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Synthesis of highly stable mesoporous aluminosilicates from commercially available zeolites and their application to the pyrolysis of woody biomass

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Abstract

Ordered mesoporous aluminosilicates have been successfully obtained via the simple combination of top–down and bottom–up approaches, using commercially available zeolites as the framework sources. The mesoporous aluminosilicates are characterized by XRD, N_2 sorption, SEM, TEM, ICP, and NMR, and have proven to have controllable aluminium contents, well-developed mesoporosity, and excellent hydrothermal stability. The hydrothermally stable mesoporous aluminosilicates, which possess the proper distribution of weak and strong acid sites, are applied as reusable heterogeneous catalysts for the pyrolysis of woody biomass. The mesoporous aluminosilicates in the present work showed good activity, selectivity, and even stability for the production of desirable organic compounds such as phenolics, in comparison to conventional HZSM-5 and Al-MCM-41.

Keywords: MMZ materials; Catalytic upgrading; Hydrothermal stability; Phenolics

1. Introduction

Since the discovery of mesoporous materials [1], there have been many researches on the synthesis and application of these materials. To be able to practically utilize such materials, they should be designed in one of three manners: via designs of their pore structures, including their pore sizes and pore shapes; designs of their morphologies; and designs of their framework structures. Basically, the framework structures are of much interest because the main functions of mesoporous materials are generated from the framework structures such as the framework compositions and atomic structures. There have been several reports on the preparation and application of different types of frameworks such as silica, metallosilicates, transition metal oxide, organic–inorganic hybrid, carbon, polymer, etc., which are designed and synthesized to optimize their applicability [2–6]. One of the most interesting approaches to the framework design is the preparation of mesoporous materials constructed with zeolitic frameworks, which may yield advantages from the synergy of the zeolites and the mesoporous materials. For example, the hydrothermal stability and acidity of the mesoporous materials are relatively low compared with those of the zeolites, which strongly influence their practical applications in industry. Several studies have reported on the preparation of zeolitic mesoporous materials. The first approach used in the preparation of zeolitic mesoporous materials is the post-reconstruction of amorphous aluminosilicate frameworks in the presence of inorganic or organic salts such as sodium chloride and tetrapropylammonium bromide [7,8]. The synthesis of zeolite particles exhibiting well-defined mesopores is also

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carried out by adding secondary templates, such as carbon black, carbon nanotube, carbon aerogel, and mesoporous carbon, during the zeolite synthesis [9–12]. Another approach is the assembly of zeolite nano-crystals in the presence of surfactants or amphiphilic polymers [13,14]. In these cases, despite several successful syntheses of hierarchical mesoporous materials that are constructed with zeolitic walls and exhibit strong acidities and excellent stabilities, only a few kinds of zeolitic frameworks have been utilized because the preparation of zeolite nano-crystals is necessary prior to the formation of mesostructures. Reported very recently was the exceptionally successful synthesis of crystalline zeolites with tuneable mesoporosity using designed amphiphilic organosilane as the structure-directing agent, suggesting catalytic applicability [15,16].

This paper demonstrates (i) a new strategy for the synthesis of ordered mesoporous materials constructed with semi-zeolitic frameworks and high aluminium contents, and (ii) the applicability of woody biomass as a catalyst of pyrolysis. The synthesis strategy involves the combination of top–down and bottom–up approaches using commercially available zeolites and a cationic surfactant (cetyltrimethylammonium bromide or CTAB) as the framework sources and the structure-directing agent, respectively, as described in Scheme 1. Commercially available zeolites are first rent into nano-units under controlled basic conditions (top–down approach). Subsequently, these zeolitic nano-units are re-assembled into highly ordered mesoporous materials in the presence of templating materials such as surfactants and amphiphilic block copolymers (bottom–up approach). The mesoporous materials from the zeolites (hereinafter referred to as "MMZ_x" in which x is the name of the zeolite used) are applied as reusable heterogeneous catalysts of the pyrolysis of bio-oil, which is still under development, but offers many benefits such as high power generation efficiency, easy storage/transport, and usability in the production of highly valuable chemicals.

