

Use of MgO to promote the oxyethylation reaction of lauryl alcohol

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Synthesis of magnesium hydroxide was performed by the precipitation method with the use of magnesium sulfate and sodium hydroxide. The influence of temperature and ratio of reagents was studied. Magnesium hydroxides, and the magnesium oxides obtained from them by thermal decomposition, were analyzed to determine their bulk density, polydispersity and particle size. The magnesium oxide with the largest surface area was tested as a catalyst in the oxyethylation of lauryl alcohol, and shown to be selective but poorly reactive in comparison with commercially available catalysts. Further studies are needed to improve its reactivity.

Keywords: magnesium hydroxide and oxide, precipitation, dispersive and structural properties, oxyethylation, catalytic activity.

INTRODUCTION

Magnesium hydroxide is one of the important precursors of magnesium oxide. It has also been successfully used as a neutralizer of acidic pollutants of water and gas, and as a bactericide¹. Its non-toxicity and high thermal stability make it suitable as an agent for reducing the flammability of polymer materials. The vast scientific and technological literature on the use of magnesium hydroxide as a new generation flame retardant provides evidence of the growing interest in this inorganic filler^{2,3}.

Magnesium oxide has recently become a subject of considerable interest because of its unique properties. MgO has found wide applications as a catalyst, as a refractory material, and in optically transparent ceramics windows⁴⁻⁶. In catalysis, magnesium oxide with large surface area and nanocrystalline structure has promising applications as a catalyst support for certain reactions, such as dry reforming, dehydrohalogenation, and oxidative dehydrogenation of butane⁷⁻⁹. The high efficiency of nanoparticle oxides results not only from their high surface area, but also from a high concentration of low-coordinated sites and structural defects on their surface¹⁰. As the particle size is scaled down to few nanometers, the constituting atoms are set in highly defective coordination environments. Most of the atoms have unfilled valencies and reside at the surface. Depending on preparation methods, MgO can exhibit quite different reactivity toward adsorbed chemicals. Therefore, a large surface area material having the most defect sites per unit area should be of interest as a catalyst and catalyst support.

Coluccia and Tench proposed a surface model for MgO¹¹ according to which there are several Mg–O ion pairs of different coordination numbers. The ion pairs of low coordination numbers are set at corners, edges, or high Miller index surfaces of the plane. Different basic sites generated by increasing the pretreatment temperature appear to correspond to the ion pairs of different coordination numbers. However, the correspondence between the catalytically active sites for different

reaction types and the coordination number of the ion pairs has not yet been definitely confirmed.

This paper presents the results of an investigation of Mg(OH)₂ and MgO synthesis by the precipitation method with the use of magnesium sulfate. The effect of selected process conditions on the physicochemical properties of magnesium hydroxide and oxide was analyzed. The magnesium oxide obtained, which had good dispersive properties and large surface area, was tested as a catalyst in the oxyethylation of lauryl alcohol. These tests were motivated by the need for effective, specific catalytic compounds, homogeneous or heterogeneous, to enable such reactions. The direct introduction of ethylene oxide is not possible; it requires the use of a catalyst to activate the substrate or the ethylene oxide itself¹². A potential catalyst must be easily removable from the product, so that it does not become an impurity. The calcium-based catalysts described in the literature have long induction times, which makes them less desirable for industrial applications¹³. Keeping the reagents, particularly ethylene oxide, at high temperature and raised pressure for a long time may lead to an uncontrolled reaction path. Moreover, oxyethylation reactions are important in industry, among other things because they can produce non-toxic, environmentally friendly surfactants¹⁴.

Magnesium oxide satisfies all of the conditions for an effective catalyst. According to literature reports, as a catalyst it is active, selective (in view of the defective microstructure and the existence of acid-base sites), high-yielding and non-toxic, with a large surface area^{7-9, 15, 16}.

