

*Dedicated to the memory of
Professor Ecaterina Ciorănescu-Nenitzescu (1909–2000)*

CATALYTIC AND ELECTRICAL PROPERTIES OF IRON OXIDE IN DEEP PROPANE OXIDATION

Cornel MUNTEANU,^{a,*} Nicolae I. IONESCU,^a Marcel FEDER,^b Lucian DIAMANDESCU,^b and
Monica CĂLDĂRARU^a

^aInstitute of Physical Chemistry “Ilie Murgulescu” of the Roumanian Academy, Spl. Independentei 202, 060021 Bucharest, Roumania, Phone/Fax (40-21) 312 1147,

^bNational Institute of Material Physics, 077125 Bucharest-Magurele, P.O.Box MG-7, Roumania

Received May 15 2009

The catalytic activity of hematite ($\alpha\text{-Fe}_2\text{O}_3$) was studied in deep propane oxidation. Propane conversion to CO_2 was more than 90% at 400°C in excess of oxygen. The AC electrical conductivity measurements performed in situ showed that at low temperature the surface conductivity is influenced by the presence of moisture in the feed which is adsorbed on the surface. Based on the conductivity data obtained in absence of oxygen coupled with information provided by Mössbauer spectroscopy, the results are discussed in terms of the redox-type mechanism.

INTRODUCTION

Liquefied petroleum gas (LPG) is used as a fuel substitute for automobiles, because of its clean combustion. The major components of the LPG are propane and butanes, the ratio of which being variable depending upon the production technology. Since in homogeneous combustion the reactivity of propane is lower than that of butanes, the concentration of propane in the auto exhaust gases is much higher. Hence, in order to control the hydrocarbon emissions from the LPG-fuelled automobiles, an efficient catalyst for total oxidation of propane at low concentration of hydrocarbon is required.

Many studies have reported earlier on the combustion of propane over different catalysts, particularly over supported noble metals¹⁻⁴ and transition metal oxides.⁵⁻⁸ In general, noble metal containing catalysts have high hydrocarbon combustion activity at low temperature, but they are more liable to deactivation by poisoning⁹ being also much more expensive. Transition metal oxide-based catalysts, however, have lower hydrocarbon combustion activity, but they are much cheaper and moreover, more resistant towards poisoning.

Iron oxide is widely known in literature as an essential component of the catalysts for selective oxidation or oxidative dehydrogenation (see for example the oxidative dehydrogenation of butene to butadiene^{10, 11} or for the dehydrogenation of ethylbenzene to styrene¹²).

The presence of iron compounds in multicomponent oxide catalysts improves their performances in hydrocarbon oxidation; the $\text{Fe}^{2+}\text{-Fe}^{3+}$ redox couple facilitates the reduction/reoxidation of other component phases having coherent interfaces, since it acts as a source and sink of electrons.¹³

In this paper we focus on the catalytic behavior in propane oxidation of hematite ($\alpha\text{-Fe}_2\text{O}_3$). AC electrical conductivity measurements in operando conditions (differential step technique) were also performed in order to follow the dynamics of the oxidation level of the oxide surface.

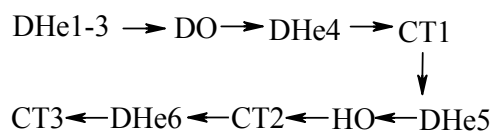
EXPERIMENTAL

$\alpha\text{-Fe}_2\text{O}_3$ (hematite) was prepared from iron hydroxide, by calcination for 7 hours at 600°C. The sample was characterized before and after the catalytic test in propane oxidation by BET method for measuring of surface area and porosity (N_2

* Corresponding author: munteanuc@icf.ro

adsorption-desorption), X-ray diffraction (XRD), Mössbauer spectroscopy, and by AC electrical conductivity measurements in operando conditions. XRD analysis was performed on a DRON X-ray powder diffractometer linked to a data acquisition and processing facility. $\text{Cu}_{K\alpha}$ radiation ($\lambda=1.540598\text{\AA}$) and a graphite monochromator have been used. The Mössbauer spectra were recorded at room temperature using a constant acceleration spectrometer and a ^{57}Co source in Rhodium matrix. $\alpha\text{-Fe}$ foil (Amersham, England) was used to calibrate the Mössbauer spectrometer in a velocity range of $\pm 10\text{mm s}^{-1}$. All spectra were analyzed by nonlinear least-square fitting in the hypothesis of Lorentzian line shape.