2. Experimental

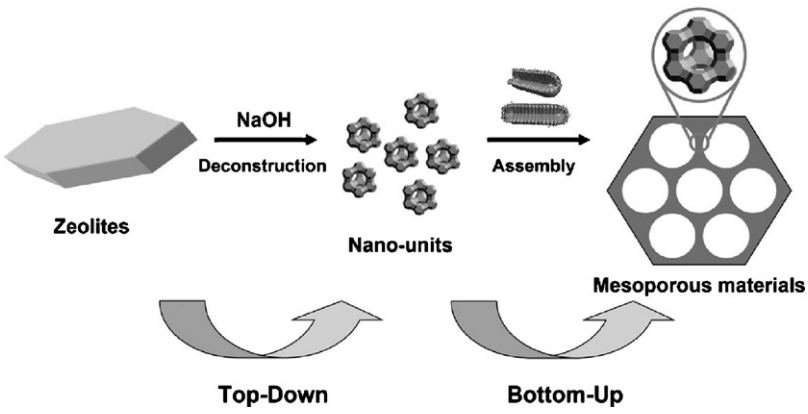
2.1. Synthesis of mesoporous materials from zeolites

The synthesis of mesoporous materials from zeolites (MMZ) was performed in this study as follows: first, various kinds of proton-exchanged zeolites such as H-beta and H-ZSM-5 were dissolved using an NaOH solution to yield a 0.5–4.0 NaOH/(Si + Al) molar ratio. The NaOH solution was prepared in typical conditions by dissolving 1.5 g of NaOH in 5.0 g of deionized water. Subsequently, 2.25 g of H-beta was added to the NaOH solution under magnetic stirring, producing a clear solution. Care should be taken during the dissolution of the zeolites using NaOH, as the zeolite solution could explode due to an exothermic reaction, especially in the case of large batch synthesis. Finally, the dissolved zeolite solution was diluted using 2.5 g of deionized water and utilized as the framework source of the MMZ materials. Then 4.6 g of cetyltrimethylammonium bromide (CTAB) was dissolved in 70 g of water. The abovementioned zeolite solution was added drop by drop into the CTAB solution under vigorous stirring, and was stirred further for 24 h at room temperature. Subsequently, the reaction mixture was heated at 373 K for 24 h. The white precipitate was filtered, washed with water, and dried at 373 K overnight. The MMZ material thus obtained was washed with an HCl/ethanol mixture and finally calcined at 823 K for 3 h to remove the surfactant. Large-batch synthesis of MMZ was also performed following the same procedure as that described above, and was likewise used for the bio-oil upgrading experiments.

The catalysts synthesized in this study were characterized as follows: X-ray diffraction (XRD) patterns were obtained with a Cu Kα X-ray source using a Rigaku D/MAX-III instrument at room temperature. The acidity was investigated using the NH_3-temperature-programmed desorption (TPD) method, using a TPD/TPR 2900 analyzer (Micromeritics Instrument Co.). N_2 adsorption/desorption isotherms were obtained at −196 °C with a Micromeritics ASAP 2000, and Brunauer–Emmett–Teller (BET) surface areas were calculated from the linear part of the BET plot. The pore size distributions were calculated using the Brunauer–Joyner–Halenda (BJH) model.

2.2. Bio-oil upgrading conditions

The biomass feedstock, the experimental apparatus and procedure, and the analytical methods have been previously described in detail [17]. The non-catalytic pyrolysis and the catalytic upgrading were conducted at the reaction temperature of 500 °C, at which the maximum bio-oil yield



Scheme 1. Schematic diagram for the synthesis of MMZ materials from conventional zeolites via combination of top–down and bottom approaches.

could be obtained. To be able to use them in the experiments, the synthesized catalysts were pelletized, crushed, and finally, screened with the use of standard sieves within the range of 1.7–2.4 mm. To evaluate the hydrothermal stability of each catalyst in the upgrading, they were again used in the experiments after regeneration at 550 °C for 12 h.

