

Effects of ZnO and MoO₃ Doping on Surface and Catalytic Properties of Manganese Oxide Supported on Alumina System

Sh. M. Ibrahim¹, G.A. El-Shobaky^{*2}, G.M. Mohamed² and N.A. Hassan²

¹Department of Chemistry, Faculty of Education, Ain Shams University, Cairo, Egypt

²Department of Physical Chemistry, National Research Center, Dokki, Cairo, Egypt

Abstract: 0.2Mn₂O₃/Al₂O₃ system was prepared by the impregnation method using finely powdered Al(OH)₃ and a calculated amount of Mn(NO₃)₂ dissolved in the smallest amount of distilled water followed by drying and calcination at 400-600°C. Six doped solids were prepared by impregnating powdered Al(OH)₃ Solids with different amounts of Zn(NO₃)₂ or (NH₄)₆Mo₇O₂₄·4H₂O followed by drying, then impregnating with Mn(NO₃)₂. The doped solids were calcined at 400-600°C. The dopant concentrations were 0.75, 1.5, and 3 mol% ZnO or MoO₃. The structural characteristics, surface and the catalytic properties of pure and variously doped solids were examined by using XRD, N₂ adsorption at 196°C and isopropanol conversion carried out at 140-280°C using a flow technique under atmospheric pressure. The obtained results revealed that the pure solids investigated and those doped with 0.75 and 1.5mol% ZnO or MoO₃ calcined at 500°C, consisted of a mixture of nanosized MnO₂ (Pyrolusite) and Mn₂O₃ (Partridgeite phase) together with κ-Al₂O₃. Increasing the calcination temperature of the variously doped solids to 600°C led to the complete conversion MnO₂(Pyrolusite) to nanosized Mn₂O₃ (Partridgeite phase). The crystallite size of manganese oxide phases varied between 3 and 56 nm. All surface characteristics of the system investigated were much affected by calcination temperature and dopant concentration. Isopropanol conversion carried out over pure and doped system calcined at different temperatures proceeded *via* dehydration and dehydrogenation yielding propene and acetone, respectively. The activity and selectivity of the various solids were much affected by the reaction temperature, calcination temperature and dopant concentration.

Keywords: Mn₂O₃/Al₂O₃ nanoparticles, dehydration, dehydrogenation, isopropanol, ZnO, Mo O – doping.

1. INTRODUCTION

Oxide solids can be considered as cheap, environmental friendly and active catalysts for a variety of chemical reactions such as oxidation reaction [1,2]. Manganese oxides are reported to be among the most efficient oxide solids for catalytic oxidation reactions [3-10]. For example, MnO₂ and Mn₃O₄ were found to be the active and stable catalysts for the combustion of organic compounds [11,12]. This behavior is attributed to the variable electronic structure and oxidation state in a variety of compounds (MnO₂, Mn₂O₃, MnO and Mn₃O₄), which shows good redox properties [8]. The catalytic properties of manganese oxides are also due to their oxygen storage capacity in the crystalline lattice [13,14].

The interaction of transition metal oxide with the support as well as with other components constituting the catalyst has a significant influence on the structure definition and the catalytic activity [13,15,16]. The most often used supports for transition metal oxide catalysts are oxides such as Al₂O₃ [17]. In previous studies, the structural characterization of pure or supported manganese oxide catalysts showed the presence of MnO₂ or mixed MnO₂/Mn₂O₃ solids as the active catalytic components [13,14]. Increasing dispersion of MnO_x on the support surface leads to a significant increase

in the catalytic activity [18,19]. Manganese oxide dispersion depends on the Mn-precursor, loading, preparation method, thermal treatment and the presence of foreign ions [13, 18].

Loading manganese oxide on to an alumina surface led to the formation of thermally stable solids, which were active in H₂O₂ decomposition [20-24]. Furthermore, Mn-oxide/Al₂O₃ catalyst with 15%MnO_x loading had higher catalytic performances towards methane combustion than Mn-oxide supported on TiO₂ and SiO₂ [8]. The high activity of Mn oxide/γ-Al₂O₃ has been attributed to the increase of active sites involved in catalytic reactions [8].

Doping with certain foreign ions, like Li₂O, Na₂O, K₂O, ZnO, MoO₃ and CeO₂ effected measurable changes in the surface and catalytic properties of a large variety of catalysts. For example, doping with ZnO of CuO/TiO₂ calcined at 600 °C resulted in an increase in the catalytic activity in isopropanol or ethanol conversion [25]. However, solid-solid interaction between Co₃O₄ and Fe₂O₃ took place at temperatures from 800°C while ZnO doped samples could produce CoFe₂O₄ at 740°C [26]. Doping NiO/TiO₂ system either with MoO₃ or CeO₂ followed by heating at 300 or 500°C brought about a considerable increase in the catalytic activity for iso-propanol conversion reaching a maximum limit in the presence of 2 or 4 mol% dopant oxide [27]. The previous solids were highly selective for isopropanol dehydration yielding propene (90-98%) with trace amounts of acetone from dehydrogenation of iso-propanol at temperatures < 250°C [27]. The treatment of Co₃O₄ with

*Address correspondence to this author at the Physical Chemistry Department, National Research Center, Dokki, Egypt; Fax: +202 3700931; E-mail: elshobaky@yahoo.com

small amounts of ZnO (2-8wt%) followed by calcinations at 500 and 700 °C exerted a progressive measurable decrease in the crystallite size of Co₃O₄ phase [28].

Doping Mn oxides with Li₂O, Na₂O, MoO₃, V₂O₅, CeO₂ and La₂O₃ have been investigated in previous studies [7,20,29-31]. It was found that La₂O₃ doping of Mn₂O₃/Al₂O₃ calcined at (400-700 °C) greatly increased the catalytic activity towards CO-oxidation and H₂O₂ decomposition [7]. Doping Mn/Al mixed oxides system with ceria enhanced the catalytic decomposition of H₂O₂ [32]. This is due to the generation of the optimal electron mobility at the surface, which was necessary to enhance the redox pathway of the reaction [32]. On the other hand, doping of manganese oxides with MoO₃ or V₂O₅ conducted at 400 °C and 600 °C brought about considerable decrease in the specific catalytic activities towards CO oxidation by O₂ and H₂O₂ decomposition [31]. MnO_x/Al₂O₃ catalysts deactivated by SO₂ was used for the selective catalytic reduction of NO with NH₃ at low temperatures [33].

The dehydration of alcohols to give ethers and olefins is a well-known acid-catalyzed reaction as well as the dehydrogenation to aldehydes or ketones over basic catalysts. Mixed oxide catalysts are more active in dehydrating alcohols than single oxide catalysts. The chemical composition, calcination temperature of mixed oxides, and doping with foreign ion are among the factors affecting the performance of the catalyst towards the conversion of alcohols [25,27,29,30,34-40]. Treatment of 0.1Mn₂O₃/Al₂O₃ with Na₂O (3 or 6 mol%) followed by heating at 500 °C led to the formation of (Na_{0.2}MnO₂), with subsequent decrease in the BET surface area and an effective increase in the catalytic activity towards conversion of ethanol and iso-propanol [30].

