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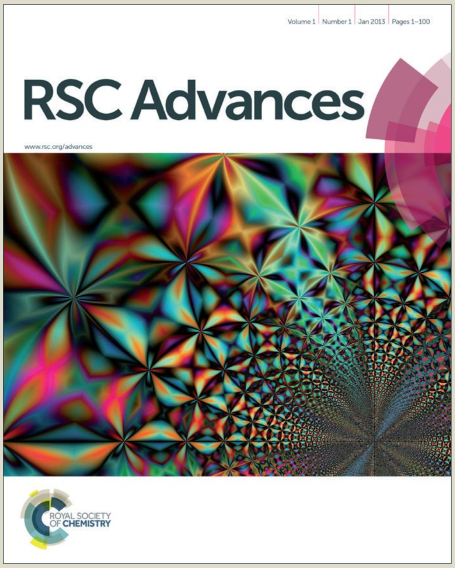

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Mg-modified ultra-stable Y type zeolite for the rapidly catalytic copyrolysis of low-rank coal and biomass

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To improve the quality of oil derived from the fast copyrolysis of low-rank coal with biomass, various metal-modified ultra-stable Y type (USY) zeolites are mixed with the samples for the copyrolysis process. It is found that Mg-modified USY zeolite shows high catalytic activity with high coking resistance ability in this study. A further treatment of Mg-modified USY zeolite by steaming process further improves the coke resistance and the catalytic activity toward production of more hydrocarbons in the pyrolytic oil. It is indicated that Al atoms in the original zeolite framework could be dislocated by the steam treatment and a new framework consisted of Al-Mg-Si could be formed on the outside of zeolite framework, which is benefit to change the physical and chemical properties of zeolite and increase the catalytic activity and coke resistance ability in the process of rapidly catalytic copyrolysis of low rank coal with biomass.

Introduction

Co-utilization of biomass and low-rank coal is gaining more and more interest in recent years as it is believed to be a good way to solve some problems regarding the utilization of coal and biomass separately. For biomass, co-utilization can increase the energy density and bulk density of the feedstock; and for coal, co-utilization can reduce CO_2 emission and ash content. To date, there have been a number of studies on copyrolysis of coal with various kinds of biomass to produce alternative fuels. In the fast copyrolysis process, it is found that the synergistic effect can increase the conversion and oil yield [1-3]. However, due to the high O/C ratio in biomass, the obtained pyrolytic oil usually contains a high amount of oxygenated compounds. To upgrade the oil, catalysts are generally applied.[4,5] One of the promising catalysts is zeolite, which always has high surface area, high pore volume and adjustable surface acidity.[6-10] It has a high potential for deoxygenizing the pyrolytic oil since its acidity can dehydrate the oxygenated compounds.[11,12] Various zeolites such as ZSM-5, USY and beta type ones have been employed for the upgrading of pyrolytic oil.[13-19]

The main problem of zeolite utilization for cracking reaction is coking, which not only results in the catalyst deactivation, but also causes the product losing in the form of carbon.[20,21] Deactivated zeolite can be regenerated by calcination, but the loss product cannot be regained. Therefore, it is necessary to improve the coking resistance ability of zeolite, especially when it is applied for the cracking of complex pyrolytic oil. Modification of zeolite by metal is considered as one way to reduce the coking since it can change the surface properties of zeolite and promote carbon to react with H_2O and other components such as H_2 and CO_2 generated during the pyrolysis process. A number of studies have been reported that the modification of zeolite by metal can reduce the amount of coke on the surface of spent zeolite. Vichaphund et al.[22] found that Co and Ni modification can reduce the amount of coke deposited on HZSM-5. Veses et al.[23] also found that by modification of the same type of zeolite by Mg, Ni, and Sn can significantly decrease the coke formation on the zeolite. In this study, to improve the quality of oil derived from the rapid copyrolysis of low-rank coal with biomass, various metal-modified USY zeolites are prepared and mixed with the coal-biomass samples directly. It is expected to find the most suitable metal to modify zeolite so that the catalyst has higher coking resistance and catalytic activity for *in-situ* catalytic upgrading of pyrolytic oil in the rapid copyrolysis process. Furthermore, a post-treatment by a steaming process for the metal modified zeolite is also performed for further improvement of its catalytic performance. A mechanism on the rapidly catalytic copyrolysis of low-rank coal and biomass by using the best metal-modified zeolite is proposed and discussed.

Experimental

Feedstock and catalysts preparation

Loy Yang coal from Australia (LY) and cedar wood from Aomori prefecture, Japan (CW) were used as feedstock. The proximate and ultimate analyses of the samples are presented elsewhere.[24] LY and CD were dried overnight at 105 °C to remove their moisture. Dried LY and CD with a weight ratio of 1:1 were mixed in a ball mill to form an evenly distributed powder. The powder was pressed to tablet, and

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Table 1 Properties of the USY zeolite.

Zeolite type	USY
Cation type	H
SiO_2/Al_2O_3 (mol/mol)*	6
Crystal Size (µm)*	0.2-0.4
BET surface area (m^2/g)	492
Micropore surface (m^2/g)	421
External surface (m^2/g)	71
Average pore size (nm)	0.68
Total acidity (mmol/g)**	0.862
Weak acid site (mmol/g)**	0.329
Medium acid site (mmol/g)**	0.436
Strong acid site (mmol/g)**	0.097

