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Characterization and activity of vanadia-promoted Pt/ZrO_2 catalysts for the water–gas shift reaction

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ABSTRACT

Pt/ZrO_2 catalysts for the water–gas shift (WGS) were promoted with various amounts of vanadia. Analyses by XRD, N_2 adsorption, Raman, and UV–vis DRS showed that vanadia is present below monolayer coverage as monovanadate and polyvanadate, with the former dominating at lower loadings, and that following monolayer formation, VO_5 species appear, with the eventual generation of V_2O_5 and ZrV_2O_7 for a vanadia weight loading of 13%. Though in all cases vanadia induced an enhancement in WGS activity, the best catalyst, that contained 3 wt.% of vanadia, gave a rate that was nearly double that of the unpromoted Pt/ZrO_2. That superior global activity probably results from the monovanadate that is the main species at low loadings. It is believed that monovanadate promotes the WGS by rendering the support's surface more oxidizing through its V–O–Zr bonds.

1. Introduction

Though used in the industry for more than a century, the water–gas shift (WGS) reaction ($CO + H_2O \Leftrightarrow CO_2 + H_2$) has lately been the object of a renewed interest as a means to remove CO from H_2 generated by the steam reforming of fuels. Current industrial WGS catalysts are not suited for that purpose, being difficult to reduce, potentially pyrophoric, easily reoxidized by steam condensation, and insufficiently active [1–3]. That is why recently, precious metal catalysts supported on various oxides have been developed.

Undoubtedly, Pt is the most studied precious metal and several reducible and unreducible oxides have been tried as supports. Indeed, both metal and support play a fundamental role in the WGS catalyzed reaction. The WGS is thought to occur through two possible mechanisms. In one of those, a redox process occurs where CO adsorbs on the precious metal and then undergoes oxidation by the support that afterward gets reoxidized by H_2O [4]. On the other hand, various groups [5,6] favor a mechanism in which a formate intermediate forms through the reaction of CO with OH groups from the support. Such OH groups would form either through the dissociation of water on oxygen vacancies in reducible oxides or through the spillover of the reducing H_2 on surface-capping oxygen [6], those processes being facilitated by the presence of precious metal. In the case of irreducible oxides, these OH groups would originate from the dissociative adsorption of water on the oxide acid–base sites [7]. However, whether the redox or the formate mechanism is believed to occur, it is desirable for the support to be easy to reduce and to possess high oxygen mobility, so that oxygen vacancies may be formed on its surface.

Amongst the potential oxides to fulfill such requirement, only few papers have focused on the use of vanadium in WGS either as a catalyst or as a promoter [8–10]. Therefore, this work presents results obtained for WGS catalysts with Pt as the metallic phase and monoclinic ZrO_2 as the support, modified with different amounts of vanadia. The objective of this study is to determine whether adding vanadia to ZrO_2 would favor the reaction, and establish a relationship between the molecular structure of the vanadia and a potential promoting effect from that oxide.

2. Experimental

The supports were obtained by suspending monoclinic ZrO_2 (m-ZrO_2) in an aqueous solution of NH_4VO_3 and $C_2O_4H_2$. Water was then removed through a rotatory evaporator, followed by drying at 120 °C and calcination at 400 °C. "xVZrO_2" will designate a support with x% in weight of vanadia. Pt (1 wt.%) was added by incipient wetness impregnation, followed by the same drying and calcination steps.

The catalysts actual chemical composition was determined by X-ray fluorescence analyses, which were carried out in a Shimadzu EDX-700 spectrometer.

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Powder XRD was carried out on a Rigaku Miniflex diffractometer that uses Cu Kα radiation (30 kV, 15 mA), the 2θ angle being incremented with 0.02° per step.

N_2 adsorption experiments at −196 °C were done with an ASAP 2010 from Micromeritics. Prior to analysis, the materials were outgassed at 5 mTorr and 150 °C for 24 h. Surface areas (S_{BET}) were determined using the BET formalism.

The Raman spectra were collected with a Jobin Yvon Horiba HR800, using a He–Ne laser (20 mW) at 632.8 nm. The Raman shift was calibrated with a silicon wafer.