AC electrical conductance G and capacitance C of 1.5cm^3 of catalyst powder (size fraction between $0.2 - 0.5\text{mm}$) were measured in operando conditions, between room temperature and 400°C with a RLC precision bridge (Tesla BM 484, 1592 Hz) during linear heating ($2^\circ\text{C}/\text{min}$) in gas flow, in various gases and in conditions simulating the catalytic experiment; this was coupled with simultaneous gas analysis. The measurements were performed by using the differential step technique (DST)¹⁴ consisting of various heating/cooling cycles and a specially designed cell.¹⁵ The cycles succession was:



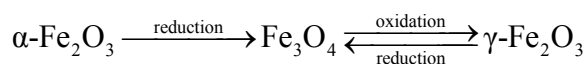
where DHe-dry helium, DO and HO dry or humid oxygen respectively, CT1-2 – the catalytic test in C_3H_8 :air 1:10 mixture and CT3 – test with propane: helium mixture (i.e. in absence of oxygen).

The catalytic tests were performed on the same batch of sample which was previously used in electrical conductivity measurements; they were done in an integral reactor between

room temperature and 450°C , with 0.5cm^3 of catalyst grains (size fraction between $0.2 - 0.5\text{mm}$), for propane:oxygen (from air) molar ratios between 2:1.8 and 1:6, at contact times between 0.75 and 2s; the gas flow was measured by using MKS mass controllers. The composition of the effluent was analyzed on line by gas chromatography (Perkin Elmer – Clarus 500) equipped with TCD and FID detectors using Hayesep Q and Molecular Sieve 5A columns.

RESULTS AND DISCUSSION

Iron oxide has two typical crystalline modifications: $\alpha\text{-Fe}_2\text{O}_3$ (hematite) and $\gamma\text{-Fe}_2\text{O}_3$ (maghemite)¹⁶. The phase transition between maghemite and hematite occurs in air approximately at 300°C and in vacuum at lower temperature (approximately 250°C)¹⁷ according with scheme:



The X-ray refinements indicated that the fresh sample contains only hematite phase (Figure 1a). After the catalytic test, the hematite phase is accompanied by $\gamma\text{-Fe}_2\text{O}_3$ phase, which is the dominant phase in the sample ($\sim 64\%$) (Figures 1b). Figures 2 show the room temperature transmission Mössbauer spectra of the fresh sample (Figure 2a) and of the same sample after its use in the series of catalytic tests (Figure 2b).

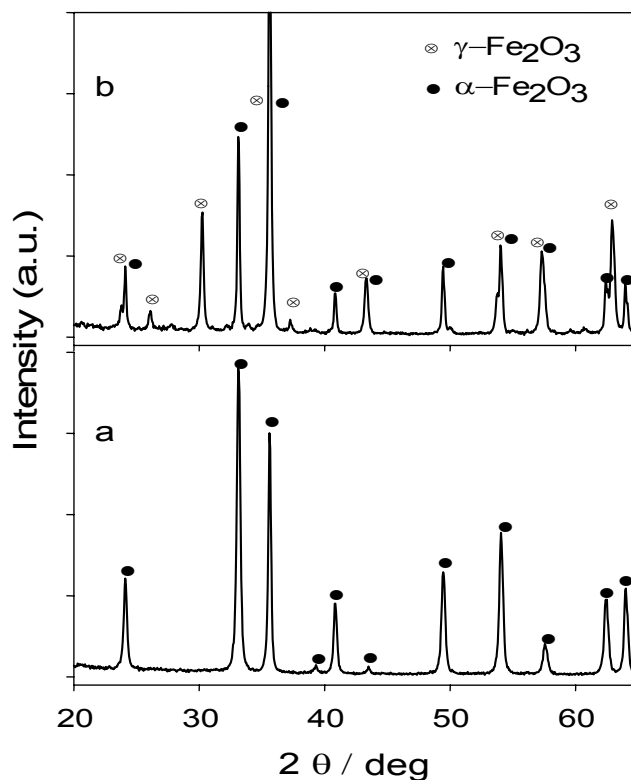


Fig. 1 – XRD analysis for $\alpha\text{-Fe}_2\text{O}_3$ sample; a – fresh, b – after the catalytic tests.