*as received; **based on the total desorbed NH_3 on NH_3-TPD

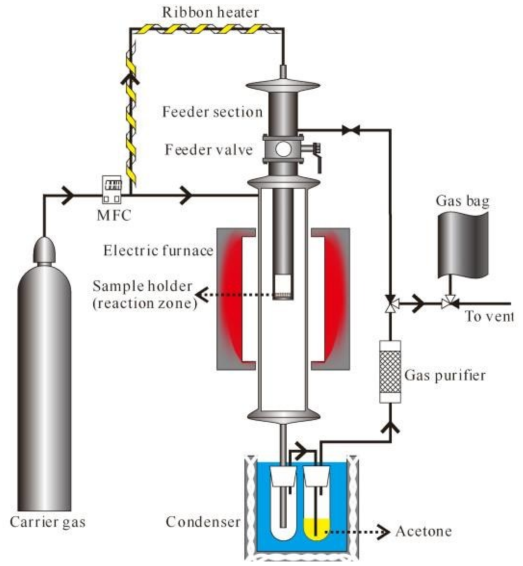

Fig.1 Schematic illustration of rapid pyrolysis reactor system.

then gently crushed and sieved in order to obtain the sample particle size of 1-2.8 mm. The remaining moisture in the sample was analyzed by using MX50 moisture content analyzer (AND, Japan).

USY zeolite with a Si/Al ratio of 6 was purchased from Tosoh Corp, Japan. Its properties are presented in Table 1. Impregnation method was used to prepare metal modified zeolite. Various metals (potassium (K), sodium (Na), magnesium (Mg), cerium (Ce), copper (Cu), iron (Fe), and molybdenum (Mo)) in the nitrate form (Wako, Japan) were used in this study. Certain amount of metal nitrate was dissolved in the distilled water until a homogeneous solution was formed and then, zeolite powder was added into it, and a slurry was obtained. The slurry was continuously stirred for 4 h and then, dried in the oven at 105 ^{o}C until all solvent was evaporated. Finally, the dried slurry was calcined at 650 ^{o}C for 2 h. Calcined powder was pressed to tablet and then gently crushed and sieved to a particle size of 1-2.8 mm. The metal modified zeolite is denoted as Me/USY where Me represents the loaded metal. The properties of the as-prepared metal modified zeolite was characterized by using X-ray diffractometry (XRD, Smartlab, Rigaku, Japan), N_2 isotherm adsorption (NOVA 4200e, Quantachrome instruments, U.S), NH_3-TPD (Belcat classic, BEL Japan Inc.) and X-ray fluorescene analysis (XRF, (Energy dispersive X-ray spectrometer, EDX-800HS, Shimadzu). The details of zeolite characterization can be found elsewhere.[17]

Post-treatment of the selected metal modified USY (Mg/USY) by steaming process was performed in a fixed bed reactor as shown in Fig.S1 in supplementary data. 3 g of Mg/USY was put in the sample holder, which was treated by saturated steam in 50 cm^3/min of argon or air as the carrier gas at the temperature of 600 ^{o}C for 4 h.

Rapidly catalytic copyrolysis process

A dropdown tube reactor was used as the rapid pyrolyzer (Fig.1). 1 g of LY-CD ball-milled sample was homogeneously mixed with 1 g of Me/USY catalyst and put in the feeder section at first. After the reaction zone was flushed by nitrogen and heated up to 600 ^{o}C, the mixture of LY-CD sample and catalyst was dropped down to the reaction zone and held there for 10 min. Volatile product was flowed out from the reactor by using 100 cm^3/min of argon and condensed in two cold trap bottles. The first bottle was used to collect the condensed tar and the second bottle filled with acetone was for trapping the tar which was not condensed in the first one. The collected tar in two bottles was mixed together for further analysis by using GC/MS (GC/MS QP2010, Shimadzu, Japan). Karl-Fisher Titration (MKS-500, KEM, Japan) was applied to analyze the water content in the liquid product. The gas product collected in the gas bag was analyzed by using a GC/TCD (GC/TCD, Agilent 7890A, USA). The details for liquid and gas product analyses can be found elsewhere.[25] The remained solid in the reaction zone was comprised of char, coke on the catalyst, and the catalyst. The total char and coke yield was obtained by measuring the weight of remaining solid before and after it was calcined at 650 ^{o}C for 2 h. The coke amount on the catalyst was calculated by assuming that the char yield was the same in the presence and absence of catalyst.

Results and discussion

Characterization of metal modified zeolite

As stated above, various metals including K, Na, Mg, Ce, Cu, Fe and Mo were applied to modify USY zeolite. As a base case, the loading amount of each metal is 3 wt%. Fig.2 shows XRD patterns of USY and metal modified USY zeolites. One can see that the similar XRD pattern is obtained for all samples, indicating that the modification by each metal with an amount of 3 wt% does not change the zeolite crystallinity and the metal species is evenly distributed on the surface of zeolite with small particle size due to the very high surface area of USY zeolite. Other researchers also reported the similar result.[22,26,27] Interestingly, as shown in Table 2, the BET surface area is increased after the zeolite is modified by metal. Other studies indicate that the loading metal on the zeolite might decrease the BET surface area slightly by pore volume occupation and/or blocking of pores and channels.[28,29] However, Son et al.[30] found that loading metal on γ-alumina support can increase the BET surface area due to the synergy effect between metal oxide and the alumina. The similar result obtained in this study might be due to the similar synergy effect since the selected USY zeolite has a high content of Al (Si/Al is about 6). In the protonic form of zeolite, protons compensate the negative

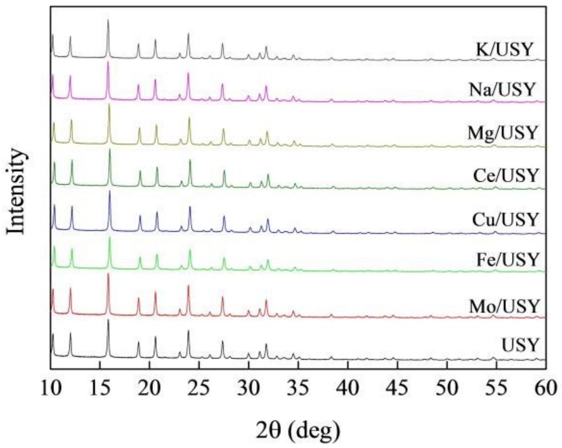

Fig.2 XRD spectra of various metal modified zeolites.

