研究与开发

水热法改性工业级 $Mg(OH)_2$ 晶体形貌研究

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摘要 以工业级 $Mg(OH)_2$ 为原料,应用水热技术对 $Mg(OH)_2$ 晶体形貌和颗粒尺寸进行改性。考察了水、乙醇和尿素 3 种水热溶剂对 $Mg(OH)_2$ 晶体的影响。通过扫描电镜(SEM)表征可知,3 种水热溶剂在一定程度上都可以改善工业级薄片状 $Mg(OH)_2$ 晶体的形貌和团聚状态。尤其是尿素对 $Mg(OH)_2$ 改性效果最为明显,在 250 ℃下改性可以得到尺寸在 10 μm,形貌非常规整的立方体晶体。

关键词 氢氧化镁;水热介质;改性;阻燃剂

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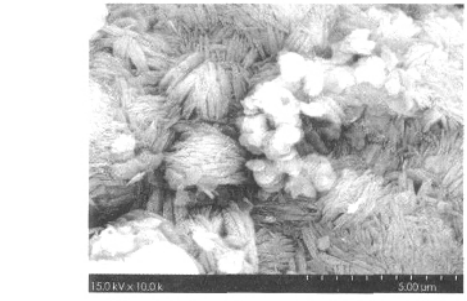
氢氧化镁作为无机添加型阻燃剂,具有阻燃、抑烟、无毒、热稳定性高的优点,越来越受到人们的关注[1-3]。但工业级的薄片状氢氧化镁表面能较高,氢氧化镁与高聚物混合时容易发生二次团聚,引起在高聚物中阻燃效率低,需要的填充量增大[4,5]。因此人们采用水热技术对工业级氢氧化镁进行改性处理[6],使氢氧化镁非极性面暴露、晶体分散均匀,晶体形貌更加规整、晶体的粒径分布更加均匀,能在材料中均匀分布而不发生二次团聚,达到高效的阻燃性能。

水热处理是利用高温高压溶液的性质,使那些在常温常压条件下不溶或难溶于水的物质溶解度提高,达到一定的过饱和度并结晶[7]。虽然在一定的水热条件下可以增加氢氧化镁晶体的溶解度,但高温条件下氢氧化镁的溶解度有限,存在着改性不完全的问题,因此需要加入一定的物质以提高其溶解性。氢氧化镁的水热介质很多,如 NaOH, $MgCl_2$, NH_4Cl, KOH, EDTA 等[8]。本文分别以乙醇、水和尿素为溶剂改性氢氧化镁,讨论以尿素为改性剂,不同的水热温度和浓度对氢氧化镁晶体形貌的影响。

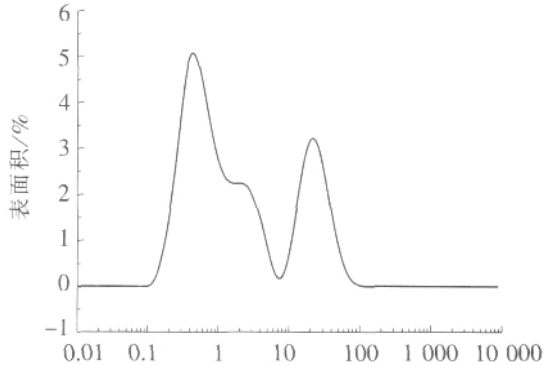
1 实验部分

1.1 原料

实验所用的氢氧化镁原料是由某化工厂提供,是利用含氯化镁废液和氨水直接沉淀制得的,原料形貌如图 1(a)所示,可见大部分为不规则片状,并且片状物之间大多呈团聚状态,比表面积 24 m^2/g,表观粒径分布集中在 1 μm 和 30 μm。



(a)



(b)

图 1 氢氧化镁原料的形貌和粒径分布

1.2 水热改性方法

实验采用内衬聚四氟乙烯、容积 100 mL 的水热反应釜,将 3.5 g 氢氧化镁、70 mL 水热介质置于水热反应釜中,密封后加热到一定的反应温度恒温 4 h,反应结束后自然冷却到室温,过滤、干燥。

