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Synthesis of Zeolites ZSM-5 and ZSM-48 from Gasification Ashes of Agricultural Wastes

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Over 800 thousand tons per year (TPY) agricultural biowastes, such as sugar cane bagasse, sugarcane leaf, rice straw, rice husk, and corn leaf, are produced in Taiwan. These biomasses are the major types of agricultural wastes and are abundantly available. However, these biowastes cause disposal and landfill problems. Gasification ashes of the agricultural biowastes containing 70-95 % amorphous silica would make the utilization system of agricultural biowaste ashes become highly economically and environmentally attractive. Experimentally, high crystallinity (99%$^+$) zeolites ZSM-5 and ZSM-48 synthesized from the reaction mixtures containing a silica source from ashes of these biowastes gasification were investigated. Tetrapropylammonium bromide (TPABr) and 1,6-diamino-hexane (C_6DN) were used as structure-directing agents in syntheses of ZSM-5 and ZSM-48, respectively. X-ray powder diffraction (XRD) and scanning electron microscopy/energy dispersive spectroscopy (SEM/EDX) data indicated that ZSM-5 or ZSM-48 with a high crystallinity can be obtained within 48 hours of crystallization in the high pressure (15-20 atm) autoclave at 393-473 K. The Si/Al ratios of synthetic zeolite products were determined by X-ray fluorescence (XRF) and induced couple plasma/mass spectroscopy (ICP/MS). It was observed that the ZSM-5 crystals are composed of hexagonal rod-shaped crystals with typically 8-13 Πm in size by SEM. In addition, ZSM-48 crystalline materials are composed of spherical aggregates of needle-shaped or rod-like crystals with typically 2-3 Πm in diameter and 6-8 Πm in length.

Keywords: Agricultural biowaste Ash, ZSM-5, ZSM-48, Resource recovery

Introduction

Agricultural biowaste, such as sugar cane bagasse (SB), sugar cane leaf (SL), rice straw (RS), rice husk (RH) or corn leaf (CL), is one of the typical types of domestic waste sources [1-9]. The use of biowaste as a fuel can decrease environmental problems, such as the CO_2 increase in the atmosphere caused by the use of fossil fuels [7,10]. Recently, over 800 TPY agricultural biowastes such as SB, SL, RS, RH, and CL were produced in Taiwan. These biomasses are the major wastes of farms and are abundantly available. However, these biowastes cause disposal and landfill problems [9,10]. If not disposed of properly, the biowastes provide a refuge for disease-carrying creatures such as mosquitoes, create fire hazards, and constrain the use of a completed landfill site. There have been several technologies proposed to solve the problems. Basically, the utilization of biowastes has been employed in the gasification to obtain syngas ($CO + H_2$), the combustion to obtain liberate energy, the controlled combustion to obtain carbon-free ash, the pyrolysis to obtain char and liquid/gas products [11-13]. Either combustion or pyrolysis of the biowastes requires the knowledge of volatile evolution behavior to control the processes [12-14]. However, a better solution from an environmental and economic standpoint is to thermally reprocess the biowastes into valuable products.

Gasification is a viable route for effective use of these biowastes in the thermal and mechanical or electrical applications [11-14]. The conversion of the biowastes into fuel gas by gasification is also a promising technology. It is advantageous to convert biowastes in solid form to gaseous form since the latter is more flexible as fuel than the former. The low-BTU gas has served as a utility fuel to power internal combustion engines. Extensions of this technology involving steam gasification include steam reforming into hydrogen-rich gas, which can be utilized as a raw material for ammonia and methanol synthesis or in fuel cells [13-15]. Gasification ashes of these biowastes containing 70-95 % high-grade amorphous silica and very low concentrations of metallic impurities would make the biowaste ashes utilization systems becoming highly economically and environmentally attractive [11-15]