UV–vis diffuse reflectance spectra were done on a Varian UV–vis-NIR Cary 500 spectrophotometer, with MgO as the reference. Edge energies were found through the plot of $[F(R_\infty)h\nu]^2$ vs. $h\nu$ [11].

Catalytic activity tests were performed in a fixed-bed flow reactor at 300 °C under differential reactor conditions (less than 13% of CO consumption). In order to avoid temperature gradients in the reactor, silicon carbide was added for dilution ($w_{cat}/w_{dil} = 1/5$) to form a small catalyst bed (<10 mm in height). Reactants flow rates and catalysts masses were varied to ensure differential conditions in order to calculate reaction rates. The feed composition was 5.49% CO, 4.10% CO_2, 9.71% H_2, 49.95% N_2 and 30.75% H_2O. Before reaction, the catalysts were reduced in H_2 at 350 °C/1 h. The reactor effluent was analyzed on-line with a GC (Agilent 6890N) equipped with a TCD [12].

3. Results

Except for $13VZrO_2$, the XRD patterns of the vanadia-promoted samples only exhibit the peaks due to m-ZrO_2. This indicates that vanadia in these supports is present under a well-dispersed state. However, $13VZrO_2$ has a peak at 20.22° that possibly results from a ZrV_2O_7 phase. It is shown in Fig. 1 along with other selected diffractograms. Indeed, it has already been reported that this compound forms, when ZrO_2 is impregnated with large amounts of vanadia [13,14]. Nevertheless, this peak could also be ascribed to V_2O_5 [15] as that phase commonly appears when higher levels of vanadia are deposited on a support [13,14].

S_{BET} values calculated from N_2 adsorption data (Table 1) show that the surface area of the supports decreases as the vanadia loading increases. This illustrates the gradual covering of the ZrO_2 surface with vanadia species. Considering the precision of BET method, $1VZrO_2$, $3VZrO_2$, and $4VZrO_2$ on the one hand, and $7VZrO_2$ and $9VZrO_2$ on the other hand essentially have the same surface area. The loss of surface area with $13VZrO_2$ compared to m-ZrO_2 is more pronounced than with the other vanadia-promoted supports. Most likely in this case, a monolayer has formed, as the vanadia content of that material is high; however, this surface area loss is too extensive to result solely from formation of a monolayer. As seen from XRD, $13VZrO_2$ probably contains a ZrV_2O_7 phase, whose formation at the expense of ZrO_2 could explain such surface area loss [13].

Table 1
Vanadia loading levels, vanadia surface densities, surface areas (S_{BET}), edge energies and Pt contents of the materials

Samples	V_2O_5 (wt.%)[a]	V_2O_5 density (V/nm^2)	S_{BET} (m^2/g)	Edge energy (eV)	Pt (wt.%)[b]
ZrV_2O_7	–	–	–	3.5	–
NH_4VO_3	–	–	–	3.1	–
V_2O_5	–	–	–	2.3	–
m-ZrO_2	–	0.00	97	5.1	0.94
$1VZrO_2$	1.19	0.82	91	3.8	0.87
$3VZrO_2$	3.13	2.20	91	3.4	0.92
$4VZrO_2$	3.97	2.82	89	3.2	0.95
$7VZrO_2$	7.27	5.35	85	2.6	1.01
$9VZrO_2$	8.59	6.42	83	2.8	0.95
$13VZrO_2$	13.14	10.33	66	2.6	0.98

[a] In the supports (determined by X-ray fluorescence).
[b] In the catalysts (determined by X-ray fluorescence).

Other than $13VZrO_2$, none of the vanadia-promoted supports shows Raman bands that do not originate from m-ZrO_2. However, the spectrum of $13VZrO_2$ features a band at 996 cm^{-1} that indicates the presence on that support of V_2O_5 [16,17] (Fig. 2).