1.3 形貌分析

晶体的形貌由 JSM-6301F 型场发射扫描电镜(加速电压 15 kV)表征;Malvern UK 2000 激光粒度

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仪测定产品的表观粒度。

2 结果与讨论

2.1 不同溶液对改性的影响

图 2 分别为采用乙醇、水、尿素溶液作为溶剂改性氢氧化镁产品 SEM 图。

由图 2 可知，水热改性后，颗粒的分散性增加，片与片之间粘连现象减少。由图 2(a)可知以乙醇为水热介质改性氢氧化镁，氢氧化镁晶体小颗粒粘附在大颗粒上，小颗粒的粒径主要集中在 400 nm 左右，而大颗粒的氢氧化镁主要集中在 1.0 μm。六方片状不规则，氢氧化镁颗粒的边缘呈椭圆形。由图 2(b)以水为溶剂改性后，晶体的颗粒主要集中在 400～800 nm，晶体的六方片状比较规整，但是部分片状之间团聚在一起。由图 2(c)尿素溶液改性氢氧化镁，晶体的厚度明显增加，而且六方片状更加规整，晶体的粒径主要集中在 600～1 000 nm。

由上可知，以乙醇为溶剂改性氢氧化镁，晶体的粒径大小分布不均匀，氢氧化镁在乙醇中的溶解度比较小，改性效果不明显；以水为溶剂改性氢氧化镁，含有部分小颗粒，但颗粒的粒径比较集中；以尿素为溶剂改性氢氧化镁，颗粒的粒径和厚度明显增加，改性效果明显增加。根据文献[8]，氢氧根离子有利于晶体的溶解结晶，乙醇，纯水和尿素溶液中氢氧根离子量逐渐增加，导致氢氧化镁的溶解结晶速度增加，促进大颗粒边缘的溶解和生长。

2.2 水热温度对改性的影响

图 3 以尿素为溶剂，分别采用 50 ℃，150 ℃，250 ℃时改性氢氧化镁的 SEM。

由图 3(a)可知，水热改性温度为 50 ℃时，氢氧化镁颗粒团聚粘连，颗粒边缘凹凸不平；改性温度为 150 ℃，晶体的粒径和厚度明显增加，颗粒分布趋于均匀；改性温度升至 250 ℃，晶体的厚度明显增加，且晶体呈立方体状，立方体状直径为 1.5 μm 左右。

根据文献[9,10]，$Mg(OH)_2$ 的水热改性过程是溶解-结晶过程，即晶体的重结晶过程[11]。粒径较小的颗粒比表面积较大，反应活性较高，在水热处理过程中不断溶解，然后以一定的方式沉积在大颗粒表面，导致粒径逐渐长大。水热温度低，晶体的溶解速度比较慢，晶体改性不完全；随着改性温度升高，大量小颗粒晶体溶解，晶体的粒径增加；当改性温度大于 150 ℃，尿素分解生成缩二脲，影响氢氧化镁晶体形貌，改性温度越高，生成杂质越多，晶体呈立方体状。

2.3 尿素浓度对改性的影响

在反应温度和反应时间一定的条件下，研究尿素浓度分别为 0.5 mol/L，1.0 mol/L，2.0 mol/L 对水热最终产物的影响，产物的形貌分别如图 4 所示。

由图 4 可知，随着尿素浓度的增加，氢氧化镁晶体粒径增加，小颗粒的量减少。以低浓度尿素溶剂改性时，出现立方体状的氢氧化镁颗粒；随着浓度的增加，颗粒量增多。

根据文献[12]，OH^- 参与了 $Mg(OH)_6^{4-}$ 的基元重组，水热反应中基元重组速率随尿素浓度增加而增加，而基元重组速率的增加必将导致晶体生长加快，反应更加充分。随着尿素浓度的增加，更多的 OH^- 离子参与水热过程，生成立方晶体量越多，晶体边缘越规整。