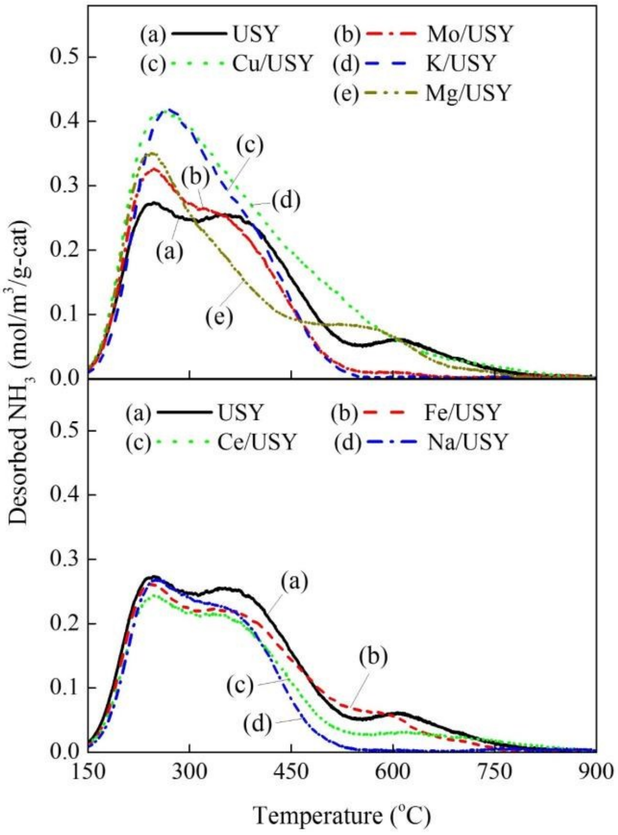

Fig.3 NH3-TPD profiles of metal modified zeolites.

charges due to the presence of alumina in the aluminosilicate framework, and such zeolites always behave as Bronsted acid sites (BAS) in some conditions.[31] When the zeolite is heated, dihydroxylation could occur on the BAS and as a result, vacant electron-acceptor sites or the Lewis acid sites (LAS) could be generated. The LAS formed by dihydroxylation may return to their original states (BAS) after rehydrated by water re-adsorption during the cooling process as illustrated in Fig.S2.[32] However, the rehydration is hindered by the presence of metal oxide, which could occupy the vacant electron-acceptor sites. These doped metal oxides can create new structures on the surface of the zeolite and result in the increase of the total surface area of the catalyst.

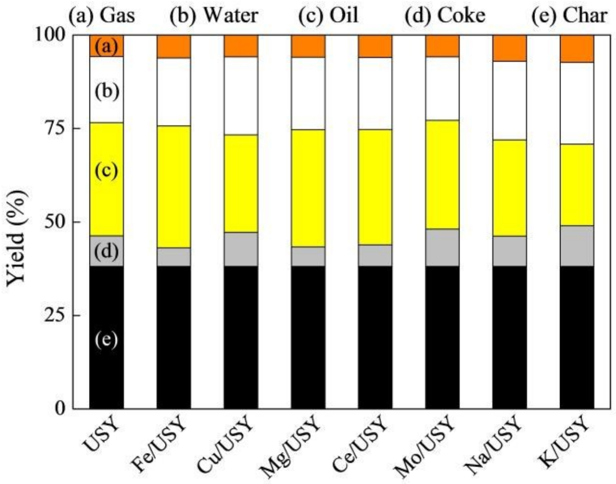

Fig.4 Product yield distribution from rapidly catalytic copyrolysis of LY-CD samples in the presence of various metal modified zeolites at 600 ^{o}C.

Table 2 BET surface areas of various metal modified USY zeolites.

Catalyst	Surface area (m^2/g)
USY	492 ± 12
Fe/USY	523 ± 10
Ce/USY	527 ± 7
Mo/USY	493 ± 11
Cu/USY	536 ± 5
Mg/USY	501 ± 15
K/USY	516 ± 11
Na/USY	531 ± 11

As shown in Fig.3, some metals can modify the surface acidity of zeolite. Especially, doping of some metals such as Cu, K, Mo, and Mg results in the increase in the low-temperature acid sites (LTAS) and the decrease in the high-temperature acid sites (HTAS). It should be noted that LTAS plays an important role to determine the activity of the zeolite-based catalyst.[17] Thus, the modifications by these metals are expected to increase the catalytic activity of USY zeolite.

Catalytic activity of metal modified zeolite

To evaluate the catalytic activity, metal modified zeolite is mixed with the ball-milled LY-CD sample and applied for the rapid copyrolysis process. Fig.4 shows the product yield distribution while Fig.5 shows the chemical compositions of the obtained pyrolytic oil from the catalytic copyrolysis process. In Fig.4, one can see that the coke amounts deposited on Cu, Mo, and K modified zeolite are increased from 8.2% (using the un-modified zeolite) to 9.1%, 10.0%, and 10.9%, respectively. It should be attributed to the higher activity of the metal modified zeolite, by which some oxygenated compounds with small molecule weight in the pyrolytic oil can be easily cracked to form coke on the surface of catalyst. Similar results can be found in the literatures.[22,29] As stated above, modification of zeolite by metal can change the surface property of the zeolite. As shown in Fig.3, the addition of Cu, K, and Mo results in the increase of the LTAS which plays an important role in deoxygenation for oil