The present work reports a study on the effect of ZnO and MoO₃ (0.75,1.5,3 mol%) on the surface and the catalytic properties of 0.2Mn₂O₃/Al₂O₃ precalcined at 400, 450, 500 and 600 °C using XRD, adsorption of N₂ at -196 °C, and catalysis of isopropanol conversion at temperatures between 140 and 280 °C.

2. EXPERIMENTAL

2.1. Materials

Manganese oxides supported on alumina having the molar composition 0.2 Mn₂O₃/Al₂O₃, was prepared by the wet impregnation method using finely powdered Al(OH)₃ solid with solutions containing known amount of Mn(NO₃)₂ dissolved in the smallest amounts of double-distilled water making a paste to avoid any possible sedimentation and to ensure the homogeneity of the samples. The paste was dried at 120 °C, then calcined at 400, 450, 500, and 600 °C for 4 h. The doped solid samples were prepared by treating known amounts of Al(OH)₃ with solutions containing different amounts of Zn(NO₃)₂·6H₂O, and (NH₄)₆Mo₇O₂₄·4H₂O dried at 120 °C. The obtained doped alumina samples were treated with solutions containing fixed amounts of Mn(NO₃)₂. The obtained solids were dried at 120 °C, then calcined at 400, 450, 500, and 600 °C for 4h. The dopant concentrations were 0.75, 1.5, and 3.0 mol% ZnO and MoO₃. The chemicals employed were of analytical grade and supplied by BDH Company. Analar isopropanol was supplied by Merck.

2.2. Techniques

X-ray powder diffractograms of pure and doped solids calcined in air at 400, 450, 500, and 600 °C were determined by using a diffractometer (type Bruker D8 Advance). The patterns were run with copper radiation (Cu K α) with second monochromator (λ = 1.5405 Å) for pure and doped solids at 40 kV and 40 mA. The crystallite size of the investigated solids was calculated from the line-broadening profile analysis of the main diffraction lines using the Scherrer equation [41]: $d = K\lambda / \beta_{1/2} \cos\theta$, where d is the mean crystallite diameter, λ the wavelength of X-ray beam, K the Scherrer constant (0.89), $\beta_{1/2}$ the full-width at half-maximum (FWHM) of the main diffraction peaks of crystalline phases present and θ is the diffraction angle.

The specific surface area (S_{BET}), total pore volume (V_p), mean pore radius (r) and pore volume distribution ($\Delta v/\Delta r$) of the solid catalysts were determined from nitrogen adsorption isotherms measured at -196 °C using Quantachrome NOVA automated gas sorbometer. Before carrying out the measurements, each sample was degassed under a reduced pressure of 10⁻⁵ Torr at 200 °C for 3 h.

The catalytic activities of various solid samples calcined at 400, 450, 500 and 600 °C were determined by using isopropanol conversion carried out at different temperatures varying between 140 and 280 °C. The catalytic reaction was carried out in a flow reactor under atmospheric pressure. Thus, a 100 mg catalyst sample was held between two glass wool plugs in a pyrex glass reactor tube of 20 cm long with 1 cm internal diameter packed with quartz fragments of 2–3 mm length. Argon gas was used as the diluent and the isopropanol vapor was introduced into the reactor through an evaporator/saturator containing the liquid at constant temperature 35 °C. The flow rate of the carrier gas was maintained at 20 ml/min. Before carrying out such catalytic activity measurements each catalyst sample was activated by heating at 300 °C in a current of argon for 1h then cooled to the catalytic reaction temperature. The reaction products in the gaseous phase were analyzed chromatographically using Perkin-Elmer Auto system XL gas chromatograph fitted with a 2m Porapak Q stainless steel column suitable for gas analysis.

3. RESULTS AND DISCUSSIONS

3.1. X-Ray Investigation of Pure and Doped Supported Solids Precalcined at Different Temperatures

X-ray diffractograms of pure and variously doped solids preheated at 400- 600 °C were carried out. Fig. (1) shows the diffractograms of pure and doped solids precalcined at 600 °C. The crystallite size and degree of crystallinity of different investigated solids are given in Table 1. Table 1 also includes the structure characteristics of the different phases present in the pure and the doped solids.

Examination of Table 1 shows the following: (i) Pure solids and those doped with 0.75 and 1.5 mol% MoO₃ or ZnO calcined at 500 °C consisted of a mixture of MnO₂ (pyrolusite phase), Mn₂O₃ (partridgeite phase) and κ -Al₂O₃ that having moderate degree of crystallinity. (ii) The solids doped with 3 mol% MoO₃ or ZnO calcined at 500 °C consisted of MnO₂ (pyrolusite phase), and κ -Al₂O₃ only. So, MoO₃ or ZnO doping of the system investigated stabilized