3 结论

采用水热技术，以乙醇、纯水和尿素 3 种水热介

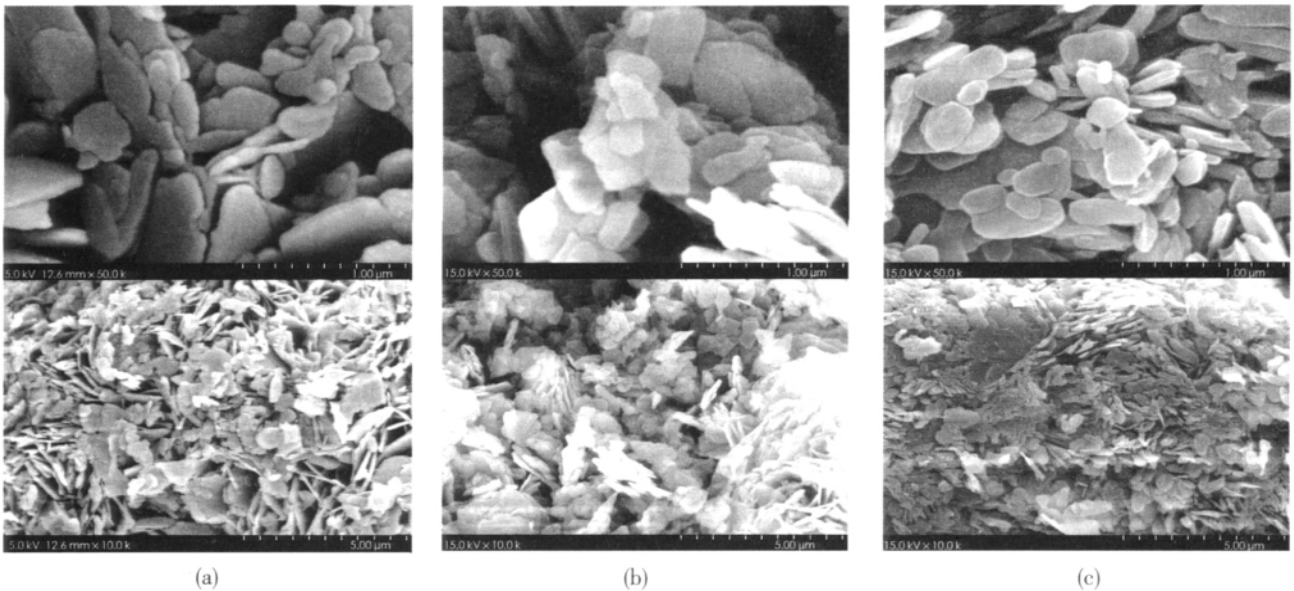
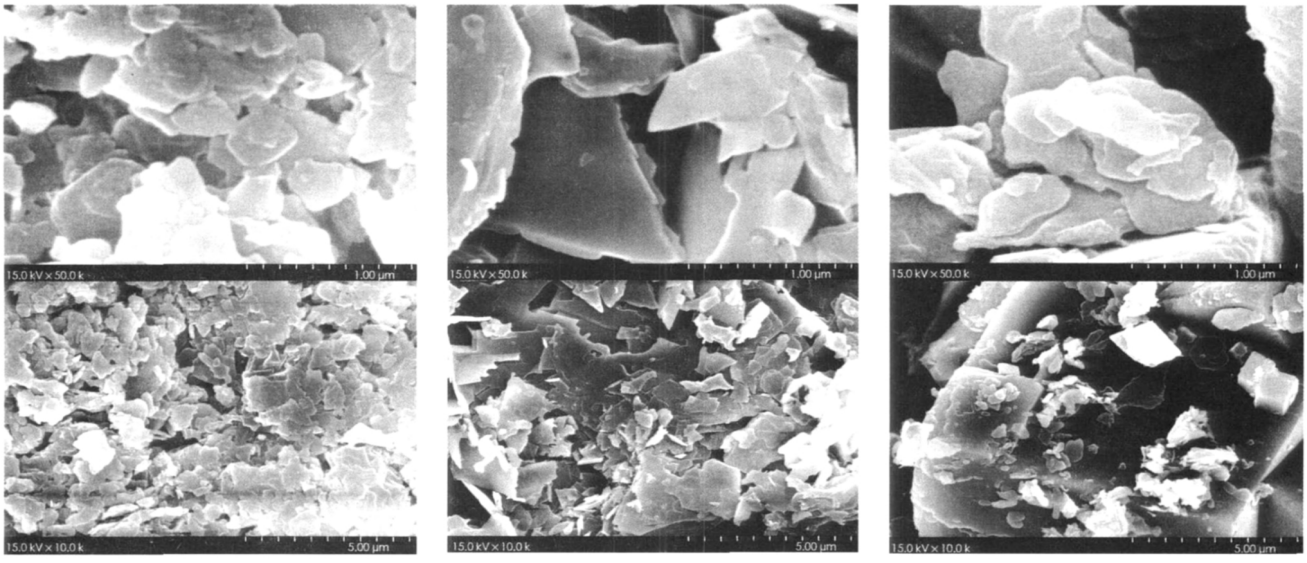
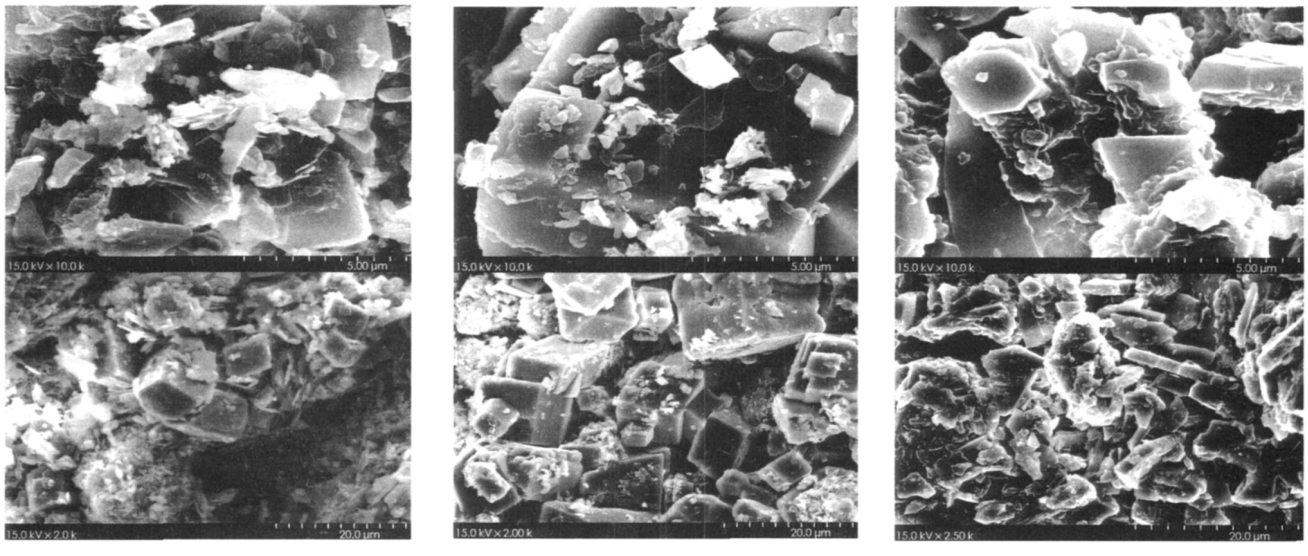