EXPERIMENTAL

Synthesis of Mg(OH)₂ and MgO

The substrates used were hydrated magnesium sulfate (analytical grade) and sodium hydroxide (also of analytical grade) in the form of solutions of appropriate concentrations, produced by POCh SA, Poland. Precipitation of magnesium hydroxide was performed in a reactor of 500 cm³ capacity equipped with a high-speed propeller

stirrer (Eurostar Digital IKA-Werke GmbH, Germany, 1800 rpm). The reaction system was thermostated in a water bath made by Julabo Labortechnik GmbH, Germany. The process temperatures used were 20, 40, 60, and 80°C. The reagents at appropriate concentrations were dosed simultaneously into the water system by means of a peristaltic pump (ISM 833A, Ismatec, Switzerland). Use of the pump permitted the maintenance of a constant substrate supply rate of 2.3 cm³/min. The concentration of the magnesium sulfate solutions was 5%. The quantity of sodium hydroxide in the solutions was determined for the stoichiometric ratio (1:1) of the reagents. As the influence of excess quantities of the reagents was also to be studied, we used reaction mixtures with reagent ratios of 1.5:1, 2:1 (excess salt), and 1:1.5 (excess sodium hydroxide).

The magnesium hydroxide precipitate was filtered off, washed and dried by the convection method or by static drying at 105°C for 6 h (in a chamber drier made by Memmert). The dried intermediate product (magnesium hydroxide) was subjected to gradual calcination in an electric furnace (Controller P320 MB1, Nabertherm GmbH, Germany) at 450°C for 2 h to obtain magnesium oxide.

Characterization of the catalysts

For all magnesium hydroxide samples and MgO, first the bulk density was determined. Bulk densities were determined using a WE-5 electromagnetic volumeter (Poland). Then the particle size distributions of the samples were determined, using a Zetasizer Nano ZS and Mastersizer 2000 (both from Malvern Instruments Ltd., UK), permitting measurements of particle diameters in ranges of 0.6–6000 nm (non-invasive backscattering technique – NIBS) and 0.2–2000 µm (laser diffraction technique) respectively. Cumulant analysis gives a width parameter known as the polydispersity, or the polydispersity index (PDI). In order to characterize parameters of the porous structure, nitrogen adsorption/desorption isotherms at 77 K and surface area (A_{BET}), pore volume (V_p) and average pore size (S_p) were determined using an ASAP 2020 (Accelerated Surface Area and Porosimetry) instrument (Micromeritics Instrument Co., USA). The surface area was determined by the multipoint BET method using the adsorption data under relative pressure (p/p_0). The BJH algorithm was applied to determine the pore volume and the average pore size.

Catalytic activity of MgO

The catalytic activity of magnesium oxide in the oxyethylation of lauryl alcohol was tested in a pressure system. The process of oxyethylation was carried out in a pressure reactor 2 dm³ in capacity (Autoclave Engineers, USA), made of acid-resistant steel. The reagents used were 98% pure lauryl alcohol (Sigma-Aldrich, Germany), and ethylene oxide from ChemoGas NV Belgium, of minimum purity 99.9%.

Syntheses of the oxyethylation of lauryl alcohol were carried out using the produced MgO as a catalyst, and using industrial catalysts for comparison purposes: a calcium catalyst (K-4/XII-O, no. 8/06, ICSO Blachownia, Poland) and NaOH (Sigma-Aldrich, Germany). Identical parameters were preset for all syntheses performed, as listed in Table 1.

Table 1. Preset parameters for the process of oxyethylation of lauryl alcohol

Name of substrate	lauryl alcohol
Mass of substrate used	300 g (1.5 mol)
Molar weight of substrate	198 g/mol
Average degree of oxyethylation	3
Catalyst	MgO
Mass of catalyst used	1.25 g (0.25% product)
Mass of ethylene oxide (assumed)	200 g (4.5 mol)
Synthesis temperature	185°C ± 5°C
Synthesis pressure, max.	400 kPa
Synthesis pressure, min.	300 kPa
Time of heating after synthesis	60 min

First the reactor was charged with 300 g of hydrophobic substrate and a catalyst in a quantity of 0.25% with respect to the product mass. After increasing the reactor temperature to 185°C, automatic dosing of ethylene oxide was commenced. Introduction of ethylene oxide in small doses of less than 20 grams is strongly dependent on the pressure (upper and lower) and temperature. Each subsequent portion of ethylene oxide was introduced into the reaction environment only when the pressure in the reactor dropped below a given value (lower pressure) and its temperature was within the preset range.