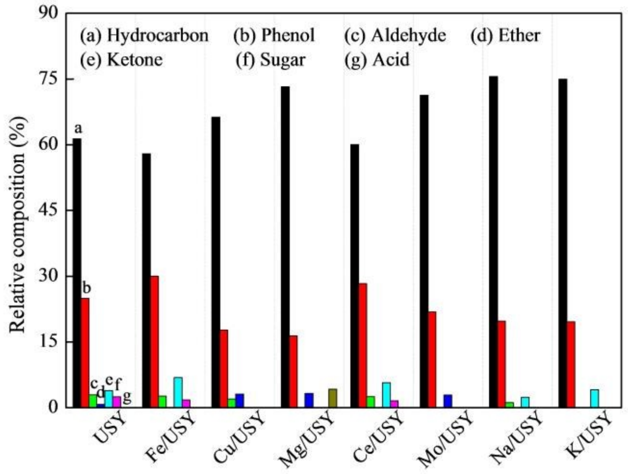

Fig.5 Chemical compositions of the obtained pyrolytic oil from rapidly catalytic copyrolysis of LY-CD samples in the presence of various metal modified zeolites at 600 °C.

upgrading process. The LTAS is related with the hydroxyl groups (Brondsted and/or Lewis sites) on the surface of the zeolite,[23] which are also benefit for the dehydration and cracking reactions. If the more LTAS is formed by the modification of metal, the cracking of some oxygenated compounds on the surface of catalyst could become more intensive so that more hydrocarbons can be produced and thus more cokes are deposited on the catalyst surface. On the other hand, as shown in Fig.4, more water is detected in the obtained pyrolytic oil, indicating that the deoxygenation process becomes more intensive on the metal modified zeolite. It should be noted here that deoxygenation should occur via dehydration reaction since the decrease of oxygenated compound is only followed by the increase of water yield. As seen in Fig.4, gas yields almost remain constants for all metal loaded zeolites, except Na/USY and K/USY with a little increase, indicating that deoxygenation reaction via decarboxylation and decarbonylation which produce CO_2 and CO, respectively, can be ignored.

Fig.5 shows the relative compositions in the pyrolytic oil, which corresponds to the results shown in Fig.4. It can be seen that the modifications of zeolite by Cu, Mo, Na, Mg, and K result in the increase in the hydrocarbon content in the pyrolytic oil from 61.4% (using the un-modified zeolite) to 66.3%, 71.3%, 75.6%, 74.8%, and 75.0%, respectively, suggesting that more oxygenated compounds in the pyrolytic oil have been converted to the hydrocarbons due to the higher activity of metal-modified zeolite.

In the case of alkali metal (i.e., Na and K) modified zeolites (Na/USY and K/USY) , it can be seen from Fig.4 that gas yields are increased from 6.4% (using the un-modified zeolite) to 7.0% and 7.3%, respectively. The increase of gas yield is attributed to the high activity of alkali metal for the gasification/reforming of some components in the pyrolytic oil through steam reforming reaction.[33-35] Generally, water will be generated by the pyrolysis process either from the remaining moisture of the sample or from the decomposition of some compounds in the pyrolytic oil. When the water contacted with the pyrolytic oil in the presence of alkali metal, steam reforming reaction will easily occur [33, 35]. Here, the increase of catalytic activity may also be resulted from the increase of BET surface area for Na/USY. As seen in Fig.3, the modification of zeolite by Na does not significantly increase the acidity of the zeolite, but results in the increase of the BET surface area by a factor of about 9% (Table 2), which will provide more space and active sites for the reaction.

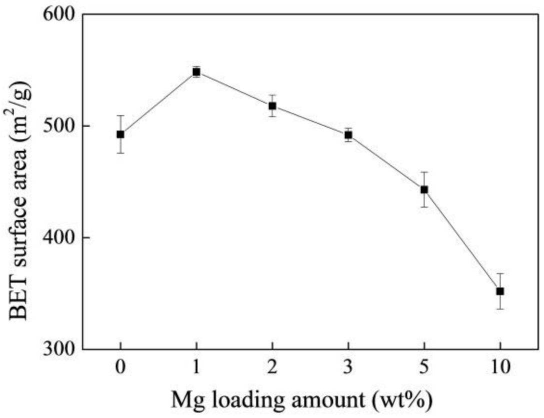

Fig.6 BET surface areas of Mg/USY zeolites with various Mg loading amounts.

Interestingly, as shown in Figs. 4 and 5, the coke amount formed on Mg loaded zeolite (Mg/USY) is much lower while the hydrocarbon content in the pyrolytic oil is significantly higher than those by using others. Similar results are also reported by Veses et al.[23] in which Mg modified zeolite shows the lowest coke deposition while the hydrocarbon contents in the obtained oil are considerably high. They suggested that the deoxygenation process is mainly occurred by decarboxylation and dehydration reactions over Mg loaded zeolite.[23] However, in this study, as seen in Fig.5, the amount of acetic acid is increased when Mg/USY zeolite is used, indicating that decarboxylation reaction is not the main route for the present case. One of the possible explanations for the high coke resistance ability of Mg/USY is as follows: Mg species in the form of MgO can easily absorb CO_2 to form carbonate and/or bicarbonate (CO_3^{2-}/HCO_3^-) due to its slight basicity[36] and the formed carbonate/bicarbonate species might react with the hydrogen atom generated from the decomposition of pyrolytic vapor and create formate/carboxylate intermediates on the surface of the zeolite.[30] Efstathiou et al.[37] reported that the formate/carboxylate formed on the surface of alumina are quite stable at certain conditions. Since the surface of the catalyst is occupied by the formate intermediates, less coke precursor can be easily attached on the surface so that the amount of deposited coke decreases to some extent. In other studies, the addition of Mg to the catalyst also shows a good effectivity as it can reduce the amount of coke significantly and thus a longer catalyst stability can be achieved.[38,39] These results indicate that Mg should be a good alternative to modify the zeolite for the pyrolytic oil upgrading.