In the early 1970s, zeolite ZSM-5 framework contains 10-membered oxygen ring channel system with a free aperture of about 6 Å, was first prepared by Mobil [16-20]. The unique pore structure and highly pure silica content of ZSM-5 has the excellent shape selectivities and catalytic properties, hydrophobicity, and thermal stability [18-22]. Zeolite ZSM-48 was first found as an impurity phase in ZSM-39 in the earth 1980s [18-24]. ZSM-48 with a two-dimensional channel structure has a framework based on the ferrierite sheets with linear non-interpenetrating 10-membered ring channels and linked via bridging oxygens located in a mirror plane [19,25]. Because of the unique pore systems, zeolite ZSM-5 or ZSM-48 has the excellent by-product shape selectivities and destruction and removal efficiency (DRE) for the hazardous organics (such as 2-

chlorophenol) in catalytic reactions [17,18,26-29]. Zeolite ZSM-48 or ZSM-5 has effective kinetic separation of xylene isomers, according to the C_8 aromatic hydrocarbons have effective molecular diameters that are close to the free diameter of ZSM-48 or ZSM-5 structure [17,30-35]. Therefore, the main objective of this work was to synthesize and characterize zeolites ZSM-5 and ZSM-48 from agricultural biowaste ashes generated from gasification. Characterization of as-synthesized ZSM-5 and ZSM-48 were also identified by XRD/XRF, SEM/EDX, and nitrogen adsorption/mercury penetration.

Experimental

Materials

Proximate and ultimate analyses of the agricultural biowastes identified by elemental analyzer (EA, F002-heraeus rapid CHN-O) are shown in Table 1. Combustibles are the main components and over 11.5 % ash residues were produced from agricultural biowaste gasification. These biowaste could easily adsorbed water and contained about 10 % moisture in the air because of its porous characteristics. Tetrapropylammonium bromide (TPABr) and 1,6-diamino-hexane (C_6DN) were used as structure-directing agents in syntheses of ZSM-5 and ZSM-48, respectively. In order to burn off the volatile organic matters and fixed carbons, some agricultural biowastes in a crucible were placed overnight in a furnace preheated to 853 K, and then the ZSM-5 or ZSM-48 zeolites were synthesized with these agricultural biowaste ashes. All the experiments were conducted with the same batch of biowastes received. TPABr (or C_6DN) and NaOH (or NaBr used to change pH value and sodium content) were high purity reagents (ACS grade, >99%). In comparison with the agricultural biowaste ashes, the high purity fumed SiO2 (>99%) was also used as different silica sources. All aqueous solutions were made in deionized water purified with a MilliQ UV plus system. The same batches of reagents were used for all reactions and the reaction gels were all prepared in exactly the same way.

Synthesis

Zeolite ZSM-5 or ZSM-48 was prepared from a reaction mixture containing a source of the agricultural biowaste ashes, TPABr or C_6DN, and deionized water. The reaction gels were vigorously agitated, transferred into 250 mL PTFE-lined stainless-steel autoclaves, sealed and left for crystallization. The PTFE flasks were precleaned to avoid seeding effects and prevent the formation of contaminating phases. The crystallization of the sodium form of ZSM-5 or ZSM-48 from a gel containing TPABr or C_6DN was carried out at 393-473 K, without stirring and under autogeneous pressure about 15-20 atm for 2-192 hr. The time of crystallization was measured after the reaction mixture had reached the required temperature. The obtained precipitates were filtered off, washed repeatedly and thoroughly with deionized water, and finally dried at 378 K overnight. Calcined ZSM-5 and ZSM-48 for further analyses were obtained after removal of the occluded organics by heating the as-synthesized zeolites at 873 K for 24 hr in an air flowing condition. The sodium forms were subsequently exchanged three times with a 1 N NH_4NO_3 solution at 298 K. The NH_4ZSM-5 or NH_4ZSM-48 was then heated for 24 hours at 823 K to obtain HZSM-5 or ZSM-48, respectively.