The fractional composition of the oxyethylates obtained was established using gas chromatography (GC). The samples studied were diluted in an appropriate solvent and the solution was injected into a chromatograph (Hewlett Packard, USA, model 5890, series 2). The column used was a high-temperature Ultra 2 type, 10 m in length and 0.25 mm in diameter.

The fractional composition of the oxyethylates obtained was established using GC/FID chromatography. This method is often found in the literature, and is used for determining the fractional composition of oxyethylates of fatty alcohols, particularly in comparing catalysts of oxyethylation processes^{17–21}.

The HP 6890 GC gas chromatograph used is equipped with a “split/splitless” injector, a flame ionization detector (FID) and a Hewlett-Packard computer workstation. Chromatographic separation of the analyzed components was obtained using a capillary chromatographic column made of fused silica, 15 m in length and 0.32 mm in internal diameter, filled with a methyl phenyl silicone stationary phase, type ZB-5HT (or ULTRA 2) with a film thickness of 0.1 µm. The conditions of analysis were as follows: (i) furnace temperature program: 120°C (1 min); 15°C/min; 380°C (10 min); (ii) injector temperature: 360°C; (iii) detector temperature: 380°C; (iv) gas flow rate through column: 2 cm³/min (argon); (v) stream split: 70:1; (vi) quantity of sample injected (manually): 0.3 µg.

The tested samples were diluted in an appropriate media, and the solution was then injected into the chromatograph. The separation temperature was programmed in the range 100–360°C, the temperature of the flame ionization detector being 380°C. The method is based on the principle that, when the chromatogram is obtained, the areas of individual peaks are measured and summed. The total sum of the areas is taken to be 100%. Assuming that all components in the sample are volatile and are visible on the chromatogram, the

area of each peak relative to the total area of all peaks corresponds to the percentage content of the analyzed substances in the sample.

RESULTS AND DISCUSSION

Dispersive properties of Mg(OH)₂ samples

To determine the conditions enabling the synthesis of Mg(OH)₂ and MgO samples with optimum properties, the influence of such parameters as temperature and quantitative ratio of reagents was tested.

Table 2 contains the dispersive parameters of magnesium hydroxide precipitated at a rate of 2.3 cm³/min, at process temperatures of 20, 40, 60 and 80°C. Moreover, magnesium hydroxide was precipitated at a stoichiometric ratio of reagents (1:1) and at ratios of 1.5:1, 2:1 (excess magnesium sulfate), and 1:1.5 (excess NaOH).

The highest temperature of 80°C produces the best morphological and dispersive properties of the final magnesium hydroxide. Sample 4A precipitated at the stoichiometric ratio of reagents was characterized by a very low bulk density of 68 g/dm³. The diameter range of the particles in this sample was 106–459 nm. The product obtained with an excess of sodium hydroxide (sample 5A) had much poorer parameters than sample 4A. Its bulk density was 367 g/dm³, while its polydispersity index (0.852) and the size of its particles in the micrometric range indicate a significant tendency to agglomeration. On the other hand, sample 6A obtained with an excess of magnesium sulfate (1.5:1) and at a temperature of 80°C exhibited much better parameters. In fact, this material had the best parameters out of all the samples obtained. The particle size distribution of this sample (Fig. 1) shows two bands. The first one covers diameters from 28 to 79 nm, and the maximum volume contribution of 21.3% comes from particles 59 nm in diameter. The presence of this band testifies to the high dispersion of particles

in sample 6A. The second band evidenced the presence of agglomerates whose diameter reached 2300 nm, but which had a low volume contribution.

Particle agglomeration can take place at every stage during liquid-phase preparation, such as nucleation and growth and the washing and drying of precipitates. Several representative theories have been proposed, including some based on crystal bridge, capillary pressure, hydrogen bond and chemical bond formation^{21,22}. Figure 2 illustrates the proposed mechanism of agglomerate formation.