Aside from the band at 230 nm due to m-ZrO_2, the UV–vis DR spectrum of $1VZrO_2$ (Fig. 3) exhibits two shoulders at 270 and 350 nm that are attributed to respectively monovanadate and polyvanadate [18,19]. In the spectrum of $3VZrO_2$, the shoulder for monovanadate is more pronounced than the one in the spectrum of $1VZrO_2$ while the one for polyvanadate is practically overshadowed by the former. This indicates that $3VZrO_2$ contains more monovanadate species than $1VZrO_2$, and that the proportion of monovanadate is higher in $3VZrO_2$ than in $1VZrO_2$. By the same argument as previously, $4VZrO_2$ contains more monovanadate than $3VZrO_2$. The same can be stated regarding polyvanadate as $4VZrO_2$ absorbs more in the 300–400 nm region than $3VZrO_2$. For vanadia contents of 7 wt.% and higher, along with an ever increasing band at 270 nm that reveals higher amounts of monovanadate, the spectra of the supports exhibit a shoulder at

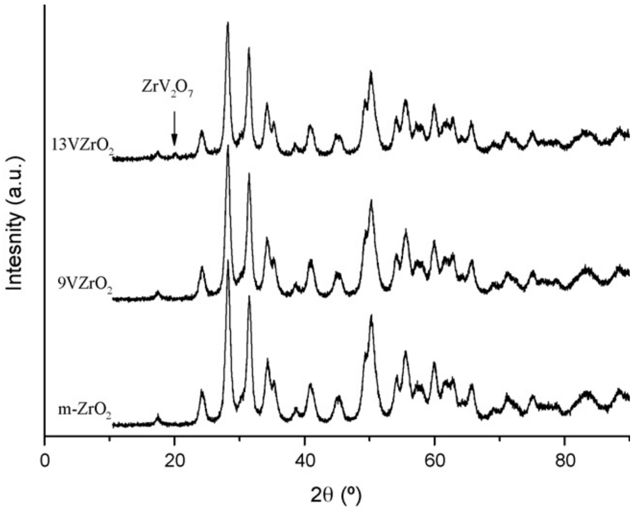

Fig. 1. X-ray diffraction patterns of the m-ZrO_2, $9VZrO_2$, and $13VZrO_2$ supports.

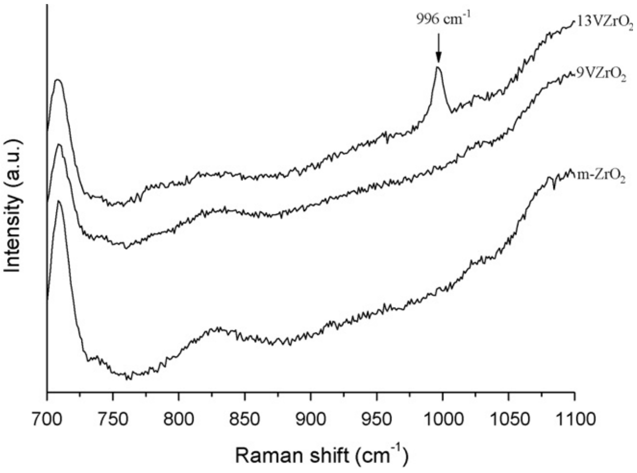

Fig. 2. Raman spectra of the m-ZrO_2, $9VZrO_2$, and $13VZrO_2$ supports.

