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Physicochemical properties and catalytic behavior of magnesia supported manganese oxide catalysts

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Abstract

A series of manganese oxides loaded on an active magnesia support was prepared by the calcination at 400–800 °C of magnesium carbonate impregnated with manganese nitrate solution. The extent of loading was varied between 16.55 wt.% and 61.34 wt.% Mn_2O_3. The samples obtained were characterized for the crystalline phase structure by X-ray powder diffractometry, the surface area by BET-analysis of nitrogen adsorption isotherms and the H_2O_2 decomposition activity by oxygen-gasometry of the reaction kinetics at 20–40 °C.

The results revealed that treatment of the Mn/Mg mixed oxide system with increasing amounts of manganese oxides followed by calcinations 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 these solids. This treatment 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 H_2O_2 decomposition reaction.

Keywords: MgO; X-ray powder diffractometry; BET-analysis; Catalytic activity

1. Introduction

Mixed oxides 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 oxides in various applications depends on the nature of the individual oxides [4], their respective ratios [1,5–8], their method of preparation [6], thermal treatment [1,5–8], and the doping with some foreign cations such as Li^+, Ag^+, Mg^{2+}, and 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. [5,10] 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 [6,16–21]. MgO support is capable forming a solid solution with some transition metal oxides due to facile diffusion of transition metal ions (T) into MgO support [22,23]. The oxide solid solution which are based MgO containing T are of special interest and are dependent on the role of electron configuration of T and the site a symmetry, T–T interaction, and also the participation of the matrix itself in the catalytic steps. It has been found that the activity per T ion varies 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 and preparation conditions

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[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 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

Four samples of manganese oxides loaded on active magnesia were prepared by impregnating a known amount of finely powdered magnesium basic carbonate with different amounts 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 6 h in each case. The amount of manganese employed, expressed as Mn_2O_3, varied between 16.55 and 61.34 wt.%. The prepared solid 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. All chemicals involved in the preparation of various catalyst samples were of analytical grade as supplied by Prolabo Company.

2.2. Techniques

An X-ray diffractograms of the different mixed solids thermally treated in air at 400, 600 and 800 °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 $2^\circ\ \text{min}^{-1}$.

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 the average particle size of the phase under investigation, B the Scherrer constant (0.89), λ the wavelength of the X-ray beam used, β the full-width half-maximum (FWHM) of diffraction peak, and Θ the diffraction angle.

The lattice parameter a of MgO phase present in the tested solids heated at various temperatures was based on the small shift in its diffraction lines and determined from the equation [32].

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

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.

The catalytic activity of the various catalysts was determined by studying the decomposition of H_2O_2 of known concentration diluted to 20 ml with distilled water. The reaction kinetics were mentioned by measuring the volume of oxygen gas liberated at different time intervals until equilibrium was attained.

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 of 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) [33], and solid–solid interaction between a small portion of Mn_2O_3 and magnesia yielding Mg_2MnO_4 according to:

$$4MgO + Mn_2O_3 + \tfrac{1}{2}O_2 \xrightarrow{600\,^\circ C} 2Mg_2MnO_4$$

(iii) The heat treatment of mixed solids at 800 °C led to formation of Mg_6MnO_8 together with MgO, Mn_2O_3, Mn_5O_8, and Mg_2MnO_4 phases. The formation of Mg_6MnO_8 took place according to: $12MgO+Mn_2O_3+1/2O_2$ 800 °C $2Mg_6MnO_8$; (iv) treatment of Mn/Mg mixed oxides system with increasing amounts of manganese oxide brought about a measurable increase in the degree of ordering of the resulting magnesium manganate compounds at 600

Table 1
The crystalline phases present in the thermal products of Mn/Mg mixed oxide solids calcined at 400–800 °C