The effect of calcination on the dispersive and the structural properties of magnesium oxide samples

The bulk densities of the magnesium oxide samples obtained were lower than those of the corresponding magnesium hydroxides, which is explained first of all by mass loss during calcination. The polydispersity

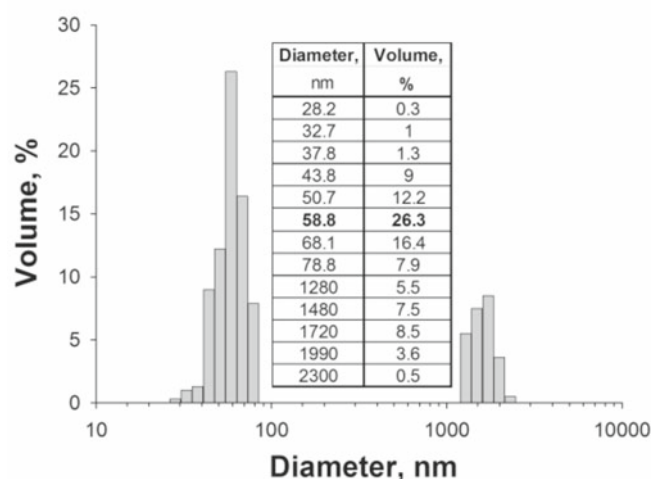


Figure 1. Particle size distribution (Zetasizer Nano ZS) of magnesium hydroxide (sample 6A), precipitated with excess magnesium sulfate at 80°C

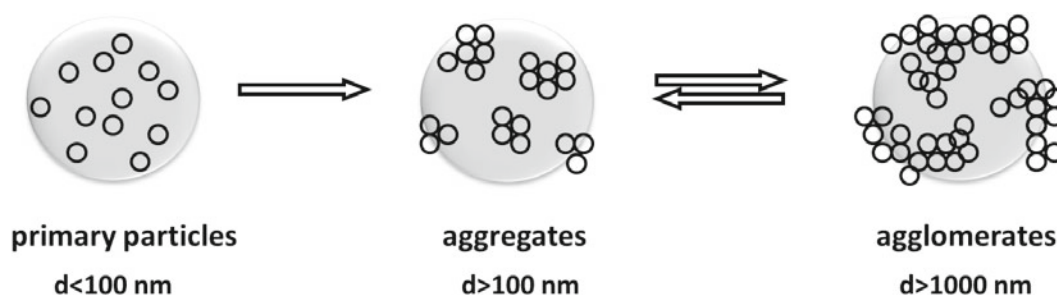


Figure 2. Mechanism of aggregate and agglomerate structure formation

Table 2. Physicochemical properties of Mg(OH)₂ precipitated with different ratios of reagents at 20, 40, 60 and 80°C

Sample No.	Precipitation process conditions		Physicochemical and dispersive properties					
	Temperature, °C	Salt/NaOH ratio	Bulk density, g/dm ³	Polydispersity index	Diameter range from Zetasizer Nano ZS, nm	Particle size from Mastersizer 2000, μm		
						d(0.1)	d(0.5)	d(0.9)
1A	20	1:1	171	0.180	122–396	2.74	7.19	22.56
2A	40		188	0.385	164–1110	2.00	4.70	28.04
3A	60		209	0.484	1280–5560	2.48	9.42	49.62
4A	80		68	0.214	106–459	2.69	6.30	26.73
5A	80	1:1.5	367	0.852	122–531	3.52	20.38	61.72
6A		1.5:1	130	0.245	28–79 1280–2300	1.83	3.73	9.83
7A		2:1	132	0.394	342–955	1.95	4.41	20.40

Table 3. Physicochemical properties of selected MgO obtained with the use of 5% solution of magnesium sulfate at 80°C

Sample No.	Precipitation process conditions			Physicochemical and dispersive properties					
	Temperature, °C	Concentration MgSO ₄ , %	Salt/NaOH ratio	Bulk density, g/cm ³	Polydispersity index	Diameter range from Zetasizer Nano ZS, nm	Particle size from Mastersizer 2000, μm		
							d(0.1)	d(0.5)	d(0.9)
4B	80	5	1:1	49	0.280	531–670	3.34	8.45	32.51
5B			1:1.5	309	0.950	122–5560	3.52	20.38	61.72
6B			1.5:1	110	0.286	122–3580	1.86	4.08	24.50
7B			2:1	98	0.426	190–2670	1.95	4.41	20.40

indices determined for the magnesium oxide samples are higher than those of the corresponding hydroxides, which indicates a deterioration in homogeneity. Higher polydispersity indices imply the presence of particles with greater diameters (see Table 3).

