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Low temperature complete combustion of dilute propane over Mn-doped ZrO_2 (cubic) catalysts

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Abstract. Combustion of dilute propane (0·9 mol%) over Mn-doped ZrO_2 catalysts prepared using different precipitating agents (viz. TMAOH, TEAOH, TPAOH, TBAOH and NH_4OH), having different Mn/Zr ratios (0·05–0·67) and calcined at different temperatures (500–800°C), has been thoroughly investigated at different temperatures (300–500°C) and space velocities (25,000–100,000 $cm^3 g^{-1} h^{-1}$) for controlling propane emissions from LPG-fuelled vehicles. Mn-doped ZrO_2 catalyst shows high propane combustion activity, particularly when its ZrO_2 is in the cubic form, when its Mn/Zr ratio is close to 0·2 and when it is prepared using TMAOH as a precipitating agent and calcined at 500–600°C. Pulse reaction of propane in the absence of free-O_2 over Mn-doped ZrO_2 (cubic) and Mn-impregnated ZrO_2 (monoclinic) catalysts has also been investigated for studying the relative reactivity and mobility of the lattice oxygen of the two catalysts. Both reactivity and mobility of the lattice oxygen of Mn-doped ZrO_2 are found to be much higher than that of Mn-impregnated ZrO_2. Propane combustion over Mn-doped ZrO_2 catalyst involves a redox mechanism.

Keywords. Combustion of dilute propane; Mn-doped ZrO_2 (cubic) catalyst; pulse reaction of propane.

1. Introduction

Owing to its cleaner combustion, liquefied petroleum gas (LPG), a mixture of propane and butanes, is used as a petrol substitute for automobiles in metropolitan cities. The reactivity of propane is less than that of the butanes, and hence the concentration of propane in the unburnt hydrocarbons in the auto-exhaust gases is much higher. For controlling the hydrocarbon emission from LPG-fuelled automobiles, an efficient catalyst for the complete combustion of propane at low concentration ($<1\%$) is essential.

A number of studies have been reported earlier on the catalytic combustion of propane over different noble metals and transition metal oxide catalysts, such as Pt or Pd/glass fibre,[1] Pt/TiO_2,[2] $Pd/SiO_2–Al_2O_3$,[3] Pt/Al_2O_3,[4] Cu, Pd or Pt modified ZSM-5,[5,6] single or mixed transition metal oxides[7–10] and transition metal oxides supported on silica fibre.[11]

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However, studies on the complete combustion of dilute propane are scarce. Recently, Taylor and O'Leary[12] reported oxidative destruction of C_1–C_4 hydrocarbons over uranium oxide-based catalysts. They observed that the oxidation activity of U_3O_8 is increased by its modification by Cr, which causes increase in the defect structure of the oxide.

Noble metal-based catalysts have, in general, high hydrocarbon combustion activity but they are expensive and more prone to deactivation by poisoning.[13,14] Whereas transition metal oxide-based catalysts are generally less active but more resistant towards catalyst poisoning and their cost is also much lower. In earlier communications, it was reported that Mn-doped ZrO_2 in its cubic form shows high activity for the combustion of butane[15] and dilute methane (1% in air),[16] as compared to that of noble metal catalysts. This work was undertaken for studying in details the complete combustion of dilute propane (0.9% propane in air) over Mn-doped ZrO_2 (cubic) catalysts. Influence of various catalyst parameters (catalyst preparation and composition) and process parameters (temperature and space velocity) on propane combustion have been investigated. Involvement of lattice oxygen from the catalyst in the combustion has also been studied.