3. Results and discussion

3.1. Characterization of mesoporous materials from zeolites (MMZ)

The powder X-ray diffraction (XRD) patterns and the SEM and TEM images of the MMZ_{beta} materials are shown in Fig. 1. The XRD patterns in Fig. 1(a) exhibit one intense peak and three or four well-resolved weak peaks that can be indexed as (1 0 0), (1 1 0), (2 0 0), and (2 1 0) reflections, which are characteristics of 2D hexagonal (*P6m*m) mesoporous materials. There was no significant change before and after the calcination, except for a slight reduction in the lattice parameter (about 3%). The nitrogen adsorption–desorption isotherms for the MMZ_{beta} materials, shown in Fig. 1(b), were Type IV, with a sharp increase in the adsorption at around $p/p_0 = 0.35$, which is typical of mesoporous solids [1]. The sample exhibited narrow BJH pore size distribution curves at around 2.8 nm after the removal of the template as shown in inset of Fig. 1(b). The TEM image in Fig. 1(d) shows well-ordered hexagonal arrays of mesopores (1D channels) and confirms that the sample had a hexagonal structure. The XRD patterns in Fig. 1(a) also show broad lines centered at $2\theta \sim 20^\circ$, which indicates that the frameworks were not atomically ordered. Interestingly, the SEM image in Fig. 1(c) indicates that the particle sizes of the MMZ_{beta} material were in the range of 100–200 nm, which is much smaller than that of the typical MCM-41 materials obtained using other framework sources such as tetraethylorthosilicate and sodium silicate. This is probably due to the many zeolitic nano-units in the reaction mixture, which might have resulted in the fast formation of the MMZ material and the disturbance of the crystal growth.

Fig. 2 shows the hydrothermal stability of the MMZ_{beta} compared with that of conventional MCM-41 obtained from sodium silicate. Surprisingly, the main feature of the XRD pattern was preserved when the MMZ_{beta} was heated to 373 K in water even for 10 d under static conditions, whereas the mesostructure was completely destroyed within 2 d in the case of MCM-41. The MMZ_{beta} material also showed an MAS ^{27}Al NMR spectrum with only a tetrahedral aluminium NMR peak centered at 55 ppm, which is very similar to that of the beta zeolite shown in Fig. 3.

The MMZ materials synthesized using other zeolites as the framework sources yielded similar XRD patterns, SEM and TEM images, and N_2 sorption results. The physicochemical properties of the MMZ materials are listed in Table 1. The Si/Al ratios of the MMZ materials are dependent on the original Si/Al ratios of the zeolites that were used as the framework sources. The MMZ materials also exhibited ion exchange and acidic