The presence of these attests to the occurrence of particle agglomeration during calcination of magnesium hydroxides. The undesirable changes are interpreted as a result of the process of agglomeration taking place on increase in temperature. Changes in the morphology and dispersion of the samples can be important when considering their application as catalysts.

Analysis of the structural properties of the samples studied confirms the effect of calcination on the microstructure of Mg(OH)₂ (Table 4). MgO samples obtained as a result of calcination had pores of sizes smaller than or comparable to those in the corresponding magnesium hydroxide samples, indicating the mesoporous character of the material, and greater pore volume. These textural changes determined the surface area of the MgO samples, which were generally larger than those in the corresponding magnesium hydroxide samples. In his paper²³ on structural changes taking place upon decomposition of nanocrystalline Mg(OH)₂ to MgO, Melgunov has reported that in the precipitated Mg(OH)₂ crystals, the surface density of Mg atoms in the face is higher than in MgO.

Magnesium hydroxide synthesis by precipitation from magnesium salt solutions, in the optimum conditions established for the process, offers the possibility of obtaining products with large surface areas. According to

Table 4. Porous structure parameters of selected magnesium hydroxide samples and their calcinates obtained using a 5% solution of magnesium sulfate at 80°C

Sample No.	BET surface area, m ² /g	Total pore volume, cm ³ /g	Mean size of pores, nm
4A	110	0.30	19
4B	156	0.42	15
5A	45	0.20	12
5B	68	0.30	10
6A	91	0.62	27
6B	269	0.92	13
7A	60	0.50	34
7B	76	0.66	32

Table 5. Lauryl alcohol oxyethylation over different catalysts (synthesis temperature 185°C, mean degree of oxyethylation $N_{av} = 3$)

Sample No.	Commercial catalyst	Catalyst concentration, %	Reaction time, min	Amount of EO introduced relative to the preset value, %	V_{av} , mol/mol·h
6B	–	0.50	88	100	2.05
–	K-4/XII-O (calcium)	0.30	46	100	3.97
–	NaOH	0.10	21	100	8.70

N_{av} – average degree of oxyethylation, denoting the average number of moles of ethylene oxide per mole of starting material; V_{av} – average rate of the oxyethylation process, expressed as the number of moles of ethylene oxide introduced into the reaction environment per mole of starting material per hour; EO – ethylene oxide.

literature data^{24,25}, the use of magnesium sulfate, besides magnesium nitrate and magnesium chloride, is most favorable for the formation of magnesium hydroxide – and hence also magnesium oxide – with small particles and large surface areas. Most probably the reason is the good water solubility of this salt, which affects the character of the nucleation. It has been proved that the oxides obtained at high temperatures show greater catalytic and adsorption activity²⁶.

Sample 6B, with its large surface area of 269 m²/g and high contribution of nanometric particles, was selected as the best for catalytic tests. WAXS²⁷ and TG/DTA²⁸ studies confirmed the purity of this sample and its well-developed crystalline structure with characteristics of periclase.

Catalytic evaluation of MgO

The catalytic activity of magnesium oxide (sample 6B) was tested in the oxyethylation of lauryl alcohol. The catalyst was found to be relatively active. A distinct decrease in the pressure observed each time after introduction of ethylene oxide into the reactor provided evidence of the progress of the reaction. The test was successful as the entire amount of ethylene oxide was dosed, but the process was slow. The time of reaction and the rate of reaction are given in Table 5, where the corresponding data for two commercial catalysts are also shown.

According to the results obtained, the use of MgO in unmodified form (sample 6A) as a catalyst is rather ineffective. The reaction initiated by magnesium oxide is very slow, and its most probable mechanism is shown in Figure 3.

