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The formation and physicochemical properties of magnesium manganates

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Abstract

The effects of calcination temperature, molar ratio and the doping by CeO_2 on the solid–solid interactions, surface and catalytic properties of Mn/Mg mixed oxide system have been studied by XRD, nitrogen adsorption at $-196\,^{\circ}C$ and the catalytic decomposition of hydrogen peroxide at 20, 30, and 40 °C.

The results revealed that the manganese oxides interacted with magnesium oxide to yield well crystallized magnesium manganates at temperatures starting from 600 °C, this reaction found to be affected by the molar ratio of the reacted oxides present and also by the dopant content. However, the treatment of the Mn/Mg mixed oxide system with increasing amounts of manganese and cerium oxides followed by calcination at 400–800 °C brought about an increase in the catalytic activity of the resulting solids, whilst the opposite effect was observed in the surface area of the investigated solids. These treatments resulted in an increase in the particle size of MgO and a decrease in both the activation energy of sintering of the investigated system and that necessary for hydrogen peroxide decomposition reaction.

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Keywords: Solid–solid interaction; Particle size; S_{BET}; Catalytic activity

1. Introduction

Manganese based systems have long attraction since they are widely used and fined many applications in several fields related to adsorption, refractories, catalysis and solid state [1–3]. The performance of mixed systems in various applications depends on the nature of the individual oxides [4], their respective ratios [1,5–8], their method of preparation [b], thermal treatment [1,5–8] and the doping with some foreign cations such as Li^+, Ag^+, Mg^{2+}, Zn^{2+} [9–14].

Manganese containing catalysts exhibit considerable activity in oxidation–reduction reactions [5,15]. The unloaded manganese oxides, although having excellent activity, are liable to a very rapid drop in their activity on enhanced sintering due to heating for prolonged time at moderate temperatures [15]. Loading the manganese oxides on to a suitable support could solve this problem. Deraz et al. [5] have been reported that the loading an alumina surface with manganese in amounts varying between 3.7 and 13.4 wt.%, expressed as MnO_2, led to the formation of thermally stable solids that were active towards H_2O_2 decomposition. These authors claimed that incorporation of manganese oxides into alumina increased the degree of dispersion of the catalytically active species and thereby hindering their grain growth. Active magnesia is considered to be the most convenient support material for a wide variety of transition metal oxide catalysts depending upon magnesia is inexpensive and relatively stable over the temperature range of interest for most catalytic reactions [4,16–21]. MgO support is capable to form a solid solution with some transition metal oxides due to facile diffusion of transition metal [T] ions into MgO support [22,23]. The solid solutions which are based MgO containing T are of special interest and are dependent on the role of T electron configuration and the site a summetry, T–T interaction, and also the participation of the matrix itself in the catalytic steps. It has been

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found that the activity per T ion various with T concentration in a way that depends on the type of reaction [24–27]. The NiO/MgO system constitutes very interesting model since NiO and MgO form ideal solid solution over the whole molar fraction range [25]. There are many factors that affect the diffusion of Ni^{+2} ions into MgO lattice as Ni precursor, the doping with some foreign cations and preparation conditions [28,29]. Also, the calcination temperature and atmosphere in contact with solid substrates affect on the composition of The NiO/MgO solid solution [30]. It has been reported that a 9.7 mol.% of NiO in the NiO/MgO catalyst has high activity and selectivity as well as excellent stability in CO_2 reforming of methane [30,31] and partial oxidation of methane [19,30]. Consequently, loading manganese oxides on to an active magnesia would be expected to modify the structural, surface and catalytic properties of the supported solid.

The present work was directed towards an investigation of the role of the calcination temperature, manganese content and the doping by cerium oxide on the solid–solid interactions, surface area and catalytic properties of Mn/Mg mixed oxides. The techniques employed were XRD analysis, the adsorption of nitrogen at −196 °C and studies of the catalytic decomposition of H_2O_2 in aqueous solution at temperatures within the range 20–40 °C.

