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Catalytic Activity of High-Surface-Area Amorphous MgO Obtained from Upsalite

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Abstract: The first aim of the research was to synthesize a pure Upsalite, which is an amorphous form of MgCO_3 , by modifying a procedure described in the literature, so that it would be the precursor of a high-surface, amorphous magnesium oxide. The results indicate that within the studied reaction conditions, the type of alcohol used as the reactant has the most pronounced effect on the yield of reaction. From the two alcohols that led to the highest yield of Upsalite, methanol gave a substantially larger surface area (794 vs. 191 $\text{m}^2 \text{g}^{-1}$). The optimized synthesis conditions of Upsalite were used to obtain MgO via thermolysis, whose activity in the transfer hydrogenation reaction (THR) from ethanol, 2-propanol and 2-pentanol to various carbonyl compounds was determined. The optimal conditions for the thermolysis were as follows: vacuum, $T = 673 \text{ K}$ as the final temperature, and a heating rate of 2 deg min^{-1} . The high-surface, amorphous magnesia ($S_{\text{BET}} = 488 \text{ m}^2 \text{g}^{-1}$) was found to be a very selective catalyst to 4-*t*-butylcyclohexanone in THR, which led to a diastereoselectivity of over 94% to the *E*-isomer of 4-*t*-butylcyclohexanol for more than 3 h, with conversions of up to 97% with either 2-propanol or 2-pentanol as the hydrogen donor. In the case of acrolein and 2-*n*-propylacrolein being used as the hydrogen acceptors, the unsaturated alcohol (UOL) was the main product of the reaction, with higher UOL yields noted for ethanol than 2-propanol.

Keywords: high surface magnesium oxide; transfer hydrogenation; α,β -unsaturated carbonyl compounds; Upsalite

1. Introduction

Although amorphous catalysts are gaining momentum in research due to the substantial number of defects in such structures and their atomic-scale structural flexibility [1–5], very few studies concerning amorphous magnesium oxide can be found. Multiple studies on the ferromagnetic properties of amorphous MgO have been performed [6–8]. It was found that this property is a result of cation vacancies in the solid, which are uncommon in crystalline MgO. Nevertheless, crystalline magnesia has several beneficial properties, such as a very high melting point (m.p. $2852 \text{ }^\circ\text{C}$) and a lack of phase transformations during thermal treatment, as is the case for alumina, zirconia, titania, etc., which is an undeniable advantage [9–11]. The high basicity of the MgO surface makes it an attractive catalyst that is used in numerous chemical processes, such as the transesterification of fats with methanol to produce fatty acid methyl esters (FAME) [12–14], the alkylation of phenol with methanol to 2,6-dimethylphenol [15,16], or the isomerization of a carbon-carbon double bond in the Shell Higher Olefin Process (SHOP) [17,18]. It is noteworthy that magnesium oxide is one of the most active metal oxides in the transfer hydrogenation reaction to carbonyl compounds using alcohols as hydrogen donors [19,20], although many other transfer hydrogenation catalysts continue to be widely investigated [21–25]. The reaction was shown to occur on supported metal and alloy catalysts, such as Au, Pt, Pd, Ru, Ag-Pd,

etc. [24] (and references therein), but magnesia is a much cheaper alternative for potential industrial applications. In contrast to the supported cobalt and copper systems studied in this reaction [24] (and references therein), magnesia is a single-component system, which does not require a multi-step synthesis and is environmentally benign. Moreover, an advantage of this oxide is that it exhibits numerous basic sites along with weak Lewis acid sites on its surface [25], which are responsible for this transfer hydrogenation and can lead to high selectivity. A study of different catalytic systems conducted by Feng et al. [26] showed that by-products were formed on those systems that had strong acidic sites, namely Pd/SiO₂, Pd/Al₂O₃, and Pd/TiO₂, whereas high selectivity of Pd/C and Pd/NaY was observed, which was attributed to the lack of numerous strong acid sites. In the case of the hydrogenation of α,β -unsaturated carbonyl compounds the chemoselectivity of the hydrogenation to the unsaturated alcohol is of great importance, which has resulted in multiple studies being conducted on this topic [27–31]. To date, no reports of catalytic properties of amorphous magnesia in transfer hydrogenation have been published. This paper aims to fill that gap.

In most studies, a relatively low surface area magnesium oxide is used. It is commonly known that increasing an oxide's surface area can lead to increased activity. In order to obtain high-surface area magnesia, several research groups have implemented different special methods of synthesis. These include attempts to synthesize high-surface MgO as a result of the thermal decomposition of oxide precursors, such as hydroxide, basic carbonates, and magnesium nitrate or oxalate, whose decomposition products have much higher surface areas than the original precursor. The presence of certain precursor impurities, e.g., chloride ions [32], has a strong influence on the size of the specific surface area of the forming magnesium oxide. The type of precursor used and the decomposition conditions, such as the rate of decomposition, the time of decomposition, and, above all, the presence or absence of a gas atmosphere during the decomposition process [33–36] are also known to affect the properties of the obtained solid. It is known that the presence of gaseous decomposition products above the formed product (H₂O, CO₂) promotes its sintering and, thus, reduces its specific surface area. Therefore, when preparing high-surface MgO, it is beneficial when the thermal decomposition of the precursor is carried out under substantially reduced pressure [37,38]. However, increasing the pressure and temperature, so that the solvent reaches supercritical conditions, is a very promising route for MgO synthesis [33,39].