The effect of metal loading amount

It is observed that Mg is a good option to modify USY zeolite since the modified zeolite can significantly reduce the coke deposition without decreasing the overall catalytic activity as indicated by high hydrocarbon content in the obtained oil. To understand the effect of metal loading amount on the catalytic activity of zeolite, various amounts of Mg are used to modify USY zeolite. Fig.6 shows BET surface areas of Mg/USY zeolite with various loading amounts. It can

Table 3 Comparison of micropore and external surfaces of Mg/USY zeolites with various Mg loading amounts.

Mg loading amount (wt%)	Micropore area (m^2/g)	External area (m^2/g)
0	421 ± 11	71
1	476 ± 12	72
2	446 ± 8	72
3	430 ± 5	71
5	398 ± 15	73
10	280 ± 15	71

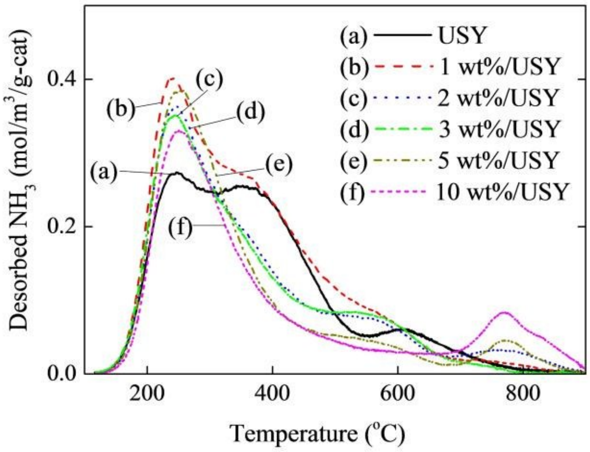

Fig.7 NH3-TPD profiles of Mg/USY zeolites with various Mg loading amounts.

be seen that the loading of Mg until a certain amount can increase the BET surface area to some extent due to the synergy effect between the metal species and the alumina species on the zeolite framework. Further increase of metal loading amount results in the decrease of BET area due to the pore blocking. Table 3 compares the micropore surface area and the external surface area of metal modified zeolites calculated by t-plot method. As seen in Table 3, the surface area of the micropore site is changed but the external surface area remains at relatively constant. At higher metal loading amount, some parts of the metal species could be agglomerated and block the micropore site and as such, the micropore surface area decreases significantly at high metal loading amount.

As seen in Fig.S3 in the supplementary data, XRD spectra of Mg/USY with various loading amounts are similar to that of the parent zeolite, indicating that no crystalline structure change occurs when the loading amount of Mg is varied. However, it should be noted that a significant change can be observed for the surface acidity as shown in Fig.7. Mg loading results in the decrease of LTAS and shifts the HTAS from about 610 to 570 °C. When the loading amount of Mg is increased to 3wt%, a new peak starts to appear at about 780 °C. The intensity of the new peak becomes stronger when the loading amount is increased to 5 and 10 wt%. This new peak might come from MgO agglomeration site.

Fig.8 shows the product yield distribution (a) and the chemical compositions of the obtained pyrolytic oil from the rapidly catalytic copyrolysis process (b). One can see that loading 1 wt% of Mg on zeolite results in a little increase of coke yield; however, with the further increase of Mg loading amount, the coke yield decreases. The increase of coke yield is attributed to the increase of catalytic activity for the cracking of some hydrocarbon components with small molecule weight in pyrolytic oil on the surface of catalyst. As seen in Fig.7, LTAS is significantly increased when 1 wt% of Mg is loaded, resulting in the increase of catalytic activity for the cracking reaction. Also, in this case, BET surface area is increased as indicated above (Fig.6). It should be noted that the hydrocarbon content in the obtained oil is also increased significantly, i.e., from 61.4% (using the un-modified zeolite) to 79.9% after USY zeolite is modified by 1 wt% Mg. Further increase in Mg loading amount results in the decrease of coke yield, but it should be noted that the hydrocarbon contents in the pyrolytic oil are also decreased a little. As seen in Figs.6 and 7, both LTAS and BET surface area decrease with the increase in Mg loading amount and as such, the catalytic activity for deoxygenation should be also decreased to some extent. However, even though the

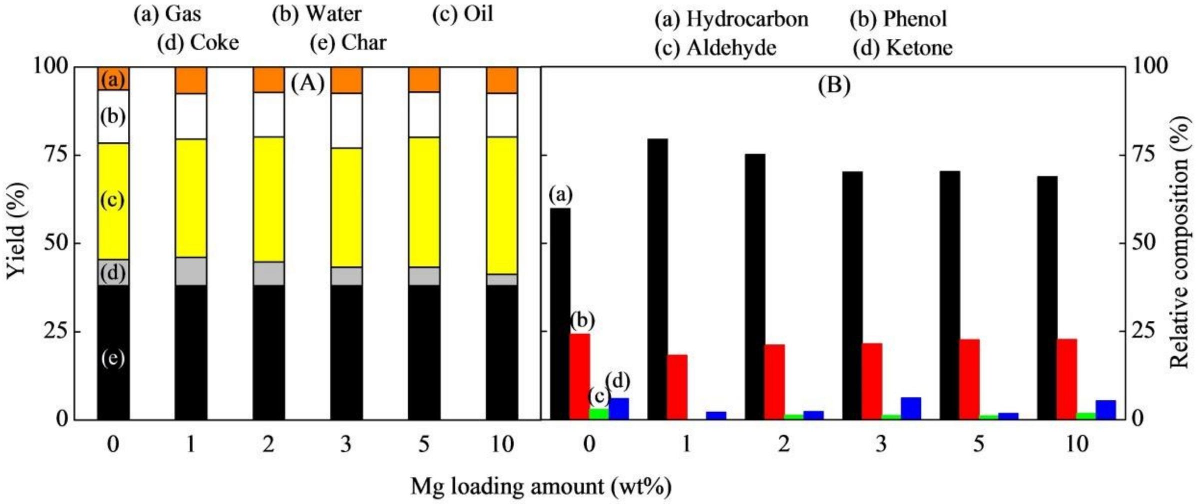

Fig.8 Copyrolysis results from LY-CD samples in the presence of Mg/USY zeolites with various Mg loading amounts. (A) Product yield distribution and (B) chemical compositions of the obtained pyrolytic oil.

