

Decomposition of H₂O₂ on Monolithic MnO_x/ZrO₂ Catalysts for Aerospace Application

Luca Micoli*, Maria Turco

Department of Chemical, Materials and Production Engineering of the University of Naples Federico II, P.le Tecchio, 80125 Napoli, Italy
luca.micoli@unina.it

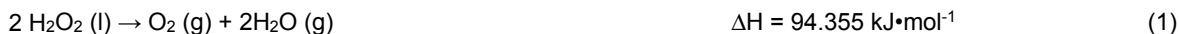
Hydrogen peroxide is widely recommended in aerospace field for propulsive applications for the high energy density and for its “green” nature due to low toxicity and low environmental impact in comparison with conventional propellants (N₂H₄, N₂O₄). Nevertheless, the presence of a catalyst is necessary for H₂O₂ decomposition due to the low kinetics of the homogeneous reaction. The catalytic activity of innovative materials for the hydrogen peroxide decomposition has been studied under the vapour phase condition at 200 °C. Catalysts are based on manganese oxides (MnO_x) dispersed on monolithic zirconia substrates. They have been developed using a precipitation technique with an improved procedure; content of the active phase was from 0.5 to 2.0 wt %.

Results obtained showed a high activity of the catalysts. The conversion was strongly depending on the space velocity and on MnO_x content on the support.

1. Introduction

Recently propulsive systems based on green propellants have seen an increased interest for space applications due to their lower toxicity, in addition they are more environmental friendly than the common propellants, such as hydrazine (Gohardani et al., 2014).

Hydrogen Peroxide (HP) is probably the most thoroughly studied propellant worldwide. Indeed, the reaction of H₂O₂ decomposition (Eq(1)) is highly exothermic and can give rise, under adiabatic conditions, to hot gaseous products at temperature depending on the concentration of the H₂O₂ /H₂O solution (T= 632-953 °C for H₂O₂ concentration of 85-98 wt %).



HP can be used as monopropellant in space propulsion systems requiring low thrust levels for satellite attitude control, station keeping, de-orbiting, and as oxidizer in bipropellant systems requiring thrust level up to 500 N (Bramanti et al., 2006), i.e. for orbit insertion manoeuvres and attitude control of more massive systems (Bonifacio, 2006).

Nevertheless, the homogeneous HP decomposition has a low kinetics and a catalyst is necessary for practical applications. Moreover, the catalysts for HP decomposition should guarantee high efficiency, long life, short response time and good thermal and mechanical properties. Therefore a proper design of catalytic system is the fundamental aspect for the development of successful propulsive systems based on HP.

In the last years, different materials based on metals (Sungyong et al., 2008) or metal oxides (Torre et al., 2008) have been investigated, among these manganese oxides on zirconia substrates seem to be very promising (Russo Sorge et al., 2004). Usually catalytic activity for propulsive applications is studied under liquid phase conditions and, apart from Micoli et al. (2013), no data are reported for vapour phase conditions: it is worth noting that the catalytic reactor must operate in large part with vaporized H₂O₂. Our previous work proposed a study on the vapour phase HP decomposition on Mn based monolithic catalysts synthesised by

different methods (Micoli et al, 2013). The present work continues that study with an analysis of the behaviour of MnOx/ZrO₂ monolithic catalysts prepared by the precipitation method with an improved procedure and tested under different conditions.

2. Experimental

2.1 Catalysts preparation and characterization

Catalysts are made by monolithic support of ZrO₂ stabilized with Y₂O₃ at 10 mol %, supplied by Céramiques Techniques Industrielles Company (France), and Mn-oxides (MnOx) as the active phase, obtained from Mn(C₂H₃O₂)₂ supplied by Sigma Aldrich. Monoliths are cylinders with an external diameter of 13 mm and internal diameter of 6 mm, length of 30 mm (CYL-30) or 60 mm (CYL-60), or honeycombs with the same external diameter of cylinder and a square channels density of 62 cm⁻², length of 30 mm (HCB-30) or 60 mm (HCB-60).

