Effect of the iron amount on the physicochemical properties of Fe–ZrO₂ aerogel catalysts for the total oxidation of Toluene in the presence of water vapor

Rimeh Ismail, Jihene Arfaoui, Zouhaier Ksibi, Abdelhamid Ghorbel, Gérard Delahay

► To cite this version:

Rimeh Ismail, Jihene Arfaoui, Zouhaier Ksibi, Abdelhamid Ghorbel, Gérard Delahay. Effect of the iron amount on the physicochemical properties of Fe–ZrO₂ aerogel catalysts for the total oxidation of Toluene in the presence of water vapor. *Journal of Porous Materials*, 2020, 27 (6), pp.1847-1852. 10.1007/s10934-020-00958-1 . hal-02954503

HAL Id: hal-02954503

<https://hal.science/hal-02954503>

Submitted on 26 Nov 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Effect of the amount of iron on the physicochemical properties of new Fe-ZrO₂ aerogel catalysts for the total oxidation of Toluene in the presence of water

Rimeh Ismail,¹ Jihene Arfaoui,^{*1} Zouhaier Ksibi,¹ Abdelhamid Ghorbel,¹ and Gérard Delahay²

¹ *Université de Tunis El Manar, Faculté des Sciences de Tunis, LR01ES08 Laboratoire de Chimie des Matériaux et Catalyse, 2092, Tunis, Tunisie*

² *ICGM, Univ Montpellier, ENSCM (MACS), CNRS, Montpellier, France
E-mail: jihene@yahoofr*

New xFe-ZrO₂ aerogel catalysts, with various amounts of iron were prepared and tested in the total oxidation of toluene. The xFe-ZrO₂ aerogel catalysts obtained exhibit the diffraction peaks of ZrO₂ tetragonal phase, a high surface area and porosity. The iron content influences the structural, textural, acidic, redox and catalytic properties of the samples. Among the iron-based catalysts, the one with 5% Fe exhibits the best activity between 300 and 550 °C with 96 % C₆H₅-CH₃ conversion to CO₂ at 550 °C.

Keywords: Fe-ZrO₂ aerogel catalysts, Fe quantity, Toluene Oxidation

The emissions of volatile organic compounds (VOCs), such as toluene, aldehydes, alcohols, ketones, ethers, halogenated and aromatic compounds, are considered as one of the main sources of air pollution¹. These substances can be issued from petroleum refineries; automotive, textile manufacturers, transportation, chemical industries and solvents using processes². Their high concentration in the air may cause a serious human health and environmental problems. Therefore, it is necessary to minimize their emissions. Catalytic oxidation is generally used in many industrial processes for the control of VOCs emissions through their selective destruction at low temperature. Two groups of catalytic materials are usually employed for VOCs oxidation: (i) supported or unsupported noble metal catalysts (mostly Pt and Pd), and (ii) transition metal oxide-based catalysts. Noting that the noble metals are characterized by a good stability and high activity at low temperatures³. Nevertheless, their high cost has limited their investigation and they have been replaced by transition metal oxide-based catalysts, such as copper oxides⁴, cobalt oxides⁵, iron oxides⁶, manganese oxides⁷ and cerium oxides⁸. These systems have been extensively explored during the past years as effective and more economic catalysts than noble metal ones for the total oxidation of VOCs⁹.

Only a few papers have been reported in the literature concerning the total oxidation of toluene, particularly in the presence of water vapor, over iron-based catalysts. In this framework: P. Djinović et al.¹⁰ have showed that the Fe quantity greatly influences the catalytic performances of bimetallic CuFe catalysts in the oxidation of toluene when the reaction was realized in the absence of H₂O. On the other hand, X. Liang et al.¹¹ have studied the effect of Fe amount and the presence of vapor H₂O on the catalytic performance of Fe-Ti-PILC in the total oxidation of toluene. Their results revealed that the catalytic activity of the samples enhanced with increasing Fe content up to a value of 3.75%. The authors have also concluded that the prepared Fe-Ti-PILC

catalysts showed high stability and superior activity at 250 and 350 °C in the presence of 50,000 ppm water vapor.

In this work, a new xFe-ZrO₂ aerogel catalyst was developed, via the one step sol-gel method associated to supercritical drying process, for the total oxidation of toluene in the presence of water vapor. The effect of Fe quantity (x = 0; 1,25; 2,5, 5 and 10 wt.%) in the physicochemical properties and catalytic performances in the C₆H₅-CH₃ oxidation of aerogel materials was investigated.