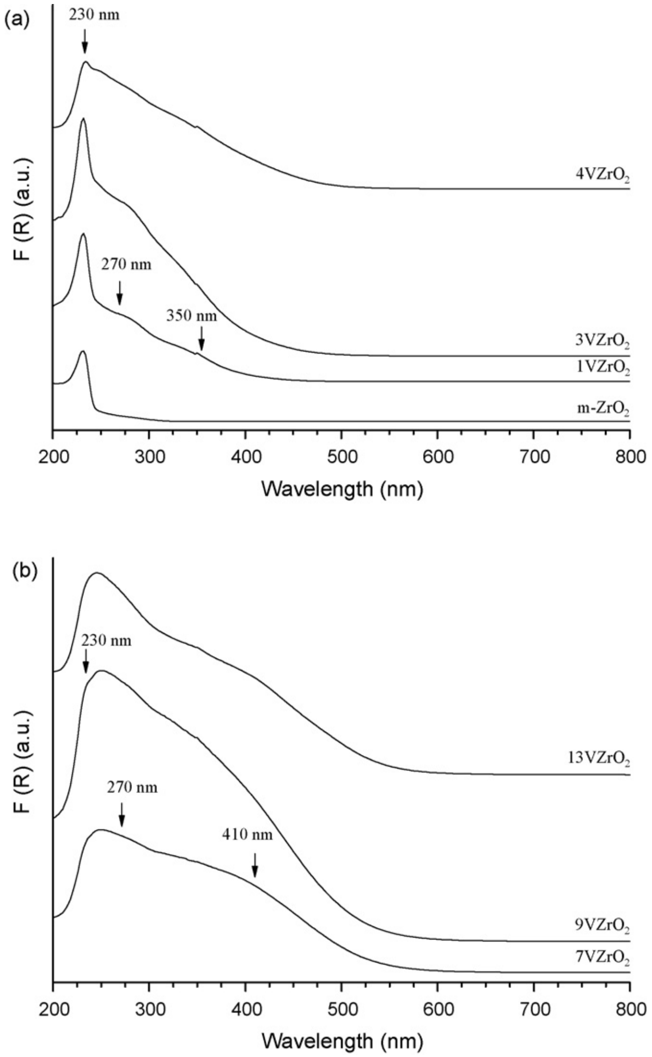

Fig. 3. UV–vis DR spectra of the (a) m-ZrO_2, 1VZrO_2, 3VZrO_2, and 4VZrO_2 and (b) 7VZrO_2, 9VZrO_2, and 13VZrO_2 supports.

410 nm that results from VO_5 units [17,19]. That VO_5 suggests that a vanadia monolayer has formed, with vanadia no longer binding to the surface.

The edge energies of the UV–vis transitions are reported in Table 1 along with data obtained for NH_4VO_3, V_2O_5, and ZrV_2O_7 reference materials. The high edge energy of 1VZrO_2, that is even larger than that of dimeric pyrovanadate in ZrV_2O_7, suggests that this material consists mostly of monovanadate. From there, the edge energy keeps decreasing with vanadia loading level, up to 7VZrO_2. This shows that as the quantity of monovanadate increases, so does the degree of polymerization of vanadia, since the edge energy of vanadia decreases with its extent of polymerization [11,13,20]. Also, the edge energy of 7VZrO_2 is significantly smaller than that of 4VZrO_2, which further suggests the presence of a monolayer in the former. Considering the precision of the method used for their determination, the edge energies of 7VZrO_2, 9VZrO_2, and 13VZrO_2 can be regarded as similar. Thus, the edge energy remains constant once a vanadia loading of 7 wt.% is reached. This is another indication that a monolayer has formed with 7VZrO_2 as in that case, additional vanadia would only form VO_5 domains that remain too small to noticeably change the edge energy. It then seems that a vanadia monolayer has appeared at a density between 2.82 and 5.35 V/nm^2.

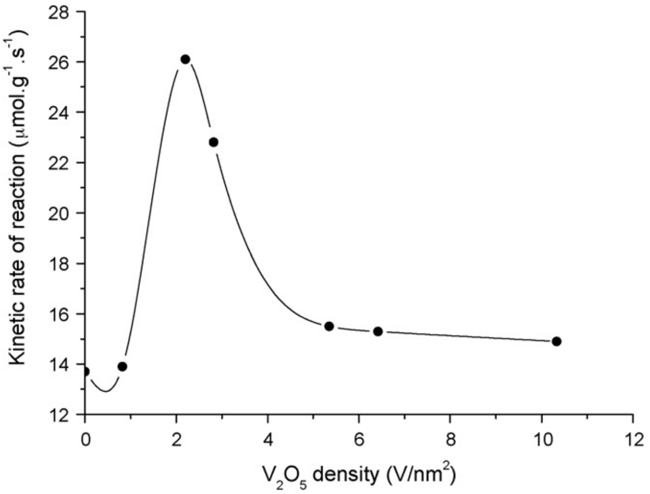

Fig. 4. Rate of reaction as a function of surface vanadia density.

The reaction rates for the WGS obtained with these catalysts as a function of surface vanadia density is plotted in Fig. 4 and illustrate the promoting effect of *vanadia*. All the catalysts contain the same amount of Pt (Table 1), allowing the comparison of their global activity. It can be seen that regardless of the amount of vanadia, an improvement in WGS activity happens compared to the vanadia-free catalyst: the rate increases with vanadia loading up to a 3 wt.% fraction, at which point it is nearly doubled, and then decreases for higher percentages.