Characterization

SiO_2 is the major components of the agricultural biowaste ashes. K_2O, Na_2O, CaO, and MgO essentially contribute to the remaining portion. The average metallic contents of agricultural biowaste ashes were evaluated by adsorption spectroscopy (AA, GBC model 908) and ICP/MS (ELAN model 5000). The Si/Al ratios of synthetic zeolite products were determined by XRF (RIGAKU Model 3063M). Morphological observations of biowaste ashes and synthetic zeolite products were examined by SEM/EDX (JEOL Model JSMr840). The void structure, pore dimensions, and surface area of ZSM-5 or ZSM-48 were measured by nitrogen adsorption and mercury penetration. The identification of the solid phases and crystallinities of zeolitic phases were evaluated by XRD (RIGAKU Model D/MAX III-V). The synthesized zeolites were scanned from 5 to 50° (2Θ) with a scan rate of 0.05° (2Θ)/s. The specific peak intensities and 2Θ values were recorded and identified by a computer library system. The percentage of crystallization of ZSM-5 or ZSM-48 was estimated as follows: Five specific peak intensities were summed, and then the total intensity was normalized to that zeolite ZSM-5 or ZSM-48 standard synthesized with pure silica.

Results and Discussion

In Taiwan, biowastes are a relatively high-volume, low-cost by-product commodity, which contains mainly silica and combustible cellulose (Table 1). Biowaste gasification of grain valuable by-products, such as syngas and high-grade amorphous silica in ashes, can be a significant biomass conversion technology because of the need to utilize agricultural waste for non-food applications including energy resources. The ashes of biowastes such as sugar cane bagasse, sugar cane leaf, rice straw, rice husk, and corn leaf contain about 70-95% silica. The X-ray diffraction pattern indicated the amorphous of the silica in rice husk. The states of silica depend on the conditions in which they have been obtained. Experimentally, the ashes obtained from the biowastes by gasification at low temperatures contain amorphous silica, whereas ash formed at higher temperature (>923 K) contains mostly crystalline silica. The crystalline silica comprise mostly crystobalite and tridymite small propertions of quartz. Biowastes on complete burning yields carbon-free white ash, which on ICP/MS or AA analysis was found to contain averagely 80.9 % SiO_2, 0.74 % Al_2O_3, 1.66 % MgO, 3.04 % CaO, 0.54 % FeO, 11.3 % K_2O, and 1.8 % Na_2O. The silica can be further extracted from biowaste ashes by a suitable alkali, such as

NaOH, was found to be very reactive for zeolite ZSM-5 or ZSM-48 synthesis.

In this study, agricultural biowaste ashes were used as a source of silica and alumina, instead of the pure chemical sources used earlier. Physical properties of the zeolites ZSM-5 or ZSM-48 synthesized from the agricultural biowaste ashes are shown in Table 2. Zeolite ZSM-48 has a unidimensional (2D) circular channel structure. The 3D straight channels of ZSM-5 have an elliptical cross section of 5.7-5.8 Å by 5.1-5.2 Å that are interconnected by zigzag channels with a nearly circular cross section and diameter of 5.5 Å and a channel length is 4.5-6.6 Å. Note that the catalysis and the selectivity of ZSM-type zeolites are determined by active sites provided by an imbalance in charge between the silicon and the aluminum ions in the framework.

Scanning electron photomicrographs of ZSM-5 and ZSM-48 synthesized from the agricultural biowaste ashes at 433 K for 48 hours are shown in Figure 1(a) and 1(b), respectively. It was observed that the ZSM-5 crystals are composed of hexagonal rod-shaped crystals with typically 8-13 Πm in size. In addition, ZSM-48 crystalline material consisted of is composed of spherical aggregates of needle-shaped or rod-like crystals with typically 2-3 Πm in diameter and 6-8 Πm in length. Figure 1 also indicates that the synthesized ZSM-5 and ZSM-48 may not be an intergrowth crystal but rather are a physical mixture of the two zeolites.