ZrO₂ and xFe-ZrO₂ aerogel samples were synthesized via the single step sol-gel method using a similar procedure to that reported in our previous work for TiO₂¹² as following: First, Zirconium (IV) butoxide (Zr(OC₄H₉)₄, Sigma-aldrich, 80 %) was mixed, under stirring at room temperature, with anhydrous ethanol (C₂H₆O, Aldrich, 99.8 %) and Ethyl acetoacetate (C₆H₁₀O₃, Fluka, > 99.5%). Then, the hydrolysis is favoured by addition of a HNO₃ aqueous solution (0.1 M). Etacac /Zr and H₂O/Zr molar ratios were fixed to 1 and 10, respectively. The prepared gel was dried in the autoclave (at T = 243 °C and P = 63 bar) to obtain ZrO₂ support. For the xFe-ZrO₂ solids, an appropriate amount of iron (III) nitrate (Fe(NO₃)₃·6H₂O, Sigma-aldrich, ≥ 99.95 %) was introduced in the mixture before the hydrolysis step. The ZrO₂ and x Fe-ZrO₂ aerogel samples were finally calcined at 550 °C for 3 h under O₂ flow (30 cc/min).

Toluene oxidation was carried out at atmospheric pressure in a fixed bed reactor using 0.02 g of catalyst, previously pretreated in situ (under air) at 200 °C for 1 h. The toluene concentration was adjusted by passing an appropriate He flow through a saturator, kept at 0.7 °C, containing toluene. The reaction was performed using a mixture of gas (total flow rate = 50 cm³/min) containing 0.01 vol % toluene (> 99.7 %), 3.4 vol % H₂O (> 99.5 %), 8 vol. % O₂ (> 99.9 %) and balance with He (> 99.9%) using a second gas line. The equivalent gas hourly space velocity (GHSV) obtained was of 60,000 h⁻¹. The catalytic activity was evaluated in terms of toluene conversion to CO₂, in the 200-550 °C temperature range, with a ramp of 6 °C/min. The composition of the effluents was monitored continuously by sampling on line to a quadrupole mass spectrometer Pfeiffer Vacuum equipped with Faraday and SEM detectors (0-200 amu).

The toluene conversion (%) is expressed as:

$$X_{\text{tol}} (\%) = \frac{[\text{Toluene}]_{\text{in}} - [\text{Toluene}]_{\text{out}}}{[\text{Toluene}]_{\text{in}}} \times 100$$

Where [Toluene]_{in} and [Toluene]_{out} are the inlet and outlet concentrations of toluene, respectively.

The concentration of CO₂ (ppm) was calculated as given below:

$$[\text{CO}_2]_{(\text{ppm})} = \frac{[I]_t - [I]_0}{[I]_{7000}} * 7000$$

Where $[I]_0$, $[I]_{7000}$ and $[I]_t$ are the intensity of CO₂ signals at inlet, outlet and at any reaction temperature (t), respectively. 7000 ppm is the inlet concentration of CO₂.

Textural properties of samples were examined by N₂-physisorption, at 77 K, using a Micromeritics ASAP 2000. The samples were degassed at 250 °C before analysis. XRD patterns of solids were recorded from $2\theta = 10^\circ$ to 80° (with a step size of 0.02°) using a Brüker AXS D8 diffractometer with CuK α radiation ($\lambda = 1.5406 \text{ \AA}$). UV-vis spectra were collected, in the 200-800 nm wavelength range, using a spectrometer Lambda 40 Perkin Elmer. Temperature programmed reduction was realized, in the 50-550 °C temperature range, using an AUTOCHEM 2920 (Micromeritics), with a mixture containing 5 vol. % H₂ in Ar (30 mL/min) and a heating rate of 10 °C/min. Prior to H₂-TPR analysis, the catalyst (0.08 g) was pre-treated under 5 vol. % O₂ in He (flow rate = 30 mL/min) at 550 °C (ramp 10 °C/min) for 30 min, then cooled down to 50 °C. Acidity of catalysts was studied by NH₃-TPD using an AUTOCHEM 2910 (Micromeritics). First, the solid was pre-treated at 550 °C (ramp 10 °C/min), during 2 h, under air flow (30 cm³/min). After, it was exposed to 5 vol. % NH₃ in He (flow rate = 30 cm³/min) for 30 min and then flushed with He (30 cm³/min) during 30 min in order to remove the physisorbed ammonia. Finally, The NH₃ desorption was done in helium flow (30 cm³/min) from 100 to 550 °C with a heating rate of 10 °C/min.