It is highly probable that the hydrophobic substrate (lauryl alcohol) connects with ethylene oxide (oxirane) and magnesium oxide to make magnesium alcoholate (laurinate) (step I). The subsequent oxirane molecules (step II), attached in the reaction of oxyethylation, coordinate the formation of the oxyethylated product. One of the two electron pairs coordinates to magnesium, taking advantage of the weak acidic properties of that metal. As a result of complex formation, the positive charge on the carbon atoms of oxirane increases. Because of the

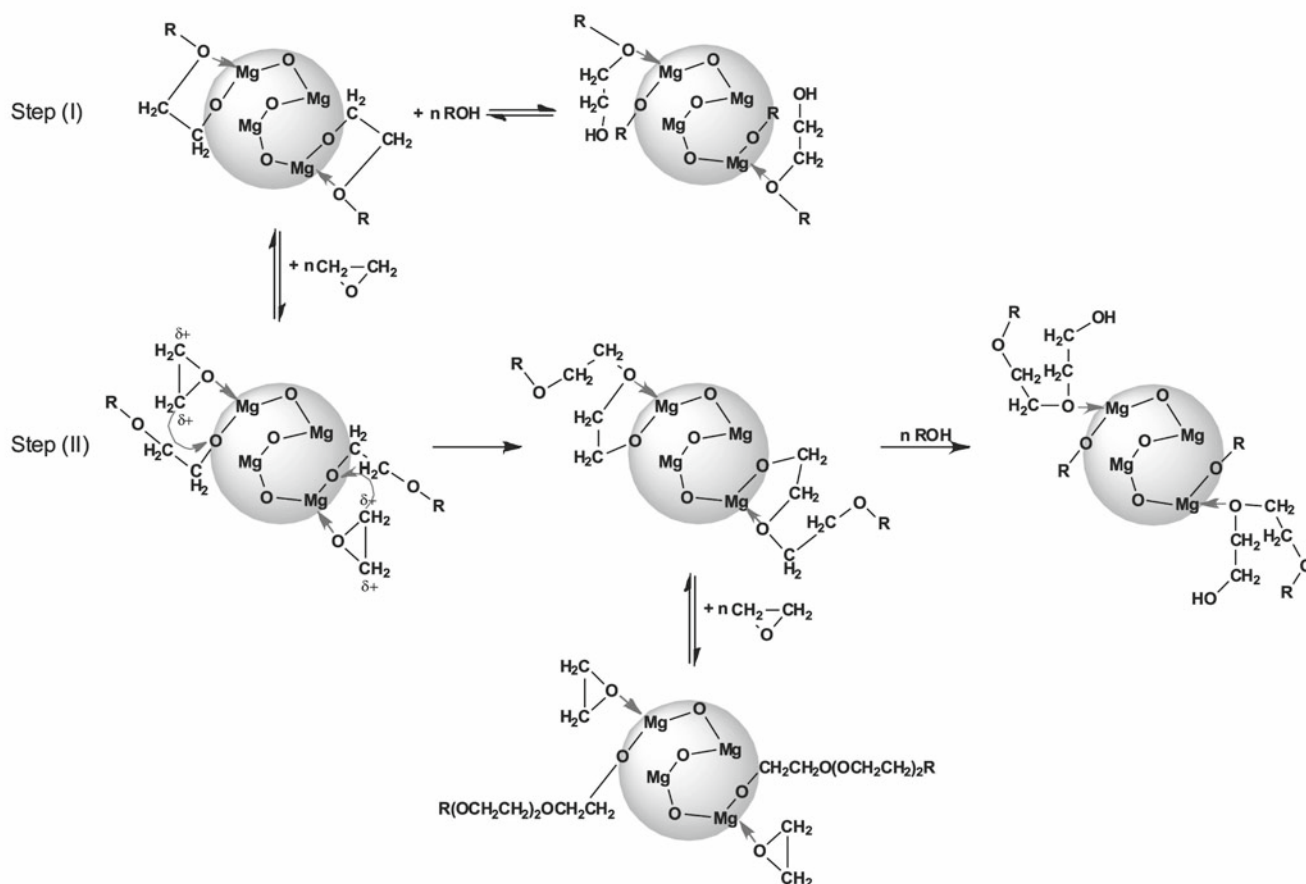


Figure 3. Mechanism of lauryl alcohol oxyethylation in the reaction catalyzed by magnesium oxide, based on²⁹ (where –OR denotes alcoholate group of the formula $-\text{OC}_{12}\text{H}_{25}$, which comes from lauryl alcohol)

increase in electrophilicity, these carbon atoms become more reactive, which facilitates the carbon-oxygen bonding.

