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Mesoporous MgO: Synthesis, Physico-Chemical, and Catalytic Properties¹

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Abstract—Mesoporous MgO was obtained via the hydrothermal synthesis using both ionogenic and non-ionogenic surfactants as structure-directing templates. The materials prepared were characterized by SEM, BET-N₂, XRD, and TG-DTA techniques. MgO particles are spherical 20- μ m aggregates of primary oxide particles well shaped as rectangular parallelepipeds. Magnesium oxide samples have the specific surface area of 290–400 m²/g and pore sizes of 3.3–4.1 nm. Their mesoporous structure remained unchanged after calcination up to 350°C. Catalytic activity of mesoporous MgO was studied in acetone condensation reaction.

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1. INTRODUCTION

Unlike the majority of mixed metal oxides, which are acidic in nature, such as silica-alumina, molecular sieves and the like, magnesium oxide catalysts and supports belong to a few solids which are weakly basic. Magnesium oxide is commonly used in the oxidation of ketones to lactones and dehydrogenation of propane over V_2O_5/MgO , in the manufacture of biodiesel, desulfurization of fuels using CoMo/MgO and NiMo/MgO catalysts, in environmental catalysis for the destruction of organophosphonates and chlorohydrocarbons, for the trapping of sulfur and carbon dioxides, and of azo dyes, as well [1–8].

Ordinary hydrothermal method of MgO production through hydroxide precipitation affords a product with a rather low surface area (no more than $100 \text{ m}^2/\text{g}$) which restricts severely its practical use. Meanwhile, a template synthesis developed in the mid-1990s to produce mesoporous molecular sieves with a high surface area and spatially ordered system of nanoscale pores, has been later successfully extended to the synthesis of non-silicate materials, including mesoporous magnesium oxide [9–12].

On applying the so called "hard" templates such as SBA-15 and CMK-3 molecular sieves in the synthesis of magnesium oxide, a structured mesoporous MgO material having a surface area of $250 \text{ m}^2/\text{g}$ could be obtained [1]. However, such two-step synthesis seems to be both a time-consuming and somewhat costly one. In contrast, the use of "soft" ionogenic or non-ionogenic templates such as cetyltrimethylammonium

bromide (CTMABr) or triblock copolymer (P123), respectively, simplifies substantially the technology to produce mesoporous MgO and thus reduces production costs.

In this regard, the aim of this work was to develop a simple and relatively inexpensive method of template synthesis of mesoporous MgO with high surface area and thermally stable mesostructure.

2. EXPERIMENTAL

2.1. Mesoporous MgO Catalyst Preparation

Magnesium nitrate hexahydrate $Mg(NO_3)_2 \cdot 6H_2O$, urea $(NH_2)_2CO$, cetyltrimethylammonium bromide (CTMABr) and Pluronic 123 block-copolymer (P123) were used. Template synthesis with CTMABr was performed as follows. 7.50 g of CTMABr was dissolved in 150 mL of water at 40°C. Then, 10.0 g of magnesium nitrate and 2.34 g of urea were added with vigorous stirring. The mixture was transferred to an autoclave and heated at 110 or 150°C for 48 h. In a parallel synthesis, 20.0 g of magnesium nitrate and 4.68 g of urea were added to the same template solution, the resulting mixture being further treated as indicated above.

The way the synthesis performed using the nonionogenic P123 was somewhat different. 8.00 g of P123 was dissolved in 250 mL of water at 40°C and the resulting solution was sonicated in the ultrasonic bath SUNKKO 3050A (50 W, 40 kHz) for 100 min. Then, 10.0 g of magnesium nitrate and 2.34 g of urea were added, and the mixture was kept in an autoclave for

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Fig. 1. XRD patterns of MgO samples obtained using P123 at 110°C (a) and 150°C (b), and CTMABr at 110°C (c).

48 h at 110° C; in a parallel synthesis, the same mixture was heated at 150° C.

As a reference sample, magnesium oxide was synthesized without template.

The resulting precipitates were filtered, washed several times with hot distilled water and dried at 110°C for 24 h. Template was then removed by the calcination of air-dry samples at 350 or 550°C for 3 h.

2.2. Catalyst Characterization

X-ray diffraction analysis was performed on a diffractometer Stoe Stadi P ($\lambda = 1.5418$ Å) in the range of $2\theta = 15^{\circ} - 75^{\circ}$ with the steps of 0.05°. Standard data processing according to the WINXPOW program included smoothing and background subtraction followed by determination of the reflex positions and relevant spacings. Adsorption measurements were performed on automatic analyzer ASAP 2000N (Micromeritics). Before the measurement, sample was evacuated at 350°C and a pressure of 10⁻³ mm Hg for 2 h. The thermal stability of the resulting samples was studied with the use of SDT Q600 TA Instruments derivatograph. 20 mg of the air-dry sample was placed in a corundum crucible and heated in the air stream. DSC-TG curves were recorded at the linear temperature rise of 10 K/min in the range 20-800°C. SEM micrographs were obtained with an electron microscope MIRA3 TESCAN.