In 2013, chemists from the University of Uppsala (Sweden) reported the preparation of amorphous MgCO₃ by reacting a suspension of MgO in CH₃OH with CO₂ under pressure [40]. The new compound was called “Upsalite” in honor of the university where it was prepared. After the removal of methanol, the product was in the form of a hard colorless gel with an unusually high specific surface area of 700–800 m² g^{−1} [40]. The authors described its use as a sorbent for drying gases and in pharmacy as a substance for the slow release of the active form of drugs [41]. The aim of our research was to optimize the synthesis conditions so as to obtain pure Upsalite, not contaminated with unreacted magnesium oxide, so that it could be applied as a magnesium oxide precursor. According to the authors' knowledge, such an application of Upsalite has not been described in the literature so far. It was expected that the thermal decomposition of this precursor with such a high specific surface area could yield a high-surface-area magnesium oxide. The most interesting, and potentially valuable in terms of applications in the chemistry of materials, property of the magnesium oxide is its activity in selected reactions. The transfer hydrogenation reaction to carbonyl compounds as hydrogen acceptors was chosen as the model reaction, which has been studied under various conditions with a wide range of catalysts [42–44]. Four acceptors, namely two α,β -unsaturated aldehydes (acrolein and 2-*n*-propylacrolein) and two ketones (acetophenone and 4-*t*-butylcyclohexanone), were selected as hydrogen acceptors.

2. Results

Upsalite was synthesized with different alcohols and within a wide range of parameters, such as volume of alcohol, CO₂ pressure, temperature, and volume of added water. The most important influence was noted when the alcohol, which had a twofold function in the synthesis (specifically, it was both a substrate as well as the solvent of the product), was changed. The impact of the alcohol used in the synthesis on the Upsalite yield and surface area is compiled in Figure 1. It can be seen that the highest yields of Upsalite were noted for MeOH and propane-1,2-diol, with 100 and 91%, respectively (Figure 1a). However, the surface area of the latter was much smaller (Figure 1b), i.e., 191 m² g^{−1} compared to 794 m² g^{−1}. The third highest yield of Upsalite was noted for ethanediol, 27% with a surface area of only 58 m² g^{−1}. The yields of Upsalite with all of the other alcohols were well below 20% and some were too small to obtain a sample for a nitrogen physisorption measurement.

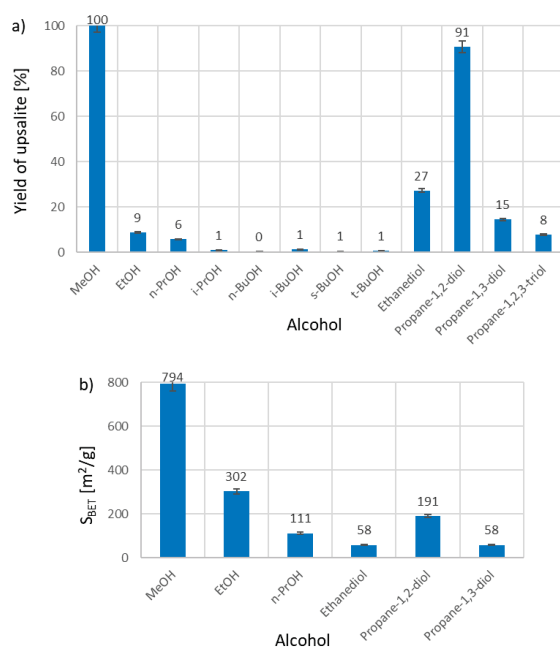


Figure 1. Influence of the type of alcohol on the reaction of carbon dioxide with magnesium: (a) yield and (b) specific surface area of the obtained Upsalite. $W_{\text{MgO}} = 2.000 \text{ g}$, $V_{\text{alcohol}} = 30 \text{ cm}^3$, $p_0 = 5.0 \text{ MPa}$, $T = 323 \text{ K}$, $t = 3 \text{ h (+16 h)}$.

Figure 1b contains the specific surface areas of all of the Upsalite samples that were obtained with a reasonable yield. It can be seen that the lengthening of the chain of the alcohol led to a decrease in the surface area; thus, in the case when ethanol was used instead of methanol, the S_{BET} dropped from 794 m² g^{−1} to 302 m² g^{−1}. A further increase in the chain led to Upsalite with a surface area to 111 m² g^{−1}. The presence of a second OH group in the molecule of the alcohol also resulted in a decrease in the surface area, i.e., for ethanol, the change to ethanediol led to decrease from 302 to 58 m² g^{−1}.

The high yield was expected for methanol due to the fact that the surface of magnesium oxide is strongly basic and alcohols are weak acids whose acidity decreases with the order of the alcohol and chain length. Therefore, the highest acidity is that of a primary, short chain molecule, such as methanol. Furthermore, it presents the smallest steric hindrance of all the studied alcohols. Indeed, it can be seen in Figure 1 that when methanol was used as a reagent and solvent of the product, the highest yield was obtained. In the case of two propanediols, the position of the OH groups was found to have a substantial effect on the specific surface area of the obtained Upsalite, and propane-1,2-diol gave a higher surface area than propane-1,3-diol and n-propanol. From the stud-

ied C3 alcohols, the lowest surface area ($58 \text{ m}^2 \text{ g}^{-1}$) was observed for propane-1,3-diol (Figure 1b). The substantial difference of the yield of Upsalite in the case of the two samples obtained using propanediols was further investigated with surface-sensitive techniques. XPS spectra of samples obtained using different alcohols and under different conditions did not reveal differences between the samples in terms of composition (Supplementary information Figure S1). However, the ATR-FTIR studies showed that in contrast to the ATR-FTIR spectrum of the Upsalite obtained using methanol (Figure 2 top curve), those of the solids obtained using propanediols contained two bands that correspond to carbonate species: one band at approx. 1420 cm^{-1} and another at a slightly higher wavenumber, i.e., 1640 cm^{-1} (Figure 2 middle and bottom curves). The latter indicated the formation of bidentate carbonate groups on the surface of Upsalites obtained with propanediols. It is noteworthy that the intensity of this band was much higher for propane-1,2-diol than for propane-1,3-diol, which corresponded to a much higher Upsalite yield. It is, therefore, concluded that the formation of bidentate species on the surface might contribute to improved reaction yields.