2. Experimental

Mn-doped ZrO_2 catalyst was prepared by mixing aqueous solutions of zirconyl nitrate and manganese acetate (Mn/Zr mole ratio varied from 0·05 to 0·67), coprecipitating metal hydroxides from the solution using tetramethyl ammonium hydroxide (TMAOH) (25%) under vigorous stirring at 30°C and a pH of 8, washing (with deionised water) and drying the resulting precipitate (at 110°C for 2 h) and finally calcining it in air at 500°C for 8 h. Other Mn-doped ZrO_2 catalysts having Mn/Zr ratio 0·25 were prepared by coprecipitating the mixed metal hydroxides from mixed aqueous solution of the respective metal nitrates, using different precipitating agents, e.g. tetramethyl ammonium hydroxide (TMAOH), (25%), tetraethyl ammonium hydroxide (TEAOH) (25%), tetrapropyl ammonium hydroxide (TPAOH) (25%), tetrabutyl ammonium hydroxide (TBAOH) (25%) and ammonium hydroxide (30%), by following the above procedure. Mn-doped ZrO_2 having the Mn/Zr ratio as 0·11 was calcined at different temperature (500–800°C) for 8 h. Mn-impregnated ZrO_2 (Mn/Zr = 0·25) was prepared by impregnating ZrO_2 with Mn-acetate by incipient wetness method and calcining at 500°C for 8 h. ZrO_2 was prepared by precipitating $Zr(OH)_4$ from an aqueous solution of zirconyl nitrate by ammonium hydroxide by a procedure similar to that described above.

The catalysts were characterized for their surface area by the single point BET method (using a Monosorb Surface Area Analyzer, Quantachrome Corp., USA) and for their crystalline phases by XRD (using a Holland–Phillips, PW/1730 X-ray generator with CuKα radiation).

Propane combustion activities of all the catalysts were measured at atmospheric pressure in a continuous fixed bed quartz-microreactor. (i.d. 10 mm) containing 0·1 g catalyst (22–30 mesh size particles), mixed uniformly with 0·4 g inert α-Al_2O_3 particles (22–30 mesh size), at different process conditions (temperature: 300–500°C and space velocity: 25000–100,000 $cm^3\ g^{-1}\ h^{-1}$, measured at NTP) using 0·9 mol% propane in air as a feed. The reaction temperature was measured by a chromel–alumel thermocouple located in the catalyst bed. The products (after condensing the water from the product stream at 0°C) were analysed by an online GC using the porapak-Q and spherocarb columns. No partial combustion product (e.g. carbon monoxide) was detected in the propane combustion over any of the catalysts.

The pulse reaction of propane (at 500°C) over the catalyst in the absence of free-O_2 as a function of pulse number was carried out in a quartz pulse micro-reactor connected to the GC, using He (30 $cm^3 min^{-1}$) as a carrier gas, following the procedure described elsewhere.[17,18] The products of the pulse reaction were analysed using a Spherocarb column and thermal conductivity detector.

3. Results and discussion

3.1 *Characterization of Mn-doped ZrO_2 catalysts*

Mn-doped ZrO_2 catalysts (with different Mn/Zr ratios) prepared using different precipitating agents and calcined at different temperatures have been characterized for their surface area and crystalline nature. The catalyst characterization data are given in table 1. From a comparison of the data, the following important observations for the effect of the precipitating agent used, and the Mn/Zr ratio and calcination temperature of the catalyst on its surface and bulk properties can be made.

– The use of TEAOH or TPAOH as the precipitating agent leads to a catalyst that is amorphous in nature, whereas when TMAOH, TBAOH and NH_4OH are used as precipitating agents, the ZrO_2 of the resulting catalyst is at least partly in cubic form. The use of TBAOH and NH_4OH results in the catalyst (with Mn/Zr = 0·25) in both cubic (major) and monoclinic (minor) forms. However, a pure cubic form of the catalyst (with Mn/Zr = 0·11–0·67) is obtained when TMAOH is used as the precipitating agent.

Table 1. Surface area and crystalline phases of Mn-doped ZrO_2 catalysts (Mn/Zr = 0·05–0·67) prepared by using different precipitating agents and calcined at different temperatures.

Mn/Zr ratio in Mn-doped ZrO_2	Precipitating agent used in the catalyst preparation	Calcination temperature (°C)	Surface area (m^2g^{-1})	Crystalline phases
0·05	TMAOH	500	74	Cubic ZrO_2 (major) and monoclinic ZrO_2 (minor)
0·11	TMAOH	500	86	Cubic ZrO_2
0·25	TMAOH	500	105	Cubic ZrO_2
0·43	TMAOH	500	91	Cubic ZrO_2
0·67	TMAOH	500	73	Cubic ZrO_2
0·11	TMAOH	600	72·4	Cubic ZrO_2
0·11	TMAOH	700	25	Cubic ZrO_2
0·11	TMAOH	800	11	Cubic ZrO_2, monoclinic ZrO_2 and MnO_2
0·25	TEAOH	500	134	Amorphous
0·25	TPAOH	500	65	Amorphous
0·25	TBAOH	500	45	Cubic ZrO_2 (major) and monoclinic ZrO_2 (minor)
0·25	NH_4OH	500	122	Cubic ZrO_2 (major) and monoclinic ZrO_2 (minor)