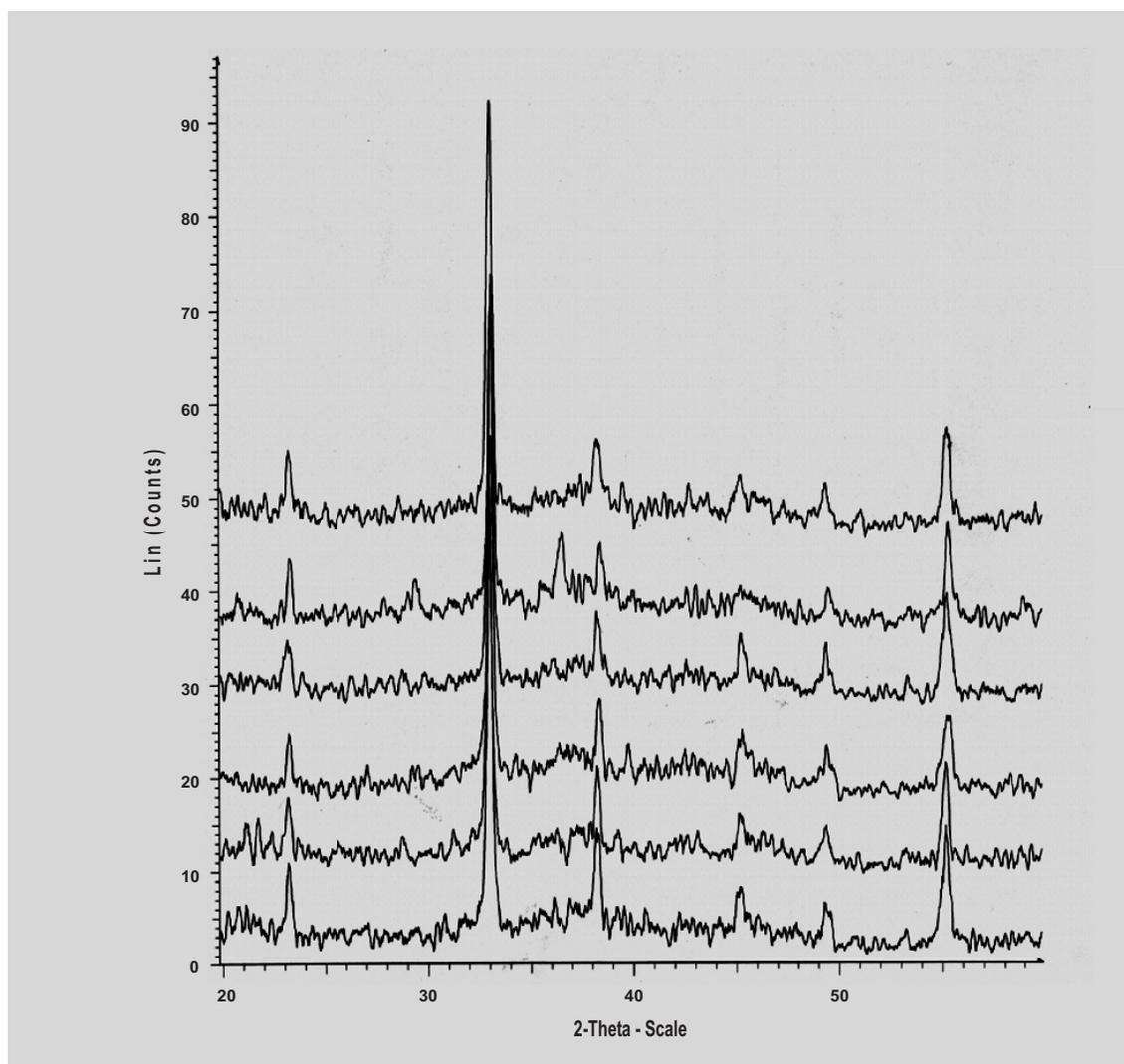


Fig. (1). X-ray diffractograms of the pure and the doped solids calcined at 600 °C

tetravalent manganese oxide. (iii) Increasing the calcination temperature of the pure and the doped solids to 600 led to the complete conversion of MnO₂ to Mn₂O₃ and conversion of κ -Al₂O₃ into γ -Al₂O₃. The conversion of MnO₂ into Mn₂O₃ took place according to $2 \text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3 + 1/2\text{O}_2$ (iv) All manganese oxides present in pure and doped solids are nanosized phases measuring crystallite sizes varying between 3 and 56 nm.

3.2. Surface Characteristics of Pure and Doped Solid Catalysts Preheated at 400–600°C

The different surface characteristics of pure and doped solids precalcined at 400, and 600°C were determined from nitrogen adsorption isotherms registered at -196°C. These characteristics include the specific surface areas (S_{BET}), total pore volume (V_p), pore volume distribution, and mean pore radius (r). The adsorption isotherms, not given here, are of type II of the Brunauer classification. Figs. (2, 3) represent the pore volume distribution curve for some selected adsorbents. The values of different surface characteristics of the investigated adsorbents are given in Table 2. Examination of Table 2 shows the following: (i) The S_{BET} of pure adsorbent suffered a significant decrease which attained

34.5% upon increasing its calcination temperature from 400 to 600°C. This decrease could be attributed to a possible increase in the crystallite size of the phases present and also to an effective pore widening. In fact, the r value increases from 18 to 34 Å upon increasing calcination temperature from 400 to 600°C. (ii) MoO₃ doping of the systems investigated followed by calcinations at 400°C resulted in limited changes in the S_{BET} values. i.e. both increase and decrease in the S_{BET} value. (iii) ZnO doping conducted at 400 °C resulted in an effective decrease in the S_{BET} value falling to a minimum value in presence of 1.5 mol% ZnO. The percentage decrease of the specific surface area due to doping with 1.5 mol% ZnO reached 31%. This decrease was accompanied by an increase in the r value from 18.2 to 24.8. The percentage increase of r value reached 36%. Thus, the observed decrease in the BET surface area of the system investigated due to ZnO doping at 400°C could be directly attributed to effective pore widening. (iv) MoO₃ doping of manganese oxide supported on alumina calcined at 600°C effected a limited increase in the S_{BET} reaching to 23.5%. This increase was accompanied by a decrease of 14% of r value. (v) ZnO-doping followed by calcination at 600°C led to limited fluctuation i.e. both increase and decrease in the

Table 1. Structural Characteristics of Different Pure and Doped Solids Precalcined at Different Temperatures

Degree of Crystallinity ^b (a.u.)	Crystallite Size ^a (nm)	Phases Present	Calcination Temperature (°C)	Solid
MnO ₂ 16 Mn ₂ O ₃ 7	MnO ₂ 11 Mn ₂ O ₃ 9	MnO ₂ , ^c Mn ₂ O ₃ , ^d κ-Al ₂ O ₃	400	0.2Mn ₂ O ₃ /Al ₂ O ₃
MnO ₂ 14 Mn ₂ O ₃ 14	MnO ₂ 30 Mn ₂ O ₃ 56	MnO ₂ , Mn ₂ O ₃ , κ-Al ₂ O ₃	500	0.2Mn ₂ O ₃ /Al ₂ O ₃
MnO ₂ 14 Mn ₂ O ₃ 12	MnO ₂ 18 Mn ₂ O ₃ 46	MnO ₂ , Mn ₂ O ₃ , κ-Al ₂ O ₃	500	0.2Mn ₂ O ₃ /Al ₂ O ₃ +0.75mol%MoO ₃
MnO ₂ 16	MnO ₂ 10	MnO ₂ , κ-Al ₂ O ₃	500	0.2Mn ₂ O ₃ /Al ₂ O ₃ + 3.0mol%MoO ₃
MnO ₂ 13 Mn ₂ O ₃ 13	MnO ₂ 3 Mn ₂ O ₃ 31	MnO ₂ , Mn ₂ O ₃ , κ-Al ₂ O ₃	500	0.2Mn ₂ O ₃ /Al ₂ O ₃ + 0.75mol%ZnO
MnO ₂ 11 Mn ₂ O ₃ 13	MnO ₂ 3 Mn ₂ O ₃ 28	MnO ₂ , Mn ₂ O ₃ , κ-Al ₂ O ₃	500	0.2Mn ₂ O ₃ /Al ₂ O ₃ + 1.5mol%ZnO
MnO ₂ 13	MnO ₂ 38	MnO ₂ , κ-Al ₂ O ₃	500	0.2Mn ₂ O ₃ /Al ₂ O ₃ + 3.0mol%ZnO
Mn ₂ O ₃ 46	Mn ₂ O ₃ 39	Mn ₂ O ₃ , γ-Al ₂ O ₃	600	0.2Mn ₂ O ₃ /Al ₂ O ₃
Mn ₂ O ₃ 47	Mn ₂ O ₃ 41	Mn ₂ O ₃ , γ-Al ₂ O ₃	600	0.2Mn ₂ O ₃ /Al ₂ O ₃ +0.75mol%MoO ₃
Mn ₂ O ₃ 43	Mn ₂ O ₃ 40	Mn ₂ O ₃ , γ-Al ₂ O ₃	600	0.2Mn ₂ O ₃ /Al ₂ O ₃ + 1.5mol%MoO ₃
Mn ₂ O ₃ 44	Mn ₂ O ₃ 41	Mn ₂ O ₃ , γ-Al ₂ O ₃	600	0.2Mn ₂ O ₃ /Al ₂ O ₃ + 3.0mol%MoO ₃
Mn ₂ O ₃ 40	Mn ₂ O ₃ 32	Mn ₂ O ₃ , γ-Al ₂ O ₃	600	0.2Mn ₂ O ₃ /Al ₂ O ₃ + 1.5mol%ZnO

^aThe value of crystallite size of the phases present were calculated from the Scherer equation [41].

