



Letter

Mn-stabilized zirconia catalysts for complete oxidation of n-butane

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Abstract

The activity of Mn-stabilized zirconia with a Mn content ranging from 5 to 50 mol-% in the complete oxidation of n-butane is investigated here. The structure sensitivity as a major factor governing the activity is proved. Multivalent Mn when present in the zirconia lattice in concentrations from 5 to 30 mol-% is found to accelerate the reaction rate to a greater extent than does bulk zirconia or bulk MnO₂ present as extra lattice component. The role of the calcination temperature on the stability of the structure and its repercussions on the catalytic activity are also demonstrated here.

Keywords: Butane oxidation; Calcination temperature; Manganese; Zirconia

1. Introduction

Ever since the introduction of stabilized zirconia systems [1-3] with a fluorite type structure into various areas of research such as gas sensors [4], thermal barrier coatings and high temperature refractories [5], very little attention has been paid to investigating their catalytic applications [6,7]. Also, it appears that hardly any attempt has been made to tailor stabilized zirconias particularly for deep oxidation reactions.

Although various perovskite type (ABO₃) oxides and noble metals are reported as efficient catalysts for the oxidation of hydrocarbons and carbon monoxide, both of them suffer from some demerits; as regards the former its poor life time and as regards the latter its high cost. In consequence, there has been an unending quest for the development of alternative catalytic materials. Recently, we have reported the preparation of Mn-stabilized zirconia systems [8] that would act as good oxidation catalysts.

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We report here our preliminary results on the catalytic activity of Mn-stabilized zirconia in the complete oxidation of n-butane, which is one of the major components of the hydrocarbons in automotive emissions. The role of the Mn content, the effect of calcination temperature and the importance of a stabilized cubic structure on the catalytic activity are described in this Letter.

2. Experimental

Pure zirconia and zirconia with varying amounts of Mn from 5 to 50 mol-% were prepared following the procedure reported in our earlier communication [8]. Briefly, stoichiometric amounts of zirconyl nitrate and manganese acetate were mixed well in aqueous form and an aqueous solution of tetramethylammonium hydroxide (25%) was added to this with constant stirring till the pH of the solution reached 8. The resultant brown coloured precipitate was filtered and washed well with deionised water and subsequently dried under vacuum at 373 K for 8 h followed by calcination at 773 K for 12 h. Chemical analysis of the sample was carried out as described elsewhere [9]. X-ray diffraction studies indicated the formation of a solid solution with cubic symmetry [8].

Catalytic test reactions for complete oxidation of n-butane were carried out using a micro-reactor operated in a steady state plug-flow mode. The powdered catalyst was pelleted, crushed and then sieved to 16 to 20 mesh before use. The reaction mixtures [n-butane (4%), N₂ (88%) and O₂ (8%)] were fed to the reactor at a gas hourly space velocity (GHSV) of 25 000 h⁻¹. The products (CO₂ and H₂O) were analyzed by an on-line gas chromatograph using a Poropak Q column. The reaction rate (expressed as $\mu\text{mol g}^{-1} \text{s}^{-1}$) was evaluated from the slope of the linear correlation between the conversion and W/F , where W is the weight of the catalyst and F is the flow rate of the reactants under steady-state conversion maintained at less than 20%.

3. Results and discussion

The results of the catalytic activity of Mn-stabilized zirconia in the complete oxidation of butane as a function of Mn content is presented in Table 1. The catalytic activity is compared with reference to the rate of the reaction and also expressed in terms of the temperature required for 50% conversion (T_{50}) and 100% conversion (T_{100}). Fig. 1 presents the conversion of n-butane with temperature in the presence of pure zirconia (curve 'f') and stabilized zirconia containing varying amounts of Mn (curves 'a' to 'e' for 20, 30, 10, 50 and 5 mol-% Mn, respectively). The rate increases almost linearly with Mn content and reaches a maximum at 20 mol-% Mn in zirconia and then starts declining slowly, as shown in Fig. 2. An increase in rate with Mn content up to 20 mol-% and then a decline shows that the

Table 1
Catalytic properties of Mn-stabilized zirconia samples

Mn content (mol-%)	Phases (XRD)	Surface area (m ² /g)	T ₅₀ ^a	T ₁₀₀ ^b	Rate ^c
0	monoclinic	62	653	823	0.98
5	cubic + monoclinic	78	566	668	6.35
10	cubic	80	480	565	19.4
20	cubic	105	445	523	26.85
30	cubic	73	460	532	24.60
50	cubic + MnO ₂	70	510	592	13.22

^a Temperature required for 50 wt.-% conversion of butane.

^b Temperature required for 100 wt.-% conversion of butane.