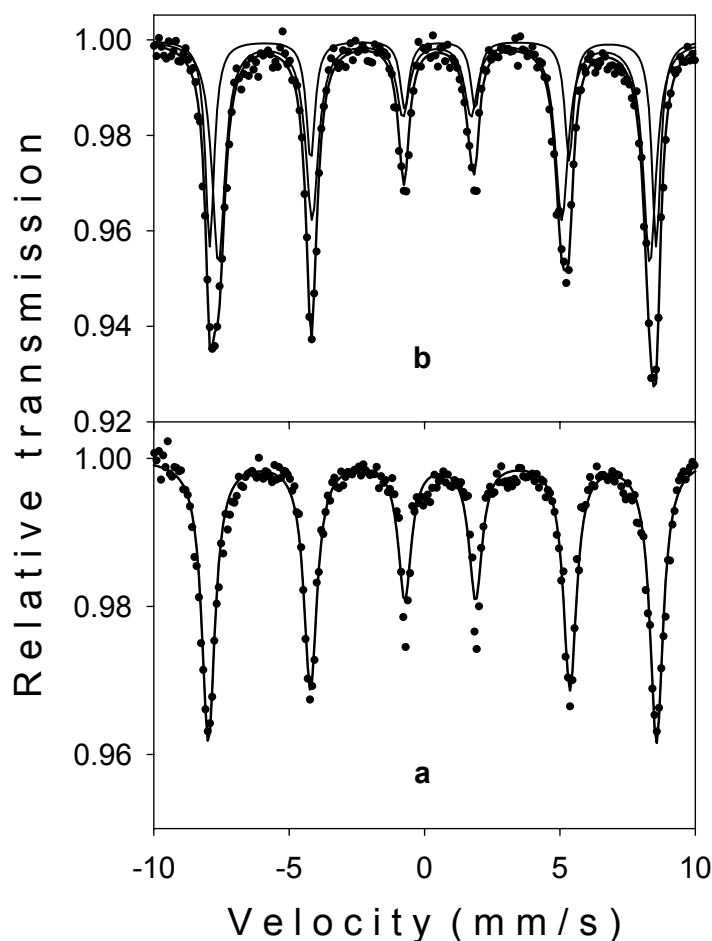


Fig. 2 – Mössbauer spectra for α - Fe_2O_3 sample; a – fresh, b – after the catalytic tests.

The Mössbauer hyperfine parameters: the magnetic hyperfine field (H_{hf}), the isomer shift (IS), the quadrupole splitting (Δ) together with the relative areas of different components, as resulted by fitting the spectra, presented in Table 1, are characteristic for Fe^{3+} ions; no Fe^{2+} species were detected in the samples.

The electrical conductivity measurements indicated that the hematite has n -type semiconductor behavior (Figure 3), which is in evidence between 100-200°C (lower conductivity in oxygen with respect to inert, due to the adsorption of electron

consuming oxygen species). At higher temperature, the trend is changed, probably associated with the existence of the plateau, indicating a phase transition. The U shape of the plots clearly indicates the surface sensitivity to water adsorption at low temperature, the decreasing arm being connected with the removal by gas flushing of the weakly adsorbed water species from the surface¹⁸, as shown by the analysis of the effluent gas.

Table 1

The Mössbauer parameters and phase composition of the fresh and tested iron oxide

Sample ID	H_{hf} (T)	IS* (mm/s)	Δ (mm/s)	Relative Areas (%)	Phase/Site assignment
α - Fe_2O_3 – fresh	51.6	0.34	-0.22	100	α - Fe_2O_3 (Fe^{3+})
α - Fe_2O_3 – tested	51.7	0.34	-0.21	35.8	α - Fe_2O_3 (Fe^{3+})
	49.4	0.29	-0.03	64.2	γ - Fe_2O_3 (Fe^{3+})
Error	± 0.3	± 0.01	± 0.01	± 0.4	