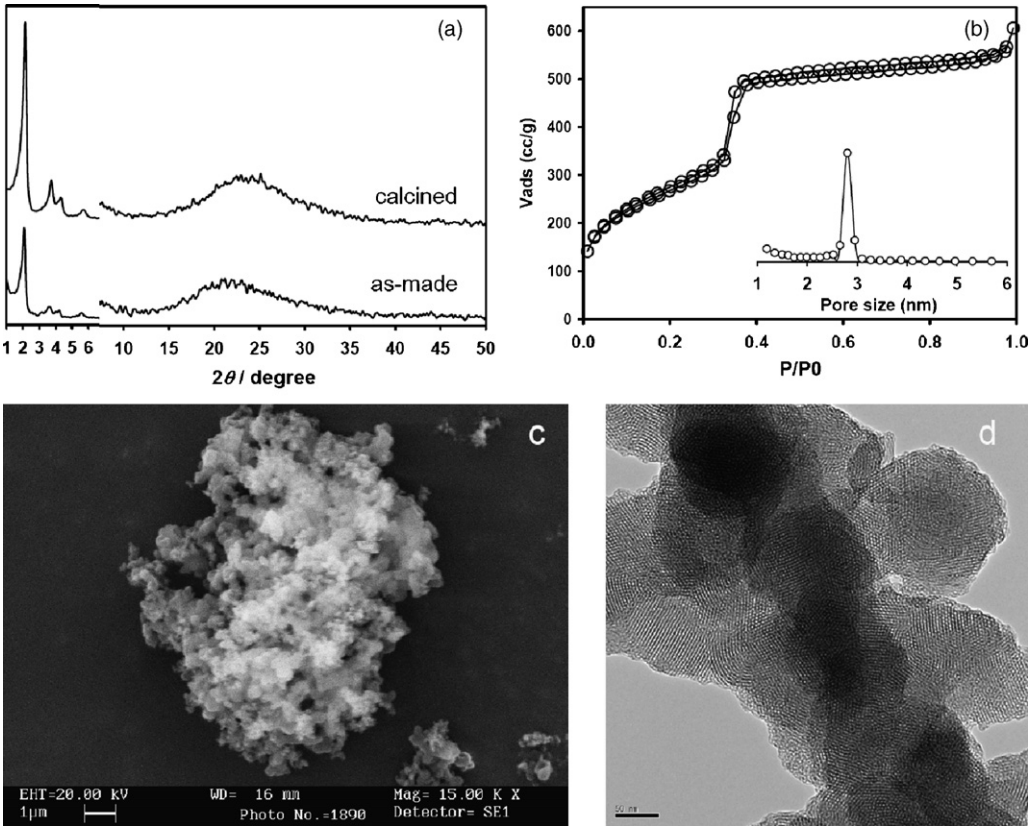


Fig. 1. (a) XRD patterns, (b) nitrogen adsorption–desorption isotherm and corresponding BJH pore size distribution, (c) SEM and (d) TEM images of MMZ_{beta}.

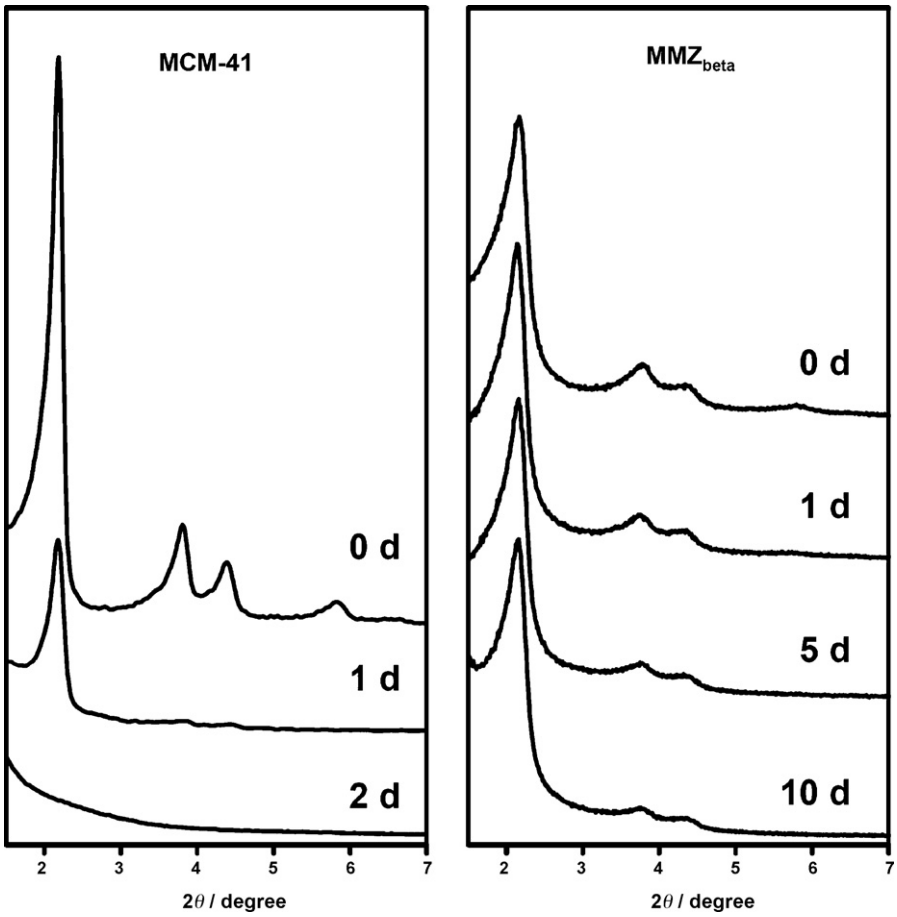


Fig. 2. XRD patterns of mesoporous materials after treating the samples in boiling water: (a) MCM-41 synthesized from sodium silicate and (b) MMZ_{beta} material.

properties similar to those of the zeolites. Highly ordered MMZ materials with other types of mesostructures such as MCM-48 and SBA-15 can also be obtained using conventional zeolites.

