processes

MDPI

Article

Synthesis and Grafted NH_2-Al/MCM-41 with Amine Functional Groups as Humidity Control Material from Silicon Carbide Sludge and Granite Sludge

Ya-Wen Lin [1], Wei-Hao Lee [1], Kae-Long Lin [2,*] and Bo-Yi Kuo [2]

[1] Institute of Mineral Resources Engineering, National Taipei University of Technology, Taipei City 106, Taiwan; urine1001@gmail.com (Y.-W.L.); whlee@ntut.edu.tw (W.-H.L.)

[2] Department of Environmental Engineering, National Ilan University, Yilan City 260, Taiwan; a0936121207@gmail.com

* Correspondence: klllin@niu.edu.tw; Tel.: +886-39357400

Abstract: Mesoporous Al/MCM-41 was synthesized by extracting silicon carbide sludge and granite sludge as the sources of silicon and aluminum. Different concentrations of aminosilane (2.5, 5, 7.5 vol.%) were used to reflux the grafted NH_2-Al/MCM-41 with amine functional groups (NH_2-Al/MCM-41). The physical and chemical characteristics were analyzed. The results confirmed that silicon carbide sludge and granite sludge can effectively synthesize Al/MCM-41 with low cost and environmental protection. Reflow grafted amine functional groups can effectively improve the surface properties of NH_2-Al/MCM-41. The moisture adsorption and desorption capacity of grafted NH_2-Al/MCM-41 with amine functional groups was also studied. Based on moisture adsorption and desorption capacity, the surface properties of NH_2-Al/MCM-41 were studied. When 5 vol.% of NH_2-Al/MCM-41 amine functional groups is added, the moisture adsorption and desorption capacity is best. When the relative humidity = 95%, the equilibrium moisture content is 39.4 kg/kg, which complies with the standard of Japanese Industrial Standard (JIS A 1475). Therefore, the use of waste derived from the industry to replace expensive commercial materials was simple and environmentally friendly, and the grafted NH_2-Al/MCM-41 with amine functional groups can be utilized in multiple applications, particularly as moisture regulation materials in building engineering.

Keywords: waste recycling; reuse; solid waste; MCM-41; functional groups; surface grafted

check for updates

Citation: Lin, Y.-W.; Lee, W.-H.; Lin, K.-L.; Kuo, B.-Y. Synthesis and Grafted NH_2-Al/MCM-41 with Amine Functional Groups as Humidity Control Material from Silicon Carbide Sludge and Granite Sludge. *Processes* **2021**, *9*, 2107. https://doi.org/10.3390/pr9122107

Academic Editor: Juu-En Chang

Received: 29 October 2021
Accepted: 21 November 2021
Published: 24 November 2021

1. Introduction

The development of urban and rural areas has been accompanied by a concentration of urban populations, and the intensive expansion of high-rise buildings has resulted in the production of large amounts of waste in related industries. For example, widely used granite stone buildings have greatly increased residual granite sludge (GS) in the stone industry. Stone slabs are polished with natural lines and gloss, as well as hardness and performance fire resistance, making them ideal building materials. These have been widely used for floors and walls in modern buildings. However, steel grit and lime milk must be added in the sawing process of granite in steel grit. The granite waste obtained from the granite cut industry is in the form of sludge, specifically GS. GS contains fine particles of small diameter, has excellent water permeability of less than 10^{-7} cm/s and has a low dehydration rate. According to Taiwan Environmental Protection Administration, the amount of GS produced in Taiwan is approximately 370,000 tonnes per year [1]. If not recycled, GS will cause environmental pollution, such as in landfills. According to the European Union (EU) environmental data, the EU's waste recycled rate is only 38%. However, more than 60% of waste is still treated as landfill. Therefore, through the target requirements of the EU environmental policy, the potential of these wastes to be managed in an environmentally sound manner and to use the secondary materials contained therein has been increased [2]. Several studies have investigated issues related to sludge management and potential new product production. GS is used industrially as a cement, zeolite LTA and biochar [3–5]. Due to the high content of silica and alumina in GS, effective use of this waste as a new material will diminish the load on the environment and will provide sustainable and greener development and it will help in preserving natural resources. In addition, in the process of silicon processed and production, silicon carbide (SiC) sludge is a by-product of the grinding process. SiC is mixed with a small amount of Al_2O_3, and the wastewater product is processed to produce a large amount of SiC sludge, which causes serious environmental pollution. According to statistics, the amount of SiC sludge produced annually exceeds 200,000 tonnes in Taiwan [1]. Due to the rapid growth of the population, the need for industrialization is also increasing. So a huge amount of solid waste is generated as a byproduct from these industries. Transportation and recycling of these wastes are very expensive. Dumping in large landfills poses an immense problem. The waste generated is hazardous and causes a negative impact on the environment. Therefore, how to recycle and reuse these wastes is very important. Efficient recycling of wastes rich in silicon and aluminum sources and generated economic value are important issues for environmental protection and sustainable management.

In order to promote its recycling, SiC sludge and GS should be manufactured into high value-added products, such as novel humidity control material. Recent research on preparing humidity control material [6,7] has led to a proliferation of relevant studies on improving comfort and saving energy in buildings [8]. The humidity regulating material has the capability of absorbing water vapor to lower the humidity once the indoor RH is more than 70%, and vice versa, it can release the adsorbed water vapor to raise the humidity when the humidity falls under RH 40% [6]. However, intelligent humidity control composite materials with high moisture adsorption ability, proper humidity control range and fast response to humidity changes are still under wide investigations [9].

Many researchers have studied other chemical techniques used different silica precursors to produce mesoporous silica, especially MCM-41. Mesoporous MCM-41 is a hexagonal, one-dimensional material with mesopores in a uniform capillary system [10]. The capillary size ranges from 2 to 10 nm. Large surface areas and excellent acidity have led to its widespread use in support materials [11]. However, the relatively high production costs of synthetic mesoporous MCM-41 materials through pure chemicals limit them to industrial applications. Therefore, it is necessary to find inexpensive procedures that can replace the synthesis and improve the electrical conductivity and hydrothermal stability. The internal space of ordered mesoporous silica can be grafted by used amine groups. Amine functionalized MCM-41 can be used to design metal complexes into ordered mesopores [12]. The presence of amine groups can greatly enhance the capability of adsorbing water vapor of the material.