– The cubic form of the catalyst (with Mn/Zr = 0·11) remains intact up to the catalyst calcination temperature of 700°C; at 800°C a small part of the cubic ZrO_2 is transformed into monoclinic ZrO_2.

– The surface area of the catalyst is also strongly influenced by the Mn/Zr ratio, precipitating agent and calcination temperature. It decreases with increasing calcination temperature and passes through a maximum on increasing the Mn/Zr ratio. The order of the surface area of catalysts (with Mn/Zr ratio = 0·25, and calcined at 500°C) prepared using different precipitating agents is as follows: TEAOH > NH_4OH > TMAOH > TPAOH > TBAOH.

The oxidation state of Mn in the Mn-doped ZrO_2 catalysts is +4.[19] Mn-doped ZrO_2 (Mn/Zr = 0·05 to 0·67) catalysts are well crystallised materials. Their XRD spectra have been given elsewhere.[19]

3.2 *Catalytic combustion of propane*

3.2a *Effect of precipitating agent:* Results showing the influence of the precipitating agent used in the preparation of Mn-doped ZrO_2 (with Mn/Zr = 0·25, and calcined at 500°C) on propane combustion are presented in figures 1 and 2.

Results in figure 1 show a strong influence of the precipitating agent on the propane conversion activity of the Mn-doped catalyst at different temperatures. The temperature required for half the propane combustion reaction (i.e. 50% conversion of propane) is

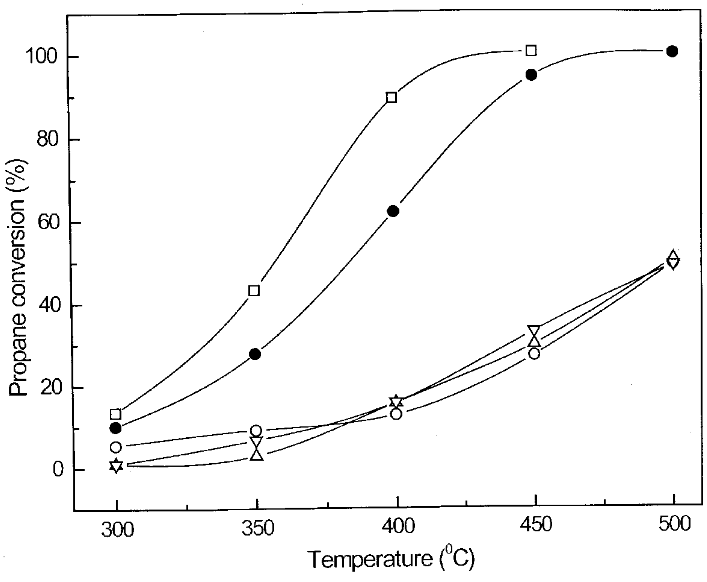

Figure 1. Temperature dependence of propane conversion in the combustion of propane (GHSV = 51,000 $cm^3\ g^{-1}\ h^{-1}$) over Mn-doped ZrO_2 (Mn/Zr = 0·25) catalyst (calcined at 500°C) prepared using different precipitating agents [TMAOH (□), TEAOH (○), TPAOH (△), TBAOH (▽) and NH_4OH (●)].