3.2. Catalytic performance in the upgrading of bio-oil

It is also noteworthy that the unique properties of MMZ materials, such as well-developed mesoporosity, a semi-crystalline framework, and high hydrothermal stability, can pose significant advantages to their catalytic applications. In this study, the applicability of MMZ materials as upgrading catalysts for woody biomass-derived bio-oil was also demonstrated. Biomass has become increasingly important in responding to concerns over the environment and security of energy supply, and today, it is the most widely used renewable energy source in the world, providing 11% of the world's primary energy supply [18,19]. The as-produced bio-oil via the fast pyrolysis of thermo-chemical conversion technologies should be upgraded because its high concentration of oxygenated compounds such as acids and carbonyls makes it unsuitable for direct use in diesel engines, gas turbines, and other transportation parts. Many researches have been carried out using zeolite-based catalysts such as ZSM-5 and Y to improve the quality of bio-oil [17,20–27]. The catalytic activities were limited, however, by the bio-oil vapor's bad accessibility due to its restricted pore size (<2 nm). To meet the requirements, mesoporous aluminosilicate Al-MCM-41 has been applied as an alternative catalyst in the pyrolysis of bio-oil [28,29], but its poor hydrothermal stability has become a serious drawback. The hydrothermal stability of the catalyst is

Table 1
Physicochemical properties of MMZ materials

Sample	Si/Al (zeolite)[a]	Si/Al (MMZ)[b]	S_{BET}[c] ($m^2\ g^{-1}$)	V_{tot}[d] ($cm^3\ g^{-1}$)
MMZ_{beta}	13.6	15.9	786	0.73
MMZ_{ZSM-5}	20.1	17.2	820	0.76
Al-MCM-41	–	30.1	866	0.83

[a] Si/Al ratios of zeolites which were used as the framework source.
[b] Si/Al ratio of MMZ materials obtained from zeolites.
[c] Calculated in the range of relative pressure (p/p_0) = 0.05–0.20.
[d] Measured at p/p_0 = 0.99.

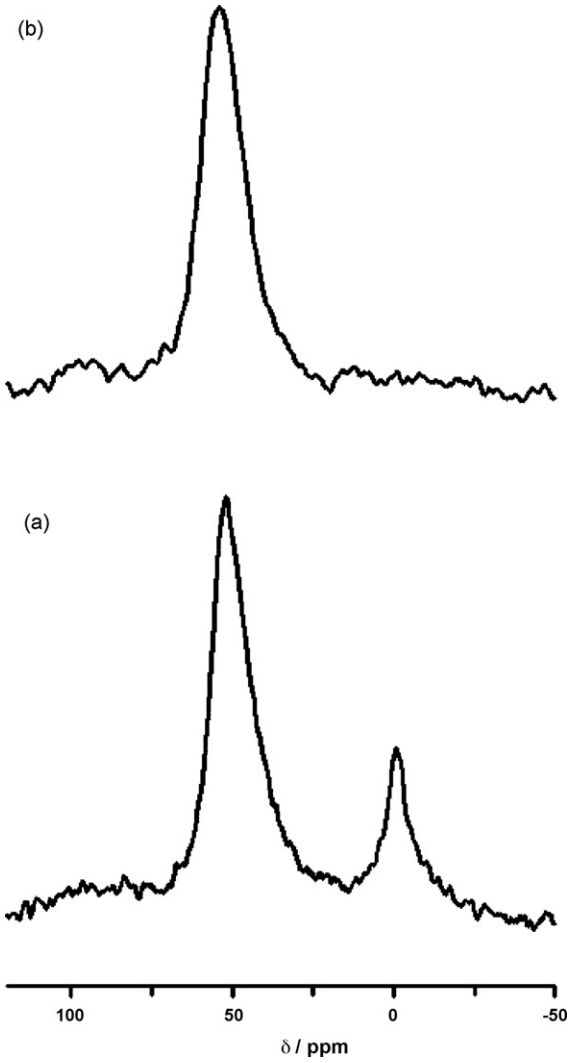


Fig. 3. MAS ^{27}Al NMR spectrums of zeolite beta (a) and MMZ_{beta} (b).