^bThe area of the main diffraction peak of the main phase was taken as a measure for the degree of crystallinity of that phase.

^cMnO₂ is pyrolusite phase.

^dMn₂O₃ is partridgeite phase.

S_{BET} value depending on the amount of ZnO added. The same trend was observed for r^{-1} values.

It is well known that MoO₃ sublimates by heating at 795°C, i.e. its vapor pressure reaches 1atm. [42]. Heating the system investigated at 600°C led to an effective migration of MoO₃ species throughout the whole mass of the doped system leading to a creation of new pores whose existence is responsible for the measurable increase in the S_{BET} and V_p of MoO₃ doped system. Figs. (2, 3) depict pore volume distribution curves ($\Delta v/\Delta r$) of some selected solids. These solids are the ones doped with 1.5 mol% MoO₃ calcined at 400 and 600°C, respectively. It is seen from these figures that $\Delta v/\Delta r$ curves consisted multimodal distribution curves having maxima at 14, and 28 Å for the adsorbent calcined at 400 °C and at 18, 36 and 45 Å for the solid calcined at 600 °C. It can also be seen that the total areas of $\Delta v/\Delta r$ curves increased upon increasing the calcination temperature from 400 to 600°C. These findings indicate that this thermal treatment led to a shift in the value of pore width towards longer values and also led to an effective increase in the volume of pores present. The same findings have been reached from the results given in Table 2 (the last two columns).

The observed changes in the structural and the surface characteristics of the system investigated due to increasing calcination temperature and doping either with ZnO or MoO₃ are expected to be followed by changes in the activity and selectivity on isopropanol conversion.

3.3. Catalytic Activity of Pure and Various Doped Solids

The catalytic activity of pure and variously doped solids were determined using the conversion of isopropanol at temperatures between 140- 280°C.

3.3.1. Catalytic Conversion of Isopropanol Over Pure and Doped Solids Calcined at Different Temperatures

The catalytic conversion of isopropanol was carried out over different solids calcined at 400, 450, 500, and 600°C. The reaction proceeded *via* dehydration and dehydrogenation producing propene and acetone, respectively. This finding indicates that the investigated solids acted as bifunctional catalysts.

Fig. (4) shows the percentage conversion of the investigated alcohol as a function of reaction temperature for pure solids calcined at 400-600°C. It is clearly shown from

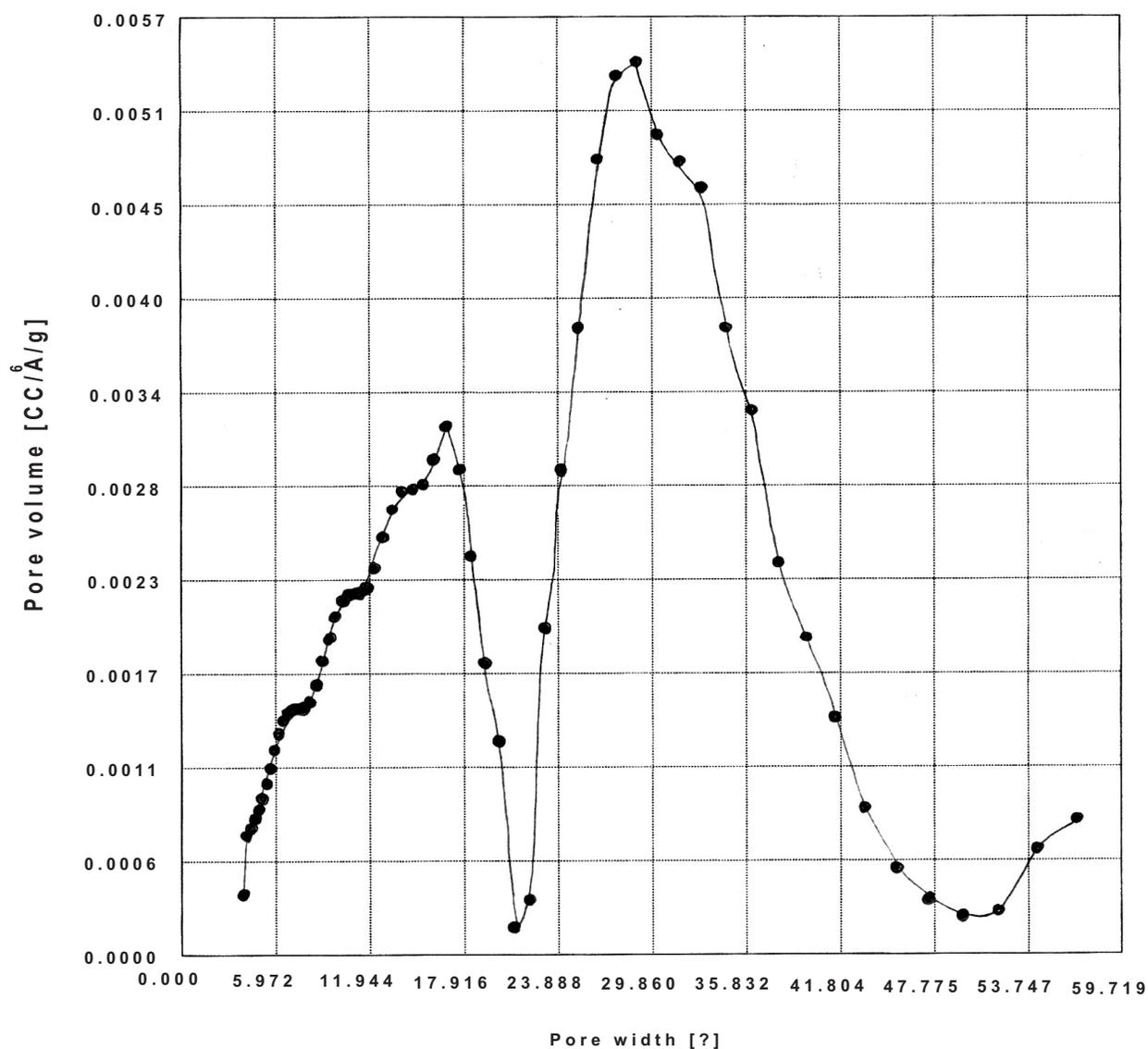


Fig. (2). Pore volume distribution curve ($\Delta V/\Delta r$ of 1.5 mol% doped MoO₃ sample calcined at 400 °C.

this figure that the solid sample calcined at 400°C had the maximum activity which decreased progressively by increasing calcination temperature. The percentage conversion measured at 205°C, taken as a measure of catalytic activity, suffered a decrease of about 23% upon increasing the calcination temperature to 600°C. The high catalytic activity of solids calcined at 400°C could be attributed to: (i) the large specific surface area of the solid calcined at 400°C (c.f. Table 2). (ii) The extremely small crystallite size of the produced MnO₂ (pyrolusite phase) and Mn₂O₃ (partridgeite phase) (c.f. Table 1). (iii) the relatively high value of surface acidity (Brønsted acid sites) [43]. (iv) the complete conversion of MnO₂ into Mn₂O₃ upon heating at 600°C. Thus, the observed progressive decrease in the catalytic activity due to increasing calcination temperature within 400-600°C could be attributed to the effective

decrease in S_{BET} , the increase of crystallite size of MnO₂ and Mn₂O₃ and the decrease of the surface acidity.