2. Experimental

2.1. Materials

Pure samples of manganese oxides loaded on active magnesia were prepared by impregnating different amounts of finely powdered manganese carbonate with a known amount of manganese nitrate dissolved in the least quantity of distilled water necessary to make a paste. The specimens thus obtained were dried to constant weight at 100 °C for 24 h and then heated in air at 400, 600 and 800 °C, respectively, for 12 h in each case. The amount of manganese employed, expressed as Mn_2O_3, varied between 16.55 and 61.34 wt.%. The prepared solids samples were designated as MgMn-I, MgMn-II, MgMn-III and MgMn-IV and contained 16.55, 28.40, 44.24 and 61.34 wt.% Mn_2O_3, respectively. One doped sample (MgMn-I) was prepared by treating a known weight of manganese carbonate with a solution containing known proportions of cerium and magnesium nitrates, then dried at 100 °C and calcined at 600 and 800 °C for 12 h. Manganese and cerium contents were 16.55 and 2 wt% expressed as Mn_2O_3 and CeO_2, respectively. All chemicals involved in the preparation of various catalyst samples were of analytical grade as supplied by Prolabo Company.

2.2. Characterization methods and techniques

An X-ray diffractograms of undoped and doped mixed solids thermally treated in air at 400 and 600 °C were obtained by using a Philips Difractometer (type PW 1390). The patterns were run with iron radiation without filter ($\lambda = 1.9373$ Å) at 36 kV and 16 mA with scanning speed in 2θ of $2^\circ\ \mathrm{min}^{-1}$.

The particle size of MgO present in the investigated solids calcined at different temperature was based on X-ray diffraction line broadening and calculated by using Scherrer equation [31];

$$d = \frac{B\lambda}{\beta \cos\theta}$$

where *d* is average particle size of the phase under investigation, *B* is the Scherrer constant (0.89), *l* is wavelength of the X-ray beam used, *b* is the full with half maximum (FWHM) of diffraction peak and Θ is the diffraction angle.

The lattice parameter “a” of MgO phase present in the tested solids heated at various temperatures was determined from the equation [32];

$$a = d\sqrt{h^2 + k^2 + l^2}$$

where *a* is the lattice parameter for the diffraction line at *d* spacing 1.106 Å.

The specific surface areas (S_{BET}) of various catalysts were determined by the conventional volumetric apparatus. Drying nitrogen was used as the adsorbate at liquid nitrogen temperature, on initially degassed samples at 150 °C for 2 h.

H_2O_2 decomposition activity of the tested catalysts was measured in solution ($H_2O_2 \rightarrow H_2O\rightarrow + 1/2O_2$). The kinetics were followed isothermally at 20, 30, and 40 °C by determining the volume of oxygen released as a function of time (up to 30 min), using a known mass of the test catalyst (20–50 mg), 20 ml of diluted H_2O_2 solution and a home-made gasometer similar to that described by Deren et al. [33].

3. Results and discussion

3.1. XRD investigation

Preliminary examination showed that magnesium basic carbonate subjected to calcination at 400–800 °C consisted mainly of MgO. The X-ray diffractograms of Mn/Mg mixed solids calcined in air at 400, 600 and 800 °C were determined. The crystalline phases produced are summarized and given in Table 1. It can be seen from Table 1 that: (i) the thermal treatment of mixed solids in air at 400 °C leads to the formation of MgO and γ-MnO_2. The relative intensities of the diffraction lines of MgO decreases and those of MnO_2 increases by increasing the amount o f manganese oxide present. (ii) An increase of the calcination temperature of the various mixed solids up to 600 °C led to the appearance of a mixture of MgO, Mn_2O_3 (partridgeite) and Mg_2MnO_4. In other words, the rise in calcination temperature to 600 °C led to both complete disappearance of γ-MnO_2 which was converted entirely into Mn_2O_3 (partridgeite) [34], and solid–solid interaction

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