This research will try to synthesize regular morphological mesoporous materials from mixed SiC sludge and GS and functionalize them with amine functional groups to improve the hydrophilic properties of the materials. In this work, the possibility of reused SiC sludge and GS produced in the technical industrial process is proposed. The purpose is to increase the potential for large-scale recovery and reuse of mixed sludge waste in the sludge treatment industry in the future. However, the novelty of our approach is the use of SiC sludge and GS as raw materials, and to functionalize them with amine functional groups. The method not only provides low-cost production and but also recycles the industrial solid waste to the environment.

2. Experimental Materials and Methods

2.1. Raw Materials and Chemicals

In this study, SiC sludge was collected from a photovoltaic manufacturing plant in Taoyuan, Taiwan. GS was collected from the stone-processed industry in Hualien, Taiwan. Sodium hydroxide powder (NaOH) and (3-aminopropyl) triethoxysilane (3-APTES, 99%) were obtained from Sigma-Aldrich. Cetyltrimethylammonium chloride (CTMACl) was purchased from Tokyo Kasei Kogyo Co. Sulfuric acid (H_2SO_4, Nippon Shinyaku Co., Ltd., Japan), ammonia (Fisher Scientific, United States), cetyltrimethylammonium bromide (CTAB, Acros Organics, United States) and anhydrous toluene (VNK Supply & Services, Malaysia).

2.2. Synthesis of NH_2-Al/MCM-41

The mesoporous silica nanomaterials studied in this article were prepared by alkali fusion and hydrothermal methods from solid waste generated in industrial processes. The alkali fusion method was used to extract silicon and aluminum sources from SiC grinding mud and stone mud and then to prepare mesoporous materials through hydrothermal reaction. The effect of surface functionalization of amine groups on the product structure and the environmental application of the product as a hydrophilic adsorbent were studied.

First, we mixed GS and SiC sludge to NaOH powder (in a weight ratio of 1:1.25) and heated it at 450 °C for 1 h to obtain alkali fused powder. An aluminosilicate precursor rich in silicon and aluminum sources was obtained from the alkali fused powder. Next, the template mixture was obtained by dispersed ammonia in distilled water contained CTAB, added the aluminosilicate precursor and stirred uniformly, and used sulfuric acid (1 M) to achieve a pH of 10. Finally, the mixed solution was placed into a high temperature autoclave, and a hydrothermal reaction was carried out at a hydrothermal temperature of 120 °C for 48 h. The resulted solid product was washed, filtered, and dried in an oven at 105 °C. Finally, the obtained powder was calcined at 550 °C for 5 h. This sample is referred to as Al/MCM-41.

Under vigorous stirring on an electromagnetic stirrer, we refluxed Al/MCM-41 (1.0 g) and 3-APTES (2.5, 5.0, 7.5 vol.%) in anhydrous toluene and kept the temperature at 120 °C. The mixture was placed in a reflux device, introduced into a nitrogen atmosphere and then refluxed at 120 °C for 12 h. The product was filtered and dried for 24 h. This sample is referred to as NH_2-Al/MCM-41.

2.3. Characterization of Materials

Field emission scanned electron microscopy (FE-SEM, JSM7001F, Japan) and transmission electron microscopy (HR-TEM, JEM2000FXII, Japan) were used to examine the surface morphology of the sample. An XRF fluorescence analyzer (Rigaku® RIX 2000, Japan) was used to measure the chemical element composition of the raw materials. The powder X-ray diffraction (XRD) pattern was obtained by used a Rigaku MiniFlex 600 diffractometer with Cu Kα radiation. The solid-state ^{27}Al MAS NMR measurement was performed at the resonance frequency of (NMR, Solid State NMR 400, Germany). In the material grafted with amine functional groups on the surface, an elemental analyzer (elementar vario EL cube, Germany) was used to confirm the carbon, hydrogen and nitrogen contents of the organic groups. Nitrogen adsorption isotherms were measured with a Micromeritics Tristar 3000, and the specific surface area and pore size distribution were calculated by the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods. The moisture adsorption and desorption curve was drawn with reference to Japanese Industrial Standard (JIS A 1475:2004) Method of test for hygroscopic sorption properties of building materials stipulated by the Japanese Industrial Standard/Japanese Standards Association. The moisture adsorption and desorption capacity of the material in different humidity environments (RH% = 0–95%) at 23 °C was tested, and the feasibility of the material as a building material was discussed.

3. Results and Discussion

3.1. Characterization of Raw Material

In order to achieve the stability and reliability of the experiment, we collected more than 100 kg of raw material samples, and tested the basic physical properties of the raw materials after drying, grinding in a cylindrical ball mill and passing them through a 100 mesh circular sieve (passed 149 µm) (Table 1). The results showed that the pH values of SiC sludge and GS were 7.61 and 8.52, respectively. It was found that SiC sludge and GS are all alkaline materials. In addition, the proportions of SiC sludge and GS are 2.55 and 2.92, respectively. The particle size of SiC sludge was mainly 44–590 μm, accounting for 87.89% of the total; and the particle size of GS was mainly 37–177 μm, accounting for 84.93% of the total, and the particle size was less than about 37 μm, accounting for 13.38% of the total. In addition, in order to improve the uniformity of the material, all used materials were sieved through 200 mesh before use. Figure 1 shows the particle size of the raw materials tested before sieving. Table 2 shows the XRF results of the raw materials, confirming that the raw materials contain a large amount of SiO_2 and Al_2O_3, which can be used as an alternative source for the synthesis of NH_2-Al/MCM-41 through the extraction of the alkali fusion system [13].

Table 1. T Basic characteristics of SiC sludge and GS.

Sample	pH (1:10)	Specific Gravity	Density (g/cm^3)	Moisture (%)	Fineness (m^2/kg)	Loss on Ignition (%)
Silicon Carbide Sludge	7.61	5.55	1.44	0.03	353.8	0.08
Granite Sludge	8.52	2.92	1.66	0.01	519.8	0.10