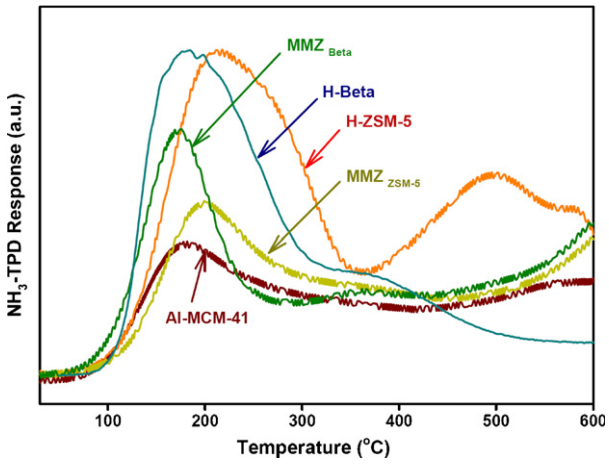


Fig. 4. Ammonia temperature programmed desorption (NH_3-TPD) curves of catalysts.

highly essential in the pyrolysis of bio-oil due to the high reaction temperature and the production of water during the reaction. In this regard, the MMZ materials are expected to be excellent catalysts in the pyrolysis of bio-oil.

In this study, the direct upgrading of biomass-derived bio-oil was carried out using different catalysts. The results are shown in Table 2. It was found that the bio-oil yields decreased with the use of all the catalysts whereas the gas yields increased, compared to the results of the non-catalytic pyrolysis. In particular, ZSM-5 contributed to a more significant reduction of the bio-oil due to its promotion of cracking reactions because of its strong acidic properties, as shown in Fig. 4. The ammonia temperature-programmed desorption (TPD) results indicate that the MMZ materials possessed both weak and strong acid sites. However, the amounts and strength of MMZ materials are less than those of precursor zeolites, which may be due to the disordered framework structures and less exposures of Al sites in MMZ materials. It was clear that the hydrothermal stability of the catalyst affected the upgrading of the bio-oil. The

Table 2
Product distribution from catalytic pyrolysis

Catalyst	Condition[a]	Residence time (cat g min/g vapor)	Yield (wt%)			
			Oil	Water content[b]	Gas	Coke
Non-catalytic pyrolysis	–	–	59.2	25.3	20.4	–
ZSM-5 (25)	F	3.0	41.5	42.4	37.5	0.5
MMZ_{ZSM-5} (26)	F	3.0	47.7	35.1	29.5	2.0
	R1	3.0	46.0	35.3	31.0	2.2
	R2	3.0	46.5	34.9	30.6	2.0
MMZ_{beta} (62)	F	3.0	48.6	35.7	28.6	2.0
	R1	3.0	47.3	36.3	29.2	2.3
	R2	3.0	47.0	35.9	28.3	2.1
Al-MCM-41 (30)	F	3.0	47.9	38.0	30.8	1.0
	R1	3.0	50.5	31.0	28.1	1.0
	R2	3.0	51.8	29.1	28.6	1.0

[a] F: fresh catalyst; R1: after 1st regeneration; R2: after 2nd regeneration.
[b] wt% on bio-oil basis.