* IS is given relative to α -Fe standard

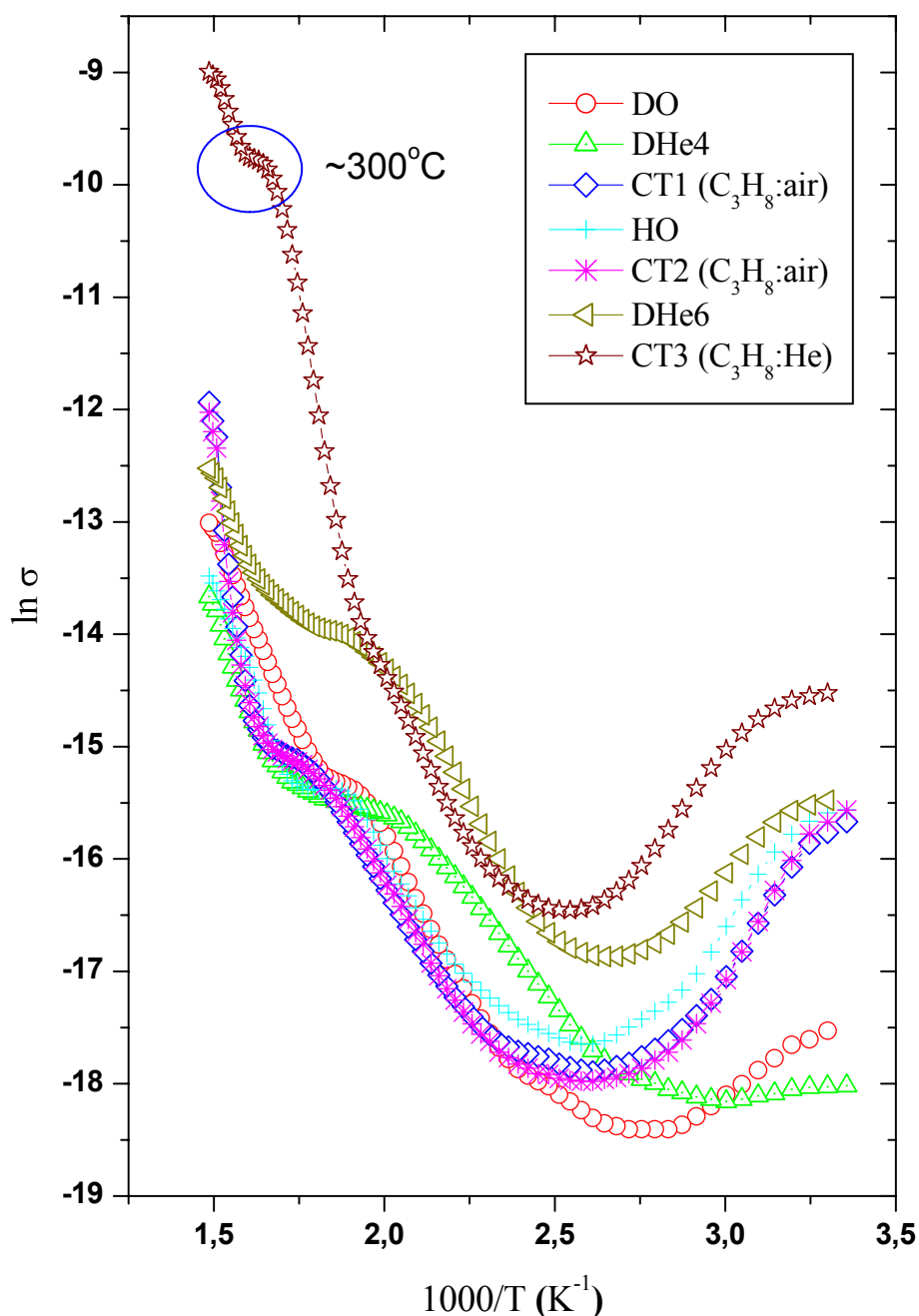


Fig. 3 – Arrhenius plots of conductivity for α -Fe₂O₃ in different atmospheres.

The capacity data, coupled with effluent analysis confirm this statement, showing that in the low temperature region, the weakly adsorbed water species desorbs from the surface by heating – see the low temperature peaks, Figure 4. The increasing part is connected with the increased mobility of the surface dipoles (e.g. water molecules) while the decreasing part is related with their desorption¹⁴.