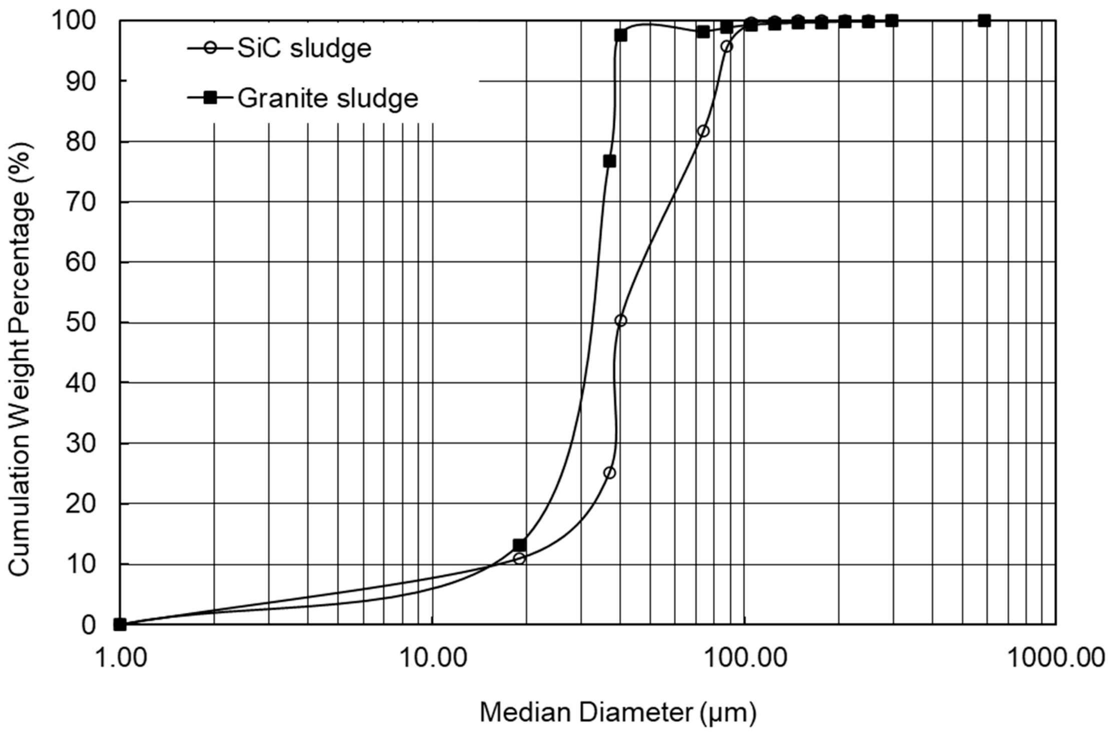


Figure 1. Particle size distribution of SiC sludge and GS.

Table 2. Chemical composition of raw materials.

Composition (%)	Silicon Carbide Sludge	Granite Sludge
SiO_2	98.70	70.40
Al_2O_3	0.52	15.20
MgO	N.D.	0.70
SO_3	0.05	0.11
K_2O	0.01	4.26
Fe_2O_3	0.52	3.18
TiO_2	0.01	0.47
CaO	0.07	2.56
Na_2O	N.D.	2.88

3.2. Total Metals and TCLP Leaching Concentration of Raw Materials

Table 3 shows the total metals and the TCLP leaching concentration of raw materials. The results showed that the SiC sludge was mainly Cu with a content of 1029.65 mg/kg. According to NIEA R201.13C and the toxicity characteristic leaching procedure (TCLP), the GS and SiC sludge were subjected to heavy metal leaching procedures, and flame atomic absorption spectrometry was used to test the heavy metal leaching of all materials. Table 3 shows the leaching concentration of raw materials. From the leaching concentration of heavy metals in TCLP, SiC sludge had a relatively large amount of Cu leaching, and its leaching amount was 8.29 mg/L. The GS had only trace amounts of Cu and Zn leaching out. According to the results of the TCLP leaching test, the leaching concentrations all met the regulatory limit of the Taiwan Environmental Protection Agency and has the potential for resource reuse.

Table 3. The total metals and TCLP leaching concentration of raw material.

Total Metal (mg/kg)	Pb	Cr	Cu	Zn	Cd	Ni
Silicon Carbide Sludge	N.D.	N.D.	1029.65	20.02	N.D.	4.29
Granite Sludge	N.D.	N.D.	111.54	145.86	N.D.	N.D.
TCLP (mg/L)	**Pb**	**Cr**	**Cu**	**Zn**	**Cd**	**Ni**
Silicon Carbide Sludge	N.D.	N.D.	8.29	0.10	N.D.	0.03
Granite Sludge	N.D.	N.D.	0.40	0.70	N.D.	N.D.
Regulatory Limits	5.00	5.00	15.00	–	1.00	–

3.3. Crystal Phase of NH_2-Al/MCM-41

Figure 2 shows a small-angle XRD pattern of grafted NH_2-Al/MCM-41 with amine functional groups. The result showed that the main characteristic peak of $d_{(100)}$ at 2θ of 2.32° indicated an ordered hexagonal mesoporous structure [14]. At 2θ of 2.32°, 3.92°, 4.56° and 6°, there are characteristic peaks of $d_{(110)}$, $d_{(200)}$ and $d_{(210)}$, respectively, indicated the typical XRD spectra of mesoporous materials [15]. The $d_{(100)}$ interplanar spacing of grafted NH_2-Al/MCM-41 without amine functional groups was calculated to be 3.84 nm, and the pore wall thickness was 0.77 nm (Figure 2a). It is proved that the Al source enters and strengthens the NH_2-Al/MCM-41 framework structure. The highly ordered mesoporous framework is due to the addition of CTAB. Insufficient or excessive amounts destroy the micelle structure and reduce the order of the pore structure [16]. In addition, 2θ between 3–5° has two secondary characteristic peaks, the lattice positions of which are $d_{(110)}$ and $d_{(200)}$. This is the influence of the change in surfactant accumulation parameters and CTAB dilution, which promotes the slow hydrolysis rate of the silicon source [17]. When the addition amount of grafted NH_2-Al/MCM-41 with 2.5 to 7.5 vol.% amine functional groups is calculated (Figure 2b), the main characteristic peak $d_{(100)}$ exists at 2θ of 2.18–2.28°. Therefore, the NH_2-Al/MCM-41 retains ordered hexagonal pores and characteristics [18]. However, when the number of amine functional groups increases, it indicates that the amine functional groups enter the pore surface and cause the $d_{(200)}$ characteristic peak to disappear. Previous studies have shown that the intensity of the significant peak of NH_2-Al/MCM-41 is reduced, which proves that amine functional groups mainly appear in mesoporous channels [19].