Catalyst	Calcination temperature (°C)	Crystalline composition[a]
MgMn-I	400	MgO (j), γ-MnO_2 (d)
MgMn-II	400	MgO (j), γ-MnO_2 (d)
MgMn-III	400	MgO (j), γ-MnO_2 (d)
MgMn-IV	400	MgO (j), γ-MnO_2 (d)
MgMn-I	600	MgO (j), Mn_2O_3 (partirdgeite, d), Mg_2MnO_4 (t)
MgMn-II	600	MgO (j), Mn_2O_3 (partirdgeite, d), Mg_2MnO_4 (m)
MgMn-III	600	MgO (j), Mn_2O_3 (partirdgeite, d), Mg_2MnO_4 (d)
MgMn-IV	600	MgO (j), Mn_2O_3 (partirdgeite, d), Mg_2MnO_4 (j)
MgMn-I	800	MgO (j), Mn_2O_3 (partirdgeite, d), Mn_5O_8 (t), Mg_2MnO_4 (m), Mg_6MnO_8 (t)
MgMn-II	800	MgO (j), Mn_2O_3 (partirdgeite, d), Mn_5O_8 (t), Mg_2MnO_4 (d), Mg_6MnO_8 (m)
MgMn-III	800	MgO (j), Mn_2O_3 (partirdgeite, d), Mn_5O_8 (t), Mg_2MnO_4 (j), Mg_6MnO_8 (d)
MgMn-IV	800	MgO (j), Mn_2O_3 (partirdgeite, d), Mn_5O_8 (t), Mg_2MnO_4 (j), Mg_6MnO_8 (d)

[a] d: dominant, j: major, m: minor, and t: trace.

and 800 °C. These results could be attributed to enhanced increase in the mobility of magnesium and manganese ions.

3.2. Particle size and lattice parameter analyses

The effect of the concentration of manganese oxides and calcination temperature on the lattice parameter *a* and the particle size of MgO have been investigated and the results obtained are given in Table 2. It is clear from Table 2 that: (i) The lattice parameter and particle size of MgO phase present in the investigated mixed oxide solids calcined at 400, 600, and 800 °C increase by increasing both the calcination temperature and amount of manganese oxide present. this increase was more pronounced for the mixed oxide solids calcined at 800 °C. (ii) The extent of increase in the lattice parameter and the particle size of MgO phase decrease progressively by increasing the calcination temperature of the investigated solids. The maximum increase in the particle size and the lattice parameter of MgO phase due to treatment with increasing amounts of manganese oxide attained 91, 49, and 17% and 26.4×10^{-2}, 18.8×10^{-2}, and 13×10^{-2}% for the solids calcined at 400, 600, and 800 °C, respectively.

Table 2
Lattice parameter and particle size of MgO phase present in various Mn/Mg mixed oxide solids calcined at 400–800 °C

Catalyst	Calcination temperature (°C)	Lattice parameter (Å)	Particle size (Å)
MgMn-I	400	4.2005	70
MgMn-II	400	4.2028	85
MgMn-III	400	4.2063	98
MgMn-IV	400	4.2116	134
MgMn-I	600	4.2132	110
MgMn-II	600	4.2152	109
MgMn-III	600	4.2169	130
MgMn-IV	600	4.221	164
MgMn-I	800	4.2168	180
MgMn-II	800	4.2188	189
MgMn-III	800	4.2205	195
MgMn-IV	800	4.2223	210

The observed increase in both the lattice parameter and the particle size due to increasing the amount of manganese oxide present in the tested solids might be attributed to dissolution of some of manganese oxides in the lattice of MgO forming MnO–MgO solid solution having the formula $Mn_xMg_{1-x}O$. In fact, the ionic radii of Mg^{2+} and Mn^{2+} are 0.65 and 0.80 Å, respectively [32]. So, the dissolution of a small amount of manganese oxide in the lattice of MgO should be normally accompanied by an expansion in its lattice with subsequent increase in the lattice parameter and the particle size of MgO phase. The decrease in the extent of augmentation of the lattice parameter and the particle size of MgO phase due to increasing the heat treatment in the range of 400–800 °C could be attributed to solid–solid interactions between Mn and Mg oxides at temperatures of 600 °C and above to produce magnesium manganate compounds.