The C₆H₅-CH₃ conversion and CO₂ concentration as function of the reaction temperature over xFe-ZrO₂ aerogel catalysts are displayed in Figure. 1A and 1B, respectively.

Based on the Mars-Van Krevelen (MVK) mechanism, which has been widely used for describing the catalytic oxidation of VOC over metal oxides,¹³⁻¹⁴ the reaction procedure includes two independent reactions steps: the oxidation of VOC molecules to CO₂ and H₂O by surface oxygen species on catalyst (surface lattice oxygen and surface adsorbed oxygen), and the reaction between the reduced sites and oxygen from gas phase to form surface oxygen species. Therefore, the surface oxygen species and the reducibility of catalyst (that is related to the release of surface oxygen species) are the key factors which govern its reactivity in the total oxidation of COVs. The surface acidity of catalysts is known to play also an important role in this reaction, as the presence of acid sites could facilitate both the sorption of COV at the catalyst surface and the breaking of carbon-carbon bonds which promotes the CO₂ production^{17,15}

As it can be seen in Fig 1A and 1B, ZrO₂ support exhibits low C₆H₅-CH₃ conversion to CO₂ (50 % at 550 °C) which can be related to the low reactivity of its acidic sites in this reaction. When Fe species are introduced on the catalyst, the toluene conversion to CO₂ increases with both the reaction temperature and Fe content (until 5 % wt. Fe). This underlines the key role of iron species in the total oxidation of toluene. In fact, these species contribute to the growing of surface oxygen

species and lead to the creation of new acidic and redox sites at Fe-ZrO₂ surface. This promotes the adsorption of toluene molecule and increases the active site amount. Similar results have been already reported by X. Liang et al.¹¹ who have demonstrated that the activity of Fe-Ti-PILCs solids, in the total oxidation of toluene (tested in the 250-350 °C temperature range), was initially enhanced with increasing Fe content up to a value of 3.75 %. Interestingly, a maximum of 96 % C₆H₅-CH₃ conversion at 550 °C was obtained over the novel 5Fe-ZrO₂ aerogel catalyst demonstrating its good stability and superior activity at high temperature (>450 °C) in the presence of 3.4 % water vapor.

Figure 1. (A) Toluene conversion and (B) CO₂ concentration (ppm) as function of temperature reaction over the samples.

In general, the increase of specific surface area results in the enhancement of catalytic activity. Textural properties of solids are given in table 1. As it can be seen, all the samples calcined at 550 °C exhibit high specific area ($\geq 93 \text{ m}^2/\text{g}$) and large pore volume ($\geq 0.26 \text{ cm}^3/\text{g}$), indicating of their developed texture and good thermal stability. It should be that the surface area of xFe-ZrO₂ catalysts slightly decreases with the increase of iron content, but remains above $90 \text{ m}^2/\text{g}$. The loss of the surface area can be explained by the blocking of some pores of the zirconia support by the iron oxide crystallites as explained earlier¹⁶.

Based on the N_2 adsorption-desorption isotherms at 77 K and pore size distribution curves of $xFe-ZrO_2$ aerogel catalysts, presented in Figures 2 and 3, respectively, it can be concluded that all the samples, which are characterized by a type IV isotherms according to IUPAC classification and a hysteresis loops type H1, are mesoporous materials with a monomodal (case of ZrO_2 , $1.25Fe-ZrO_2$, $2.5Fe-ZrO_2$ and $10Fe-ZrO_2$) or bimodal (for $5Fe-ZrO_2$) pore size distributions.

Figure 2. N_2 adsorption-desorption isotherms of samples.

It is worthy to note that the pores of solids become larger by increasing the Fe loading (Figure. 3). This result can be explained by the existence of strong interactions between zirconia and iron which affect the porosity of catalysts ¹².

Figure 3. BJH pore size distribution curves of samples.