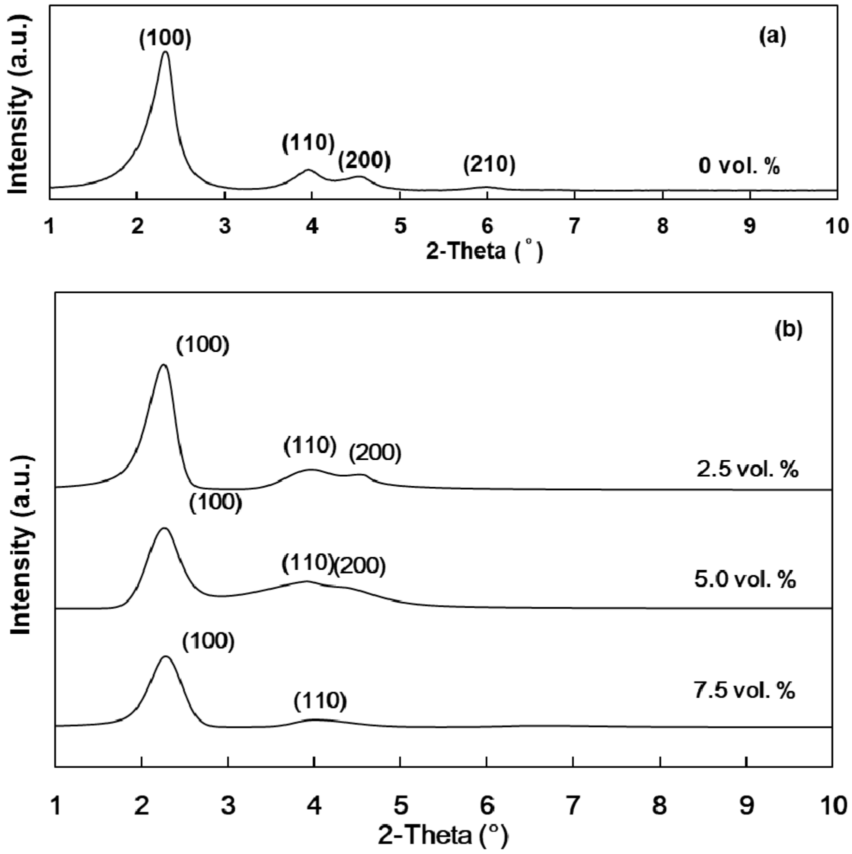


Figure 2. Small-angle XRD patterns of grafted NH_2-Al/MCM-41 with different amine functional groups. (**a**) 0 vol %; (**b**) 2.5 vol.%–7.5 vol.%.

Figure 3 shows a FTIR spectra of grafted NH_2-Al/MCM-41 with 5.0 vol.% amine functional groups. The presence of functional groups was identified using FTIR analysis (Figure 3). In the Figure, broad absorption bands focused at 3412 cm^{-1} indicate the presence of –OH functional groups [19]. The absorption peaks observed at 693 and 2928 cm^{-1} correspond to the vibration of the N–H group confirming formation. The observed peak at 1066 cm^{-1} is assigned to Si–O–Si associated with the formation of a condensed silica network [12].

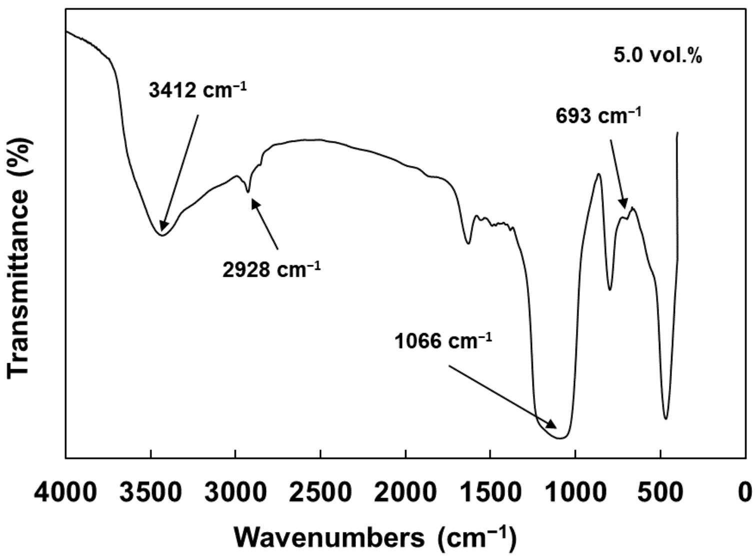
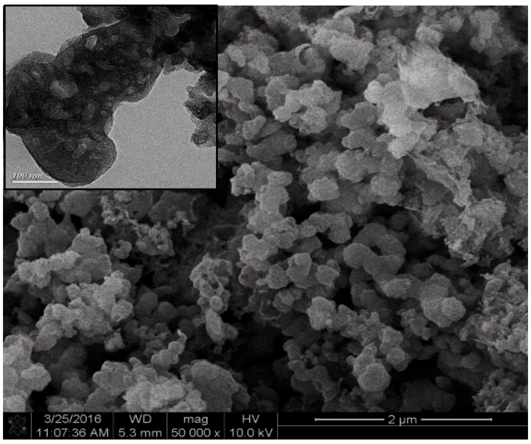


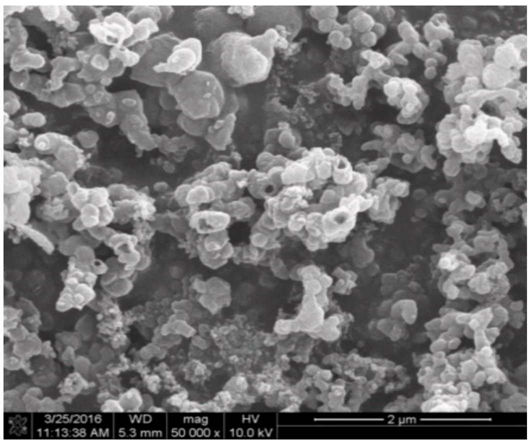
Figure 3. FTIR spectra of grafted NH_2-Al/MCM-41 with 5.0 vol.% amine functional groups.