catalytic activity decreases in the case of Mg loading amount as much as 10 wt%, the hydrocarbon content in the obtained pyrolytic oil is still higher than that in the case of the parent USY zeolite.

Reusability of Mg modified zeolite

Coke deposition is still observed on the surface of Mg/USY even though the amount is much lower than those on other metal modified zeolites. As the coke deposition will deactivate the catalyst, regeneration process is necessary to regain the catalytic activity. In this study, the spent zeolite is regenerated by calcination at 650 ^oC in

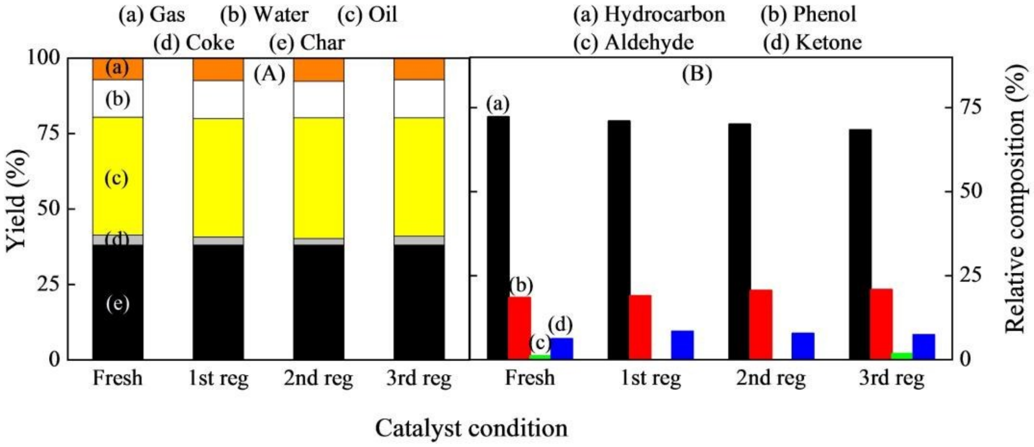

Fig.9 Catalytic performance of the regenerated Mg/USY zeolites. (A) Product yield distribution and (B) chemical compositions of the obtained pyrolytic oil.

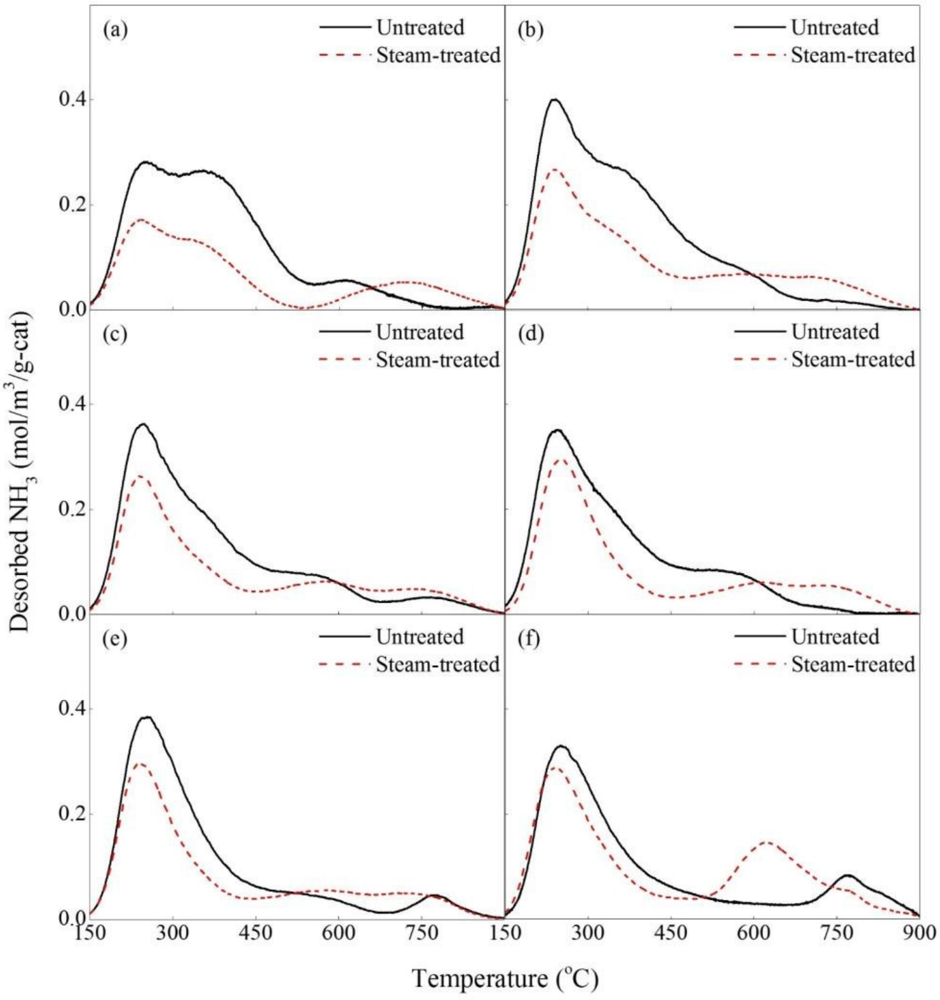

Fig.10 Comparison of NH3-TPD profiles of zeolite before and after treated by steaming process for (a) USY, (b) 1 wt%Mg/USY, (c) 2 wt%Mg/USY, (d) 3 wt%Mg/USY, (e) 5 wt%Mg/USY, and (f) 10 wt%Mg/USY.