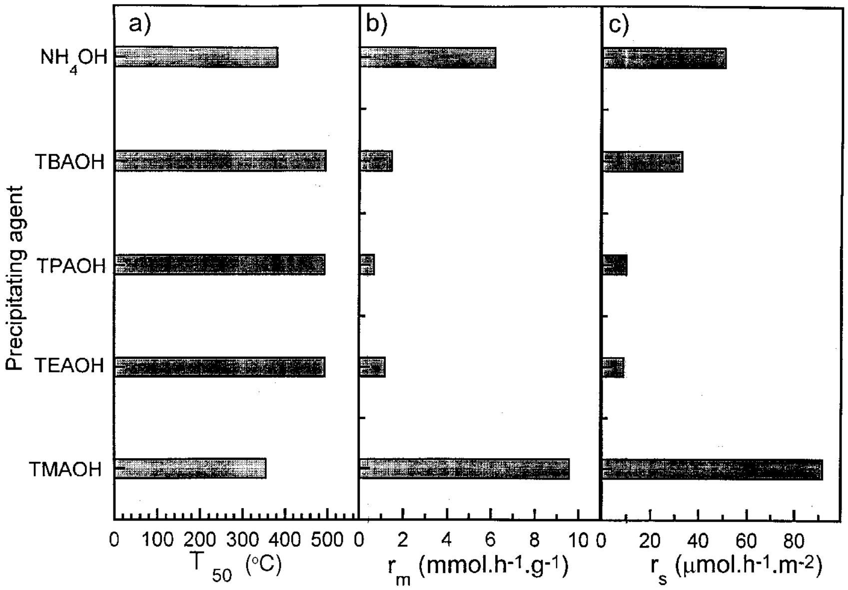

Figure 2. Effect of precipitating agent used in the preparation of Mn-doped ZrO_2 (Mn/Zr = 0·25) catalyst (calcined at 500°C) on (**a**) the temperature required for 50% (T_{50}) conversion of propane, (**b**) propane conversion rate (at 350°C) based on the mass of catalyst (r_m), and (**c**) propane conversion rate (at 350°C) based on the surface area of catalyst (r_s) in the combustion of propane (space velocity: 51,000 $cm^3\ g^{-1}\ h^{-1}$).

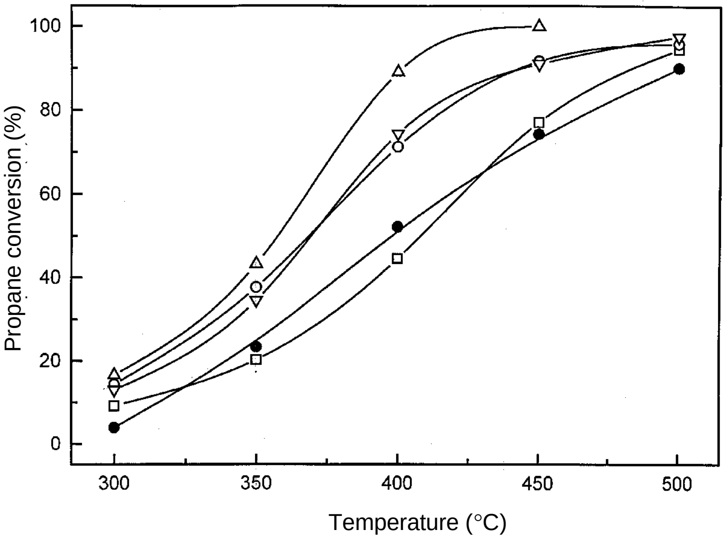

Figure 3. Temperature-dependence of propane conversion in the combustion of propane (GHSV = 51,000 $cm^3\ g^{-1}\ h^{-1}$) over Mn-doped ZrO_2 catalyst (prepared using TMAOH and calcined at 500°C) with different Mn/Zr ratios [Mn/Zr = 0·05 (□), 0·11 (○), 0·25 (△), 0·43 (▽) and 0·67 (●)].

lowest for the catalyst prepared using TMAOH (figure 2a). The rate of propane conversion in the combustion reaction when expressed in terms of the amount of propane converted per hour per unit mass or per unit surface area of the catalyst is also highest for the catalyst prepared using TMAOH. The order of preference for the different precipitating agents is as follows.

Order based on the rate per unit mass: TMAOH > NH_4OH > TBAOH > TEAOH > TPAOH.

Order based on the rate per unit surface area: TMAOH > NH_4OH > TBAOH > TPAOH ≥ TEAOH.

The results clearly show that the most preferred precipitating agent for the preparation of the catalyst, which shows highest propane combustion activity, is TMAOH and the next preferred precipitating agent is NH_4OH.