4. Discussion

As argued previously, the improved rate of reaction of the WGS with the vanadia-promoted catalysts over Pt-supported monoclinic zirconia can only be due to the molecular structure of the support's surface with the better catalysts: the presence of vanadia, regardless of its state and quantity, results in higher WGS global activities. However, the vanadia-promoted catalysts do not improve the rate of reaction to the same extent. Indeed, superior results are reached at low-intermediate vanadia levels of 3–4 wt.%. It thus seems that it is the nature and the amount of the doping vanadia species that determines the level of activity enhancement. As seen from UV–vis DRS, below monolayer coverage, vanadia is present under the form of monovanadate and polyvanadate, with the former being predominant at lower vanadia loadings and with an increased proportion of the latter at higher loadings. From the molecular structure standpoint, monovanadate consists of one V=O bond and three V–O–Zr bonds while polyvanadate features one V=O bond, two V–O–V bonds, and one V–O–Zr bond. Most likely, the V=O bond plays little role in the promotion of the WGS, or else the rate would rise between Pt/1VZrO_2 and Pt/4VZrO_2 as more and more V=O bonds are present. The highest rate occurs with 3VZrO_2 that consists mostly of monovanadate, which thus appears to be the vanadia species that has the highest promoting effect. A lesser improvement is found with Pt/4VZrO_2 over Pt/ZrO_2 compared to 3VZrO_2. However, UV–vis DRS showed that 4VZrO_2 contains more monovanadate but also more polyvanadate than 3VZrO_2. Polyvanadate then seems to be at least less active than zirconia or else Pt/4VZrO_2 would give a higher rate than Pt/3VZrO_2. Like the vanadyl groups, the V–O–V bonds do not seem to take part in the improvement of the global activity since in polyvanadate domains, those bonds are much more numerous and accessible to the reactants than the V–O–Zr ones. The promoting effect of vanadia would then find its origin mostly in the presence of V–O–Zr bonds, which would explain why monovanadate is more active than polyvanadate, since the former contains three times as many of such bonds as the latter. Furthermore, the V–O–Zr bonds in monovanadate are more readily accessible than the ones in polyvanadate in which most of those bonds are situated underneath V–O–V and V═O bonds, thus being shielded from potential reactant molecules. Once a vanadia monolayer is formed, the promoting effect of vanadia starts to wane as all the additional vanadia generates VO_5 units that do not contain any V–O–Zr bond and that render inaccessible some of the previously active V–O–Zr bonds from the monolayer.

That apparent preeminent role of the V–O–Zr bonds in the promotion of the global activity would be compatible with the WGS happening through a redox mechanism. Indeed, it has been shown that such V–O–support bonds are generally decisive in vanadia-catalyzed oxidation reactions [20,21]. Nevertheless, it is possible as well that the presence of vanadia results in a support with enhanced reducibility where oxygen vacancies and OH groups would form more easily, thus favoring a process occurring through the formate mechanism [5,6]. Still from the formate mechanism standpoint, vanadia could also heighten the activity of the WGS by favoring the diffusion of OH and H, formed by the dissociation of water on the irreducible m-ZrO_2, on the support's surface for reaction with CO adsorbed on Pt [7].

The lack of activity of O in V═O is probably in part due to the strength of that bond whose stretching Raman shift occurs at 996 cm^{-1} for V_2O_5 (and 1010–1040 cm^{-1} for monovanadate and polyvanadate [16,22]) compared to 620 cm^{-1} and 800 cm^{-1} for V–O–V [16,20] and 930 cm^{-1} for V–O–Zr [20]. Though more weakly bound in V–O–V than in V–O–Zr, oxygen in the former bond does not seem to participate either in the WGS: only the oxygen in V–O–Zr appears active. Thus, the catalytic improvement found in the case of Pt/4VZrO_2 would result from the V–O–Zr bonds present in monovanadate and, to a lesser extent, on the edges of the polyvanadate domains. The difference in activity between the oxygen atoms in V–O–V and in V–O–Zr could be the result of the higher electronegativity of V compared to Zr, which would generate a higher electron density around the oxygen in the latter bond, thus rendering that oxygen more effective for redox processes [23].