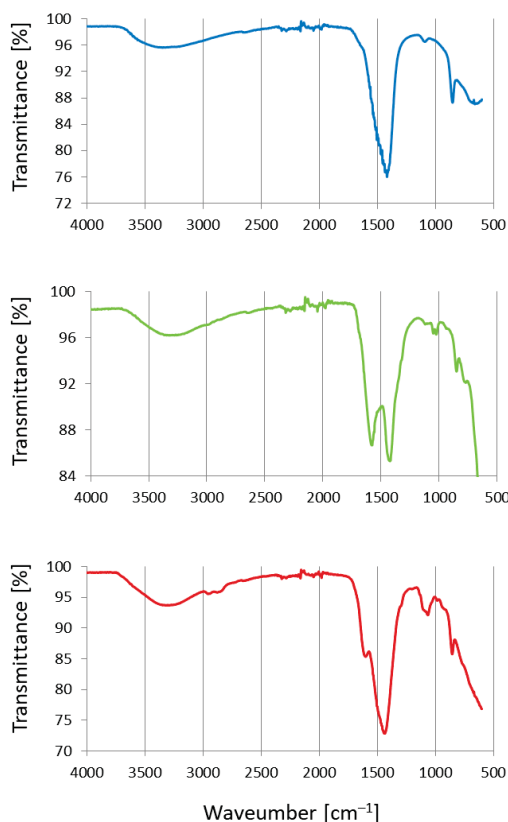


Figure 2. ATR-FTIR spectra of Upsalite obtained using methanol, propane-1,2-diol, and propane-1,3-diol.

In order to optimize the yield and surface area of the Upsalite that could be used as a precursor of MgO, the variables of Upsalite synthesis were studied in the following ranges: volume of methanol: $20\text{--}50 \text{ cm}^3$; pressure: $0.5\text{--}5.0 \text{ MPa}$; and temperature: $298\text{--}353 \text{ K}$. It can be seen that the optimal synthesis values for these parameters were: 30 cm^3 , 5.0 MPa , and 323 K . Values of the impact of each parameter on the surface area are provided in Supplementary Information, Table S1. The Upsalite with the highest surface area, namely $794 \text{ m}^2 \text{ g}^{-1}$, was used to obtain magnesium oxide via thermolysis. The influence of the following parameters of thermolysis on the surface area of the obtained MgO were investigated: atmosphere (flowing nitrogen or vacuum), heating rate, and final temperature. The results indicate that the most favorable conditions of the thermolysis were: vacuum

(1.33 Pa), 2 deg min^{−1}, and 673 K. Under such conditions, magnesium oxide with a surface area of 488 m² g^{−1} was obtained. Values corresponding to other studied conditions are provided in Supplementary Information, Table S2. The diffraction pattern of the obtained solid (Figure 3a top) was a typical pattern for amorphous magnesium carbonate [45] and did not contain any other phases. Pair Distribution Function (PDF) analysis of the diffraction pattern of the Upsalite measured using Mo radiation showed that the close-range ordering of Upsalite (within the achieved resolution) resembled the ordering in MgCO₃ crystals. The pattern of magnesium oxide obtained from this Upsalite (Figure 3a bottom) showed markedly broadened maxima pointing to an Fm3m structure of lattice parameter 4.249(3) Å, slightly bigger than that of crystalline MgO (4.211 Å; PDF#780430). Standard analysis, e.g., Williamson–Hall plot showed no significant microstrain and ordered domain size of approx. 2 nm. Debye–Waller factor estimation suggested that the disorder had a mostly thermal character with mean square displacements of 0.15 Å². The average size estimate from the Williamson–Hall plot pointed to approx. 55 elementary cells forming a spherical domain or 104 cells forming a cube, and corresponded to a surface area of 674 m² g^{−1}. This was only slightly more than the BET result and suggests a rather narrow size distribution. Conchoidal fracture can be seen in the SEM image of both the Upsalite (Figure 3b top) and the freshly synthesized MgO (Figure 3b bottom). The EDX analysis showed that the obtained solids had no impurities and had the composition of magnesium carbonate (Figure 3c top) and magnesium oxide (with a minor contribution from carbon, which was always present; Figure 3c bottom), respectively.