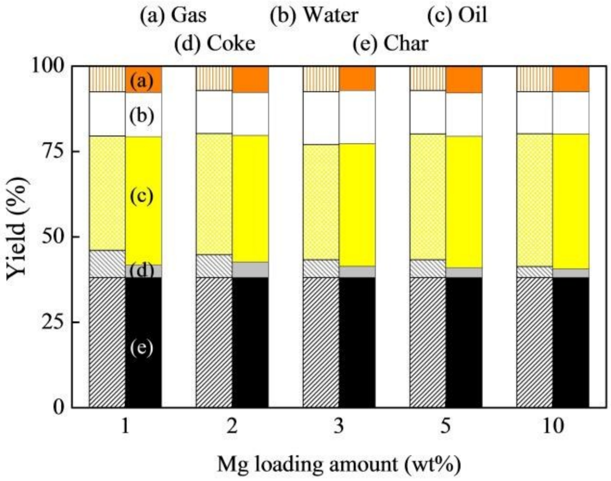

Fig.11 Product yield distribution from rapidly catalytic copyrolysis of LY-CD in the presence of Mg/USY (shaded graph) and steamed Mg/USY zeolites (solid graph).

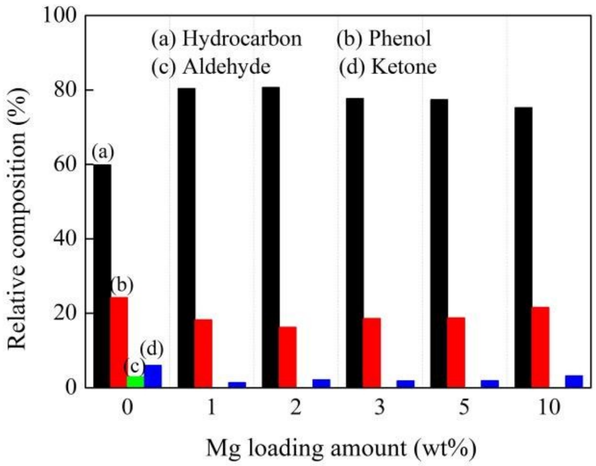

Fig.12 Chemical compositions in the obtained pyrolytic oil from rapidly catalytic copyrolysis of LY-CD in the presence of steam-treated Mg/USY zeolite.

Table 4 Comparison of coke yield and hydrocarbon content in the obtained oil for the untreated and steam-treated Mg/USY at various Mg loading amount.

Mg loading amount (wt%)	Coke yield (%)		Hydrocarbon content (%)	
	Untreated	Treated	Untreated	Treated
0	7.4	3.9	59.9	65.3
1	8.0	3.7	79.6	80.9
2	6.7	4.6	75.2	80.7
3	5.2	3.3	70.3	77.7
5	5.2	2.9	70.4	77.4
10	3.2	2.5	68.9	75.3

air for 2 h. Fig.9 shows the catalytic performance of fresh and regenerated 3wt% Mg/USY zeolites. It can be seen that the regenerated catalyst has almost the same coking resistance ability and the obtained hydrocarbon content in the obtained pyrolytic oil is also only decreased slightly, indicating that the regeneration process can regain the catalytic activity as the original one. NH_3-TPD profile and BET surface area of the regenerated catalyst also show the similar properties as the fresh one. A slight decrease in hydrocarbon content in the pyrolytic oil might be attributed to the volatilization of Mg species since alkali and alkaline earth metal species are known to be easily volatilized during the heat treatment.[24,34,40] For comparison, the stability test is also conducted for 3 wt% Cu/USY and the results are shown in Fig.S4. One can see that the regenerated Cu/USY exhibits a stable performance until the 3rd regeneration, indicating that the spent Cu/USY can be also regenerated as spent Mg/USY. However, it should be noted that the obtained hydrocarbon content in the pyrolytic oil is still high for Mg/USY even after it is reused for 3 times.

The effect of steam treatment for Mg/USY zeolite

As indicated above, Mg/USY zeolite can effectively reduce the amount of coke while make the obtained pyrolytic oil contain high hydrocarbon content. However, it is still necessary to further increase the coke resistance so that more product can be recovered. Sazama et al.[41] found that less coke will be deposited on the surface of the metal modified zeolite after it is further treated with steaming process, by which the acidic property of zeolite could be significantly changed so that the catalytic performance is promoted.[42-46]

Fig.10 shows NH_3-TPD profiles of Mg/USY with various Mg loading amounts before and after steaming process. One can see that the total acid amount decreases for each Mg loading amount. Interestingly, for 10 wt% Mg/USY, a quite strong peak appears at about 620 ^{o}C, which might come from the new formed framework between dislocated Al and Mg species. Sazama et al.[41] reported that metal oxide structures on the zeolite surface might reorganize themselves dramatically by the Al dislocation from the zeolite framework. The steaming process can release the framework Al atom, which can encapsulate other metal ions located in the cationic sites and stabilize the adjacent framework Al atoms.[41,47] As seen in Fig.S5, based on XRF analysis, Si/Al ratio on the surface of steam-treated zeolite is lower than the untreated one due to the dislocation of Al from the main framework to the outer surface. In the cases of untreated metal loaded zeolites, metal oxide structures are formed above the Si sites (see Fig.S2) and thus they might hinder the Si atoms. As a result, Si/Al on the zeolite surface tends to decrease along with the increase of metal loading amount (Fig.S5). When the metal loaded zeolite is steamed, metal oxide might capture the dislocated Al to form a new framework of Al-Me-Si. Due to the structure rearrangement, the oxide structure above the Si atoms are opened and thus more Si can be detected by XRF. As such, the detected Si/Al ratio is also higher for the high metal loading amount (5 and 10 wt%) after the zeolite is steam-treated. The structure rearrangement between modified metal and the extra-framework Al (EFAl) to form a new framework of Al-Me-Si could also provide new active sites for the reaction and thus, as shown in Fig. S6, a higher surface area is formed for the steam-treated metal loaded zeolite.