The product of the oxyethylation is a mixture of a number of derivatives with different content of ethylene oxide, in which the amount of particular homologues depends on the catalyst used²⁹. Subsequently, it is necessary to use the notion of mean oxyethylation degree, providing information on which fraction has been dominant. If the catalyst is selective, a narrow distribution of homologues is obtained. With the use of the currently available catalysts, irrespective of the hydrophobic substrate, it is possible to obtain a product in which the target component makes up a maximum amount of 30% wt./wt. in the mixture of oxyethylates^{12, 30}. In our experiment the synthesis was performed with a mean degree of oxyethylation of 3.

Consequently, the content of oxyethylated product containing three molecules of ethylene oxide was as high as 19.30% (Table 6). It should be noted, however, that a very similar percentage was also obtained for the compound with two molecules of oxirane (19.24%), which for products of this type is a satisfactory result indicating a narrowing of the distribution of homologues. The analogous product obtained using NaOH (a catalyst used industrially) is found to have contents of 12.93% and 12.20% for the respective fractions. Moreover, the superior selectivity of the MgO catalyst compared with NaOH is evidenced by, as well as the narrowing of the distribution of homologues, the content of unreacted starting material. The content of the original alcohol in the product obtained using MgO as catalyst was 14.72%, compared with 17.82% in the case of NaOH (Table 6).

Table 6. Distribution of homologues in the product of lauryl alcohol oxyethylation ($N_{\text{av}} = 3$) using MgO, NaOH and K-4/XII-O as catalysts. GC/FID analysis

Oxyethylates of lauryl alcohol	Fractional composition, %		
	Type of the catalyst		
	MgO	NaOH	K-4/XII-O (calcium)
Alcohol C-12/0	14.72	17.82	13.01
C-12/1	14.95	12.05	8.32
C-12/2	19.24	12.20	14.50
C-12/3	19.30	12.93	21.64
C-12/4	15.01	10.05	19.91
C-12/5	9.02	7.52	12.33
C-12/6	4.40	6.88	6.42
C-12/7	1.79	5.02	2.08
C-12/8	0.63	4.91	0.89
C-12/9	0.26	3.23	0.35
C-12/10	0.11	2.12	0.29
C-12/11	0.05	1.80	0.04
C-12/12	traces	1.26	traces
Other components	0.52	2.21	0.22

where, for example, C-12/2 denotes oxyethylate of C12 alcohol with 2 moles of ethylene oxide attached

Generally speaking, the oxyethylates, particularly oxyethylates of alcohols, are always a mixture of homologues with different degrees of polyoxyethylation. This results from the different reactivity of the starting material and the various homologues, which take part in parallel reactions with ethylene oxide and propagation of the oxyethylene chain. It is possible to improve the reactivity

and obtain a narrower distribution of homologues with the use of appropriate catalysts^{31, 32}.

The lauryl alcohol oxyethylate obtained demonstrates good quality and relatively small distribution of oxyethylene homologues (narrow-fraction oxyethylates). The tested catalyst (MgO, sample 6B) was shown to be selective in the process of oxyethylation, but its activity was much too low relative to that of the commercially available catalysts, which precludes its use in the present form as a technological material. The most probable explanation is that the acidic properties of magnesium are too weak and prevent realization of the process of insertion. Studies aimed at improving the catalytic behavior of MgO will be continued, including with the use of modifying agents – oxides of other metals (e.g. alumina) or pure metals.

CONCLUSIONS

The results of the experiments show the significant influence of experimental conditions on the properties of the final products. The product with optimum properties was obtained when the synthesis was performed at 80°C in the presence of an excess of the salt. The process of calcination was found to affect the dispersive properties of magnesium oxide; moreover the porous structure parameters were improved. The magnesium hydroxide samples with the best physicochemical parameters (sample 6A) contained particles with diameters of 28–79 nm and surface area (BET) of 91 m²/g. The corresponding magnesium oxide (sample 6A) contained particles of greater diameter (122–3580 nm), and its surface area was 269 m²/g. The catalyst studied proved to be selective in the oxyethylation of lauryl alcohol, but poorly reactive. Further studies are needed to improve its reactivity.

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