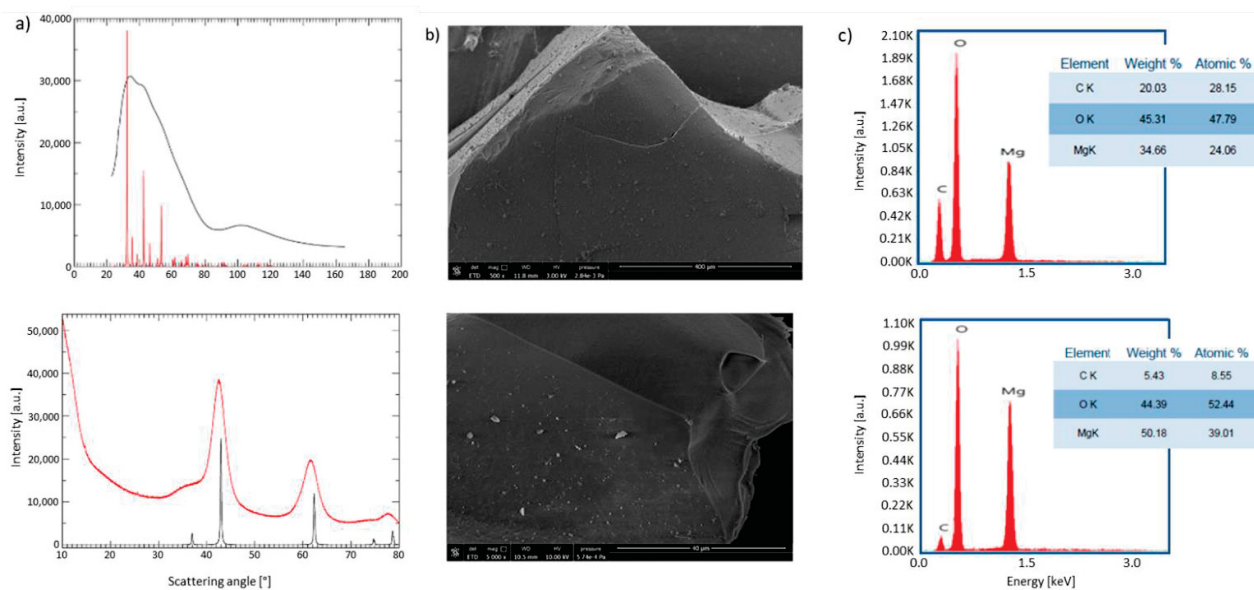


Figure 3. Obtained Upsalite and MgO obtained from it: (a) diffraction patterns, (b) SEM images (500 times magnification), and (c) EDX results.

Figure 4a depicts the results, namely the TG and DTG curves (top), of thermal decomposition of Upsalite in argon with a simultaneous MS detection of signals $m/z = 18$ and $m/z = 44$ (bottom), which corresponded to water and carbon dioxide, respectively. It can be seen that the decomposition of Upsalite was preceded by desorption of gases, such as water and CO₂, with a maximum at approx. 430 K (line 1). The maximum rate of the thermal decomposition occurred at around 670 K (line 2). The evolution of CO₂ was the most intensive at this temperature (Figure 4a, bottom).

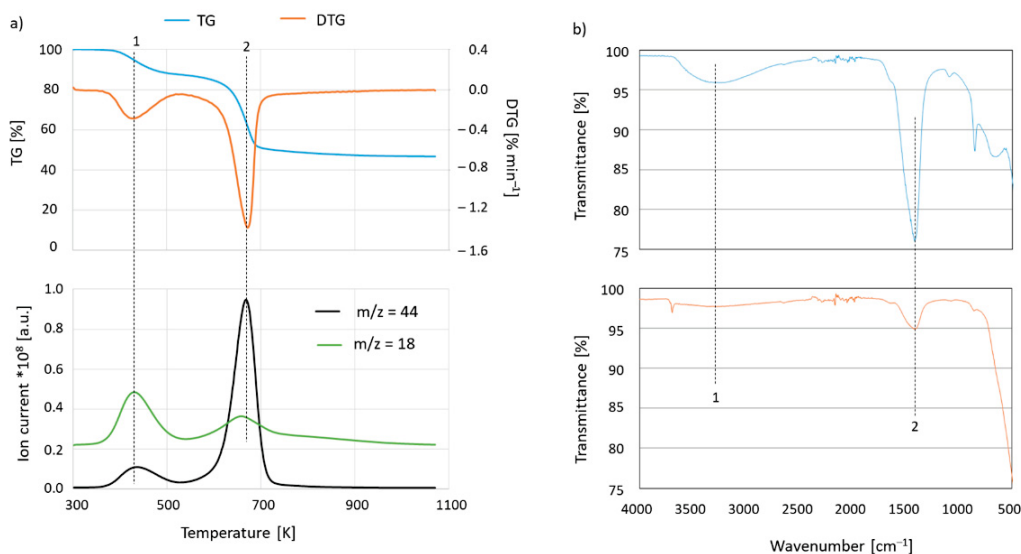


Figure 4. Results: (a) thermal analysis: TG and DTG curves (top) and MS curves (bottom) and (b) ATR-FTIR spectra of the optimized Upsalite (top) and optimized MgO (bottom) obtained from that Upsalite.

The broad band between 3000 and 3500 cm^{-1} in the ATR-FTIR spectrum of the Upsalite indicated the presence of a wide range of types of OH groups on the surface of this solid (Figure 4b, line 1). The carbonate region also had a pronounced signal (Figure 4b, line 2). In contrast, the obtained MgO had few OH groups and the sharp band at 3690 cm^{-1} was ascribed to isolated OH groups [46]. Some carbonate species were present on the surface of the MgO, which was not surprising considering the basicity of the oxide and its inevitable interaction with CO_2 from the atmosphere. The acidic/basic properties of the surface were further probed with benzoic acid and *n*-butylamine to determine the total concentration of sites whose acidic strength fell in the range of $0.8 < \text{H}_0 \leq 4.8$ and whose basic strength was within the range of $26.5 \leq \text{H}_- < 33.0$. These studies showed that the concentrations of the acidic and basic sites on the surface of this oxide were 295 and 400 $\mu\text{mol g}^{-1}$, respectively. Considering the specific surface area of MgO (488 $\text{m}^2 \text{g}^{-1}$), this translates to 0.605 and 0.820 $\mu\text{mol m}^{-2}$, respectively.