Testing in propane:air 1:10 mixture influences the surface conduction for the low temperature

domain but it has no any noticeable effect above 100°C (see DHe4, CT1 in Figure 3). However, testing again (CT2) after the treatment in humid oxygen induces surface sensitization, since the next reference cycle in inert (DHe6) showing much higher values indicates a considerable surface reduction. To confirm this statement, an experiment was performed in absence of oxygen (CT3 – propane:helium cycle). As shown, the values between 110-240°C are practically superposed on DHe6

values, but at higher temperature they are much higher due to the surface reduction by propane. This is confirmed also by the capacity data (Figure 4), surface reduction resulting in increased surface capacitance. These clearly indicate that surface reduction by propane in absence of oxygen occurs above 240°C, while in presence of oxygen, this effect appears at much higher temperature. The in-

flexion point at 300°C must be due to the transition of phase as indicated by XRD and Mössbauer spectroscopic data.

Catalytic results obtained in a separate series of experiments performed on the same batch of sample indicate that iron oxide is active in deep propane oxidation, with more than 90% conversion to CO₂ in excess of oxygen (Figure 5).

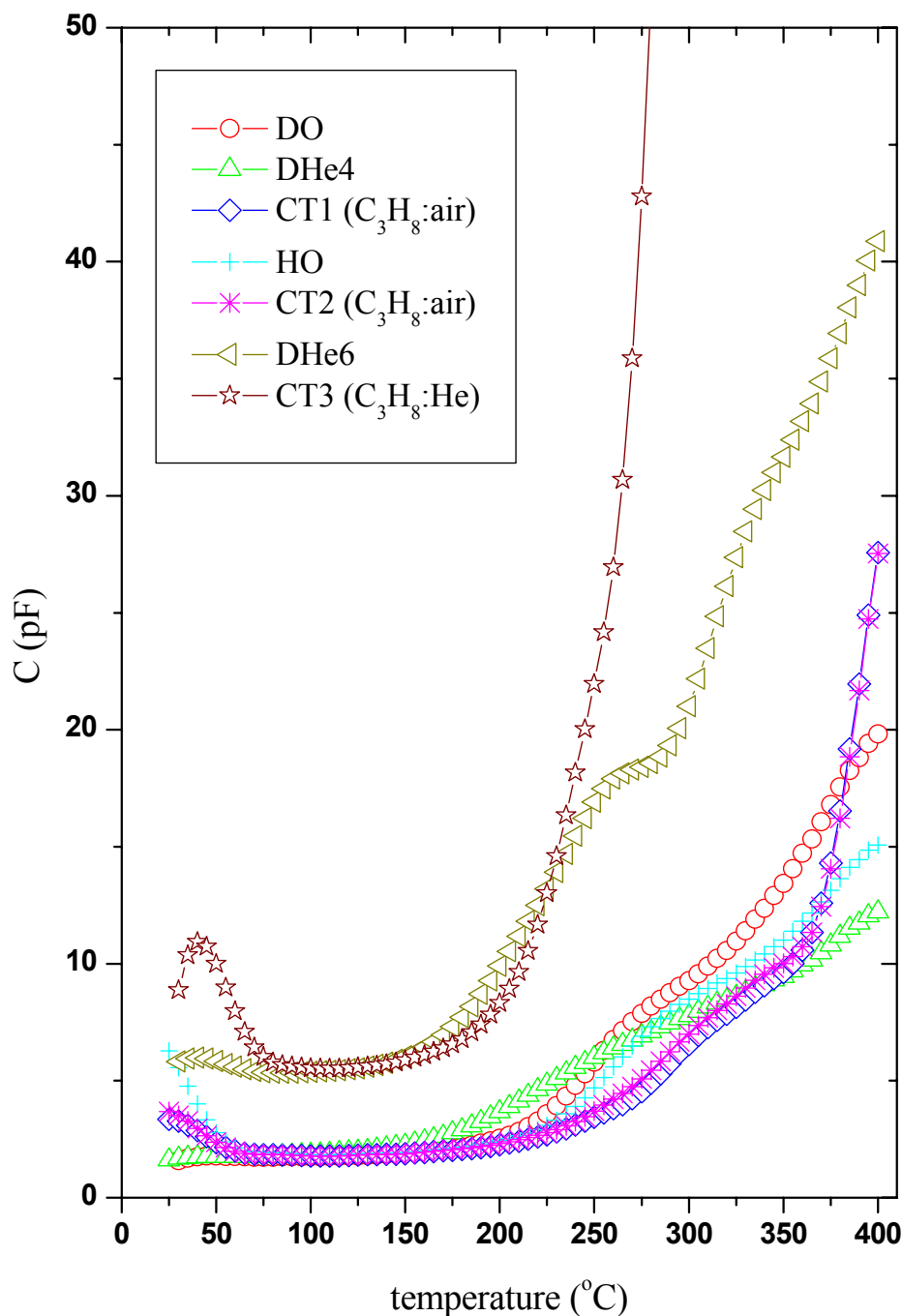


Fig. 4 – Variation of apparent capacity during heating for α -Fe₂O₃.

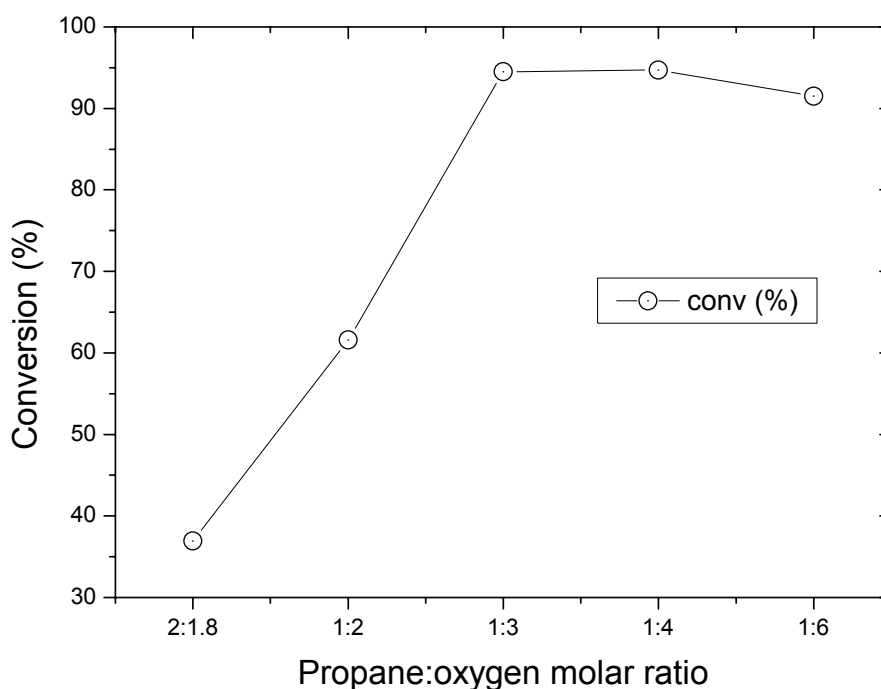


Fig. 5 – Propane oxidation on α -Fe₂O₃ at 400°C, contact time 0.75s.