It is interesting to note from the results (figures 2b, c and table 1) that the catalyst, which shows highest propane combustion activity, is in the pure cubic form, whereas the

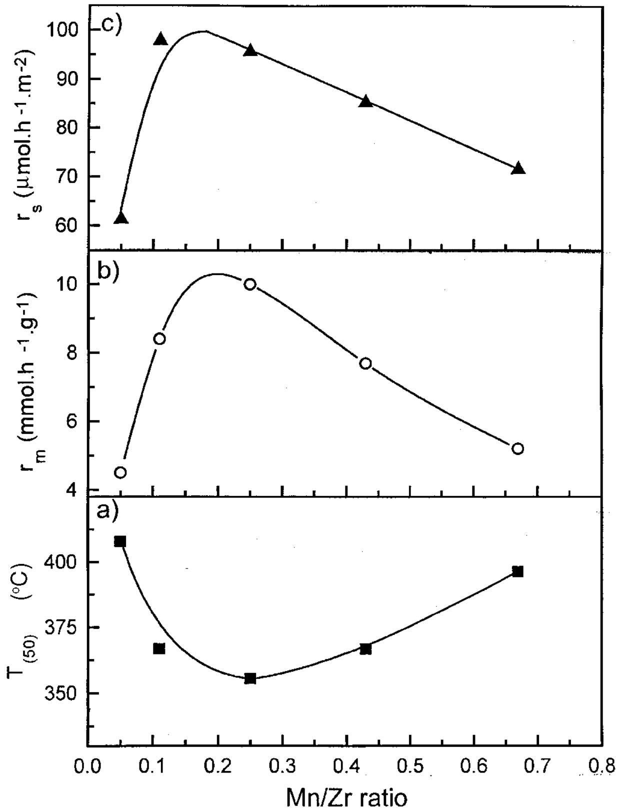

Figure 4. Effect of the Mn/Zr ratio of Mn-doped ZrO_2 catalyst (prepared using TMAOH) and calcined at 500°C) on (**a**) the temperature required for 50% conversion (T_{50}) of propane, (**b**) propane conversion rate (at 350°C) based on the mass of catalyst (r_m), and (**c**) propane conversion rate (at 350°C) based on the surface area of catalyst (r_s) in the combustion of propane.

catalysts, which show very low propane combustion activity, are in amorphous form and those that show intermediate performance are in both cubic and monoclinic forms.

3.2b *Effect of Mn/Zr ratio:* Results showing the temperature-dependence of propane conversion in the combustion reaction over the Mn-doped ZrO_2 catalyst (prepared using TMAOH and calcined at 500°C) with different Mn/Zr ratios are presented in figure 3. Dependence of the temperature required for half the reaction and also of the propane combustion activity up on the Mn/Zr ratio of the catalyst (prepared using TMAOH and calcined at 500°C) is shown in figure 4.

The results show strong influence of the Mn/Zr ratio on the catalytic performance of Mn-doped ZrO_2 catalyst in propane combustion. When the Mn/Zr is increased, the activity of the catalyst, expressed in terms of the temperature required for half the propane combustion reaction or the propane conversion rate, passes through a maximum at an Mn/Zr ratio of about 0·2 (figure 4).

3.2c *Effect of catalyst calcination temperature:* Results in figures 5 and 6 show strong effect of catalyst calcination temperature, particularly above calcination temperatures of 600°C, on propane combustion activity of Mn-doped catalyst (Mn/Zr = 0·11). Increase in the calcination temperature from 500 to 600°C has no significant effect on the catalytic activity. However, further increase in the temperature above 600°C results in sharp decrease in the catalytic activity. The observed very small activity (at 350°C) of the catalyst calcined at 800°C (figure 6b) is not only because of the sintering