The optimized MgO was used in a series of catalytic studies of transfer hydrogenation. There are several parameters that affect the result of the reaction, namely the reactivity of the acceptor, the structure of the donor, the donor: acceptor ratio, the time of the reaction, and the reaction temperature. For this reason, all of these parameters were studied using amorphous MgO as the catalyst. The hydrogen acceptors for the reactions were carefully selected based on the fact that, by studying them, additional information about the catalyst and reaction mechanism could be obtained. In the case of acetophenone, its hydrogenation product was sensitive to the presence of acidic sites, on which its transformation to styrene was observed. Therefore, the catalytic test with this compound could be used to probe the surface of the amorphous MgO for the existence of acidic Brønsted sites, which were not found on crystalline MgO. On the other hand, 4-*t*-butylcyclohexanone could be used to determine which side the attack on the carbonyl group came from, i.e., the attack from the axial position would lead to the formation of the *E*-diastereoisomer, whereas that from the equatorial position resulted in the formation of the *Z*-diastereoisomer.

In order to compare the reactivity of donors, two alcohols were used, namely 2-propanol and 2-pentanol, with the donor acceptor molar ratio (D/A) equal to 6 or 8, and the catalytic tests were performed at the boiling point of the donor, because it was used in large excess. In the case of the former donor, the reaction temperature was 355 K, whereas it was 392 K for the latter. Therefore, the effect of the discrepancy in the temperatures overlapped with the effect of the donor structure. The separation of the effects led to

the conclusion that the alcohol with the longer chain was a poorer donor when tested at the lower temperature, as described by us in [19]. This effect was not tested again in the current study. Instead, each of the donors was tested at its boiling point, which is the most pragmatic way of conducting the synthesis in an industrial setting.

The results of activity tests of the obtained MgO in liquid phase transfer hydrogenation of acetophenone with 2-pentanol and 2-propanol are shown in Figure 5. Under the studied conditions, it can be seen that the yield with 2-pentanol was much higher than with 2-propanol. The yield of 1-phenylethanol after 30 min of reaction was 70 and 14% for 2-pentanol and 2-propanol, respectively. In the case of 2-pentanol, the maximum yield of the desired product was reached already after 60 min of reactions and stayed constant until 360 min. In contrast, in the case of 2-propanol, the yield of 1-phenylethanol increased with reaction time and reached 46% after 360 min of reaction, which was more than twice the value observed after 30 min of reaction (Figure 5).

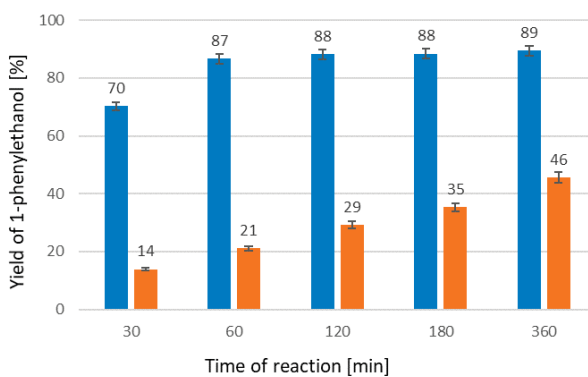


Figure 5. Liquid phase transfer hydrogenation of acetophenone with 2-pentanol (blue) or 2-propanol (orange) in the presence of MgO derived from Upsalite. $W_{\text{MgO}} = 100$ mg, 5 mmol of acceptor, D/A = 8.

In contrast to the carbonyl group in acetophenone, the one in 4-*t*-butylcyclohexanone experienced strain, i.e., the angles typical for sp^2 hybridization were restricted by the cyclic ring. Since the reduction in the latter to 4-*t*-butylcyclohexanol released the molecule from this strain (sp^3 hybridization), it was more reactive than acetophenone. The results of the obtained MgO in hydrogen transfer of 4-*t*-butylcyclohexanone from 2-propanol showed that the sum of the yields of 4-*t*-butylcyclohexanols increased with the time of the reaction within the studied interval (Figure 6a). After 5 min of reaction, the conversion of 4-*t*-butylcyclohexanone was 11% and the only products of the reaction were the appropriate cyclohexanols. In fact, in the whole studied interval, the contribution from other products was negligible and the conversion of the ketone increased with time to 95% after 180 min. It should be emphasized that under the synthesis conditions, with the entire studied interval of time, the ratio of the stereoisomers was much higher than the equilibrium value, i.e., 78% (Figure 6b). This indicates that such a catalytic process could be implemented for preferential synthesis of the *E*-diastereoisomer.

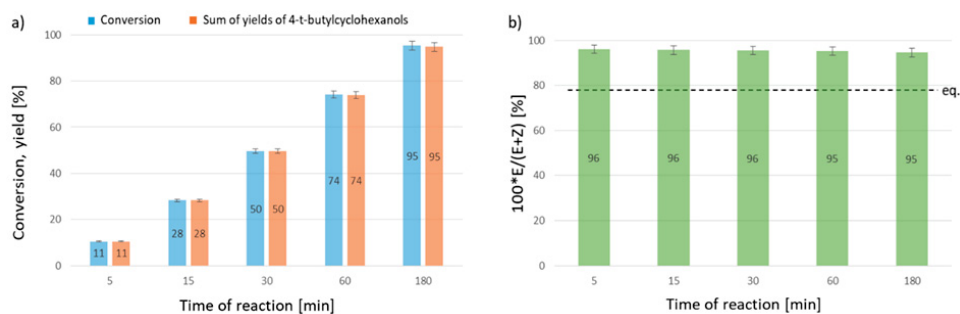


Figure 6. Liquid phase transfer hydrogenation of 4-*t*-butylcyclohexanone with 2-propanol in the presence of MgO derived from Upsalite: (a) conversion of 4-*t*-butylcyclohexanone and sum of yields of 4-*t*-butylcyclohexanols, and (b) diastereoselectivity; $W_{\text{MgO}} = 100 \text{ mg}$, 2.5 mmol of acceptor, $D/A = 8$.