The role of calcination temperature in the catalytic activity of the heavily doped solids (doped with 3mol% ZnO or MoO₃) was investigated and the results are illustrated in Fig. (5a, b) as percentage conversion of isopropanol as a function of reaction temperature. Similar to the pure solids the catalytic activity of heavily doped solids decreased progressively by increasing their calcination temperature within 400-600°C. The decrease was, however, less pronounced (about 11%) as compared to that observed for the pure solids (23%). The observed decrease in the catalytic activities of heavily doped solids due to increasing their calcination temperature could also be attributed to the significant increase in the crystallite size of manganese oxide phase (c.f. Table 1), the decrease in their specific surface area and the decrease in surface acidity.

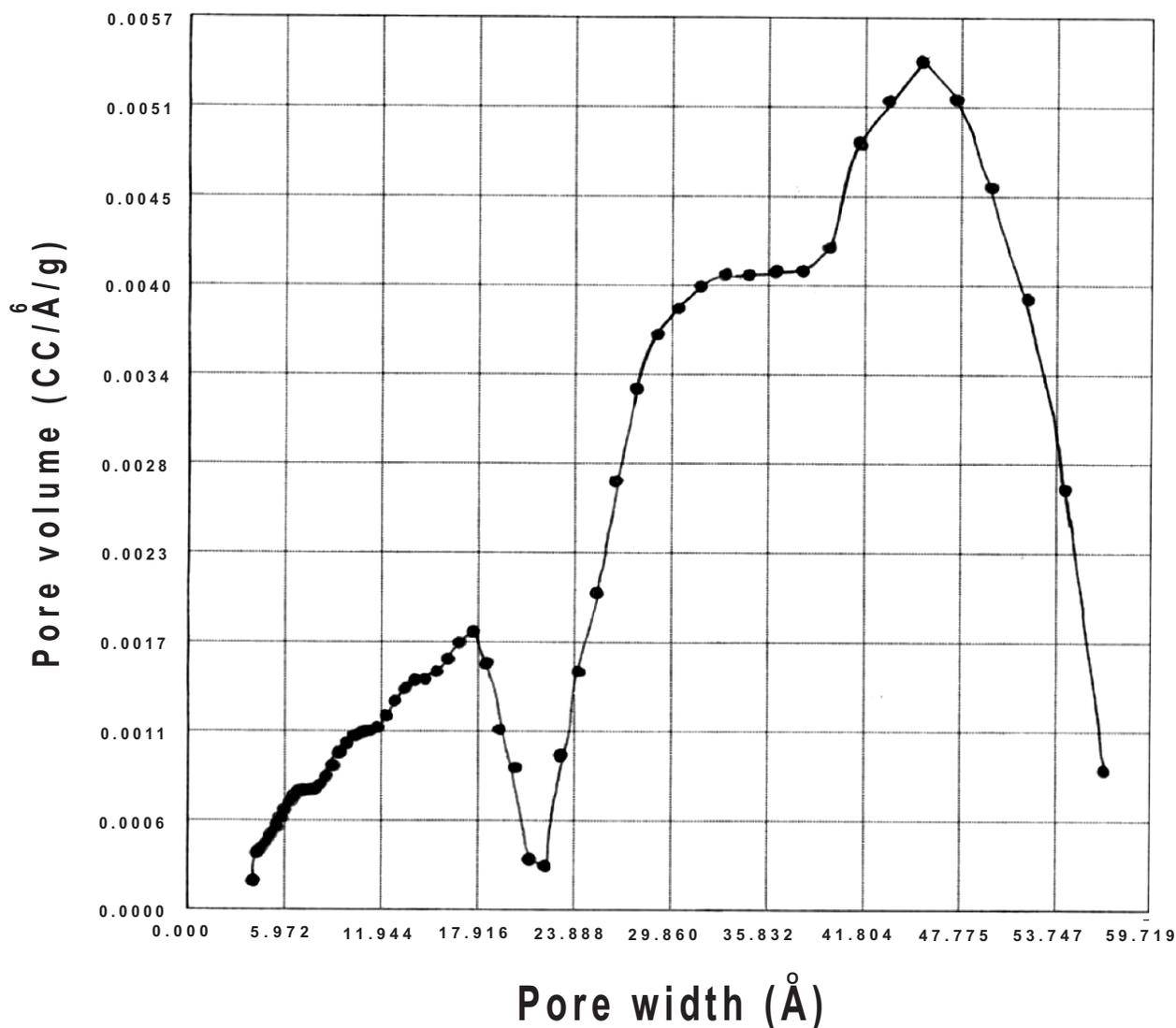


Fig. (3). Pore volume distribution curve ($\Delta v/\Delta r$ of 1.5 mol% doped MoO_3 sample calcined at 600 °C.

The role of dopant concentration on the activity was investigated *via* following the percentage conversion as a function of reaction temperature for the reaction carried out over the solids doped with 0.75, 1.5 and 3mol% MoO_3 or ZnO and calcined at 500°C. The results obtained are graphically illustrated in Fig. (6a, b). It is shown from these figures that the increase in the dopant concentration resulted in a corresponding increase in the catalytic activity. The percentage conversions measured for the reactions carried out at 205°C attained 59.5%, 67.4%, 75.2% and 79.5% for the pure sample and the samples doped with 0.75, 1.5 and 3mol% MoO_3 , respectively. The values measured were 59.5, 68.9%, 75%, and 80.3% for the pure sample and the samples doped with 0.75, 1.5 and 3mol% ZnO , respectively. These findings indicate that MoO_3 and ZnO doping resulted in almost the same increase in the catalytic activity. The increase in the catalytic activity of the system investigated calcined at 500°C due to doping either with ZnO or MoO_3

could be tentatively attributed to the significant decrease in the crystallite size of manganese oxide phases and also to a possible stabilization of MnO_2 by heating at 500°C in the presence of 3mol% ZnO or 3mol% MoO_3 (c.f. Table 1).