The active phase was dispersed on the monolithic supports by a precipitation technique (Micoli et al., 2013) using a modified procedure that allows to avoid a preliminary washcoating. This procedure permits to obtain a uniform dispersion of the active phase and high MnOx uptakes for each precipitation step. The honeycomb support was introduced into a 0.65 M aqueous Mn(C₂H₃O₂)₂ solution ($V = 100$ mL) under stirring at 50 °C. Then 2 mL of concentrated NH₄OH solution was slowly added drop by drop to favour a lower precipitation rate of Mn(OH)₂ and a stronger adhesion onto the support. Afterwards the material was drained and oven dried at 120 °C for 2 h. This procedure was repeated three (P3) or five (P5) times to obtain high Mn content. Then samples were thermally treated in air flow (6 L h⁻¹) for 2 h at 500 rpm to promote the decomposition of Mn(OH)₂ into Mn-oxides. The evaluation of the MnOx content was obtained from the weight increase of the support with an accuracy of ±0.05 wt %.

Average Mn oxidation state of the active phase were evaluated by Temperature Programmed Reduction (TPR) measurements using a laboratory apparatus with a 2 % H₂/Ar flow (150 cm³ min⁻¹) and heating rate of 10 °C min⁻¹ up to 800 °C. The catalysts were loaded in a quartz down-flow cell properly designed to allow the analysis on the entire monolith.

2.2 Catalytic activity measurements

Catalytic activity tests were carried out with vaporized solutions of hydrogen peroxide in the experimental apparatus shown in Figure 1.

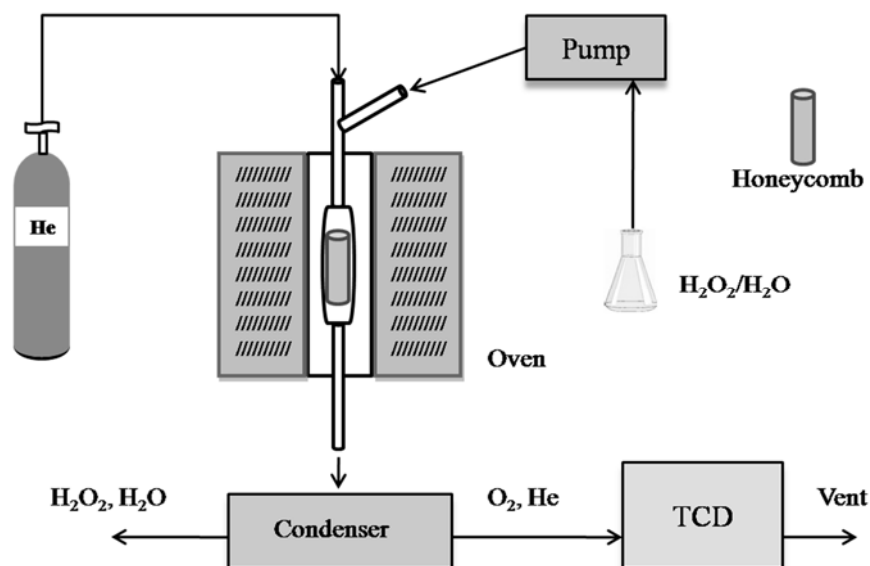


Figure 1: Apparatus for H₂O₂ decomposition tests

The reactor was a glass tube (i.d. = 0.6 cm, l = 40 cm) with a central enlarged section (i.d. = 1.4 cm, l = 8 cm) in which the honeycomb catalyst was precisely accommodated. The reactor was properly designed to allow

both the vaporization and preheating of the feed mixture. Feed flow rates of 223 and 280 mL min⁻¹ were obtained starting from H₂O₂ solution (50 wt %) pumped to the reactor with a flow of He as carrier. The feed flow composition was constant (H₂O₂ 11.3 mol %, H₂O 21.4 mol %, He balance) corresponded to contact times (τ), calculated as the reactor volume and reactant gas flow rate ratio, reported in Table 1 for monoliths of 30 and 60 mm. Catalytic tests were carried out at 200°C.