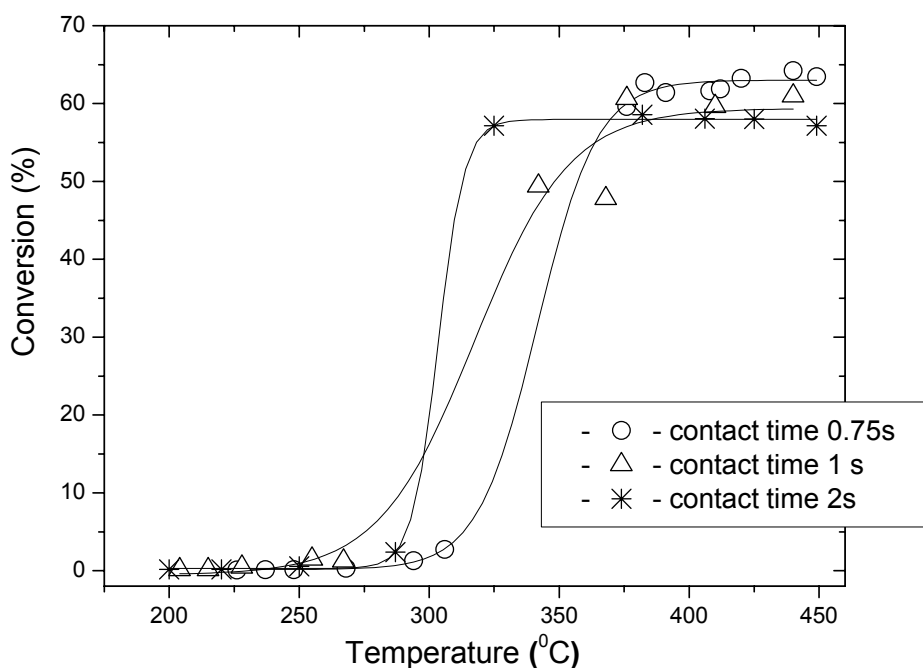


Fig. 6 – Propane oxidation on α -Fe₂O₃, propane:oxygen ratio – 1:2.

For a propane:oxygen ratio of 1:2 the hydrocarbon conversion is around 60%, with 80% selectivity to CO₂, the rest being C₁-C₃ products. Propane conversion is slightly higher at lower contact time (Figure 6). This is probably due to the fact that a longer residence time of the hydrocarbon on the surface blocks some of the active sites.

A high local exothermal effect indicating the onset of oxidation (corresponding to a sharp increase of temperature by about 50°C with respect to the programmed one) was noticed between 275–325°C (depending on the residence time) and associated with a sharp increase of conversion (Figure 6). This sharp temperature increase is diminished on

increasing the residence time; as mentioned before, this suggests either that in the latter case some of the active sites might be blocked by strongly adsorbed hydrocarbon-derived species (and consequently the activity is diminished by coke formation), or that the iron phase is more reduced in this case. The decrease of the propane:oxygen ratio (2:1.8) induces a slight increase of selectivity to C_1 - C_3 products (30%), but at much lower conversion (35%).

After the catalytic tests the surface area of the hematite increased, suggesting that α to γ transition must be accompanied by the change in particle size. At the same time, a change in pore size distribution was noticed, after the catalytic test the larger pores being transformed in smaller pores, probably by coke formation, but the pore volume is higher (Figure 7).

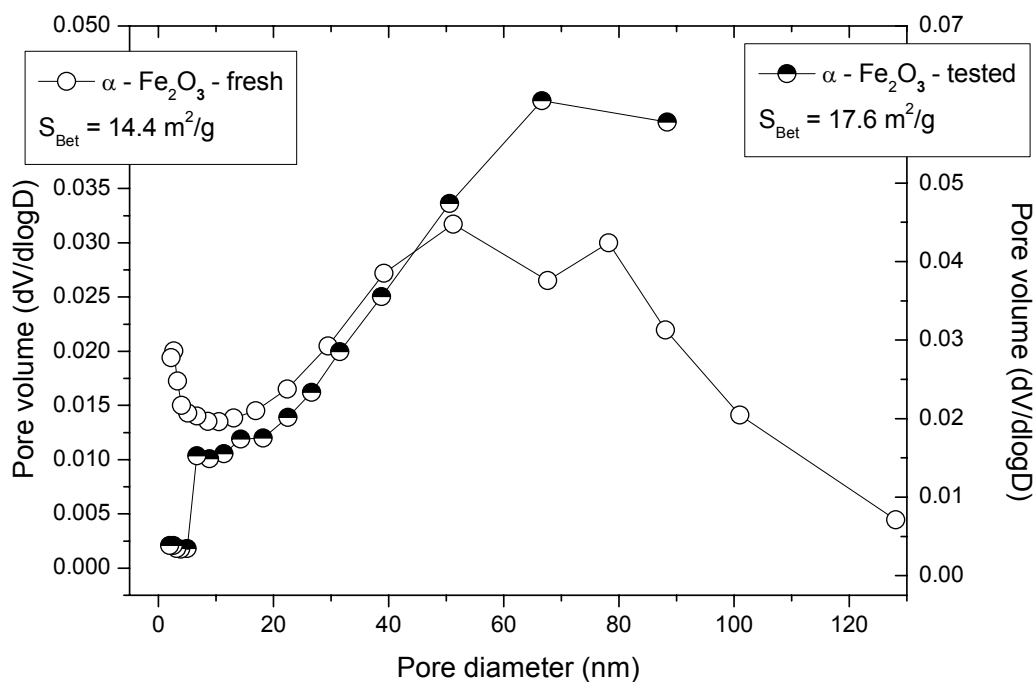


Fig. 7 – Pore volume distribution (N_2 adsorption-desorption) for α - Fe_2O_3 samples.