^c Rate of the reaction (expressed as $\mu\text{mol g}^{-1} \text{s}^{-1}$) was evaluated from the slope of the linear correlation between the conversion and W/F , where W is weight of the catalyst and F is the flow rate of the reactant under steady-state conversion maintained at less than 20%.

activity depends mainly on the stable structure of the catalyst resulting from an optimum amount of Mn rather than on the surface area or the amount of active element. An alternative proposition for the higher activity of Mn-stabilized zirconia relatively at lower temperatures includes the possibility of enhanced adsorption sites for one of the reactants involved in the rate limiting process. This would be logical if oxygen vacancies or oxygen vacancy–acceptor pairs at or near the surface were the adsorption sites.

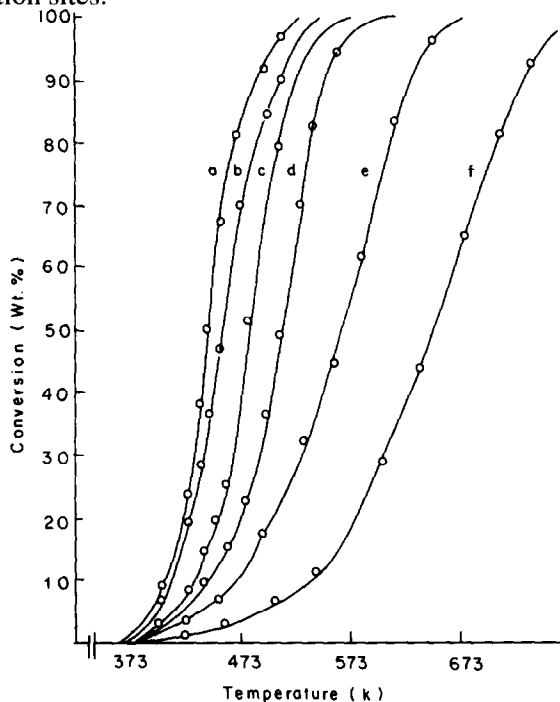


Fig. 1. Conversion of n-butane as a function of temperature over pure zirconia (curve 'f') and Mn–ZrO₂ samples with Mn content of 20, 30, 10, 50 and 5 mol-%, respectively (curves 'a' to 'e'). Feed composition: n-butane (4%), N₂ (88%) and O₂ (8%); GHSV: 36 000 h⁻¹.

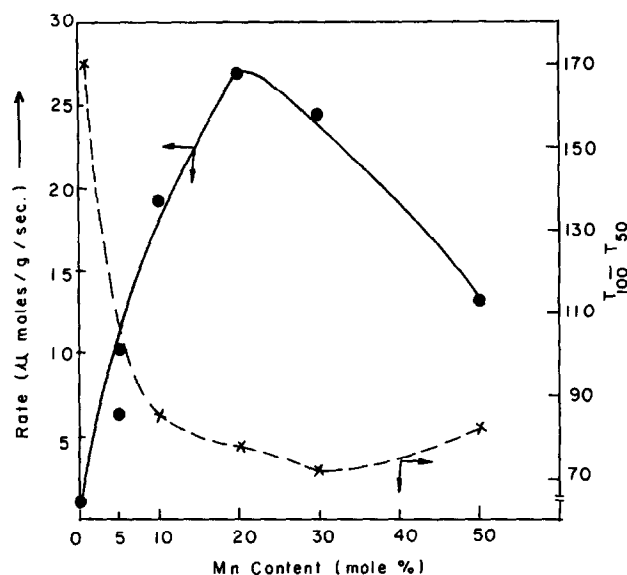


Fig. 2. Variation of reaction rate and $T_{100} - T_{50}$ for oxidation of n-butane as a function of Mn content in Mn-stabilized zirconia.

Fig. 2 also shows the variation of $T_{100} - T_{50}$ as a function of Mn content. We have chosen $T_{100} - T_{50}$ as a relative measure of the activity response to the inlet temperature. It can be seen that the temperature response to the rate of oxidation of n-butane over samples with Mn content ranging from 10 to 30 mol-% is similar to that found in precious metal catalysts with a steep rise in activity with a lower light off temperature [10]. However, the behaviour of the catalyst with lower and higher amount of Mn is similar to that of perovskite type or binary oxides with a lower slope. It is likely that the rate determining step depends on the optimum amount of Mn content required to obtain the solid solution. Since the catalysts are active at lower temperatures it is apparent that the rate equation which is most fitting is

$$r = kP_{C_4}$$

where the reaction rate largely depends on the n-butane partial pressure. Although the participation of the lattice oxygen cannot be ruled out, the reaction is mainly operated by adsorbed oxygen in the present case and the reaction is facile at lower temperatures. The rate dependence on the oxygen partial pressure and the possible mechanism of oxidation involving multivalent Mn in the lattice will be presented in detail later.