图 2 乙醇、水、尿素溶液改性氢氧化镁的形貌



(a)50 ℃　(b)150 ℃　(c)250 ℃

图 3　不同水热温度改性的氢氧化镁



(a)0.5 mol/L　(b)1.0 mol/L　(c)2.0 mol/L

图 4　不同的尿素浓度改性的氢氧化镁

质改性工业级氢氧化镁，改性后氢氧化镁晶体的粒径分布均匀，分散性提高。尤其是尿素作为水热介质时，随着改性温度和尿素浓度的提高，晶体改性效果越明显，氢氧化镁晶体变为规整的立方体结构。

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Analysis on the Chinese Patents in Fluorochemical Industry

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Abstract: Chinese patents by foreign multinational corporations in the fluororchemical field are statistically analyzed. Main enterprises in fluorochemical industry, international technological market distribution and the developing trend of this industry are analyzed; status of the patent application in the fluorochemical enterprises at home and abroad are compared to find out the difference in the core field of the fluorochemical industry, and its corresponding countermeasures are also put forward.

Keywords: flurochemical industry; patent; analysis

Study on Drying Processes of High Reinforcing Silica from Amination of Fluosilicic Acid

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2.Yunnan Yuntianhua International Chemical Co. Ltd, Kunming 650113)

Abstract: High reinforcing white carbon black is prepared from phosphate fertilizer by-product fluosilicic acid. Influence of drying methods, including oven drying, vacuum drying, spray drying and solvent exchange drying on the specific surface area and size of silica white are studied in order to obtain a silica white of low agglomeration and good quality. Experimental results indicate that solvent exchange drying can prevent silica white from forming hard agglomerate, the silica white obtained through solvent exchange drying is small in size and large in specific surface area. Meanwhile hard agglomeration mechanism of silica white among the four drying processes is also discussed.

Keywords: silica white; fluosilicic acid; amination; drying

Performance, Processing and Application of Fluoro Resin (Continue 21)

Qian Zhimian

(Shanghai City Plastics Institute, Shanghai 200090)

Abstract: Principle, method and equipment of compression, injection, vacuum, transmission and rotatory molding for fluorinated ethylene-propylene (FEP) are reviewed.

Keywords: fluorinated ethylene-propylene resin; compression; injection; vacuum; transmission; rotation; molding

Synthesis of Antipsychotic Drug Risperidone

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Abstract: A process for risperidone synthesis was designed and validated. 6-Fluoro-3-(4-piperidinyl)-1,2-benzisoxazole hydrochloride was synthesized from 4-piperidinecarboxlic acid through acetylation, chlorination, Fiedel crafts reaction, hydrolysis, oximation and cyclization. 3-(2-Chloroethyl)-6,7,8,9-tetrahydro-2-methyl-4H-pyrido[1,2-**a**]pyrimidin-4-one was synthesized from 2-aminopyridine in 2 steps of condensation and hydrogenation reduction. Risperidoneis obtained from the two compounds through condensation, in the total yield of 12%. 1,2-Dichloroethane is used as a solvent for the separation with palladium on carbon as the best catalyst, the best dosage is 5% by mass. The process conditions are mild and raw materials are easily available, which is suitable for industrialization production.