The catalytic activity of the mesoporous sample of magnesium oxide calcined at 500° C was evaluated in a gas phase conversion of acetone into isophorone. It was carried out in a flow system at 500° C, 0.101 MPa, and acetone WHSV of 2 h⁻¹. The composition of the reaction products was determined by GLC on a Kristal 2000M apparatus.

3. RESULTS AND DISCUSSION

XRD pattern for the synthesized MgO samples are shown in Fig. 1. Two peaks at $2\theta = 43^{\circ}$ and 62° indicate the formation of MgO phase. Also, the reflex at $2\theta = 21^{\circ}$ accounts for the presence of Mg(OH)₂ phase, however its low intensity suggests MgO being a predominant phase in the prepared material. Besides, the broadened reflections indicate small particle size of the synthesized material.

Noteworthy, the positions of main peaks in XRD patterns for the three samples of magnesium oxide are similar to those for the periclase-type phase. This also evidences that the use of templates of different in nature does not affect the final phase composition of MgO material.

Figure 2 shows the low-temperature N_2 adsorption-desorption isotherms obtained for MgO samples. SEM micrographs of these samples are given in Fig. 3, and their textural and morphological characteristics are summarized in table.

The identifying features of N_2 adsorption isotherms on magnesium oxide synthesized at two different temperatures using both CTMABr and P123 templates are characteristic of type IV mesoporous materials according to IUPAC classification. All samples exhibit the wide hysteretic loops of E-type by de Boer's classification [13] in 0.4–0.8 range of the relative pressure (*a*–*d* adsorption–desorption isotherms in Fig. 2). This type of hysteresis is due to the bottle-shape pores with narrow equisized openings but with the different diameters of pores in their wide part.

On lowering the synthesis temperature down to 110° C, another narrow hysteresis loop of C-type appears on the adsorption-desorption isotherms in the range of p/p_0 from 0.8 to 1.0 for all samples (isotherm *a* and *b*). Such a loop is characteristic of slit-shaped pores. As to the reference MgO sample which was syn-



Fig. 2. N₂ adsorption-desorption isotherms of the samples prepared using P123 (*a*, *b*) at 110°C (*a*), 150°C (*b*), CTMABr (*c*, *d*) at 110°C (*c*), 150°C (*d*), and of the reference sample (*e*).

thesized without template, it has no mesopores at all (isotherm *e* in Fig. 2).

Thus, on performing the hydrothermal synthesis at 150° C and using non-ionogenic P123 template, the magnesium oxide with specific surface area of $300 \text{ m}^2/\text{g}$ and with equisized mesopores could be prepared (table).

On the other hand, the hydrothermal synthesis at 150° C in the presence of ionogenic CTMABr template yields a material with rather low specific surface area (isotherm *d*) which is very close to that for the reference sample prepared without template: 23 and 22 m²/g, respectively (table). This result seems to be connected with the features of micelle formation in

the solutions of an ionogenic template which depends not only on surfactant concentration but also on the temperature of reaction. This assumption is confirmed by the textural data obtained for the sample synthesized in the presence of the same CTMABr template but at a temperature of 110°C (isotherm *c* in Fig. 2). Indeed, this sample has the largest surface area of ca. $400 \text{ m}^2/\text{g}$ and two types of pores, i.e., both bottle and slit types.

Apart from the synthesis temperature and the type of surfactant used as a template, the starting concentration of components represent not less important factor for the formation of MgO mesoporous structure. Thus, on doubling the amount of reagents used, the specific surface area of the synthesized material increases almost by 4 times (samples 4 and 5 in table), the shape of adsorption-desorption isotherm being the same.

This very fact is evident to reflect the strong influence of reactant starting concentrations on the rate of hydroxide precipitation and as a consequence on the number of nucleation centers for the metal hydroxide deposition which leads to a reduction in the size of its primary particles.

There is no doubt, a crucial factor that determines ultimately the most important textural characteristics of a prepared material—specific surface area and pore size, are the conditions of the final stage, i.e., its annealing to remove the spent template from of the assynthesized porous solid. The textural characteristics of sample 3 (table) calcined at two different temperatures are as follows:

Temperature, °C	$S, m^2/g$	D _{pore} , nm
350	395	3.8
550	130	5.5

It is evident, the more severe conditions of annealing the stronger degradation of mesoporous MgO tex-



Fig. 3. SEM images of mesoporous MgO prepared at 110°C using CTMABr template.

No.	Template	Synthesis conditions	Crystal morphology ^a	D _{pore} , nm	<i>S</i> , m ² /g
1	P123	110°C, US ^b	Fine white spheres	4.1	336
2	P123	150°C, US	Fine white spheres	3.4	338
3	CTMABr	110°C	Fine white spheres	3.8	395
4	CTMABr	150°C	Fine white spheres	3.3	23
5 ^c	CTMABr	150°C	Large white spheres	3.7	88
6	—	150°C	White powder	—	22

Characteristics of mesoporous MgO samples

^a Annealing at 350°C, ^b sonicated template solution, ^c double amounts of both magnesium nitrate and urea used.

ture: pore size increased and surface area decreased sharply, although it did remain considerable.