The computed values of the particle size of MgO present in the different mixed oxide solids calcined at 400, 600, and 800 °C allowed the calculation of the activation energy of sintering of MgO via direct application of the Arrhenius equation

$$d = A \exp\left(-\frac{E_s}{RT}\right)$$

where *d* is the particle size of MgO calcined at temperature *T*, *A* the frequency factor of Arrhenius equation and E_s is the activation energy of sintering process of MgO. This equation can be converted into the following form:

$$\ln d = \ln A - \frac{E_s}{RT}$$

Plotting $\ln d$ against $1/T$ in the range of 400–800 °C for different solids as given in Fig. 1, a straight line is obtained whose slope determines the value of E_s. The computed values of E_s were found to be 25, 22, 17, and 15 kJ/mol for MgMn-I, MgMn-II, MgMn-III, and MgMn-IV, respectively. These values indicate that increasing the amount of manganese oxides in the system up to 61.34 wt.% brought about a decrease in E_s of 40% demonstrating that the manganese species increased the sinterability of the magnesia

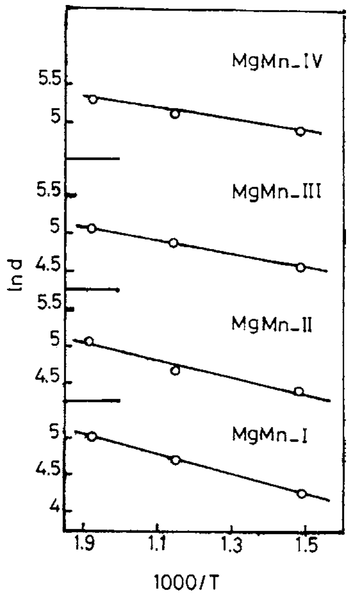

Fig. 1. Variation of ln *d* with 1/*T* for various Mn/Mg mixed solids.

support i.e. manganese oxides when present over the range 16.55–61.34 wt.% facilitated the sinterability of Mn/Mg mixed oxide solids. Thus, the sintering process is normally accompanied by grain growth of a catalyst support, thereby reducing the specific surface area of the investigated system [5].

3.3. BET surface area

The specific surface area of the various solids was determined via BET-analysis [34] of nitrogen adsorption isotherms measured at −196 °C. The effect of the calcination temperature and the extent of loading on the specific surface area is better represented by plotting the values of S_{BET} for the different adsorbent as a function of both the calcination temperature and the amount of manganese oxide present in the system. The results obtained are illustrated graphically in Figs. 2 and 3 which clearly indicate that the specific surface areas of the MgO-supported manganese oxides decreased on increasing both the calcination temperature from 400 to 800 °C and the amount of manganese oxides present. This decrease was more pronounced for the mixed solids containing 61.34 wt.% Mn_2O_3 and calcined at 800 °C.

The decrease in the specific surface area of given porous solids due to an increase in the calcination temperature could be attributed to grain growth of their particles [5,35]. The fact that the particle size of MgO phase increased by increasing both the calcination temperature and the amount of Mn oxides present. However, another factor cannot be overlooked is the effect of solid–solid interaction between the manganese and magnesium oxides. Conversion of a portion of the magnesia into magnesium manganate compound via the interaction with Mn_2O_3 might decrease the specific surface of the tested solid. In fact, XRD measurements revealed that the formation of magnesium manganate compounds increased to an extent proportional to the amount of manganese present. Similar results have been reported by Deraz, in the case of Mn/Al mixed oxide solids [5].

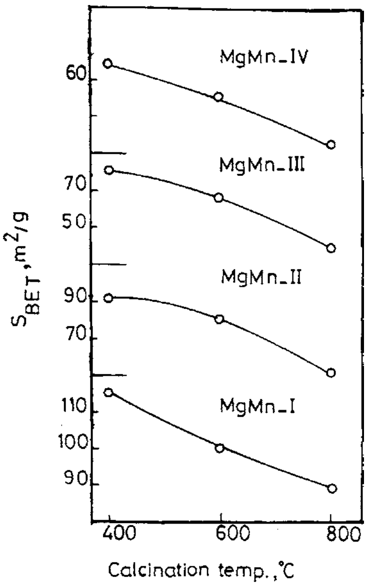

Fig. 2. Variation of S_{BET} as a function of calcination temperature for various Mn/Mg mixed solids.

3.4. Hydrogen peroxide decomposition activity

Preliminary experiments showed that MgO calcined at 400–800 °C showed no measurable catalytic activity for H_2O_2 decomposition conducted at temperatures up to 40 °C.