The XRD analysis (Figure 4) reveals that both the diffraction peaks related to monoclinic and tetragonal phases of ZrO_2 (m- ZrO_2 and t- ZrO_2) are detected at $2\theta = 24.38^\circ$ (110), 28.26° (-111), 31.56° (111), 41.07° (102), 45.21° (-202), 54.09° (300), 55.60° (130), 65.68° (320) [PDF 89-9066] and $2\theta = 30.33^\circ$ (101), 34.67° (002), 50.37° (112), 60.09° (211), 62.57° (202) [PDF 79-1769], respectively, in the X-ray diffraction patterns of ZrO_2 . However, only the typical peaks of the t- ZrO_2 phase are observed in the case of $xFe-ZrO_2$ aerogel catalysts. This result, demonstrating a stabilization of ZrO_2 tetragonal phase, known by its metastability at low temperature, could indicate the existence of strong interactions between Fe and ZrO_2 which modify the structure

Table 1. Textural properties of the samples

Sample	BET surface area ($m^2 g^{-1}$)	Total pore Volume (cm^3/g)	Average Pore diameter (Φ_{pore} , Å)
ZrO_2	107	0.33	88
$1.25Fe-ZrO_2$	111	0.26	90
$2.5Fe-ZrO_2$	107	0.29	104
$5Fe-ZrO_2$	93	0.28	92
$10Fe-ZrO_2$	95	0.32	134

of zirconia. It should be also mentioned that the XRD analysis did not reveal the presence of characteristic peaks of metallic Fe or its oxides, which is in good agreement with a previous study ¹⁷ and indicates the high dispersion of iron species at zirconia surface.

Figure 4. XRD patterns of samples.

DR UV-vis spectroscopy (Figure 5) is used to examine the nature and environment of Zr and Fe species. The ZrO_2 shows a typical absorption band in 200-250 nm range, which is attributed to $O^{2-} \rightarrow Zr^{4+}$ charge transfer transition in zirconia ¹⁸. The new bands observed at higher wavelengths in the UV-vis spectra of $xFe-ZrO_2$ solids correspond to iron species. Hence, the bands situated at $\lambda < 300$ nm can be attributed to Fe species in tetrahedral and octahedral coordinations ¹⁹. Fe_xO_y aggregates or clusters display an absorption band at $300 < \lambda < 400$ nm², whereas, the band located at $\lambda > 400$ nm indicates the presence of aggregates of αFe_2O_3 iron oxide ². It should be noted that the αFe_2O_3 aggregates are obtained only in the case of $10Fe-ZrO_2$ catalyst which demonstrates that the increase of the iron amount influences the nature of Fe species and consequently affects the catalytic performances of $xFe-ZrO_2$ in the total oxidation of toluene as confirmed by the catalytic test results.

Figure 5. DRUV-Vis spectra of samples.

It is well established that the catalytic activity of metal oxide catalysts strongly depends on their acidic and redox properties²⁰⁻²¹. Therefore, the reducibility and surface acidity of xFe-ZrO₂ were studied using H₂-TPR and NH₃-TPD techniques. The results are illustrated in Fig.6 and Fig.7, respectively.

As shown in the H₂-TPR profiles of samples (Figure. 6), no H₂ consumption peaks are detected for ZrO₂ support since Zr⁴⁺ is a non-reducible cation²². However, for the xFe-ZrO₂ solids, new peaks are appeared at different temperatures and are attributed to the reduction of various iron species. Therefore, the peaks at low temperatures (between 90 and 450 °C) can be ascribed to the reduction of Fe₂O₃ to Fe₃O₄ and the peaks at higher temperatures (> 450 °C) can be attributed to Fe₃O₄ → FeO → Fe⁰ transformations²³. This demonstrates that the addition of Fe contributes to the creation of redox sites at xFe-ZrO₂ surface. These sites were found active in the total oxidation of toluene and their nature and reactivity seem to be affected by the amount of Fe. It can be also suggested, in line with the UV-vis results, and that the amount of iron influences the nature, the dispersion and/or the oxidation state of iron species seeing that the position, the number and the intensity of H₂ consumption peaks change with increasing the iron quantity.

Figure 6. H₂-TPR profiles of samples.

In Fig. 7., ZrO₂ and xFe-ZrO₂ samples show a broad NH₃ desorption peak between 100 and 450 °C which can be attributed to NH₃ desorbed from weak (at T ≈ 200 °C) and medium (at T ≈ 300-400 °C) acid sites²⁴. It should be underlined that the intensity of this peak is higher in case of the samples containing iron indicating the creation of new acidic sites at ZrO₂ surface by the Fe addition. It is known that acid sites provide protons or accepting electron pairs from the toluene molecule which is crucial for its further oxidation.

Figure 7. NH₃-TPD profiles of samples.

In this work, new well-structured xFe-ZrO₂ aerogel catalysts with high surface area, large porosity and good thermal stability were successfully synthesized by the one step sol-gel method and tested in the total oxidation of toluene in the presence of H₂O. It was found that the addition of iron affects the structural and textural properties of xFe-ZrO₂ catalysts, contributing to the creation of actives acidic and redox sites at their surfaces. This addition consequently enhances the activity of the total oxidation of toluene. Interestingly, high conversion of C₆H₅-CH₃ to CO₂ (96 % at 550 °C), in the presence of water vapor, was obtained over the novel 5Fe-ZrO₂ aerogel catalyst.