The effluents from the reactor passed through an ice trap and an anhydrous KOH trap for the removal of H₂O and not converted H₂O₂, the remaining gas mixture containing He and O₂ was sent to a Thermal Conductivity Detector (TCD) for the continuous analysis of O₂. From the concentration of O₂, the H₂O₂ decomposition rate and then the percentage conversion was calculated (Micoli et al., 2013).

Table 1: Contact times for catalytic tests with a feed flow rate of 223 mL min⁻¹(τ_1) and 280 mL min⁻¹(τ_2)

Sample	τ_1 , s	τ_2 , s
Honeycomb 30 mm length	0.50	0.38
Honeycomb 60 mm length	1.00	0.76
Cylinder 30 mm length	0.23	0.18
Cylinder 60 mm length	0.46	0.36

3. Results and discussion

3.1 Synthesis and characterization of the catalysts

In Table 2 were reported results of catalysts preparation. As expected the MnOx content increases from 3 to 5 precipitation steps. Nevertheless, the lower geometric area of the cylindrical monoliths than honeycombs suggests the formation of multilayer of the active phase even though the content is approximately the same for P3 and P5 samples.

Table 2: Characteristics of monolithic catalysts

Sample	Length, mm	Precipitation steps	MnOx content, wt %
CYL-30-P3	30	3	0.88
CYL-60-P3	60	3	0.94
CYL-30-P5	30	5	1.23
CYL-60-P5	60	5	1.79
HCB-30-P3	30	3	0.95
HCB-60-P3	60	3	1.01
HCB-30-P5	30	5	1.55
HCB-60-P5	60	5	1.66

According to literature data thermal treatment of Mn hydroxide at 500 °C leads to the formation of Mn(III) oxides (Mn₂O₃) (Fritsch et al., 1996). However, in the present case Mn oxides are obtained by treating precipitated Mn(OH)₂ at 500°C in air flow: In these conditions the oxidizing action of O₂ can be counteracted by the reducing action of acetate ions that could be adsorbed on the precipitate. This effect together with the slow kinetics of Mn oxides inter-conversion (Xinli Hao et al., 2011), can lead to the formation of a less oxidized MnOx phase, that is Mn₃O₄.

TPR measurements allowed to calculate Mn oxidation state (Mn_{o.s.}) from the amount of H₂ consumed, considering that the average Mn oxidation state after reduction under these conditions is Mn(II) (Xinli Hao et al., 2011) according to the following equation:

$$Mn_{o.s.} = \frac{2 \text{ mol}_{H_2 \text{ consumed}}}{\text{mol}_{Mn}} + 2 \quad (2)$$

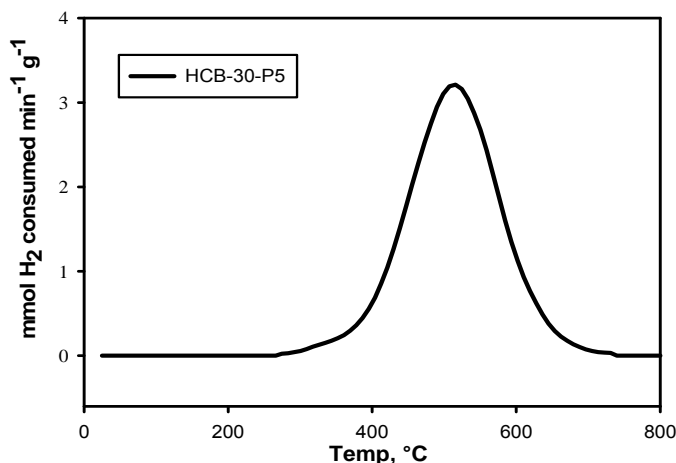


Figure 2: TPR profile of HCB-30-P5 sample

For all samples the average Mn oxidation state was approximately 2.66 that corresponds to Mn_3O_4 phase. TPR measurement showed approximately the same profile for all samples. For instance in Figure 2 is shown the TPR profile of HCB-30-P5 sample. It presents a signal with a maximum at about 515 °C and a total amount of H_2 consumed of about $67 \mu\text{mol g}^{-1}$. The pure monolithic supports gave no TPR signals under these conditions.