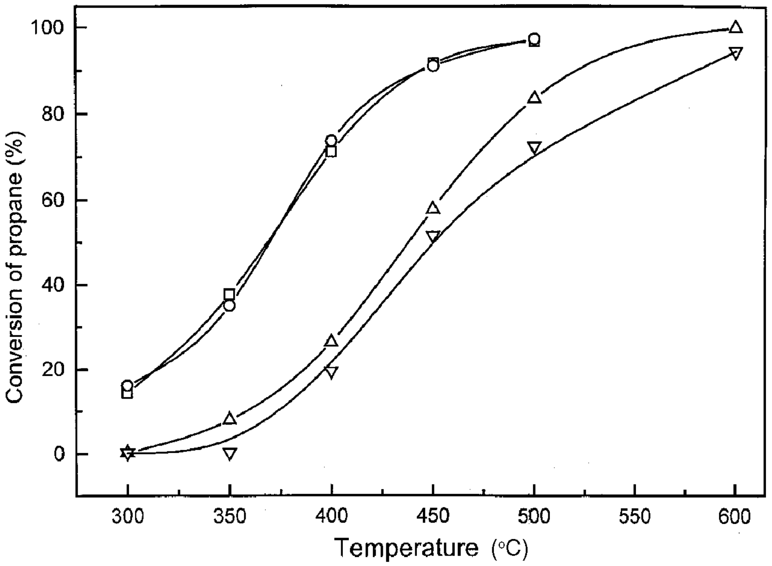

Figure 5. Temperature dependence of propane conversion in the combustion of propane (GHSV = 51,000 $cm^3\ g^{-1}\ h^{-1}$) over Mn-doped ZrO_2 (Mn/Zr = 0·11) catalyst (prepared using TMAOH) calcined at different temperatures [500°C (□), 600°C (○), 700°C (△) and 800°C (▽)].

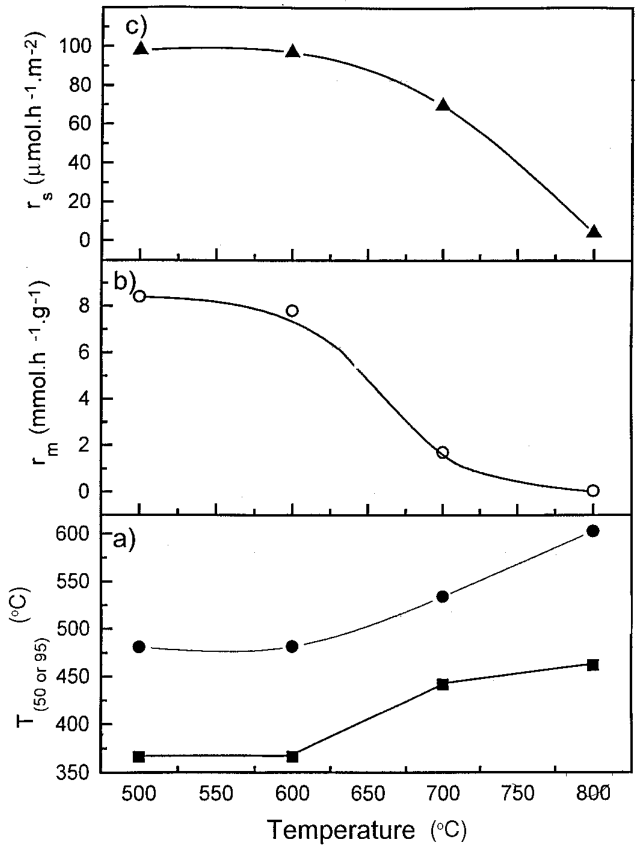

Figure 6. Effect of calcination temperature of Mn-doped ZrO_2 (Mn/Zr = 0·11) catalyst (prepared using TMAOH) on (**a**) the temperature required for 50% (■) and 95% (●) conversion of propane (T_{50} and T_{95} respectively), (**b**) propane conversion rate (at 350°C) based on the mass of catalyst (r_m), and (**c**) propane conversion rate (at 350°C) based on the surface area of catalyst (r_s) in the combustion of propane (space velocity: 51,000 $cm^3\ g^{-1}\ h^{-1}$).

of the catalyst at the higher temperature but also because of the structural transformation of the catalyst producing monoclinic ZrO_2 and MnO_2 phases (figure 6c and table 1).

3.2d *Effect of space velocity:* Results showing the effect of space velocity on propane conversion at different temperatures in propane combustion over Mn-doped catalyst (Mn/Zr = 0·25) prepared using TMAOH and calcined at 500°C are presented in figure 7. The space velocity effect shows strong dependence upon the reaction temperature, the effect being more pronounced at lower temperatures.