References and Notes

1. P. Doggali, Y. Teraoka, P. Mungse, I. K. Shah, S. Rayalu, N. Labhsetwar, *J. Mol. Catal. A. Chem.* **2012**, 358, 23.
2. C. Hea, F.W. Zhanga, L.Yue, X.S. Shanga, J.S.Chena, Z.P. Hao, *Appl. Catal. B. Environ.* **2012**, 111-112, 46.
3. J. N. Armor, *Appl. Catal. B.* **1992**, 1, 221.
4. Y. Wang, Z. Wen, H. Zhang, G. Cao, Q. Sun, J. Cao, *Catalysts* **2016**, 6, 2.
5. F. Yu, Z. Qu, X. Zhang, Q. Fu, Y. Wang, *J. Energy Chem.* **2013**, 22, 845.
6. B. Solsona, T. Garcia, R. Sanchis, M.D.Soriano, M. Moreno, E. Rodriguez-Castellon, S.Agouram, A. Dejoz, J.M. Lopez Nieto, *Chem. Eng. J.* **2016**, 290, 273.
7. V.P. Santos, M.F.R. Pereira, J.J.M.Orfao, J.L. Figueiredo, *Appl. Catal. B environ.* **2010**, 99, 353.
8. C. H.Wang, S.S. Lin, *Appl. Catal. A Gen.* **2004**, 268, 227.
9. Y. Wang, J. Cao, S.Wang, X. Guo, J. Zhang, H. Xia, S. Zhang, S. Wu, *J. Phys. Chem. C.* **2008**, 112, 17804.
10. P. Djinić, A. Ristić, T. Žumbar, V. D.B.C. Dasireddy, M. Rangus, G. Dražić, M. Popova, B. Likozar, N. Z. Logar, and N. Tušar, *Appl. Catal. B. Environ.* **2020**, <https://doi.org/10.1016/j.apcatb.2020.118749>,
11. X. Liang, F. Qi, Peng Liu, GaolingWei, Xiaoli Su, LingyaMa, Hongping He, Xiaojun Lin, Yunfei Xi, Jianxi Zhu, Runliang Zhu, *Appl. Clay. Sci.* **2016**, <http://dx.doi.org/10.1016/j.clay.2016.05.022>

12. J. Arfaoui, A. Ghorbel, C. Petitto, G. Delahay, *Appl Catal , Environ.* **2018**, 224, 264.
13. Pei and J.S.S Zhang, *Hvac&r. Res*, **2011**, 17, 476
14. J.C.S, Wu, T.Y, Chang, *Catal.Today*, **1998**, 44,111.
15. A.K. Neyestanaki, N. Kumar, L.-E. Linfors, *Appl. Catal. B* , **1995**, 7, 95.
16. J. Arfaoui, L. Khalfallah-Boudali, A. Ghorbel, G. Delahay, *J. Phys. Chem. Sol.* **2008**, 69, 1121.
17. W. Zhao, Q. Zhong, Y.X. Pan, R. Zhang, *Chem. Eng. J.* **2013**, 228, 815.
18. Z. Guerra-Que, G. Torres-Torres, H. Pérez-Vidal, I. Cuauhtémoc-Lopez, A. Espinosa de los Monteros, J. N. Beltramini and D. M Frias-M´arquez, *RSC Adv.* **2017**, 7, 3599.
19. M. Schwidder, S. Heikens, A.D. Toni, S. Geisler, M. Berndt, A. Bruckner, W. Grunert, *J. Catal.* **2008**, 259, 96.
20. H.H. Vogue, C.R. Adams, *Adv. Catal.* **1967**, 17, 151.
21. S.L.T. Anderson, *J. Catal.* **1986**, 98, 138.
22. Y. Zheng, X. Zhu, H. Wang, K. Li, Y.H.Wang, Y.G. Wei, *J. Rare Earth.* **2014**, 32, 842.
23. F. Yang, J.L. Hang, T. Odoom-Wubah, Y.L. Hong, M.M. Du, D.H Sun, L.S Jia, Q.B. Li, *Chem. Eng. J.* **2015**, 269, 105.
24. J. Arfaoui, L. Khalfallah-Boudali, A. Ghorbel, *Appl. Clay Sci.* **2010**, 48, 171.