Keywords: risperidone; antipsychotic drug; synthesis

Study on Morphology of Industrial Grade $Mg(OH)_2$ Crystals Modified by Hydrothermal Method

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Abstract: A method of hydrothermal modification on industrial grade Mg $(OH)_2$ particles in ethanol, water and urea solution was investigated. Influence of morphology and size of hydrothermal products was studied. According to SEM, morphology and aggregation

of $Mg(OH)_2$ crystals were improved greatly. Effects of urea solution was obvious, size was increased up to 10 μm and morphology of $Mg(OH)_2$ was cube crystal at the temperature of 250℃.

Keywords: magnesium hydroxide; hydrothermal medium; modification; flame retardant

Effect of Plasticizer Amount on the Performance of TPCS/PCL Blended Material

Liu Yingchun

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Abstract: Thermosplastic crosslinked starch (TPCS) and polycaprolactone (PCL) are blended to prepare a biodegradable material. Results show that plasticizer has obvious effect on the mechanical performance of the materials: tensile strength is descended, and extension at break is raised; compared with water, glycerin can improve obviously extension at break; increasing plasticizer glycerin is helpful to enhance water resistance of the raw materials, but slightly decrease the degradation performance of the raw materials.

Keywords: crosslinked starch; polycaprolactone; plasticizer; performance

Experiment on Sodium Hydrosulphite Waste Water Treatment by Photic-catalytic Oxidation-Biochemistry and Its Application

Jiang Bing

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Abstract: Treatment of organic rich sodium hydrosulfite wastewater with high COD_{Cr} was studied and the method was applied in the production. The results indicated that the COD_{Cr} of sodium hydrosulfite wastewater could be reduced over 80 percent by photic-catalytic oxidation-biochemistry treatment with wastewater from the production of chloro-alkali, i.e. chlorine water as oxidant. Actual production shows that the COD_{Cr} of wastewater after treatment is less than 150 mg/L and meets the requirements of discharge. Wastewater is treated by waste chlorine water, which costs low in the treatment of sodium hydrosulphite.

Keywords: sodium hydrosulfite; waste water; treatment; photot catalysis oxidation

Coordinating Reaction of 5-Fluorouracil-Porphyrin with Copper (Ⅱ) and Its Catalysis

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Abstract: Apparent rate constant and apparent activation energy are determined in the coordinate reaction of 5-fluorouracil porphyrin with Cu (Ⅱ) by spectrometry method. Equilibrium constant and related thermodynamic parameters in the formation of metal porphyrin are determined with a mobile equilibrium method, catalysis of Cd(Ⅱ) on the reaction and effect of different solvents on the reaction ratio are discussed. Results show that activation energy in the coordinate reaction of H_2P and Cu (Ⅱ) E_a=64.13 kJ/mol, reactive $\triangle_r H_m$= - 20.552 kJ/mol, $\triangle_r S_m$ = 6.787 J/mol; Cd^{2+} has catalysis on the reaction, when the Cd^{2+} concentration is not big, rate constant k has the linear relationship with Cd^{2+} concentration; the smaller the dielectric constant is, the bigger the reaction rate is.

Keywords: porphyrin-copper (Ⅱ); kinetics; thermodynamics; equilibrium parameter; activation energy; catalysis

Catalytic Synthesis of Isooctyl Choloroacetate by Solid Super Acid

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Abstract: Isooctyl choloroacetate was synthesized by choloroacetic acid and isooctanol with our self-made solid super acid as the catalyst. Effects of catalyst amount, ratio of the reaction materials isooctanol and choloroacetic acid, water carrying agent amount and reaction time on esterification were discussed. Results showed that TiO_2-SO_4^{2-} had good catalytic performance, the best reaction conditions were as follows: at the conditions of chloroacetic acid amount 0.15 mol, n(isooctyl alcohol): n(chloroacetic acid)=1.1: 1.0, mass of the catalyst is 1.2% of the total reactants, water carrying agent was 10 mL, reaction time was 2.5 h. Yield of isooctyl chloroacetate reached 98% under such conditions. The catalyst could be recycled 5 times and the yield of isooctyl choroacetate was not reduced obviously.

Keywords: solid super acid; isooctyl choroacetate; catalytic esterification