Figure 7 depicts the results obtained for the same acceptor, i.e., 4-*t*-butylcyclohexanone, but with 2-pentanol as the hydrogen donor. It can be seen that the conversion of this compound with 2-pentanol was higher than that observed for 2-propanol (Figure 6a). The value for 5 min was 25%, and after 30 min, a value of 82% was attained (Figure 7a). Additionally, in the case of this donor, the value of the ratio describing the relative amount of the *E*-diastereoisomer was above 94% during the entirety of the studied reaction time interval (Figure 7b).

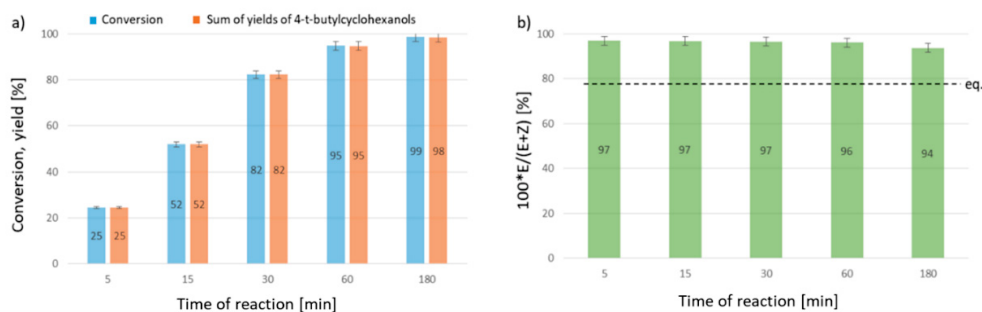


Figure 7. Liquid phase transfer hydrogenation of 4-*t*-butylcyclohexanone with 2-pentanol in the presence of MgO derived from Upsalite: (a) conversion of 4-*t*-butylcyclohexanone and sum of yields of 4-*t*-butylcyclohexanols, and (b) diastereoselectivity; $W_{\text{MgO}} = 100 \text{ mg}$, 2.5 mmol of acceptor, $D/A = 8$.

In contrast to the liquid phase studies that were performed at a fixed temperature, i.e., the boiling point of the donor, the temperatures of the gas phase studies were conducted at temperatures above the boiling points of all reactants and, hence, the same temperatures were studied for both donors. The activity of the MgO obtained from the Upsalite was studied in the hydrogen transfer from ethanol and 2-propanol to acrolein. It can be seen that, as in the case of crystalline MgO, the amorphous MgO, higher conversion of acrolein was attained when ethanol was used as the hydrogen donor. A discussion regarding these two hydrogen donors in THR to acrolein was conducted by us in a previous study [20]. In the case of this reaction, the potential products were the saturated aldehyde, saturated alcohol, and unsaturated alcohol, which was the desired product due to the fact it is more valuable than the other two products [20]. It was favorable that under the reaction conditions, the unsaturated alcohol was the main product with yields of over 60% at 573 and 623 K. The conversion increased with temperature throughout the entire studied range. It is noteworthy that the contribution of the saturated alcohol was higher when 2-propanol was used as the hydrogen donor than in the tests with ethanol in the entire temperature range (Figure 8a,b).

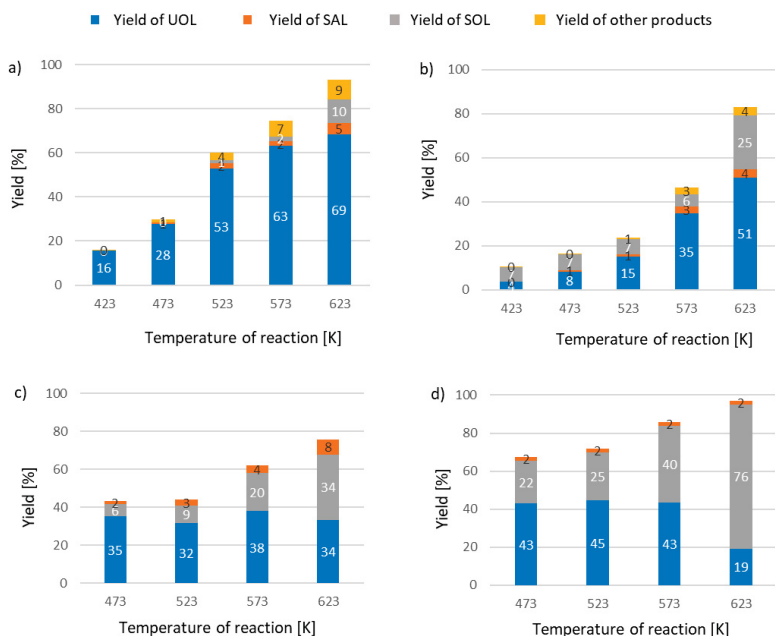


Figure 8. Activity of MgO in transfer hydrogenation of acrolein (a,b) and 2-*n*-propylacrolein (c,d) with ethanol and 2-propanol, D/A = 6.