3.4. SEM Images of NH_2-Al/MCM-41

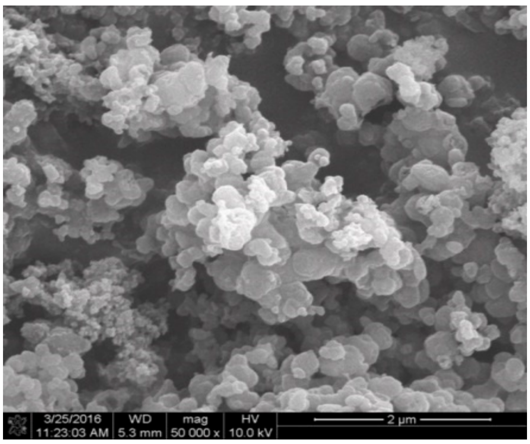
Figure 4 shows SEM images of grafted NH_2-Al/MCM-41 with amine functional groups. The grafted NH_2-Al/MCM-41 without amine functional groups is spherical in appearance and exhibits agglomeration of fine particles, which is a typical form of mesoporous materials [20]. In addition, the calculated average particle size range is approximately 0.09–0.36 nm. The small image in Figure 4a shows the TEM observation results. The results showed a complete and ordered honeycomb hexagonal structure, indicating a typical porous structure and highly ordered mesopores [21]. The results confirm the successful synthesis of MCM-41 with a long-range order and two-dimensional hexagonal pore structure [22]. When the additional amount of grafted NH_2-Al/MCM-41 with 2.5 to 7.5 vol.% amine functional groups is calculated (Figure 4b–d), the particle size is approximately 0.13–0.30 μm. The spherical particles of grafted NH_2-Al/MCM-41 with amine functional groups is usually used for adsorption studies [23]. However, grafted NH_2-Al/MCM-41 with amine functional groups show different morphologies where most of the nanoparticles are aggregated, compared to the grafted NH_2-Al/MCM-41 without amine functional groups. In addition, when the amount of amine functional groups increased, the phenomenon of particle-to-particle bonding and agglomeration becomes more obvious; the particle size is about approximately 0.13–0.30 μm. However, the results showed that there is no difference in the morphology of NH_2-Al/MCM-41 grafted by amine functional groups. Compared with MCM-41 reported by other researchers, the FE-SEM image of the synthesized NH_2-Al/MCM-41 showed that the mesoporous structure did not change significantly after grafted the amine functional groups, the results showed that the basic hexagonal unit structure of MCM-41 was retained after grafting [19,24,25].



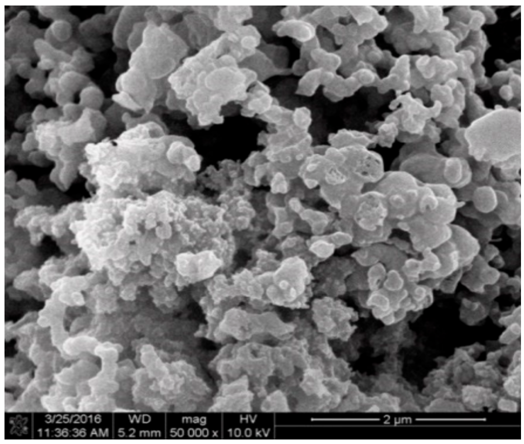
(**a**) 0 vol.%



(**b**) 2.5 vol.%



(**c**) 5 vol.%



(**d**) 7.5 vol.%

Figure 4. SEM image of grafted NH_2-Al/MCM-41 with different amine functional groups.

3.5. Pore Size Distribution of NH_2-Al/MCM-41

Figure 5 shows the pore size distribution and N_2 isotherm adsorption-desorption curve of grafted NH_2-Al/MCM-41 with amine functional groups. The results show that the average pore size is 12.20, 9.75 and 9.31 nm, and the average pore volume is reduced from 0.103 to 0.063 cm^3/g after calculation by the BJH method. When the NH_2-Al/MCM-41 has a smaller pore volume and pore diameter, fewer nitrogen molecules condense in the pore structure. There are organic groups in the framework, and water molecules can still be adsorbed on the surface of periodic mesoporous organic silica, water molecules first adsorb on the surfaces of silicate units prior to those of organic groups and finally the mesopores are filled by capillary condensation of water molecules. The grafted amine functional groups are bonded to the surface of the molecular sieve, resulting in dense amine functional groups in the pore walls and thus a decrease in specific surface area of 30.57, 34.12 and 24.45 m^2/g. However, the average pore volume and average pore diameter are relatively small. After grafted amine functional groups NH_2-Al/MCM-41, the BET surface area, total pore volume and pore diameter decrease [12]. In addition, the nitrogen isothermal adsorption and desorption curve of NH_2-Al/MCM-41 belongs to the type IV isothermal adsorption and desorption curve of medium-sized pore adsorption materials [16,26], which has a hysteresis loop of the H4 type, and the nitrogen adsorption and desorption curve showed typical mesoporous characteristics [27]. According to the measurement of nitrogen adsorption and desorption, the average pore diameter is approximately 3.98 nm, and a large number of mesopores distributed in the range of 3–20 nm can apparently improve the water adsorption performance [9]. Table 4 shows the pore structure parameters of grafted NH_2-Al/MCM-41 with amine functional groups.

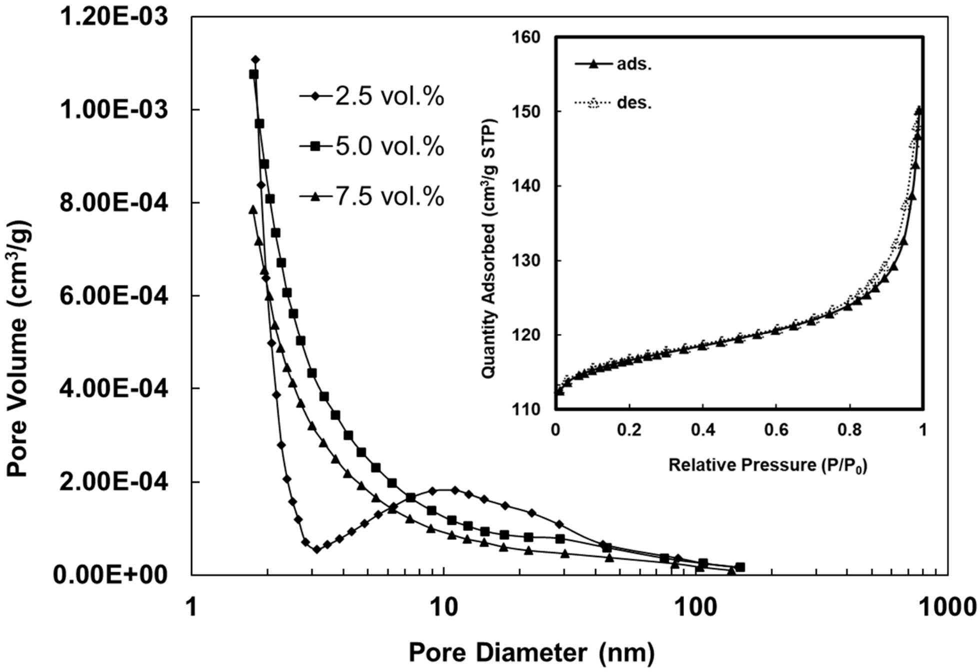


Figure 5. Pore size distribution and N_2 isotherm adsorption-desorption curve (5.0 vol.%) of grafted NH_2-Al/MCM-41 with different amine functional groups.