Apart from the optimum amount of active element, the calcination temperature also plays an important role in controlling the structure and texture which in turn show significant influence on the catalytic activity. This is illustrated in Fig. 3, where the oxidation activity of a Mn-stabilized zirconia (20 mol-% Mn) sample calcined at different temperatures (curves a, b, c and d correspond to the catalysts calcined at 773, 873, 973 and 1073 K, respectively) are represented. The catalyst calcined at 773 and 873 K where a single cubic phase exists, are quite active. Then,

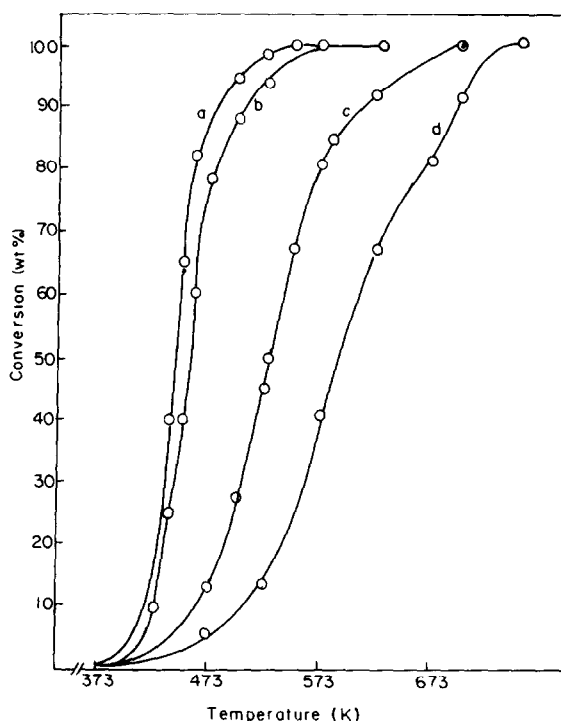


Fig. 3. Effect of calcination temperature on the activity of Mn-stabilized zirconia with 20 mol-% of Mn. Curves 'a' to 'd' correspond to samples calcined at 773, 873, 973 and 1073 K, respectively.

the activity gradually declines as the calcination temperature is increased to 973 K, when the structural transformation of fluorite (cubic) to the monoclinic phase begins with a consequent reduction in the surface area. At 1073 K, the material transforms completely to the monoclinic phase and the activity further deteriorates.

An interesting feature of the above studies is that it is the optimum amount of Mn which could stabilize zirconia into the cubic phase that is important for obtaining a better activity. When monoclinic zirconia was impregnated with the same amount of Mn, the activity was meagre. Also, a sample with a very low amount of Mn with monoclinic zirconia impurities and the one with very high amount of Mn as a separate phase of MnO_2 along with cubic zirconia were not active.

The major point to be discussed here is what makes the Mn-stabilized zirconia with cubic structure so active. The fundamental phenomenon behind the stabilization and the ensuing activity is the oxygen mobility. This type of oxygen mobility arises due to the creation of defect sites. Such a creation of defect sites will have a tremendous impact on the catalytic properties [11,12]. If a foreign ion in a crystalline lattice has a net charge difference from that of the host ion it replace, an ionic defect must be introduced for charge compensation. As a result of the increase in the concentration of ionic defects, the ionic conductivity is increased. To achieve this through the creation of defect sites, introduction of lower valent ions of yttrium, magnesium or calcium is known in the literature. In the present case, the advantage

of using multivalent Mn is two fold. First of all, it generates defect sites enhancing the oxygen mobility and secondly, it easily undergoes a redox cycle due to its ease of reduction when present as a part of the zirconia lattice which is confirmed by our temperature-programmed reduction studies. This is in particular due to the presence of both Mn^{3+} and Mn^{4+} ions in the zirconia lattice [13,14]. It is inferred that adsorption of butane and oxygen occurs simultaneously on the catalyst surface so that, at one site Mn^{3+} gets oxidized to Mn^{4+} and at the other site Mn^{4+} gets reduced to Mn^{3+} . Thus, a reduction–oxidation cycle is facilitated. In a somewhat similar study on the Mn–MgO system both Mn^{3+} and Mn^{4+} dispersed on MgO were found to be more favourable for the complete oxidation of carbon monoxide as compared to the pure oxides [15], but, unlike the supported Mn oxide, in our samples Mn appears to be a part of the ZrO_2 cubic structure.

4. Conclusions

1. The Mn-stabilized zirconia solid solutions with multivalent manganese in the zirconia lattice is a suitable catalyst for the complete oxidation of n-butane.
2. The catalytic activity is sensitive to the structure rather than to the texture or the amount of active element.
3. The increased activity is believed to be due to the oxygen ion mobility, the origin of which could be ascribed to the creation of defect sites in the lattice.
4. The easy redox ability of Mn in the ZrO_2 lattice also plays a synergistic role in achieving better activity in the oxidation reaction.

Further studies to understand the mechanism of oxidation involving multivalent Mn stabilized in the cubic structure of zirconia, the redox characteristics, the ionic conductivity and the long-term activity stability of the system are under progress.

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