Figs.11 and 12 show the catalytic performance of steam treated Mg/USY zeolites. One can see that the coke amount deposited on the catalyst surface decreases from 8.0 (without steam treatment) to 3.7, 4.6, 3.3, 2.9, and 2.5% for 1, 2, 3, 5, and 10wt% Mg/USY, respectively, after they are treated by steam as shown in Table 4. Bazyari et al.[44] also observed the similar results. As indicated above, the main sources for the coke formation are the cracking of hydrocarbon components with lower molecular weights in the pyrolytic oil, and these components also have less diffusion limitation.[44] These cracking products may polymerize with each other and then dehydrogenate and aggregate to form coke on the acid sites of the zeolite.[48] When the zeolite is treated by steam, some parts of the acid sites are removed out from the structure due to dealumination. The decrease of acid sites may reduce the dehydrogenation chance of the cracking species since the amount of acid sites as the counterpart of the dehydrogenated cracking product become limited.[44]. As a result, the total amount of deposited coke on the zeolite surface decreases to some extent. In other words, the optimum amount of acid sites should be existed for the metal modified zeolite as a catalyst for the rapidly catalytic copyrolysis of low-rank coal and biomass.

On the other hand, as shown in Fig.12 and Table 4, the decrease of coke deposition on the steam-treated catalyst results in the increase of hydrocarbon content in the obtained pyrolytic oil. As indicated above, steaming process can reduce the acid sites and as such, dehydrogenation of hydrocarbon to coke is inhibited and more hydrocarbons remain in the final pyrolytic oil. These results indicate that Mg is very suitable metal to modify the zeolite for the rapidly catalytic copyrolysis of low rank coal and biomass, and the post-treatment of catalyst by steam can effectively increase the catalytic performance by increasing the coke resistance of the zeolite.

Conclusions

Various kinds of metals (K, Na, Mg, Ce, Cu, Fe, and Mo) are applied for the modification of USY zeolite to improve the catalytic activity as well as the coke resistance. Performance test is focused on the coke yield and hydrocarbon content in the oil. The results indicate that the modification of zeolite by metal can change the surface properties of the zeolite. Some metals, such as Cu, Na, K, Mg and Mo can increase the LTAS for improvement of the catalytic activity of the zeolite. Mg modified USY zeolite shows the best performance in this study. It is found that the deposited coke on the surface of the zeolite is decreased while the hydrocarbon content in the obtained pyrolytic oil is increased when the zeolite is modified by Mg. It is suggested that the adsorption of CO_2 to form carbonate and/or bicarbonate sites for hindering the formation of formate/carboxylate as the coke precursor in the presence of Mg species should be the main reason for the coking resistance. Also, Mg modified zeolite also shows a good stability even though a slight decreasing catalytic activity can be observed due to the volatilization of minor Mg species. Further treatment of the zeolite by steaming process increases the coke resistance. It is observed that steaming process results in the decrease in the surface acidity of the zeolite. Steaming process can cause the dealumination, and in the presence of modified metal species, a new Al-Me-Si framework can be formed after steaming process. In the case of Mg modification, the formation of the new framework may hinder the metal agglomeration and results in the increase of BET surface area. Furthermore, the decrease of acid site by steam treatment also limit hydrocarbon species attaching on it for generation of coke. As a result, the amount of deposited coke is decreased and more hydrocarbon can be detected in the obtained pyrolytic oil. This study indicates that the modification of USY zeolite by Mg and post steam-treatment of the catalyst can significantly increase the catalytic performance of the zeolite for assisting rapid copyrolysis of low rank coal and biomass.

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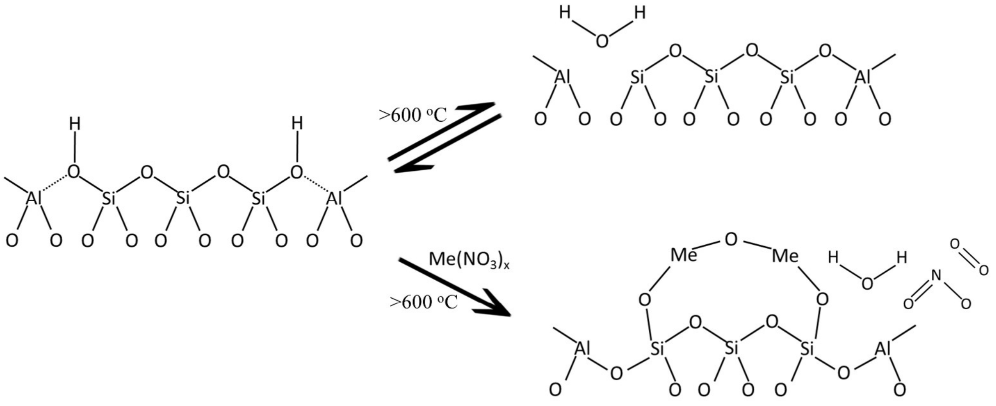

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