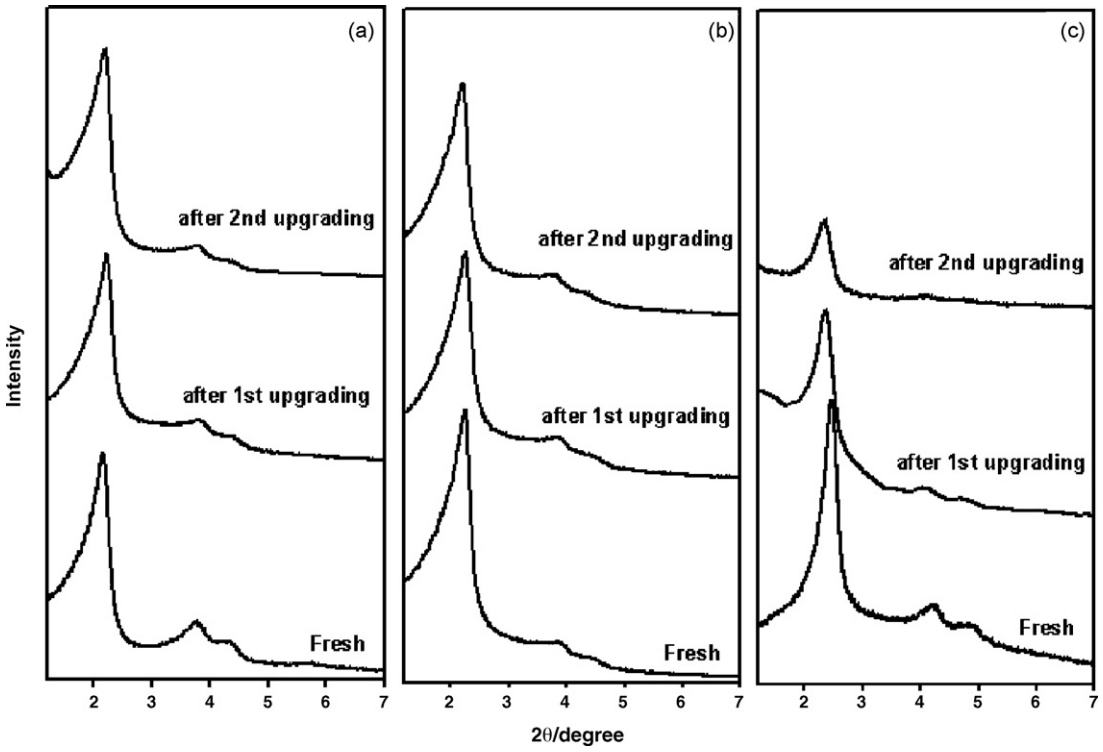


Fig. 5. XRD patterns of different mesoporous catalysts after reaction: (a) MMZ_{ZSM-5}, (b) MMZ_{beta} and (c) Al-MCM-41.

regenerated MMZ catalysts maintained their activity for the bio-oil and gas yields, whereas the regenerated Al-MCM-41 induced a gradual increase in the bio-oil and decrease in the gas yield, similar to the case of the non-catalytic pyrolysis. This might have been due to the considerable difference in the stability of the mesoporous catalysts, as shown in Fig. 5. The hexagonal framework structures of Al-MCM-41 were significantly destroyed based on the regeneration-upgrading cycles, whereas those of the MMZ catalysts were remarkably retained. From Table 2, it could also be seen that the more stable bio-oils with less oxygen were produced by the conversion of the oxygen in the bio-oil largely to H_2O after the catalysis by the ZSM-5 and MMZ materials. It was noteworthy that on one hand, ZSM-5 exhibited the most excellent activity in the deoxygenation of the bio-oil, compared to the other mesoporous catalysts, but on the other hand, it was unfortunately responsible for the lowest organic fraction. In view of these facts, it can be seen that the excess strong acid sites in the catalyst may rather negatively affect the upgrading process. The MMZ and Al-MCM-41 catalysts showed a good degree of deoxygenation, but only the MMZ catalysts exhibited maintainable activity after regeneration, which might also have been due to the difference in their hydrothermal stability.