Table 4. The pore structure parameters of grafted NH_2-Al/MCM-41 with different amine functional groups.

Sample	Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Diameter (nm)
2.5 vol.%	30.57	0.103	12.20
5.0 vol.%	34.12	0.094	9.75
7.5 vol.%	24.45	0.063	9.31

In addition, Rahimi et al. used TGA to analyze the organic content of MCM-41 and NH_2-MCM-41 nanostructures [12]. The results showed that the NH_2-MCM-41 revealed higher weight loss compared to that of MCM-41. Weight loss observed at above 150 °C for NH_2-MCM-41 was related to the decomposition of the amine group anchored to the pore walls [28]. The weight loss obtained below 150 °C for both ungrafted and grafted MCM-41 corresponded to the desorption of water molecules [19]. It is confirmed that the NH_2-Al/MCM-41 exhibits relatively higher thermal stability.

3.6. ^{27}Al Solid-State NMR of NH_2-Al/MCM-41

Figure 6 shows the ^{27}Al NMR spectrum of NH_2-Al/MCM-41. When the chemical shift of the NH_2-Al/MCM-41 sample is 53 ppm, it has tetrahedral coordination. When the chemical shift occurs at 0 ppm, it is shown as the octahedral coordination of aluminum, and the hydrolysis and condensation of NH_2-Al/MCM-41 in the synthesis stage affect its coordination [29]. In addition, the chemical shift at 52 ppm is due to the addition of amine functional groups. Different positions of chemical shifts can distinguish aluminum atoms as tetrahedrons or octahedrons in the framework [30]. When the aluminum atom is in the form of a tetrahedron, a chemical shift occurs at 56 ppm. The figure showed that as the addition of amine functional groups increases, the chemical shift produced is still consistent with Al/MCM-41, indicating that the addition of amine functional groups does not affect the NH_2-Al/MCM-41 framework structure, and the Al coordination mode with the tetrahedral structure is still maintained [31].

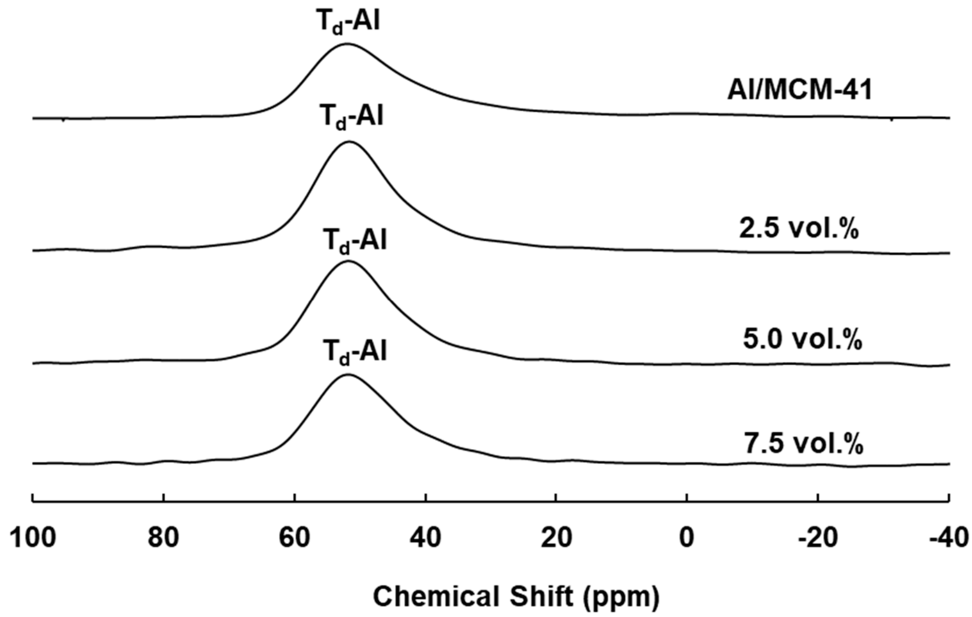


Figure 6. ^{27}Al NMR spectra of grafted NH_2-Al/MCM-41 with different amine functional groups.

3.7. Equilibrium Moisture Content Curve and Humidity Control Performance of NH_2-Al/MCM-41

This study is based on the Japanese Industrial Standards (JIS A 1475) for the determination of the equilibrium moisture content of building materials. The ambient temperature was constant at 23 °C with different ambient humidity (RH% = 10%, 33%, 55%, 75%, 85%, 95%) to determine the equilibrium moisture content of NH_2-Al/MCM-41. Figure 7 shows the equilibrium moisture content curve of grafted NH_2-Al/MCM-41 with different amine functional groups. With the addition of amine functional groups from 2.5 vol.% to 7.5 vol.% (RH% = 95%), the equilibrium moisture content range is 37.3–39.4 kg/kg. The figure showed that when the amount of amine functional groups is increased to 7.5 vol.%, the equilibrium moisture content showed a downward trend. However, the addition of amine functional groups at 5 vol.% has the best moisture adsorption and desorption capacity, and as the relative humidity rises from 10% to 95%, its equilibrium moisture content is 39.4 kg/kg. It is possibly that the number of grafted amine functional groups is more appropriate to coordinate with the number of Si-OH groups on the surface of Al/MCM-41. Therefore, when the amount of amine functional groups is 5 vol.%, the concentration of amine functional groups grafted to NH_2-Al/MCM-41 is more prone to capillary condensation, so it has better moisture adsorption and desorption capacity under high relative humidity. Moreover, water molecules hardly adsorbed on amine. In contrast, water molecules can be adsorbed on the surfaces of periodic mesoporous organosilicas in spite of the presence of organic groups within the frameworks [32]. In this case, water molecules first adsorb on the surfaces of silicate units prior to those of organic groups and finally the mesopores are filled by capillary condensation of water molecules though the surfaces are more hydrophobic than those of ordered mesoporous silicas [17].