3.2 Catalytic activity

Catalytic tests have been carried out operating at two flow rate corresponding to the contact times reported in Table 1. H_2O_2 conversion values were shown in Figures 2 and 3 for cylindrical and honeycomb monoliths respectively.

Results on cylindrical catalysts indicated that at the lower flow rate (223 mL min^{-1}) the decomposition of H_2O_2 was complete for 60 mm length samples for all MnOx contents, while on 30 mm length catalysts conversions of about 93 % and 98 % were obtained for CYL-30-P3 and CYL-30-P5 samples respectively. Increasing the feed flow rate (280 mL min^{-1}) conversions decreased drastically for all samples, giving values between 23 and 30 %. It can be noted that by increasing of the precipitation steps, from 3 to 5, and the length of monoliths, from 30 to 60 mm, H_2O_2 conversion increased. This was due both to the higher amount of active phase in P5 samples than P3 and to the higher contact time for 60 mm samples than 30 mm.

Results of the H_2O_2 decomposition tests on honeycomb monoliths were shown in Figure 3. At the lowest flow rate 60 mm length samples gave complete conversion, even at low MnOx content. Honeycombs of 30 mm length gave conversions lower than previous monoliths but still high: 98 % for HCB-30-P5 and 89 % for HCB-30-P3 sample.

As expected, the increasing of flow rate led to the reduction of the H_2O_2 conversion for all the samples that however were still noticeable values higher than those obtained for cylindrical monoliths. Sample HCB-60-P5 gave a conversion of 74 % at $\tau_2 = 0.76 \text{ s}$. Results on monoliths HCB-30-P3 and HCB-60-P3 showed that the conversion increased from 28 % to 36 % thanks to the higher contact time of 60 mm length sample and probably also for the little bit higher content of the active phase.