Bio-oil is an unstable complex that contains corrosive acids, phenolics, aromatic hydrocarbons, carbonyls, and other heavier oxygenates. Until now, many researchers have grouped the different organic compounds in bio-oil into desirables such as phenolics, alcohols, and hydrocarbons, and undesirables such as acids, carbonyls, PAHs, and heavier oxygenates [28,29]. In this study, the quality of bio-oil was assessed by means of its oxygenates, aromatics, and phenolics. Generally, since the oxygenates such as carbonyls and acids are responsible for many side-reactions in the aging procedure and for corrosion in diesel engines or gas turbines, these compounds should be removed. Most aromatic hydrocarbons are toxic and mutagenic compounds. On the other hand, phenolics can be considered very attractive compounds due to their commercial applicability (e.g., as adhesives, adhesive additives, and resins). Fig. 6 shows the chemical composition of bio-oils produced through non-catalytic pyrolysis and upgrading. From Fig. 6, it can be seen that with the use of the catalysts, the oxygenate yields decreased whereas the phenolics yields increased, compared to the results of non-catalytic pyrolysis. In particular, the MMZ catalysts exhibited pronounced activity in both the production of phenolics and the reduction of oxygenates, even though the amount of acid sites in ZSM-5 was the highest among those of the other catalysts. These results indicate that the pore size and the consequent high accessibility of MMZ catalysts also have a

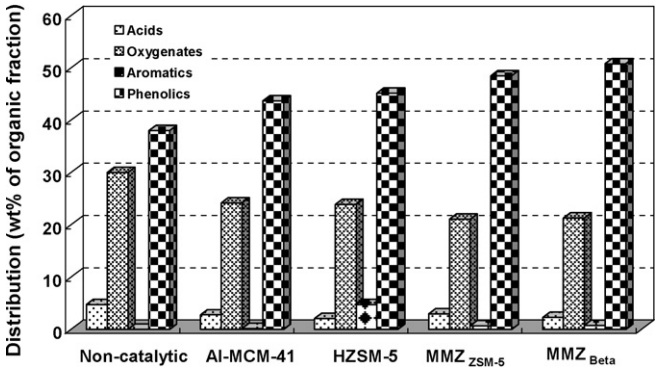


Fig. 6. Effect of catalyst type on the chemical composition of bio-oils.

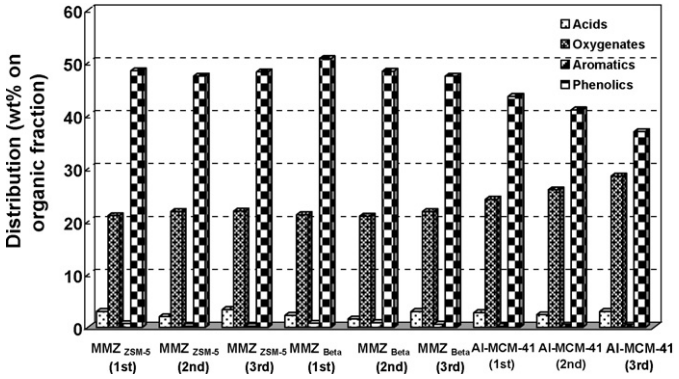


Fig. 7. Effect of the catalytic condition on the chemical composition of bio-oils.

considerable effect on their catalytic activity. At the same time, ZSM-5 induced an increase in the aromatics yield via the consecutive reactions, i.e., the cracking of the light organics, oligomerization, cyclization and hydrogen or hydride transfer, and aromatization. Consequently, it appears that MMZ catalysts are more effective in producing green fuels and highly valuable chemicals. Fig. 7 shows the stability of the mesoporous catalysts during pyrolysis. The activity and selectivity for desirable phenolics of MMZ catalysts were maintainable even after two regenerations, whereas those of Al-MCM-41 were lowered by the level of the non-catalytic pyrolysis due to the mesostructural collapse, as shown in Fig. 5(c).

4. Conclusion

This paper provides not only a general route to an ordered mesoporous aluminosilicate (MMZ) with attractive advantages such as well-developed mesoporosity, excellent hydrothermal stability, and high aluminium contents using commercially available zeolites as the framework sources, but also a new design concept for hierarchical nano-structured materials. The MMZ materials used in this study showed excellent catalytic activity, stability and selectivity for the specific compounds during the catalytic upgrading of bio-oil. In consideration of both their selectivity of phenolics and organic fraction yield, and reduction of undesirable compounds such as oxygenates, MMZ catalysts are considered promising catalysts in the upgrading of bio-oil. In this study, moreover, the high catalytic activities of the MMZ catalysts were maintained through the regeneration-upgrading cycles, whereas the activity of Al-MCM-41 significantly decreased.

Acknowledgement

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