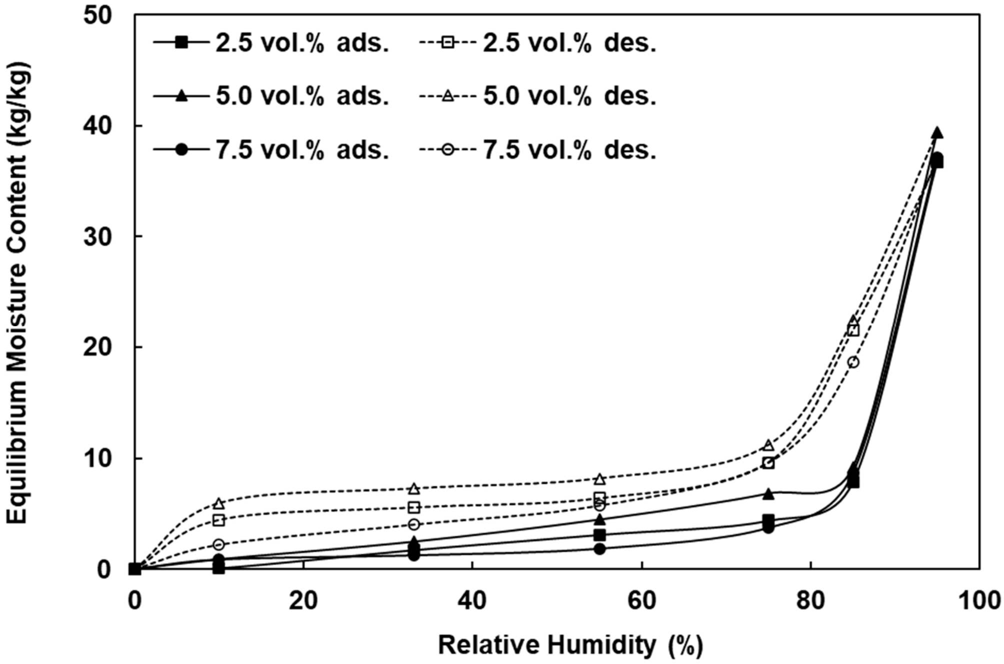


Figure 7. Equilibrium moisture content curve of grafted NH_2-Al/MCM-41 with different amine functional groups.

4. Conclusions

In this work, the possibility of reused SiC sludge and GS produced in the technical industrial process is proposed. The purpose is to increase the potential for large scale recovery and reuse of mixed sludge waste in the sludge treatment industry in the future. This research uses SiC sludge and GS as a raw material of silicon and aluminum, and explores the feasibility of extracting Si and Al sources from this material by alkali fusion treatment. A hydrothermal and reflux grafted method was used for the synthesis of NH_2-Al/MCM-41, and the macro- and microscopic properties and humidity control performance were analyzed. The synthetic NH_2-Al/MCM-41 located at $d_{(100)}$, $d_{(110)}$, and $d_{(200)}$, showed the characteristic peak of mesoporous materials. When the concentration of the amine functional groups is 5.0 vol.% in the mixed solution, the average pore size of the NH_2-Al/MCM-41 was 9.75 nm, and the surface area was 34.12 m^2/g. The equilibrium moisture content (39.4 kg/kg) of the humidity control test met Japan Industrial Specifications (JIS A 1475), which mark the potential to be a humidity-controlling building material. The results showed that the recycling of SiC sludge and GS generated in industrial processes can effectively replace chemicals and can also be used as a new application.

Author Contributions: Y.-W.L.: writing—original draft, methodology, conceptualization. W.-H.L.: supervision. K.-L.L.: resources, writing—commenting and editing. B.-Y.K.: validation, investigation, methodology. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by Ministry of Science and Technology of Taiwan, for supporting this research financially (Contract No. MOST-107-2221-E-197-002-MY3).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

References

1. Environmental Protection Administration, R. O. C. (Taiwan). 2021. Available online: https://www.epa.gov.tw (accessed on 9 May 2021).
2. Oficjalna Strona Internetowa Unii Europejskiej. Available online: https://ec.europa.eu/environment/topics/waste-and-recycling_pl (accessed on 8 May 2021).
3. Clausi, M.; Fernández-Jiménez, A.M.; Palomo, A.; Tarantino, S.C.; Zema, M. Reuse of waste sandstone sludge via alkali activation in matrices of fly ash and metakaolin. *Constr. Build. Mater.* **2018**, *172*, 212–223. [CrossRef]
4. Rozhkovskaya, A.; Rajapakse, J.; Millar, G.J. Synthesis of high-quality zeolite LTA from alum sludge generated in drinking water treatment plants. *J. Environ. Chem. Eng.* **2021**, *9*, 104751. [CrossRef]
5. Xue, J.; Wang, H.; Li, P.; Zhang, M.; Yang, J.; Lv, Q. Efficient reclaiming phosphate from aqueous solution using waste limestone modified sludge biochar: Mechanism and application as soil amendments. *Sci. Total Environ.* **2021**, *799*, 149454. [CrossRef] [PubMed]
6. Lan, H.; Zhang, Y.; Cheng, M.; Li, Y.; Jing, Z. An intelligent humidity regulation material hydrothermally synthesized from ceramic waste. *J. Build. Eng.* **2021**, *40*, 102336. [CrossRef]
7. Castellano, J.; Sanz, V.; Cañas, E.; Sánchez, E. Assessment of humidity self-regulation functionality for ceramic tiles. *J. Eur. Ceram. Soc.* **2021**, in press. [CrossRef]
8. Yang, L.; Yan, H.; Lam, J.C. Thermal comfort and building energy consumption implications—A review. *Appl. Energy* **2014**, *115*, 164–173. [CrossRef]
9. Lin, Y.W.; Lin, K.L.; Cheng, T.W.; Chen, C.Y.; Lo, K.W. Synthesis and environmental applications of aluminum-containing MCM-41 type material from industrial waste containing silicon and aluminum. *J. Non. Cryst. Solids* **2021**, *569*, 120954. [CrossRef]
10. Du, C.; Yang, H. Investigation of the physicochemical aspects from natural kaolin to Al-MCM-41 mesoporous materials. *J. Colloid Interface Sci.* **2012**, *369*, 216–222. [CrossRef]
11. Pirouzmand, M.; Anakhatoon, M.M.; Ghasemi, Z. One-step biodiesel production from waste cooking oils over metal incorporated MCM-41; positive effect of template. *Fuel* **2018**, *216*, 296–300. [CrossRef]
12. Rahimi, Z.; Zinatizadeh, A.A.; Zinadini, S.; van Loosdrecht, M.; Younesi, H. A new anti-fouling polysulphone nanofiltration membrane blended by amine-functionalized MCM-41 for post treating waste stabilization pond's effluent. *J. Environ. Manag.* **2021**, *290*, 112649. [CrossRef]
13. Panek, R.; Wdowin, M.; Franus, W.; Czarna, D.; Stevens, L.A.; Deng, H.; Liu, J.; Sun, C.; Liu, H.; Snape, C.E. Fly ash-derived MCM-41 as a low-cost silica support for polyethyleneimine in post-combustion CO_2 capture. *J. CO_2 Util.* **2017**, *22*, 81–90. [CrossRef]
14. Zhou, C.; Gao, Q.; Luo, W.; Zhou, Q.; Wang, H.; Yan, C.; Duan, P. Preparation, characterization and adsorption evaluation of spherical mesoporous Al-MCM-41 from coal fly ash. *J. Taiwan Inst. Chem. Eng.* **2015**, *52*, 147–157. [CrossRef]
15. Karnjanakom, S.; Suriya-umporn, T.; Bayu, A.; Kongparakul, S.; Samart, C.; Fushimi, C.; Abudula, A.; Guan, G. High selectivity and stability of Mg-doped Al-MCM-41 for in-situ catalytic upgrading fast pyrolysis bio-oil. *Energy Convers. Manag.* **2017**, *142*, 272–285. [CrossRef]
16. Chen, H.; Yang, H.; Xi, Y. Highly ordered and hexagonal mesoporous silica materials with large specific surface from natural rectorite mineral. *Microporous Mesoporous Mater.* **2019**, *279*, 53–60. [CrossRef]
17. Kimura, T.; Suzuki, M.; Maeda, M.; Tomura, S. Water adsorption behavior of ordered mesoporous silicas modified with an organosilane composed of hydropHobic alkyl chain and hydropHilic polyethylene oxide groups. *Microporous Mesoporous Mater.* **2006**, *95*, 213–219. [CrossRef]
18. Amama, P.B.; Lim, S.; Ciuparu, D.; Pfefferle, L.; Haller, G.L. Hydrothermal Synthesis of MCM-41 using Different Ratios of Colloidal and Soluble Silica. *Microporous Mesoporous Mater.* **2005**, *81*, 191–200. [CrossRef]
19. Ebrahimi-Gatkash, M.; Younesi, H.; Shahbazi, A.; Heidari, A. Amino-functionalized mesoporous MCM-41 silica as an efficient adsorbent for water treatment: Batch and fixed-bed column adsorption of the nitrate anion. *Appl. Water Sci.* **2017**, *7*, 1887–1901. [CrossRef]

