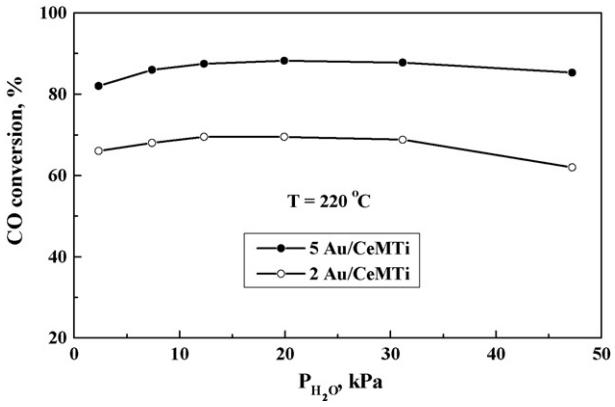

Fig. 9. Effect of partial pressure of H_2O (H_2O/CO ratio) on the CO conversion at 220 °C of the gold ceria-modified mesoporous titania catalysts.

the CO conversion. The different gold loadings strongly influence the catalytic activity. The higher gold loading could probably provide larger number of active sites located at the Au/ceria-modified mesoporous titania interface, which could be the most important because the perimeter interfaces around Au particles act as the site for reaction [24,25]. The role of perimeter interface between Au particles and the support is emphasized as a unique reaction site for the reactants adsorbed separately, one on Au and another on the support surface.

The effect of the space velocity and water vapor partial pressure on WGS activity was studied at 220 °C. Fig. 8 presents the effect of contact time on WGS activity at 220 °C over the studied gold/ceria-modified mesoporous titania catalysts. The tests were performed with different space velocities of 2000, 4000 and 8000 h^{-1}. The sample with higher gold content (5Au/CeMTi) demonstrated lower decrease in CO conversion than 2Au/CeMTi sample when the space velocity was increased. However, it should be noted that the decrease of space velocity to its initial value (2000 h^{-1}) can make the CO conversion completely recovered. This result is related to the stable activity of the catalyst. The effect of contact time on the degree of CO conversion for 2Au/CeMTi sample is noticeable.

The results obtained for the influence of six different H_2O/CO ratios on the CO conversion at 220 °C are presented in Fig. 9. Very interesting results on the degree of conversion over all the range of investigated water vapor partial pressures were obtained. No significant changes in CO conversion can be seen. The sample with higher gold content (5Au/CeMTi) manifests unexpectedly high CO conversion even at rather low H_2O/CO ratios. Long period catalytic activity test carried out over the Au/CeMTi catalyst during 2 weeks confirms its high stability. Moreover, the presence of a higher content of water in the reaction mixture does not retard the activity of the Au/CeMTi catalysts. The catalysts exhibit good tolerance towards a high concentration of water.

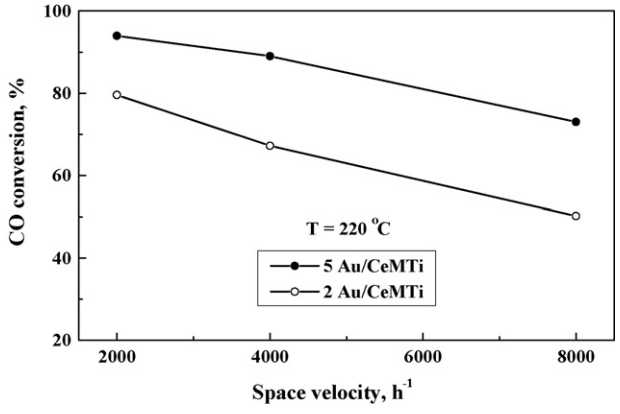

Fig. 8. Effect of contact time on the CO conversion at 220 °C of the gold ceria-modified mesoporous titania catalysts.

4. Conclusions

The ceria-modified mesoporous titania is of much interest as potential support for gold-based catalyst and strongly improves the catalytic performances due to: (i) the beneficial role of ceria additive in decreasing the degree of crystallinity of mesoporous titania and decreasing its particle size; (ii) the strong effect on the reducibility of the support owing to the interaction of ceria additive with the mesoporous titania; (iii) a high degree of synergistic interaction between ceria and mesoporous titania. The high and stable WGS activity could be related to the high stability of the gold dispersion and to larger number of active sites located at the Au/ceria-modified mesoporous titania interface. The Au/ceria-modified mesoporous titania catalytic system is found to be highly active catalyst for WGSR.

Acknowledgments

This work was financially supported by the European Program of InterReg III (Programme France-Wallonie-Flandre, FW-2.1.5), and the Interuniversity Attraction Poles Program (P6/17)-Belgian State-Belgian Science Policy. The support from the National Science Fund at the Ministry of Education and Science of Bulgaria (project X-1320), the Joint Research Project between the Commissariat general des relations internationals (CGRI), Belgium and Bulgarian Academy of Sciences, the National Natural Science Foundation of China (No. 20473041) and the National Basic Research Program of

China (No. 2003CB615801) and Wallonia Region government are greatly acknowledged.

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