Our previous studies showed that with crystalline MgO as the catalyst, the presence of a substituent in the number 2 position in an acrolein derivative enhances its chemoselective reduction to the unsaturated alcohol [20]. Therefore, hydrogen transfer in the presence of the obtained high-surface, amorphous MgO between ethanol or 2-propanol and 2-*n*-propylacrolein was also studied. The results are presented in Figure 8c,d. It is noteworthy that the desired product was the main product at temperatures up to 573 K regardless of the alcohol used. In the case of the highest temperature, the SOL: UOL ratio was 1 with ethanol and 4 for 2-propanol. This was probably caused by the fact that 2-propanol is a better hydrogen donor than ethanol, as was previously observed for crystalline MgO [20]. In the case of 2-*n*-propylacrolein, the reverse order was observed [20]. This was experimentally checked for the amorphous magnesia, and the results showed that the same is true for this catalyst. The difference may be the result of one or a combination of multiple factors, such as reaction conditions, catalyst surface properties, etc., which will form a part of future investigations. The conversion of 2-*n*-propylacrolein was higher for 2-propanol at all studied temperatures. It can be seen that when ethanol was used as the hydrogen donor, the yield of the saturated aldehyde changed from 2% at 473 K to 8% at 623 K (Figure 8c), whereas it was constant when 2-propanol was the donor (Figure 8d) and was equal to 2%. The UOL:SOL ratio was noticeably higher for acrolein than for 2-*n*-propylacrolein because it is less reactive and, hence, more selective.

3. Materials and Methods

3.1. Catalyst Preparation

Upsalite precursor. Upsalite was synthesized from low-surface area, high purity MgO prepared from $\text{Mg}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ (puriss p.a., Aldrich, Poznan, Poland) and concentrated NH_3 aqueous solution (25%, p.a. POCh Gliwice, Gliwice, Poland) using a method that enables the removal of most of the metal cationic impurities of the starting magnesium nitrate according to the procedure described in detail elsewhere [47].

Prior to the Upsalite synthesis 2.90 g/50 mmol of $\text{Mg}(\text{OH})_2$, i.e., the precursor of MgO, was placed in a quartz beaker and calcined in a muffle furnace at $873 \pm 2 \text{ K}$ for 6 h in air. To produce the amorphous MgCO_3 (Upsalite), a sample of MgO, taken from a muffle furnace, was placed into an autoclave (200 cm^3 capacity) together with a magnetic element and the

volume of anhydrous methanol (p.a., POCh Gliwice, Gliwice, Poland) was calculated, and was usually found to be 30 cm³. Next, the reaction vessel was purged three times with CO₂ (99.9% purity, Multax, Stare Babice, Poland) and pressurized with this gas until a given pressure had been reached. The autoclave was placed on a magnetic hot plate stirrer and heated for 3 h at a given temperature with constant stirring. Afterwards, the content of the autoclave was stirred for 16 h. After slow depressurization of the autoclave, it was emptied. The slightly viscous and transparent colorless sol was dried at 343 K for 12 h in a laboratory dryer under normal pressure. A transparent colorless gel was obtained and used for characterization experiments as well as MgO synthesis.

MgO from Upsalite. Synthesis of MgO by thermal decomposition of Upsalite was performed in a quartz tube (i.d. 15 mm) in which a sample of Upsalite (c.a. 2.5 g) was inserted between two layers of quartz wool. The tube was placed horizontally in an electrically heated furnace (Carbolite Gero, Hope, Great Britain) and the temperature was increased at a heating rate from 1 to 10 deg min^{−1} in either a stream of nitrogen (3 dm³ h^{−1}) or in a vacuum (1.33 Pa, rotary pump), and held for 1 h at the final temperature.

A schematic version of the procedure is shown in Figure S2 in the Supplementary Information section.

3.2. Catalytic Activity Measurements

Liquid phase transfer hydrogenation with 100 or 200 mg of MgO was performed in a one-piece glass reactor (15 cm³ capacity) equipped with a magnetic bar and a condenser connected with nitrogen-vacuum line. For quantitative determination of the compositions of post-reaction mixtures, *t*-butylbenzene was used as an internal standard. The details of measurements are given elsewhere [19,48].

Vapor phase transfer hydrogenation was performed in a glass tubular reactor (i.d. 7.0 mm) with a glass thermocouple pocket (o.d. 4.0 mm) placed in its axis. The space between them was filled with the grains of MgO (0.15–0.30 mm, 250 mg) diluted with grains of quartz in a 1:1 vol. ratio. All operations with the catalyst were performed in a stream of dry nitrogen to exclude its contact with humidity. During the reaction tests, a stream of nitrogen (3 dm³ h^{−1}) was passed through the reactor. Reaction products were condensed at 243 K in glass receivers, which were kept in a dry ice-2-propanol bath. A solution of liquid reactants was dosed into the reactor chamber using a microdosing pump with a liquid hourly space velocity (LHSV) of 3 h^{−1}. The catalytic tests were performed at the temperature range 423–673 K. To ensure that the compositions correspond to steady-state conditions, the catalyst was kept at the lowest reaction temperature in the stream of reactants for 60 min before samples were taken for analysis.

3.3. Catalyst Characterization

3.3.1. Nitrogen Physisorption

The specific surface area and pore distribution of each sample were determined by nitrogen physisorption performed on an ASAP 2020 instrument (Micromeritics Instrument Corp., Norcross, GA, USA). The procedure was previously described in [49]. Nitrogen (p/p₀ = 0.01–1.00) was dosed onto a degassed sample (degassing conditions: 323 K, 10 h) at 77 K.