20. Gao, L.; Shi, Z.; Etim, U.J.; Wu, P.; Han, D.; Xing, W.; Mintova, S.; Bai, P.; Yan, Z.; Yan, Z. Beta-MCM-41 micro-mesoporous catalysts in the hydroisomerization of n-heptane: Definition of an indexed isomerization factor as a performance descriptor. *Microporous Mesoporous Mater.* **2019**, *277*, 17–28. [CrossRef]
21. Bedoya, J.C.; Valdez, R.; Cota, L.; Alvarez-Amparán, M.A.; Olivas, A. Performance of Al-MCM-41 nanospheres as catalysts for dimethyl ether production. *Catal. Today* **2021**, *4*. in press. [CrossRef]
22. Liu, Y.; Li, C.; Peyravi, A.; Sun, Z.; Zhang, G.; Rahmani, K.; Zheng, S.; Hashisho, Z. Mesoporous MCM-41 derived from natural Opoka and its application for organic vapors removal. *J. Hazard. Mater.* **2021**, *408*, 124911. [CrossRef]
23. Szegedi, A.; Popova, M.; Goshev, I.; Klébert, S.; Mihály, J. Controlled drug release on amine functionalized spherical MCM-41. *J. Solid State Chem.* **2012**, *194*, 257–263. [CrossRef]
24. Bao, Y.; Yan, X.; Du, W.; Xie, X.; Pan, Z.; Zhou, J.; Li, L. Application of amine-functionalized MCM-41 modified ultrafiltration membrane to remove chromium (VI) and copper (II). *Chem. Eng. J.* **2015**, *281*, 460–467. [CrossRef]
25. Yang, S.; Wu, Y.; Aierken, A.; Zhang, M.; Wu, Y. Adsorption of Ni (II) using amine-functionalized MCM-41 optimized by response surface methodology. *Desalination Water Treat.* **2016**, *57*, 8526–8539. [CrossRef]
26. Cychosz, K.A.; Guillet-Nicolas, R.; García-Martínez, J.; Thommes, M. Recent advances in the textural characterization of hierarchically structured nanoporous materials. *Chem. Soc. Rev.* **2017**, *46*, 389–414. [CrossRef] [PubMed]
27. Li, H.; Ai, M.; Liu, B.; Zheng, S.; Zong, G. Water vapor sorption on surfactant-templated porous silica xerogels. *Microporous Mesoporous Mater.* **2011**, *143*, 1–5. [CrossRef]
28. Parida, K.M.; Mallick, S.; Pradhan, G.C. Acylation of anisole over 12-heteropolyacid of tungsten and molybdenum promoted zirconia. *J. Mol. Catal. A Chem.* **2009**, *297*, 93–100. [CrossRef]
29. Birjega, R.; Ganea, R.; Nenu, C.; Pop, G.; Jitianu, A. Al-MCM-41 synthesis using Al-isopropoxide as Al source. *Stud. Surf. Sci. Catal.* **2002**, *141*, 151–158.
30. Naranov, E.R.; Sadovnikov, A.A.; Maximov, A.L.; Karakhanov, E.A. Development of micro-mesoporous materials with lamellar structure as the support of NiW catalysts. *Microporous Mesoporous Mater.* **2018**, *263*, 150–157. [CrossRef]
31. Ivanova, I.I.; Kolyagin, Y.G.; Kasyanov, I.A.; Yakimov, A.V.; Bok, T.O.; Zarubin, D.N. Time-Resolved In Situ MAS NMR Monitoring of the Nucleation and Growth of Zeolite BEA Catalysts under Hydrothermal Conditions. *Angew. Chem.* **2017**, *129*, 15546–15549. [CrossRef]
32. Kimura, T.; Saeki, S.; Sugahara, Y.; Kuroda, K. Organic modification of FSM-type mesoporous silicas derived from kanemite by silylation. *Langmuir* **1999**, *15*, 2794–2798. [CrossRef]