The role of reaction temperature on the selectivity of pure and variously doped solids calcined at 500°C was studied and the results obtained are graphically illustrated in Fig. (7a, b). The selectivity of pure and doped solids are mainly dependant on the reaction temperature. Generally, the dehydration selectivity decreases by increasing reaction temperature falling to minimum values for the reaction carried out at 160°C. The decrease was, however, more pronounced for MoO_3 doping. Then it increases progressively by increasing reaction temperature within 200-280°C. On the other hand, it can also be seen from Fig. (7b) that the dehydrogenation selectivity increases progressively by increasing reaction temperature showing a maximum value at 160-200°C. The increase was, however, more

Table 2. Surface Characteristics of Various Investigated Adsorbents

Adsorbent	Calcination Temperature (°C)	S _{BET} (m ² /g)	V _p (ml/g)	r ⁻ (Å)
0.2Mn ₂ O ₃ /Al ₂ O ₃	400	192	0.175	18
0.2Mn ₂ O ₃ /Al ₂ O ₃ +0.75mol%MoO ₃	400	203.5	0.197	19
0.2Mn ₂ O ₃ /Al ₂ O ₃ + 1.5mol%MoO ₃	400	176.0	0.161	18
0.2Mn ₂ O ₃ /Al ₂ O ₃ + 3.0mol%MoO ₃	400	200.5	0.190	19
0.2Mn ₂ O ₃ /Al ₂ O ₃ + 0.75mol%ZnO	400	150.4	0.165	22
0.2Mn ₂ O ₃ /Al ₂ O ₃ + 1.5mol%ZnO	400	132.2	0.164	25
0.2Mn ₂ O ₃ /Al ₂ O ₃ + 3.0mol%ZnO	400	165.6	0.184	22
0.2Mn ₂ O ₃ /Al ₂ O ₃	600	125.9	0.215	34
0.2Mn ₂ O ₃ /Al ₂ O ₃ +0.75mol%MoO ₃	600	147.8	0.253	34
0.2Mn ₂ O ₃ /Al ₂ O ₃ + 1.5mol%MoO ₃	600	155.1	0.264	31
0.2Mn ₂ O ₃ /Al ₂ O ₃ + 3.0mol%MoO ₃	600	155.5	0.229	30
0.2Mn ₂ O ₃ /Al ₂ O ₃ + 0.75mol%ZnO	600	131.0	0.213	33
0.2Mn ₂ O ₃ /Al ₂ O ₃ + 1.5mol%ZnO	600	114.9	0.181	32
0.2Mn ₂ O ₃ /Al ₂ O ₃ + 3.0mol%ZnO	600	119.0	0.192	32

pronounced for the solid doped with 3mol% MoO₃. The dehydrogenation selectivity was found to decrease progressively by increasing reaction temperature within 200-280°C falling to very small value. It is worth mentioning to that MoO₃-doping resulted in a very significant increase in the dehydration selectivity and a sudden drop in the dehydrogenation selectivity. These findings could be attributed to the acidic nature of MoO₃ leading to an effective enhancement in the dehydration selectivity with subsequent drop in the dehydrogenation selectivity.

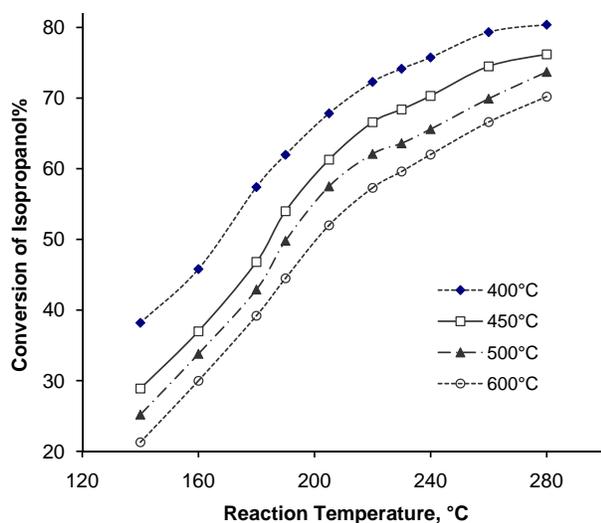


Fig. (4). Effect of calcination temperature on % of catalytic conversion of isopropanol carried out over pure 0.2Mn₂O₃/Al₂O₃

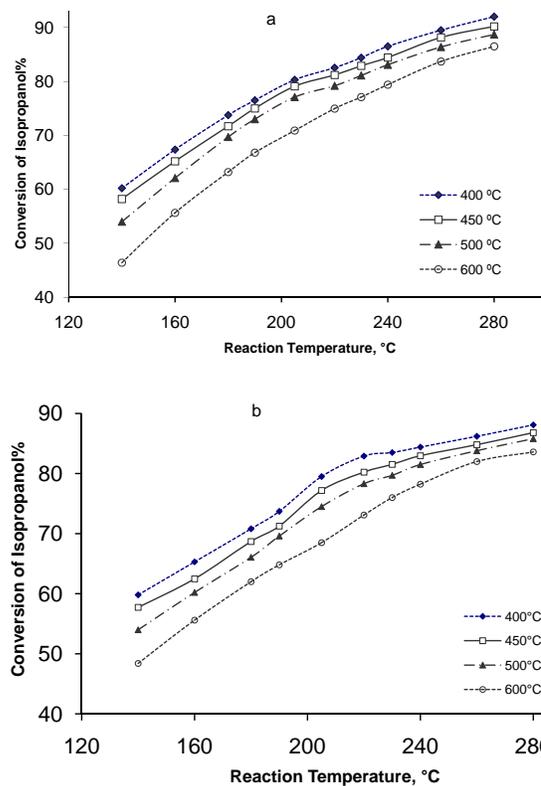


Fig. (5). Effect of calcination temperature on % of catalytic conversion of isopropanol carried out over (a) 3 mol% ZnO doped 0.2Mn₂O₃/Al₂O₃, and (b) 3 mol% MoO₃ doped 0.2Mn₂O₃/Al₂O₃.

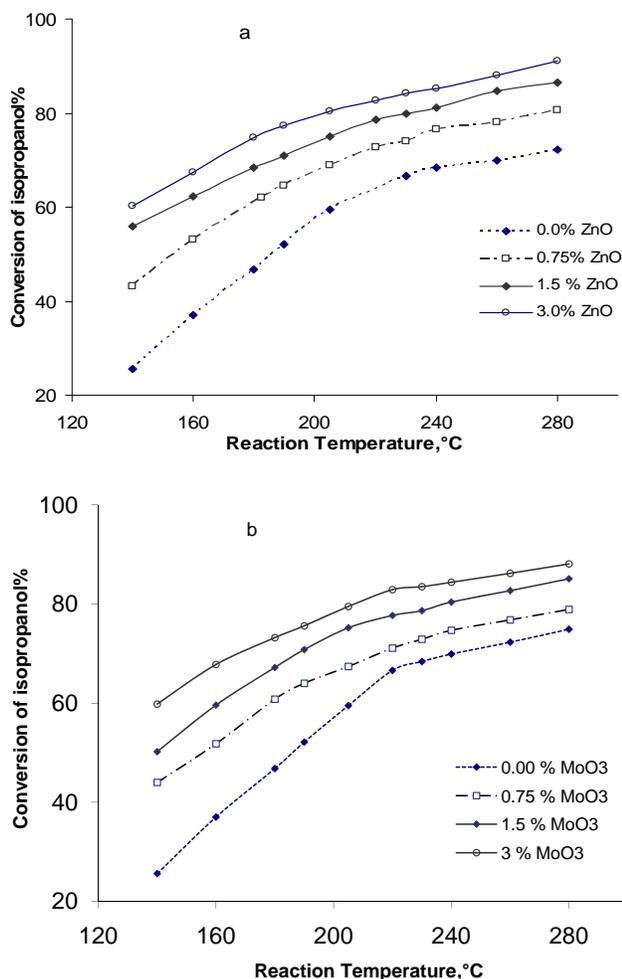


Fig. (6). Percentage conversion of isopropanol as a function of reaction temperature carried out over (a) pure and ZnO doped $0.2\text{Mn}_2\text{O}_3/\text{Al}_2\text{O}_3$ calcined at $500\text{ }^\circ\text{C}$, and (b) pure and MoO_3 doped $0.2\text{Mn}_2\text{O}_3/\text{Al}_2\text{O}_3$ calcined at $500\text{ }^\circ\text{C}$.

