3d Transition-metal oxide-stabilized zirconia as novel catalysts for complete oxidation of hydrocarbons

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A new series of zirconia based fluorite type oxides stabilized by Cr, Mn, Fe, Co or Ni are found to be active for complete oxidation of hydrocarbons.

While zirconia has considerable prominence in chemical technology,[1] very little is known about its application in the field of oxidation catalysis.[2] Recently, Trovarelli and coworkers,[3] have reported the use of zirconia doped in ceria as an improved catalyst for the combustion of methane compared to that of individual oxides. Although, noble-metal catalysts are well established in the oxidation of hydrocarbons, considerable efforts are being directed to find non-noble-metal catalysts as economic alternatives. Significant investigations have been carried out in this direction and perovskite and spinel type oxide materials have been shown to be promising catalysts.[4–6] The major disadvantages of these catalysts are their low surface area, poor catalytic lifetime and poor mechanical strength. Here, we report the synthesis and application of novel oxide materials of fluorite structure based on zirconia and stabilised with 3d transition-metal ions. The present investigation establishes that active elements like manganese, cobalt or iron when present in a suitable matrix like zirconia as a solid solution act as reactive sites for redox processes; furthermore the resulting catalysts do not sinter or become deactivated, unlike known metal oxides/mixed-metal oxides.

The stabilized zirconia catalysts were prepared by mixing aqueous solution of $Zr(NO_3)_2$ and nitrates of Cr, Mn, Fe, Co or Ni, in the molar ratio of 80 : 20, to which aqueous tetramethylammonium hydroxide (25%) was added under vigorous stirring up to pH 8. The resultant precipitate was washed with deionised water, dried at 383 K for 24 h and subsequently calcined at 773 K for 8 h. For comparison, a Pt/ZrO_2 sample was prepared by impregnation of ZrO_2 with a H_2PtCl_6 solution to a level of 0.5 mass% Pt. The physicochemical characterization of the samples was carried out by X-ray diffraction, TG–DTA, temperature programmed reduction, SEM and N_2 adsorption (BET) techniques.[7,8] The powder X-ray diffraction patterns of the catalysts indicated the formation of a cubic phase, whereas the TG–DTA studies indicated the role of the 3d transition-metal ions in inhibiting sintering of the samples.[8] TPR profiles showed the ease of reduction of the respective 3d transition-metal atoms and the SEM photographs indicated the presence of uniform particles with sizes ranging from 0.5 to 1.0 μm. The N_2 adsorption–desorption isotherms of the samples indicated that these samples are mesoporous having a surface area in the range 90–120 m^2 g^{-1} (Table 1).

The oxidation of *n*-butane was carried out in a tubular, quartz microreactor of the down-flow fixed-bed type in the temperature range 423–723 K using 200 mg of stabilized zirconia as catalyst with the catalyst first preheated to 673 K for 12 h. The reaction mixtures [butane (4%), N_2 (76%) and O_2 (20%)] were admitted to the reactor at a GHSV of 36 000 h^{-1}. The products were analysed by an on-line gas chromatograph using a 10 m poropak Q column.

Fig. 1 compares the activity of Pt/ZrO_2 [curve (*a*)] with that of various stabilized zirconia samples [curves (*b*)–(*f*)] and of pure zirconia [curve (*g*)] in the complete oxidation of *n*-butane as a function of inlet gas temperature. The Pt-zirconia has the lowest light-off temperature while pure zirconia (monoclinic) and Cr- and Ni-stabilized zirconia show a catalytic response only at high temperatures. However, the performance of Mn-stabilized zirconia [Fig. 1(*b*)] is nearly as good as that of the

Table 1 Catalytic properties of fluorites, perovskites and Pt/ZrO_2 catalysts in the oxidation of *n*-butane

Catalyst	Phase	Surface area/m^2 g^{-1}	$T_{50}{}^a$/K	$T_{100}{}^b$/K	Rate^c
ZrO_2	monoclinic	56	653	823	0.98
$Zr_{0.8}Cr_{0.2}O_2$	fluorite	118	550	648	10.42
$Zr_{0.8}Mn_{0.2}O_2$	fluorite	105	445	523	26.85
$Zr_{0.8}Fe_{0.2}O_2$	fluorite	102	523	603	18.60
$Zr_{0.8}Co_{0.2}O_2$	fluorite	98	498	583	22.35
$Zr_{0.8}Ni_{0.2}O_2$	fluorite	96	581	698	12.69
$LaCoO_3$	perovskite	26	573	763	4.96
$LaMnO_3$	perovskite	28	558	703	5.20
$Pt/ZrO_2{}^d$	monoclinic	48	423	475	30.12

[a] Temperature required for 50% conversion of *n*-butane. [b] Temperature required for 100% converson of *n*-butane. [c] Rate of the reaction (μmol g^{-1} s^{-1}) was evaluated from the slope of the linear correlation between the conversion and *m*/*f*, where *m* is mass of the catalyst and *f* is the flow rate of the reactant under steady-state conversion maintained at < 20%. [d] Pt/ZrO_2 was prepared by doping 0.5 mass% of Pt metal on zirconia by the incipient wet technique.