Table 3 indicated that ZSM-5 or ZSM-48 with a high crystallinity identified by XRD pattern could be also obtained from mixed agricultural biowaste ashes in the autoclave at 433 K for 48 hours. Figure 2 shows that X-ray diffraction patterns (identified by the five main peaks) of ZSM-5 or ZSM-48 synthesized from mixed agricultural biowaste ashes at 433 K for 48 hours. Experimentally, it was also found that an increase in temperature, to some extent, enhances the crystallization rate. The syntheses of ZSM-5 or ZSM-48 from a reaction mixture with C6DN ions were also investigated. A comparison of the X-ray diffraction patterns for ZSM-5 with that for ZSM-48 formed using the same organic cations (i.e., C6DN) indicated that the most intense peaks for the two zeolites were different. The positions of the two main peaks were $2\theta = 23.7$ and 21.3 for ZSM-5 and ZSM-48, respectively. This difference makes it possible to distinguish between zeolites ZSM-5 and ZSM-48. It was also observed that pure ZSM-5 or ZSM-48 could be obtained only with Si/Al ratio >60 or >350, respectively. It has been also reported that the preparation of crystalline ZSM-5 or ZSM-48 require the Si/Al ratio >10 or >350, respectively, to products contamination with other silicates, notably crystalline ZSM-11 [17-20].

Conclusion

Zeolite ZSM-5 or ZSM-48 with a high crystallinity was synthesized from a reaction mixture containing a silica source from mixed gasification ashes (containing about 70-95% silica) of agricultural biowastes, such as sugar cane bagasse, sugar cane leaf, rice straw, rice husk, and corn leaf. XRD and SEM/EDX data indicated ZSM-5 or ZSM-48 with a high crystallinity could be obtained with a 48-hour crystallization time in the autoclave at 393-473 K. The ZSM-5 crystals were composed of hexagonal rod-shaped crystals with typically 8-13 Πm in size by SEM. In addition, ZSM-48 crystalline materials were composed of spherical aggregates of needle-shaped or rod-like crystals with typically 2-3 Πm in diameter and 6-8 Πm in length. It was observed that pure ZSM-5 or ZSM-48 was obtained only with Si/Al ratio >60 or >350, respectively.

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Table 1. Proximate and ultimate analyses of the agricultural biowastes in Taiwan

	SB	SL	RS	RH	CL
Proximate analysis (wt%)					
Combustibles	82.6	87.0	75.6	72.9	82.3
Moisture (W)	10.3	11.2	9.9	9.5	10.9
Ash	7.1	11.8	14.5	17.6	6.8
Ultimate analysis (wt%)					
Carbon	47.4	45.6	42.0	46.9	42.4
Hydrogen	6.4	6.1	6.5	6.7	6.0
Oxygen	46.1	46.8	50.8	45.8	51.0
Nitrogen	<0.01	1.5	0.7	0.3	0.6
Sulfur	<0.01	<0.01	<0.01	0.2	<0.01
Chlorine	0.3	0.2	0.1	0.1	0.1
[a] High heating value (MJ/kg)	17.8	16.4	15.2	18.2	14.8
[b] Low heating value (MJ/kg)	16.1	14.7	13.5	16.5	13.2

Note: 1. "SB", "SL", "RS", "RH", and "CL" denote sugarcane bagasse, sugarcane leaf, rice straw, rice husk, and corn leaf, respectively.

2. Results are all normalized to 100%.

[a] High heating value (HHV) = $\{33.5[C]+142.3[H]-15.4[O]-14.5[N]\}\times 10^{-2}$.

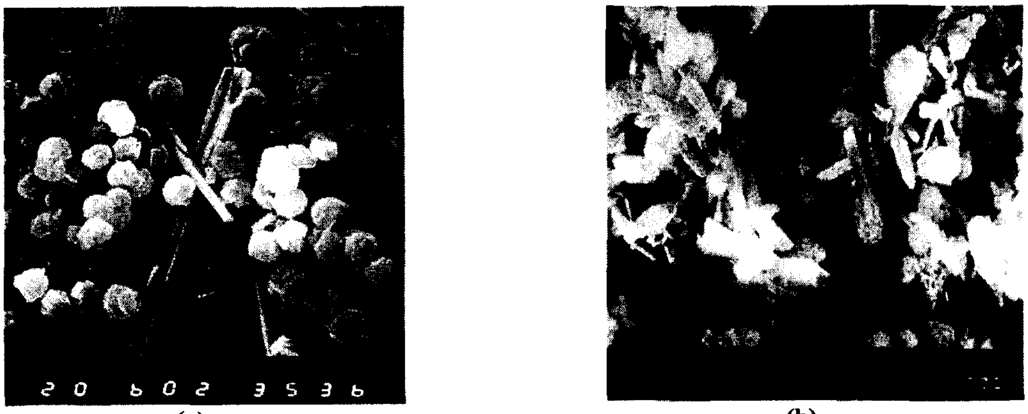
[b] Low heating value (LHV) = HHV-$\{6[9H+W]\times 4.184\times 10^{-3}\}$.