3.3 *Pulse reactions of propane*

In order to study the possibility of involvement of the lattice oxygen of the catalyst in propane combustion, a pulse reaction of propane in the absence of free-O_2 over Mn-doped ZrO_2 (Mn/Zr = 0·25) was carried out. A number of pulses of pure propane were passed one after another at fixed intervals of time (8 min) over the catalyst at 500°C and conversion of propane was measured as a function of pulse number. A similar pulse reaction of propane was also carried out in case of Mn-impregnated ZrO_2 catalyst (Mn/Zr = 0·25) for the purpose of comparing the reactivity of the lattice oxygen of both the catalysts. The results of the pulse reaction over the two catalysts are presented in figure 8.

From the results, the following important observations can be made.

- Among the two catalysts, the initial propane conversion activity (i.e. the propane conversion in the first pulse) of Mn-doped ZrO_2 is much higher than that observed for Mn-impregnated ZrO_2.

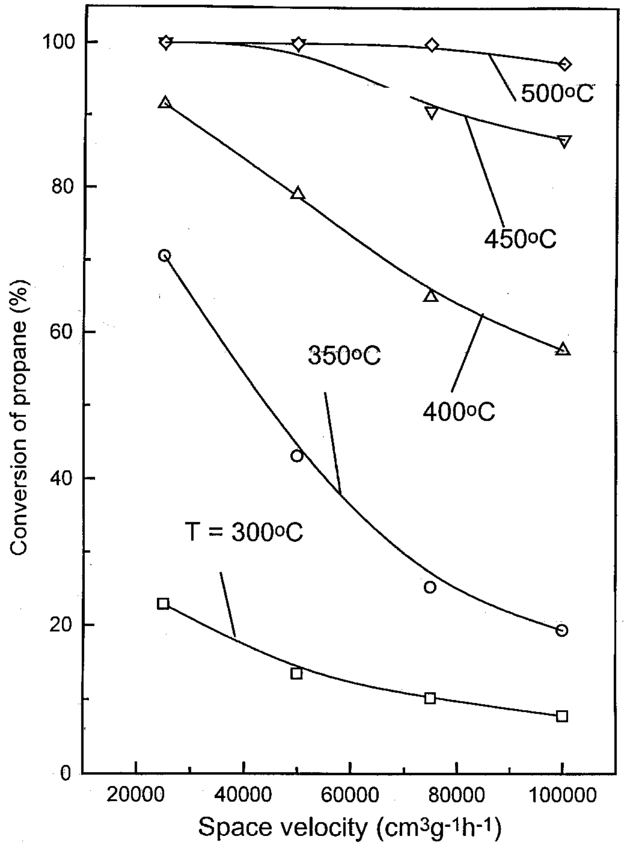

Figure 7. Effect of space velocity on propane conversion in the propane combustion over Mn-doped ZrO_2 (Mn/Zr = 0·25) catalyst (prepared using TMAOH and calcined at 500°C) at different temperatures.

- For both the catalysts, propane conversion is sharply decreased on increasing the pulse number because of the consumption of lattice oxygen at or close to the catalyst surface.
- After the 12th pulse, when the Mn-doped ZrO_2 catalyst is aged at 500°C for 1 h in a flow of pure He and the pulse experiments then continued, there is a sharp increase in the propane conversion for the 13th pulse, after which the propane conversion is sharply decreased with increasing the pulse number. In case of the Mn-impregnated ZrO_2 catalyst, no sharp increase however, but a continuous decrease in the propane conversion is observed, even for the 13th pulse.
- After the 16th pulse, when the Mn-doped ZrO_2 catalyst is reoxidized by air at 500°C for 1 h, and then the pulse experiments continued, the catalyst is found to regain its initial activity for the 17th pulse. However, for the subsequent pulses, propane conversion over the catalyst is sharply decreased with increasing the pulse number. Similar behaviour is also shown by the Mn-impregnated catalyst.