5. Conclusion

By depositing vanadia on zirconia, improved global activities of the WGS have been obtained. Among the various vanadia species present, monovanadate appears to contribute the most to the promoting effect, while polyvanadate and VO_5 seem less active than zirconia. As such, the higher activities occur for lower vanadia loadings, when monovanadate is the predominant species. Part of the promoting effect of vanadia likely stems from the enhanced reducibility that this oxide brings to the support's surface. Furthermore, if the WGS indeed happens through a redox mechanism, then the superior activity of monovanadate could find its origin in the presence in that species of numerous and accessible V–O–Zr bonds. These V–O–Zr bonds would be particularly active in the redox process owing to the high electron density of its O atoms.

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References

[1] A.A. Phatak, N. Koryabkina, S. Rai, J.L. Ratts, W. Ruettinger, R.J. Farrauto, G.E. Blau, W.N. Delgass, F.H. Ribeiro, Catal. Today 123 (2007) 224.
[2] Y. Sato, K. Terada, S. Hasegawa, T. Miyao, S. Naito, Appl. Catal. A 296 (2005) 80.
[3] W. Ruettinger, X. Liu, R.J. Farrauto, Appl. Catal. B 65 (2006) 135.
[4] T. Bunluesin, R.J. Gorte, G.W. Graham, Appl. Catal. B 15 (1998) 107.
[5] T. Shido, Y. Iwasawa, J. Catal. 141 (1993) 71.
[6] S. Ricote, G. Jacobs, M. Milling, Y. Ji, P.M. Patterson, B.H. Davis, Appl. Catal. A 303 (2006) 35.
[7] G.G. Olympiou, C.M. Kalamaras, C.D. Zeinalipour-Yazdi, A.M. Efstathiou, Catal. Today 127 (2007) 304.
[8] N. Ballarini, A. Battist, F. Cavani, A. Cericola, C. Lucarelli, S. Racioppi, P. Arpentinier, Catal. Today 116 (2006) 313.
[9] T. Utaka, T. Okanishi, T. Takeguchi, R. Kikuchi, K. Eguchi, Appl. Catal. A 245 (2003) 343.
[10] A.M. Silva, A.M. Duarte de Farias, L.O.O. Costa, A.P.M.G. Barandas, L.V. Mattos, M.A. Fraga, F.B. Noronha, Appl. Catal. A 334 (2008) 179.
[11] X. Gao, I.E. Wachs, J. Phys. Chem. B 104 (2000) 1261.
[12] A.M. Duarte de Farias, A.P.M.G. Barandas, R.F. Perez, M.A. Fraga, J. Power Sources 165 (2007) 854.
[13] A. Khodarov, J. Yang, S. Su, E. Iglesia, A.T. Bell, J. Catal. 177 (1998) 343.
[14] J.R. Sohn, S.G. Cho, Y.I. Pae, S. Hayashi, J. Catal. 159 (1996) 170.
[15] K.V.R. Chary, G. Kishan, T. Bhaskar, C. Sivaraj, J. Phys. Chem. B 102 (1998) 6792.
[16] M.V. Martinez-Huerta, X. Gao, H. Tian, I.E. Wachs, J.L.G. Fierro, M.A. Banares, Catal. Today 118 (2006) 279.
[17] K.J. Chao, C.N. Wu, H. Chang, L.J. Lee, S.-F. Hu, J. Phys. Chem. B 101 (1997) 6341.
[18] Z. Wu, H.-S. Kim, P.C. Stair, S. Rugmini, S.D. Jackson, J. Phys. Chem. B 109 (2005) 2793.
[19] Y. Segura, L. Chmielarz, P. Kustrowski, P. Cool, R. Dziembaj, E.F. Vansant, J. Phys. Chem. B 110 (2006) 948.
[20] H. Tian, E.I. Ross, I.E. Wachs, J. Phys. Chem. B 110 (2006) 9593.
[21] B.M. Weckhuysen, D.E. Keller, Catal. Today 78 (2003) 25.
[22] J.H. Kwak, J.E. Herrera, J.Z. Hu, Y. Wang, C.H.F. Peden, Appl. Catal. A 300 (2006) 109.
[23] I.E. Wachs, Catal. Today 100 (2005) 79.