Table 2. Properties of ZSM-5 or ZSM-48 synthesized from agricultural biowaste ashes

	ZSM-5	ZSM-48
Ring pore opening	10	10
Pore dimension (Å)	5.1-5.8	5.3-5.7
Si/Al ratio	60-100	350-500
Pore volume (mL/g)	0.18-0.21	0.13-0.16
Surface area (m^2/g)	400-500	800-1000

Table 3. Crystallinity of synthesized ZSM-5 and ZSM-48 zeolites

Zeolite type	Silica source	Crystallinity
HZSM-5	SiO_2	99^+
HZSM-5	Mixed agricultural biowaste ashes	99^+
HZSM-48	SiO_2	99^+
HZSM-48	Mixed agricultural biowaste ashes	99^+



(a) (b)

Figure 1. SEM photographs of (a) ZSM-5 and (b) ZSM-48 synthesized from mixed agricultural biowaste ashes at 433 K for 48 hours.

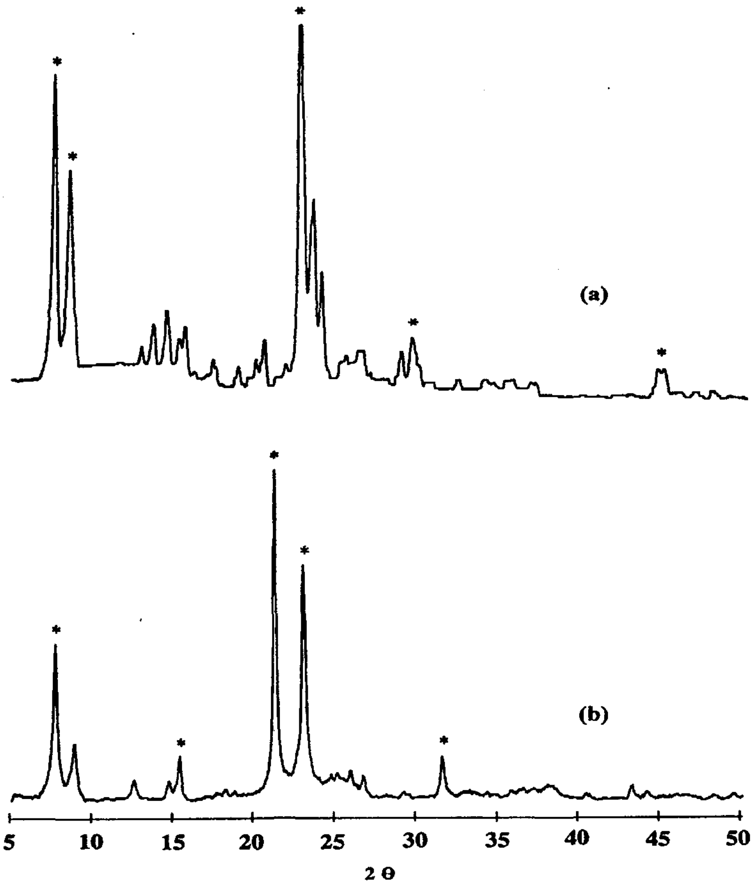


Figure 2. X-ray diffraction patterns of (a) ZSM-5 and (b) ZSM-48 synthesized from mixed agricultural biowaste ashes at 433 K for 48 hours. * Denotes the five characteristic peaks of ZSM-5 or ZSM-48.