3.3.2. X-ray Diffraction

XRD data were collected on D5000 diffractometer (Bruker AXS GmbH, Karlsruhe, Germany) equipped with Cu tube (40kV, 40mA) and LynxEye strip detector. The diffraction patterns for the obtained Upsalite and MgO were measured within the scattering angle ranges 20–160° and 10–90°, respectively, with a step of 0.02 deg. in the continuous scan mode. The Upsalite data were measured with both: Mo (wavelength 0.7107 Å) and Cu (1.5418 Å) radiation; the former required subtraction of a scattering from sample holder. The data from the measurement with the former type of radiation were used for

Pair Distribution Function (PDF) analysis. Based on the obtained diffraction patterns, a Williamson–Hall plot was obtained and the Debye–Waller factor was estimated.

3.3.3. Secondary Electron Microscopy-Energy Dispersive X-ray Spectroscopy (SEM-EDX)

The obtained Upsalite and magnesium oxide were subjected to SEM-EDX studies. They were imaged with a magnification of 500 times and higher with a Quanta FEG 250 from Field Electron and Ion Company, FEI, Hillsboro, OR, USA. The images and EDX spectra were acquired with the following values of accelerating voltage: 10 keV, working distance: 11 mm, spot size 3.

3.3.4. X-ray Photoelectron Spectroscopy (XPS)

The purity of the surface of the obtained solids was probed using X-ray Photoelectron Spectroscopy (Thermo Scientific, Waltham, MA, USA). Survey spectra of MgCO_3 and MgO , as well as the detailed regions (C 1s, O 1s and Mg 2p), were acquired with a pass energy of 200 and 50 eV, respectively, and a step of 1 eV and 0.1 eV, using a K-Alpha instrument.

3.3.5. Attenuated Total Reflectance-Fourier Transform InfraRed Spectroscopy (ATR-FTIR)

Spectra in the range of 450 to 4000 cm^{-1} of both the Upsalites and MgO samples were acquired using a UATR Spectrum Two instrument (PerkinElmer, Waltham, MA, United States). The background spectrum was collected and subtracted automatically. The force gauge of 100 was used for collecting a series of four scans (resolution: 4 cm^{-1}) from samples without pretreatment.

3.3.6. Titration Measurements

The strength and concentration of the basic and acidic sites on the surface of the obtained MgO was determined according to the procedure described elsewhere [49].

3.4. Reagents and Solvents

Anhydrous toluene used for titrimetric measurements was dried via the distillation of commercial toluene (p.a., POCh Gliwice, Gliwice, Poland) in the presence of benzophenone and metallic sodium in dry nitrogen atmosphere. The distillate was stored under nitrogen in a Schlenk type container. A small amount (1 g per 1 dm^3 of MeOH) of an aqueous solution (85%) of phosphoric (V) acid was added to methanol to neutralize methylamines, and methanol was distilled prior to use. Ethanol (99.8%, p.a.) and 2-propanol (p.a), both from POCh Gliwice (Gliwice, Poland), were used as received. Higher alkanols were commercial products (Aldrich, Poznan, Poland, and Reanal, Budapest, Hungary) with purities higher than 99%. They were dried over freshly calcined K_2CO_3 , distilled under nitrogen atmosphere, and kept over anhydrous molecular sieves. Ethanediol (p.a., POCh Gliwice, Gliwice, Poland), propane-1,2-diol (puriss., VEB Apolda, Apolda, Germany) and propane-1,3-diol (>98%, Fluka, Buchs, Switzerland) were dried by distillation under reduced pressure. Propane-1,2,3-triol (85%, p.a., POCh Gliwice, Gliwice, Poland, glycerol) was distilled twice under reduced pressure, b.p. 461–2 K/13 hPa.

4. Conclusions

The synthesis of high-surface-area, amorphous magnesia from Upsalite was performed. The synthesis of both Upsalite and the magnesia were optimized. The results indicate that the type of alcohol and the location of the OH groups in their molecules are of key importance in terms of attaining a high Upsalite yield and surface area. The atmosphere and rate of thermolysis of Upsalite were significant factors in obtaining a high-surface, amorphous MgO . The composition of this oxide, the presence of functional groups on its surface, and the total concentration of active sites were determined, and its activity in the vapor and liquid phase hydrogen transfer to carbonyl compounds was tested. It was shown that it is a very selective catalyst in this reaction. In the case of the reaction of acetophenone and 4-*t*-butylcyclohexanone with 2-pentanol, it gave conversions

that were higher than 85% after only 60 min of reaction with less than 1% of products other than 1-phenylethanol and 4-*t*-butylcyclohexanols, respectively. In the case of transfer hydrogenation of 4-*t*-butylcyclohexanone with either 2-pentanol or 2-propanol, the diastereoselectivity of the reaction was higher than 90% for 180 min.

5. Patents

Polish patent pending: application nr. P437346 from 19.03.2021 entitled: “Method of obtaining high surface area magnesium oxide”.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/catal11111338/s1>, Table S1: Influence of reaction parameters on the yield of Upsalite and its surface area, Table S2: Upsalite thermolysis results ($S_{\text{BET}} = 794 \text{ m}^2 \text{ g}^{-1}$). Influence of atmosphere, decomposition pressure and sample heating rate on the size of the specific surface area of the formed magnesium oxide., Figure S1: XPS results (survey spectra) of Upsalite samples obtained: (a) using different alcohols ($T = 323 \text{ K}$, $p = 5.0 \text{ MPa}$ and $V = 30 \text{ cm}^3$), and (b) under different conditions with methanol (changed variable is provided over the spectrum)., Figure S2: Step-by-step procedure of amorphous MgO preparation.

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