The observed sharp decrease in propane conversion with increasing pulse number and a complete regeneration of the catalyst, regaining its initial activity, clearly indicate that propane combustion over both the catalysts involves a redox mechanism (Mars and van Krevelen cycle), involving the following reactions:

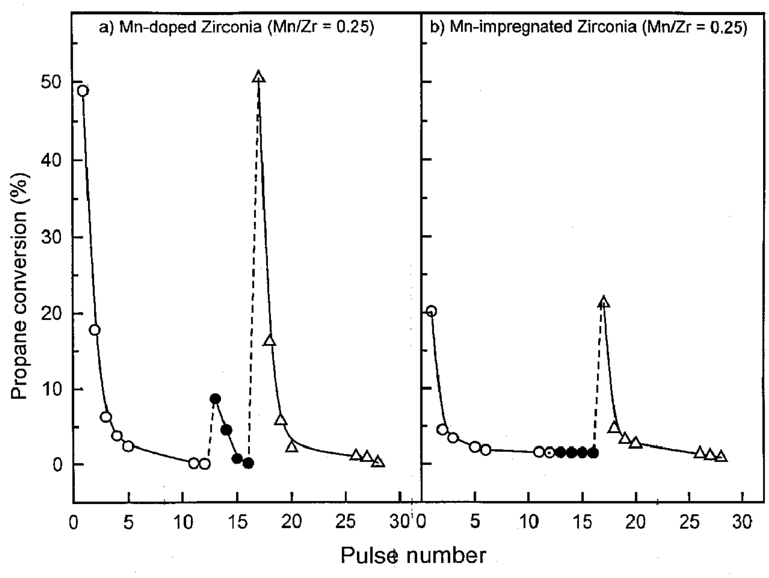

Figure 8. Variation of propane conversion (at 500°C) with pulse number in the reaction of pure propane (in the absence of free-O_2) with (**a**) Mn-doped ZrO_2 (Mn/Zr = 0·25) catalyst (prepared using TMAOH and calcined at 500°C) and (**b**) Mn-impregnated ZrO_2 (Mn/Zr = 0·25) catalyst (calcined at 500°C) in a pulse micro-reactor [for the fresh catalyst (○), after aging the deactivated catalyst under He at 500°C for 1·0 h (●) and after reoxidizing the deactivated catalyst by air at 500°C for 1·0 h and flushing with pure He for 0·5 h (△)].

$$C_3H_8 + 10(O_L) \rightarrow 3CO_2 + 4H_2O + 10\,(\square), \tag{1}$$

$$10\,(\square) + 5O_2 \rightarrow 10\,(O_L), \tag{2}$$

where $\square$ is the anion vacancy and O_L is the lattice oxygen.

The observed somewhat higher propane conversion activity of both the reoxidized catalysts may be due to a small amount of oxygen adsorbed on the catalysts during the reoxidation.

The two catalysts however differ very markedly in their initial propane conversion activity (i.e. the reactivity of their lattice oxygen) and also in their reactivation by the thermal aging treatment. The deactivated (due to the consumption of the lattice oxygen at or close to the surface) Mn-doped ZrO_2 catalyst is partially reactivated by the thermal aging treatment but such reactivation is not observed in case of the Mn-impregnated ZrO_2 catalyst. The observed reactivation of the Mn-doped ZrO_2 catalyst is attributed to the transfer of sub-surface lattice oxygen to the catalyst surface during the thermal treatment. This clearly shows that the mobility of lattice oxygen in case of the Mn-doped ZrO_2 catalyst is much larger than that in case of the Mn-impregnated ZrO_2. In our earlier studies also, it is shown that the methane combustion activity of Mn-doped ZrO_2 is much higher than that of Mn-impregnated ZrO_2.[16] This work clearly shows that the mobility of lattice oxygen in ZrO_2 is increased because of Mn-doping.

4. Conclusions

Mn-doped ZrO_2 (cubic) is a promising catalyst for the combustion of dilute propane and hence for controlling propane emissions from LPG-fuelled vehicles. Propane combustion activity of this catalyst is strongly influenced by the precipitating agent used in the catalyst preparation, Mn/Zr ratio of the catalyst and also by the calcination temperature of the catalyst and consequently by the cubic and/or monoclinic ZrO_2 phase present in the catalyst. The catalyst prepared using TMAOH as a precipitating agent, with Mn/Zr mole ratio of about 0·2 and calcined at 500–600°C, is found to show the best performance in propane combustion. Propane combustion over the catalyst involves redox (Mars and van Krevelen) mechanism. The doping of Mn in ZrO_2 greatly enhances the mobility of lattice oxygen in Mn-doped ZrO_2 catalyst.

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