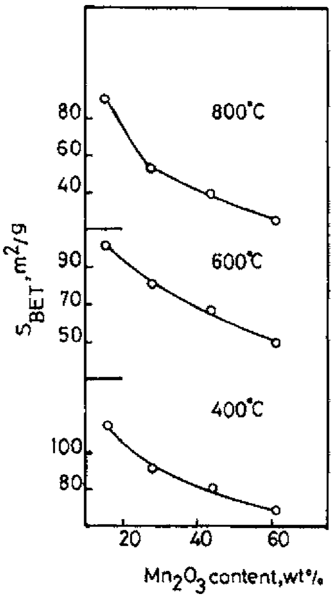

Fig. 3. Variation of S_{BET} as a function of Mn_2O_3 content for various Mn/Mg mixed solids calcined at 400, 600, and 800 °C, respectively.

Table 3
Activation energy for catalytic decomposition of H_2O_2 over various mixed oxides calcined at 400, 600, and 800 °C

Catalyst	Calcination temperature (°C)	E_a (kJ mol^{-1})	Reaction temperature (°C)
MgMn-I	400	25	20–30
MgMn-II	400	19	20–30
MgMn-III	400	14	20–30
MgMn-IV	400	7	20–30
MgMn-I	600	32	20–40
MgMn-II	600	25	20–40
MgMn-III	600	19	20–40
MgMn-IV	600	12	20–40
MgMn-I	800	40	20–40
MgMn-II	800	31	20–40
MgMn-III	800	15	20–40
MgMn-IV	800	18	20–40

However, the unloaded manganese oxides obtained after thermal treatment of manganese nitrate at 400 °C exhibited excellent catalytic activity for H_2O_2 decomposition at temperatures starting from 20 °C. But the solid lost its catalytic activity completely on heating in air at temperatures above 600 °C. These results may be attributed to enhanced sintering of the manganese oxide crystallites and clearly indicate the necessity of using a catalyst support [5]. Hence, the magensia is considered to be a convenient support material for this reaction and manganese oxides and various magnesium manganate compounds represent the catalytically active constituents of the investigated system.

The kinetic of H_2O_2 decomposition in the presence of the various solids calcined at 400, 600, and 800 °C were monitored by measuring the volume of O_2 librated at different time intervals at a fixed temperature until equilibrium was attained. Such catalytic reactions were carried at 20–40 °C and in all cases the reactions were found to follow first-order kinetics. It was possible to determine the value of reaction rate constant (k) in the presence of a given solid catalyst under specified conditions from the slopes first-order plots. Such values of k enabled the activation energy (E_a) for H_2O_2 decomposition to be calculated the corresponding values being listed in Table 3. It is clear from this table that the E_a for most solids calcined at temperatures ranging between 400 and 800 °C decreased. This confirms the observed increase in the catalytic activity of these solids as a result of the treatment with increasing amounts of Mn oxides. However, the magnitude of the catalytic reaction rate constant per unit surface area ($\bar{k}$) was considered in order to avoid the change in the value of S_{BET} of various catalysts.

The effect of manganese content on the catalytic activity of the different solids calcined at 400, 600, and 800 °C is well illustrated by Fig. 4. This figure represents the relationship between the reaction rate constant per unit surface area at 30 °C ($\bar{k}_{30\,^\circ C}$) as a function of manganese content for solid catalysts calcined at different temperatures.

It is clear from this figure that initially $\bar{k}_{30\,^\circ C}$ increased progressively as a function of the amount of manganese present. The maximum increase in the $\bar{k}_{30\,^\circ C}$ due to the treatment with increasing amounts of Mn oxides attained 153, 192, and 283% for the solids calcined at 400, 600, and 800 °C, respectively.

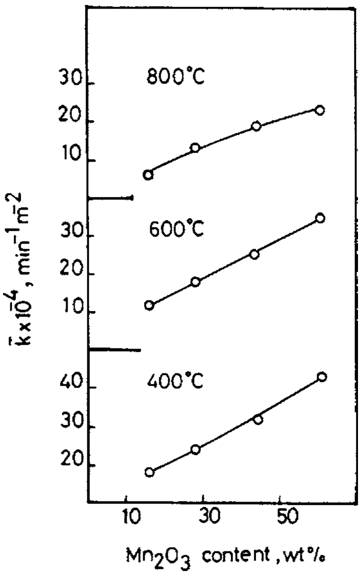

Fig. 4. Variation of $\bar{k}$ for H_2O_2 decomposition at 30 °C as a function of Mn_2O_3 content for various Mn/Mg mixed solids calcined at different temperatures.