4. CONCLUSIONS

The followings are the main conclusions that could be drawn from the results obtained

1. Pure and variously doped solids calcined at $400\text{ }^\circ\text{C}$ consist of a mixture of MnO_2 , Mn_2O_3 and $\gamma\text{-Al}_2\text{O}_3$ and turned to Mn_2O_3 and $\gamma\text{-Al}_2\text{O}_3$ upon heating at $600\text{ }^\circ\text{C}$.
2. ZnO and MoO_3 doping increased the thermal stability of MnO_2 calcined at $500\text{ }^\circ\text{C}$. The crystallite size of manganese oxides in different solids calcined at $400\text{--}600\text{ }^\circ\text{C}$ varied between 3 and 50nm depending on dopant concentration and calcination temperature.
3. The different surface characteristics of the system investigated were much influenced by calcination temperature and doing with either ZnO or MoO_3 .
4. Pure and doped solids acted as active catalysts for the dehydrogenation and the dehydration of isopropanol. The doping process increased the activity to an extent proportional to the dopant concentration. This process modified the selectivity of the doped solids.

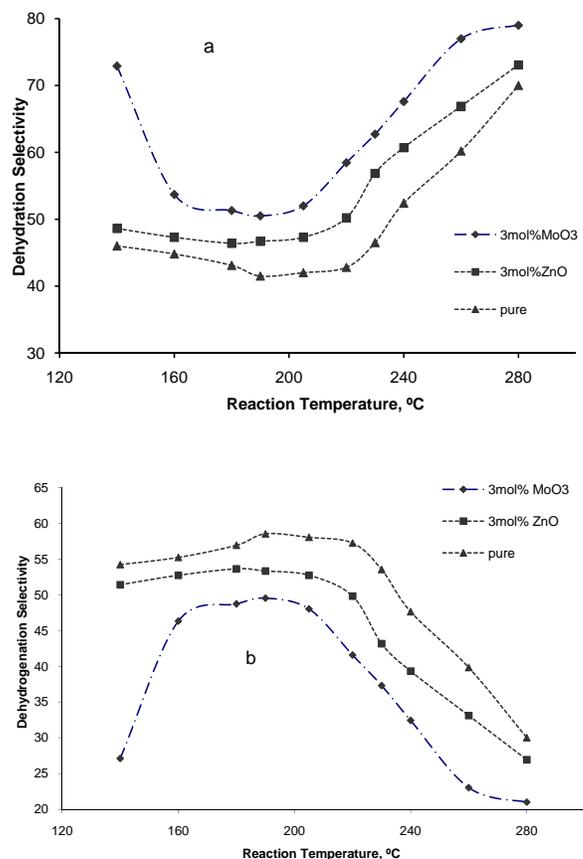


Fig. (7). Dehydration selectivity (a), dehydrogenation selectivity (b) over pure, 3 mol % ZnO and 3mol % MoO_3 doped $0.2\text{Mn}_2\text{O}_3/\text{Al}_2\text{O}_3$ calcined at $500\text{ }^\circ\text{C}$.

REFERENCES

- [1] Baltanas, M.A.; Stiles, A.B.; Katzer, J.R. Development of supported manganese oxides catalysts for partial oxidation: Preparation and hydrogenation properties. *Appl. Catal.*, **1986**, *28*, 13.
- [2] Karlsson, H.T.; Rosenberg, H.S. Flue gas denitrification. Selective catalytic oxidation of nitric oxide to nitrous oxide. *Ind. Eng. Chem. Process. Res. Dev.*, **1984**, *23*, 808.
- [3] Craciun, R. Structure/activity correlation for unprompted and CeO_2 promoted $\text{MnO}_2/\text{SiO}_2$ catalysts. *Catal. Lett.*, **1998**, *55*(1), 25.
- [4] Hadjiivanov, K.; Lavalley, J. C. "FT-IR Spectroscopic study of CO adsorption on monoclinic Zirconia of different hydroxylation degrees". *Catal. Commun.*, **2001**, *2*(3-4), 129.
- [5] Gelin, P.; Primet, M. Complete oxidation of methane at low temperature over noble metal based catalysts: a review. *Appl. Catal. B*, **2002**, *39*(1), 1.
- [6] Machocki, A.; Ioannides, T.; Stasinska, B.; Gac, W.; Avgouropoulos, G.; Delimaris, D.; Grzegorzczak, W.; Pasieczna, S. Manganese-lanthanum oxides modified with silver for the catalytic combustion of methane. *J. Catal.*, **2004**, *227*(2), 282.
- [7] Radwan, N.R.E. Effects of La_2O_3 -doping on physicochemical surface and catalytic properties of nickel and manganese oxides supported on alumina. *Appl. Catal. A. Gen.*, **2004**, *257*, 177.
- [8] Hu, J.; Chu, J.; Shi, L. Effects of carrier and Mn loading on supported manganese oxide catalysts for catalytic combustion of methane. *J. Nat. Gas Chem.*, **2008**, *17*, 159.
- [9] Trawczyńska, J.; Bielaka, B.; Mista, W. Oxidation of ethanol over supported manganese catalysts—effect of the carrier. *Appl. Catal. B Environ.*, **2005**, *55*, 277.
- [10] Finocchio, E.; Busca, G. Characterization and hydrocarbon oxidation activity of coprecipitated mixed oxides $\text{Mn}_3\text{O}_4/\text{Al}_2\text{O}_3$. *Catal. Today*, **2001**, *70*, 213.