The results of thermogravimetric study on the mesoporous MgO samples are shown in Fig. 4. In the reference sample obtained without template (Fig. 4, profile a'), endoeffect in the range $100-130^{\circ}$ C is due to water removal; two endopeaks at 375 and 425°C are owing to conversion of Mg(OH)₂ and decomposition of MgCO₃ impurity, respectively [14].

TG-DSC study was performed with MgO samples synthesized applying with both P123 (Fig. 4, curve b') and CTMABr (Fig. 4, curve c') templates. In both cases, the endothermic peaks at 400–440°C originate from the decomposition of magnesium hydroxide and carbonate mixture. In addition to these peaks, the exothermic effects at 490 and 525°C are also present and correspond to complete combustion of P123 and CTMABr templates, respectively. In the case of P123 template used, exopeak at 230°C and endopeak at 285°C are present at TG-DSC profiles. They are probably due to the partial oxidation of pure organic



Fig. 4. DSC-TG profiles of MgO samples prepared without template (a, a') and using P123 (b, b') and CTMABr (c, c').

template, and decomposition of pure organic template, respectively.

Thus, the results of thermal analysis and adsorption measurements showed that the P123 non-ionogenic template seems to be preferred for the synthesis of mesoporous MgO at 150°C: the obtained solid has high surface area and uniform pores; besides, the surfactant applied in the synthesis could be removed at a lower temperature than in the case of CTMABr ionogenic template.

The catalytic activity in the condensation of acetone was evaluated using the sample 3 of mesoporous MgO (table). The catalytic conversion of acetone is well documented to be a multistep process [15]. Diacetone alcohol as a primary product of acetone selfcondensation then successively converts into secondary mesityl oxide, wherein both steps occur upon both the acidic and basic active centers. Furthermore, mesityl oxide gives isobutylene and acetic acid on acidic active sites.

In the presence of the basic centers, acetone conversion occurs to give a large variety of cyclization products, in particular, isophorone and methyl phenols. As it was shown by GLC analysis, at about 40% acetone conversion on mesoporous MgO isophorone and methylphenol were formed with a selectivity of about 33% while the selectivity to isobutylene is 3% only. This ratio of product selectivity enables one to conclude that the surface of mesoporous magnesium oxide possesses sufficient number of strong basic centers and at the same time a small amount of aprotic acidic centers.

4. CONCLUSION

Thus, the nature of template, the synthesis temperature, the concentration of starting reactants and conditions to remove the spent templates are all key factors to obtain mesoporous MgO catalysts having a surface area of about 400 m²/g. Morphology of magnesium oxide particles is seemed to be very peculiar: they are the 20- μ m spherical aggregates of primary nanoparticles composed of primary oxide species in the form of rectangular parallelepipeds. The prepared

mesoporous MgO showed good activity and selectivity in the catalytic conversion of acetone to isophorone and other products that require the presence of both basic and acidic active sites.

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REFERENCES

- 1. J. Li, W.-L. Dai, and K. Fan, J. Phys. Chem. C 112, 17657 (2008).
- 2. C. Pak, A. T. Bell, and T. D. Tilley, J. Catal. **206**, 49 (2002).
- 3. T. Klicpera and M. Zdražil, J. Catal. 206, 314 (2002).
- 4. M. Bhagiyalakshmi, J. Y. Lee, and H. T. Jang, Int. J. Greenhouse Gas Control **4**, 51 (2010).
- I. V. Mishakov, A. F. Bedilo, R. M. Richards, et al., J. Catal. 206, 40 (2002).

- C. Gao, W. Zhang, H. Li, et al., Cryst. Growth Des. 8, 3785 (2008).
- X. Li, W. Xiao, G. He, et al., Colloids Surf. A: Physicochem. Eng. Asp. 408, 79 (2012).
- H. Jeon, D. J. Kim, S. J. Kim, and J. H. Kim, Fuel Process. Technol. 116, 325 (2013).
- 9. D. Gu and F. Schüth, Chem. Soc. Rev. 43, 313 (2014).
- Y. Shi, Y. Wan, and D. Zhao, Chem. Soc. Rev. 40, 3854 (2011).
- 11. P. T. Huyen, E. Callone, R. Campostrini, et al., Eur. Phys. J. Appl. Phys. **64**, 10405 (2013).
- 12. G. Wang, L. Zhang, H. Dai, et al., Inorg. Chem. 47, 4015 (2008).
- 13. Physical and Chemical Aspects of Adsorbents and Catalysts, Ed. by B. G. Linsen (Academic, New York, London, 1970; Mir, Moscow, 1973).
- 14. G. I. Kapaev, Cand. Sci. (Chem.) Dissertation (Russ. Chem. Technol. Univ., Moscow, 2009).
- 15. G. S. Salvapati, K. V. Ramanamurty, and M. Janardanarao, J. Mol. Catal. **54**, 90 (1989).