CONCLUSIONS

In this study the catalytic activity of α - Fe_2O_3 and in situ measured electrical properties were investigated in deep propane oxidation with the aim of evidencing the potential application of this oxide as a catalyst for auto-exhaust gases of vehicles using LPG as a fuel and also to find mechanistic details of its action.

In spite of the fact that no Fe^{2+} ions were detected in the used catalyst by Mössbauer spectroscopy, the final presence of γ - Fe_2O_3 clearly indicated that propane combustion on iron oxide occurs via a redox-type process. This is also supported by the electrical conductivity/capacity data, particularly in absence of oxygen in the feed.

The high propane conversion to CO_2 for rich-in-oxygen mixtures recommends iron oxide to be used as a catalyst for removing traces of hydrocarbon from auto-exhaust gases.

Acknowledgements: The authors are grateful to Dr. József Kovács for the BET and porosity measurements. C. Munteanu is grateful to CNCSIS, Roumania for financial support under the grant TD 252/2007.

REFERENCES

1. T.F. Garetto, E. Rincón and C.R. Apesteguía, *Appl. Catal. B: Environmental*, **2004**, *48*, 167.
2. M. Schmal, D.A.G. Aranda, F.B. Noronha, A.L. Guimaraes and R.S. Monteiro, *Catal. Lett.*, **2000**, *64*, 163.
3. A. Scarpa, R. Pirone, G. Russo and D.G. Vlachos, *Combustion and Flame*, **2009**, *156*, 947.
4. P. Vernoux, F. Gaillard, L. Bultel, E. Siebert and M. Primet, *J. Catal.*, **2002**, *208*, 412.
5. V.R.Choudhary, S.Banerjee and S.G.Pataskar, *Appl. Catal. A: General*, **2003**, *253*, 65.
6. M. Baldi, E. Finocchio, F. Milella and G. Busca, *Appl. Catal. B: Environmental*, **1998**, *16*, 43.
7. M.R. Morales, B.P. Barbero and L.E. Cadús, *Appl. Catal. B: Environmental*, **2006**, *67*, 229.

8. M. Alifanti, J. Kirchnerova, B. Delmon and D. Klvana, *Appl. Catal. A: General*, **2004**, 262, 167.
9. M.F.M. Zwinkels, S.G. Jaras and P.G. Menon, *Catal. Rev. Sci. Eng.*, **1993**, 35, 319.
10. M. Misono, K. Sakata, F. Ueda, Y. Nozawa and Y. Yoneda, *Bull. Chem. Soc. Jpn.*, **1980**, 53, 648.
11. H.H. Kung, M.C. Kung and B.L. Yang, *J. Catal.*, **1981**, 69, 506.
12. E.H. Lee, *Catal. Rev.*, **1973**, 8, 285.
13. N.I. Ionescu and M. Caldararu, "Heterogeneous Selective Oxidation of Lower Olefins", Roumanian Academy Printing House, 1993, p. 81.
14. M. Caldararu, G. Postole, M. Carata, C. Hornoiu, N.I. Ionescu, T. Jouhakova and A. Redey, *Appl. Surf. Sci.*, **2003**, 207, 318.
15. M. Caldararu, D. Sprinceana, V.T. Popa and N.I. Ionescu, *Sens. Actuat. B*, **1996**, 30, 35.
16. I.S. Lim, G.-E. Jang, C.K. Kim and D.-H. Yoon, *Sens. Actuat. B*, **2001**, 77, 215.
17. S. Sugiyama, K. Kastuma, N. Fukuda, T. Shono, T. Moriga and H. Hayashi, *Catal. Comm.*, **2001**, 2, 285.
18. M. Caldararu, G. Postole, C. Hornoiu, V. Bratan, M. Dragan and N.I. Ionescu, *Appl. Surf. Sci.*, **2001**, 181, 255.