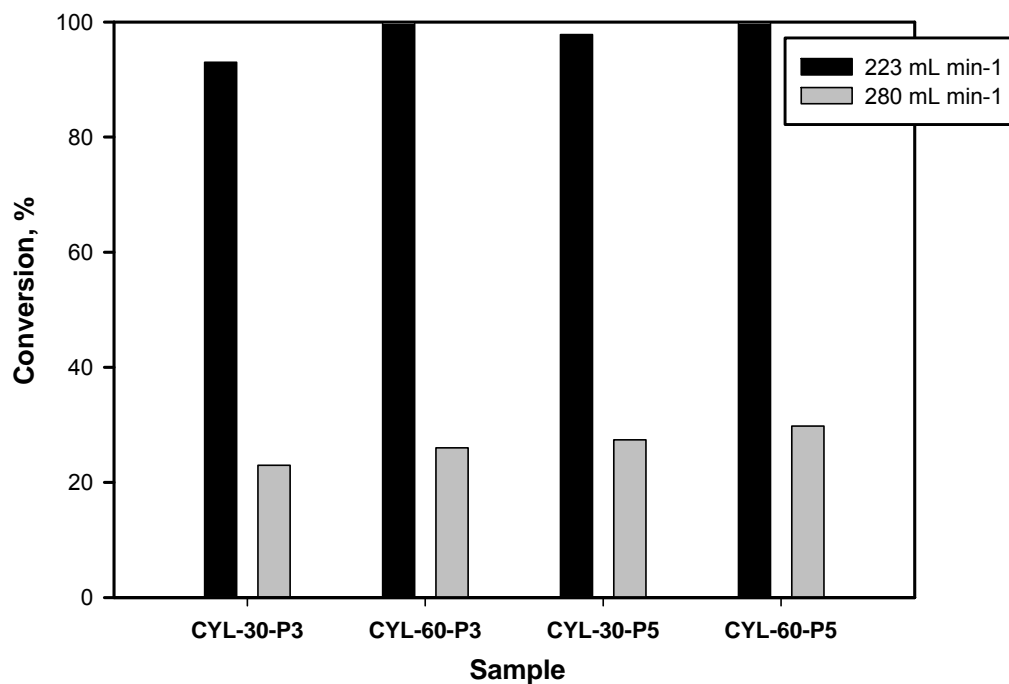


Figure 3: Results of H₂O₂ decomposition tests on cylindrical monoliths at two flow rate (223 and 280 mL min⁻¹)

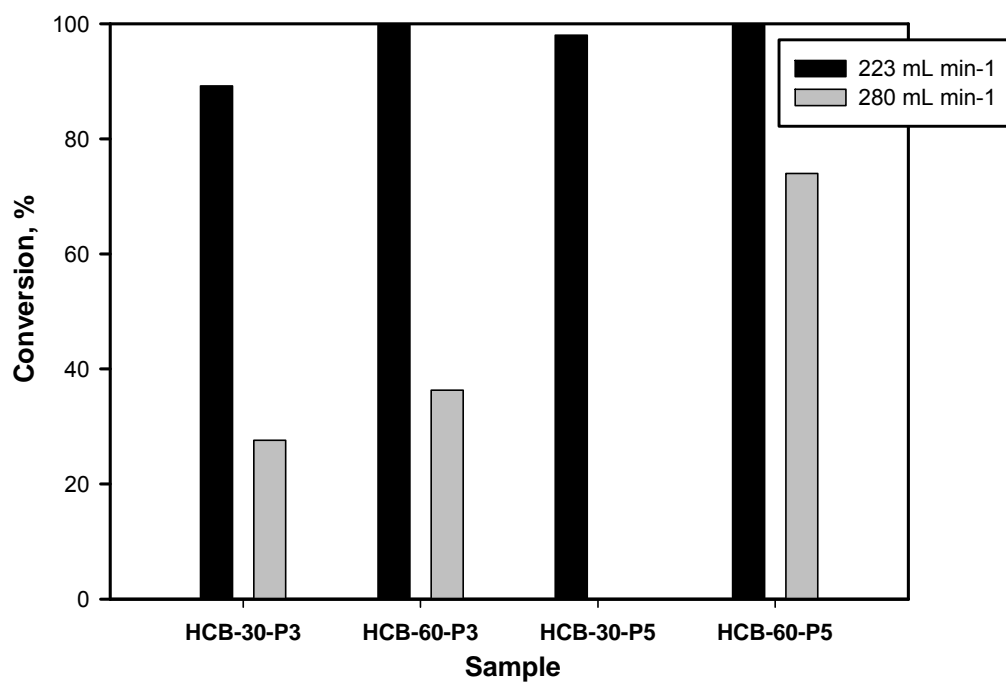


Figure 4: Results of H₂O₂ decomposition tests on honeycombs monoliths at two flow rate (223 and 280 mL min⁻¹)

If we compare honeycomb 30 mm length and cylinder 60 mm length at similar contact times (0.36 and 0.38 s respectively), it can be noted that the honeycomb shape of the support allowed to reach higher value of H₂O₂ conversion with lower content of the active phase and shorter length.

4. Conclusion

In this work the catalytic decomposition of H_2O_2 under vapour phase conditions at 200 °C have been investigated on cylindrical and honeycomb monoliths. The catalysts were prepared employing a new precipitation procedure leading to obtain high contents of MnO_x active phase uniformly dispersed on the substrate. Catalysts are based on manganese oxides (MnO_x) dispersed on monolithic zirconia substrates with cylindrical and honeycomb shape. The results indicate that the conversion was strongly depending on the space velocity and on MnO_x content. The shape of monolithic substrate also influences the catalytic activity and honeycomb shape allows to reach higher value of H_2O_2 conversion with lower content of the active phase and shorter length in comparison to the cylindrical one.

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