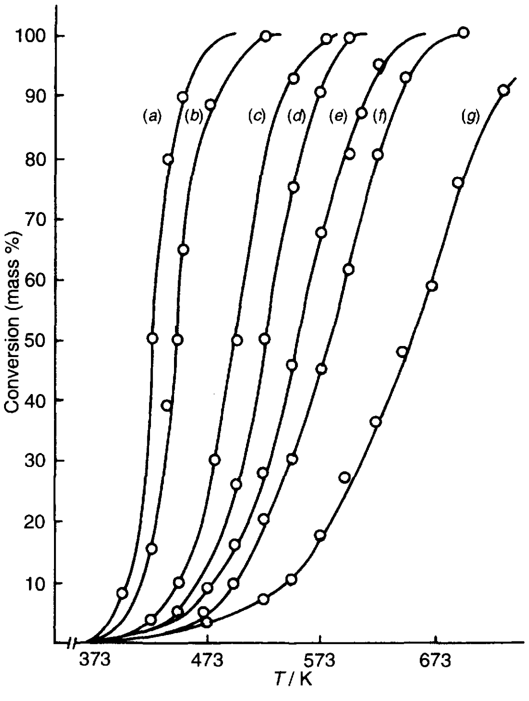

Fig. 1 Conversion of *n*-butane as a function of temperature over Pt/ZrO_2 (*a*), Mn (*b*), Co (*c*), Fe (*d*), Cr (*e*) and Ni (*f*) stabilized zirconia and pure zirconia (*g*). Feed composition : butane (4%), N_2 (76%), O_2 (20%); GHSV 36 000 h^{-1}.

noble-metal doped zirconia while Co- and Fe-stabilized zirconia have medium activity. A better way to compare the activity of the samples is to find the temperatures required for fixed conversion. Table 1 presents temperatures at which 50 and 100% conversion of butane to CO_2 occurs under the conditions above. The rate data presented in Table 1 show that the activity is not related to the surface area of the catalysts but to some other intrinsic properties. As a control experiment, the oxidation activity of the well known perovskite type oxides containing Mn and Co were also tested and the results are also included in Table 1. By comparing the activity exhibited by bulk oxides of manganese or cobalt to those of the Co- and Mn-containing perovskites (ABO_3) (Table 1) it is clear that the present catalyst series is superior and particularly, the activity of Mn-stabilized zirconia is fairly close to that of Pt-doped zirconia, with Co- and Fe-stabilized zirconia showing somewhat less activity. It is thus evident that the mere presence of an element which is redox active is not the only criterion for obtaining improved activity. Probably, a stable structure coupled with fairly high surface area, the presence of oxygen ion vacancies, and an accessible redox pair leads to high oxidation activity.

Fig. 2 compares Mn-ZrO_2 in the fluorite structure and the perovskite oxide ($LaMnO_3$) for their long term activity. The fluorite based material shows a lower tendency to deactivate compared to the perovskite material. This can be attributed the role of the 3d transition-metal ions in the inhibition of sintering particularly when they are present in the fluorite lattice. In addition, the presence of multiple oxidation states of the transition-metal ions in the fluorite structures, as confirmed by TPR studies, facilitates the redox ability of the catalysts.

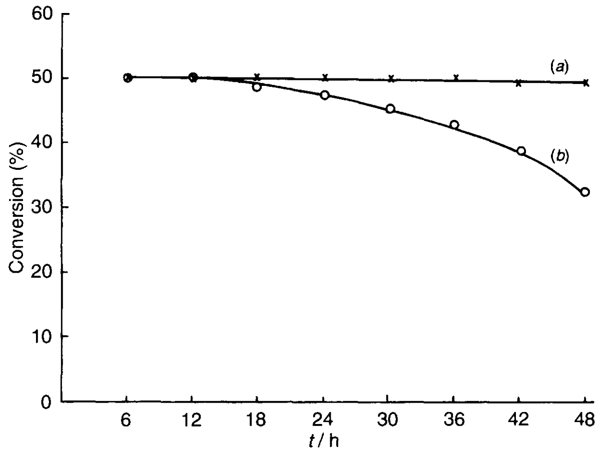

Fig. 2 A comparison of activity–stability of Mn-stabilized zirconia ($Zr_{0.8}Mn_{0.2}O_2$) with fluorite structure at 450 K (*a*) and $LaMnO_3$ with perovskite structure at 550 K (*b*) in the oxidation of *n*-butane at a GHSV of 36000 h^{-1}

For complete oxidation, surface O^- or O_2^- species need to be generated.[9] Incorporation of oxygen from the gas phase on to the oxide surface or into the lattice does not necessarily take place at the same site so that oxygen mobility is required. Such mobility is known to be created in zirconium oxide when the Zr^{4+} ion is partly substituted by other metal ions such as Y^{3+}, Mg^{2+}, Ce^{4+}, Ca^{2+} *etc.*[10–12] although these particular elements do not substantially enhance reactivity. Incorporation of transition-metal ions such as Mn or Co increases the activity mainly due to the creation of defect sites as a consequence of charge imbalance. It has been confirmed by TPR studies that 3d transition-metal ions residing in the fluorite lattice are more readily reduced at lower temperature compared to the metal ions within the individual oxides or allied catalysts of the perovskite family.

In conclusion, a series of novel catalysts belonging to the fluorite family prepared by a simple route is active as complete oxidation catalysts and found to be superior in comparison with known metal oxides or mixed-metal oxides. The improved activity is believed to be due to the ease of reducibility of the 3d transition-metal ions incorporated into the fluorite lattice, increased oxygen mobility and increased textural and structural stability of the samples. Further experiments, such as cyclic voltammetry and ionic conductivity studies to elucidate the mechanistic features of the novel catalysts, are under progress.

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