The effect of calcination temperature on the catalytic activity of the above various solids is better represented by plotting the values of $\bar{k}_{30\,^\circ C}$ for the catalysis of H_2O_2 decomposition as a function of the calcination temperature. The results obtained are depicted in Fig. 5, which clearly indicates that $\bar{k}_{30^\circ C}$ decreased on increasing the calcination temperature of the different supported solid catalysts. This decrease was most pronounced for solid containing 61.34 wt.% Mn_2O_3 and calcined at 800 °C.

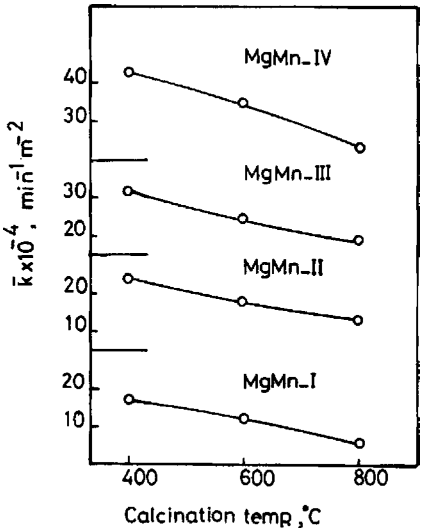

Fig. 5. Variation of $\bar{k}$ for H_2O_2 decomposition at 30 °C over calcined at different as a function of their calcination temperature.

The observed decrease in the catalytic activity may be discussed in the following terms:

1. Conversion of MnO_2 into Mn_2O_3 by increasing the calcination temperature up to 600 °C. It is well known that MnO_2 possesses the highest catalytic activity amongst transition metal oxides towards H_2O_2 decomposition [5,36].
2. Formation of sintered Mn_2O_3 crystallites [5,37,38].

The induced increase in the catalytic activity by increasing the amount of manganese present in the samples from 16.55 to 61.34 wt.% is to be expected as a result of the progressive increase in the concentration of the catalytically active part of the catalyst (manganese oxides and magnesium manganate compounds). Indeed, XRD studies showed that the formation of magnesium manganate compounds at temperatures starting from 600 °C increased by increasing the amount of Mn_2O_3 present. However, Hasan et al. have been reported that the mixed and composite manganese oxide catalysts are generally more active than the pure catalyst. These authors were found that the $NiMnO_x$ containing $NiMnO_3$ as major bulk phase and exposing mixed valency metal–oxygen surface species is shown to assume the highest H_2O_2 decomposition activity [37].

4. Conclusions

The following are the main conclusions arising from the results obtained:

1. Loading an magnesia surface with manganese in amounts varying between 16.55 and 61.34 wt.% Mn_2O_3 led to the formation of thermally stable solids that were active towards H_2O_2 decomposition.
2. The specific surface areas of Mn/Mg mixed oxide solids were found to decrease on increasing both the amount of manganese present and the calcination temperature. This decrease could be attributed to an increase in the particle size of the mixed solids.
3. The catalytic activity of Mn/Mg mixed oxide system increased progressively on increasing the manganese content from 16.55 to 61.34 wt.% Mn_2O_3 and also decreased by increasing the calcination temperature from 400 °C to 800 °C. The increase in catalytic activity was attributed to an increase the concentration of catalytically active sites (manganese and magnesium mangantes). On the other hand, the decrease in H_2O_2 decomposition activity resulted from conversion MnO_2 into sintered Mn_2O_3.
4. Manganese oxides were found to facilitate the sinterability of Mn/Mg mixed oxides to an extent proportional to their amount present.
5. Treatment of Mn/Mg mixed oxide system with increasing amounts of manganese followed by calcination at 400–800 °C led to a progressive decrease in the activation energy of H_2O_2 decomposition reaction. This decrease corresponds to the observed increased in the catalytic activity of such solids.

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