- [11] Lahousse, C.; Bernier, A.; Grange, P.; Delmon, B.; Papaefthimiou, P.; Ioannides, T.; Verkios, X.J. Evaluation of γ -MnO₂ as a VOC removal catalyst: comparison with a noble metal catalyst. *J. Catal.*, **1998**, *178*, 214.
- [12] Baldi, M.; Escribano, V.S.; Amores, J.M.G.; Milella, F.; Busca, G. Characterization of manganese and iron oxides as combustion catalysts for propane and propene. *Appl. Catal. B Environ.*, **1998**, *17*, 175.
- [13] Craciun, R.; Dulamita, N. Influence of La₂O₃ promoter on the structure of MnOx/SiO₂ catalysts. *Catal. Lett.*, **1997**, *46*, 229.
- [14] Longya, X.; Quigxia, W.; Yide, X.; Jiashng, H. Promotion effect of K₂O and MnO additives on the selective production of light alkenes via syngas over Fe/silicalite-2 catalysts. *Catal. Lett.*, **1995**, *31*, 253.
- [15] El-Shobaky, G.A.; El-Khouly, S.M.; Ghozza, A.M.; Mohamed G.M. Surface and catalytic investigations of CuO-Cr₂O₃/Al₂O₃ system. *Appl. Catal. A*, **2006**, *302*, 296-304.
- [16] Craciun, R.; Nentwich, B.; Hadjiivanou, K.; Knözinger, H. Structure and redox properties of MnOx/Yttrium-stabilized zirconia (YSZ) catalyst and its used in CO and CH₄ oxidation. *Appl. Catal. A Gen.*, **2003**, *243*, 67.
- [17] Wojciechowska, M.; Przystajko, W.; Zieliński, M. Catal. CO oxidation catalysts based on copper and manganese or cobalt oxides supported on MgF₂ and Al₂O₃. *Today*, **2007**, *119*, 338.
- [18] F. Kapteijn, F.; van Langeveld, D.; Moulijn, J.A.; Andreini, A.; vuurman, M.A.; Turek, A.M.; Jehng, J.M.; Wachs, I.E. Alumina-supported manganese oxide catalysts I. Characterization: effect of precursor and loading. *J. Catal.*, **1994**, *150*, 94.
- [19] Strohmeier, B.R.; Hercules, J. Surface spectroscopic characterization of manganese/aluminum oxide catalysts. *J. Phys. Chem.*, **1984**, *88*, 4922.
- [20] Deraz, N.M. Influence of ceria on physicochemical, surface and catalytic properties of alumina supported manganese catalysts. *Colloids Surfaces A Physicochem. Eng. Aspects.*, **2009**, *335*, 8.
- [21] Mehandjiev, D.; Zhecheva, E.; Ivanov, G.; Ioncheva, R. Preparation and catalytic activity of nickel-manganese oxide catalysts with an ilmenite-type structure in the reactions of complete oxidation of hydrocarbons. *Appl. Catal. A*, **1998**, *167*, 277.
- [22] Wang, H.-T.; Xiao, T.-C.; Su, J.-X.; Liu, W.-X.; Lu, Y.-L. Catalytic purification of flue gas from civil-used stove. *Catal. Today*, **1999**, *53*, 661.
- [23] Agarwal, S.K.; Spivey, J.J. Deep oxidation of hydrocarbons. *Appl. Catal. A*, **1992**, *81*, 239.
- [24] Watanabe, N.; Yamashita, H.; Miyadera, H.; Tominaga, S.; Removal of unpleasant odor gases using an Ag-Mn catalyst. *Appl. Catal.*, **1996**, *8*, 405.
- [25] El-Shobaky, H.G.; Ahmed, A.S.; Radwan, N.R.E. Effect of γ -irradiation and ZnO-doping of CuO/TiO₂ system on its catalytic activity in ethanol and isopropanol conversion. *Colloids Surfaces A Physicochem. Eng. Aspects.*, **2006**, *274*, 138.
- [26] Zhou, J.-P.; He, H.-C.; Lin, Y.-H.; Nan, C.-W. Effect of ZnO-doping on the reaction between Co and Fe oxides. *Mater. Lett.* **2006**, *60*, 1542.
- [27] Radwan, N.R.E.; El-Shobaky, H.G.; El-Molla, S.A. Surface and catalytic properties of pure CeO₂ and MoO₃-doped NiO/TiO₂ system. *Appl. Catal. A Gen.*, **2006**, *297*, 31.
- [28] El-Shobaky, G.A.; Ghozza, A.M. Effect of ZnO doping on surface and catalytic properties of NiO and Co₃O₄ solids. *Mater. Lett.* **2004**, *58*, 699.
- [29] El-Shobaky, G.A.; Shouman, M.A.; Ibrahim, Sh.M. Surface and Catalytic Properties of Nanocrystalline Pure and Li₂O -Doped CoO/Mn₂O₃ System. *Open Catalysis J.*, **2009**, *2*, 46.
- [30] Doheim, M.M.; Hanafy, S.A.; El-Shobaky, G.A. Catalytic conversion of ethanol and isopropanol over the Mn₂O₃/Al₂O₃ system doped with Na₂O. *Mater. Lett.*, **2002**, *55*, 304.
- [31] El-Shobaky, H.G.; Shaheen, M.W. Effect of γ -irradiation and doping with MoO₃ and V₂O₅ on surface and catalytic properties of manganese oxides. *Radiat. Phys. Chem.*, **2003**, *66*, 55.
- [32] Nasr-Allah M. DERAZ, physicochemical, surface, and catalytic properties of pure and ceria-doped manganese/alumina catalysts. *Chin. J. Catal.*, **2008**, *29*(8), 687.
- [33] Sjoerd Kijlstra, W.; Biervliet, M.; Poels, E.K.; Blik, A. Deactivation by SO₂ of MnOx/Al₂O₃ catalysts used for the selective catalytic reduction of NO with NH₃ at low temperatures. *Appl. Catal. B Environ.*, **1998**, *16*, 327.
- [34] Doheim a, M.M.; El-Shobaky, H.G. Catalytic conversion of ethanol and iso-propanol over ZnO-treated CO₃O₄/Al₂O₃ solids. *Colloids Surfaces A Physicochem. Eng. Aspects.*, **2002**, *204*, 169.
- [35] Zaki, T. Catalytic dehydration of ethanol using transition metal oxide catalysts. *J. Colloid. Interface. Sci.*, **2005**, *284*, 606.
- [36] Noller, H.; Lercher, J.A.; Vinek, H. Acidic and basic sites of main group mixed metal oxides. *Mater. Chem. Phys.*, **1988**, *18*(5/6), 577.
- [37] Youssef, A.M.; Awad, A.I.; Samra, S.E. Surface and acidic properties of some mixed oxide catalysts in relation to their catalytic activities. *Mater. Lett.*, **1990**, *10*(4/5), 175.
- [38] Berteau, P.; Delmon, B.; Dalon, J.L.; Gysel, A.V. Acid-base properties of silica-aluminas: use of 1-butanol dehydration as a test reaction. *Appl. Catal.*, **1991**, *70*(2), 307.
- [39] Satoshi, S.; Masato, T.; Toshiaki, S.; Fumio, N. Catalytic and acidic properties of silica-alumina prepared by chemical vapour deposition. *Appl. Catal.*, **1990**, *62*(1), 73.
- [40] Mostafa, M.R.; Youssef, A.M.; Hassan, A.M. Conversion of ethanol and isopropanol on alumina, titania and alumina-titania catalysts. *Mater. Lett.* **1991**, *12*(3), 207.
- [41] Cullity, B.D. Element of X-Ray Diffraction, 3rd ed., Addison-Wesley, Reading, MA, **1967**.
- [42] El-Shobaky, G.A.; Fagal, G.A.; Hassan, N.A. Solid-solid interactions in pure and Na₂O-doped MoO₃/Al₂O₃ system. *Thermochimica Acta*, **1998**, *211*, 205.
- [43] Doheim, M.M.; Ahmed, A.S.; El-Boohy, H.A.; El-Shobaky, G.A. Activity and selectivity of manganese oxides in alcohols Conversion as influenced by gamma-irradiation. *J. Radio anal. Nucl. Chem. Articles*, **2002**, *254*, 583.