

Influence of the Zeolite ZSM-5 on Catalytic Pyrolysis of Biomass *via* TG-FTIR

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Bio-oil from the pyrolysis of biomass is an important renewable source for liquid fuel. However, the application of bio-oil has been severely restricted due to its high viscosity, acidity, and low heating value. Thus, it has been necessary to upgrade bio-oil for automobile fuel *via* catalytic deoxygenation reactions. Herein, the effects of the zeolite ZSM-5 on the pyrolysis of four biomass materials (corn cob, corn straw, pine powder, and cellulose) were investigated *via* TG-FTIR (thermogravimetric analyzer coupled with a Fourier transform infrared spectrometer) to better understand the working mechanism of ZSM-5. The contents of the products of H₂O, CO, CO₂, and the C-O, C=O, and OH groups evolved with increasing pyrolytic temperature were monitored by FTIR. It was found that the relative contents of the C-O and C=O groups were decreased under the catalysis of ZSM-5, while the formations of CO, H₂O, and the OH containing compounds were promoted. To explain the regulations, reaction routes were speculated and the catalytic conversion mechanisms were deduced.

Keywords: Biomass; Catalysis; Upgrading; Mechanism; ZSM-5

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INTRODUCTION

Bio-oil from the pyrolysis of biomass is an important renewable source for liquid fuel and/or for chemicals (Huber *et al.* 2006; Mohan *et al.* 2006; Bridgwater 2012). However, the application of bio-oil has been severely restricted due to its high viscosity and acidity and low heating value. Thus, efforts had been made to upgrade bio-oil for use as an automobile fuel *via* catalytic deoxygenation reactions (Williams and Horne 1995; Vitolo *et al.* 1999; Nokkosmaki *et al.* 2000; Thring *et al.* 2000; Williams and Nugranad 2000; Karagöz *et al.* 2005; Adam *et al.* 2006; Antonakou *et al.* 2006; Huber *et al.* 2006; Nilsen *et al.* 2007; Triantafyllidis *et al.* 2007; Song *et al.* 2010; Vispute *et al.* 2010; Stefanidis *et al.* 2011; Stephanidis *et al.* 2011; Campanella and Harold 2012). The investigations focused on zeolites due to their relatively greater effect and lower cost (Williams and Horne 1995; Vitolo *et al.* 1999; Thring *et al.* 2000; Williams and Nugranad 2000; Adam *et al.* 2006; Antonakou *et al.* 2006; Nilsen *et al.* 2007; Triantafyllidis *et al.* 2007; Vispute *et al.* 2010; Stefanidis *et al.* 2011; Stephanidis *et al.* 2011; Campanella and Harold 2012).

The Li research group (Fan *et al.* 2013; Gong *et al.* 2011; Huang *et al.* 2012) had systematically investigated the effect of La/HZSM-5 catalyst on producing light olefins

from conversions of various biomass materials such as cellulose, hemicellulose, lignin, rice husk, sawdust, sugarcane bagasse, and bio-oil as well. It was found that the biomass with higher content of cellulose or hemicellulose generated more olefins than those with higher content of lignin, and the addition of lanthanum played an important role in promoting the formation of olefins. Additionally, the effect of current on transformation of bio-oil to BTX by catalysis of HZSM-5 was also investigated (Bi *et al.* 2013), and the results revealed that the methoxy, hydroxyl, and methyl groups in aromatics could be effectively removed in the current-enhanced catalytic process. Stephanidis *et al.* (2011) investigated the effect of ZSM-5 on the pyrolysis of beech wood before and after hydrothermal pretreatment. It was found that under the catalysis of ZSM-5, the contents of H₂O and CO were increased significantly, while the content of CO₂ was decreased distinctly for both raw and pretreated beech wood. The contents of the C=O containing components (acids, aldehydes, and ketones) were decreased remarkably under ZSM-5 catalysis in both systems; the content of esters was increased in the raw beech wood system but remained almost unchanged in the pretreated system. For components containing C-O-C bonds, the furan content was increased in both of the raw and pretreated systems; the content of other ethers was only increased by a modest degree in the raw beech wood system but was decreased remarkably in the pretreated system. For the components containing C-OH bond, the content of phenols was decreased, but the content of alcohols was increased for both systems. The formation of aromatics was promoted obviously in both systems. In the Williams' work (Williams and Horne 1995), the contents of H₂O, CO, and CO₂ were all increased remarkably during the pyrolysis of wood waste *via* ZSM-5 catalysis. However, for the pyrolysis of Lignocel HBS 150-500, Stefanidis *et al.* (2011) observed that the CO content was increased, the CO₂ content changed very little, and the generation of H₂O was only weakly promoted by ZSM-5 catalysis. The concentration of acids, aldehydes, and ketones were decreased remarkably, but esters were more generated under the catalysis of high surface area of ZSM-5. Phenols and alcohols were more generated. The concentration of furans was decreased under the catalysis of low surface area of ZSM-5, but increased by high surface area of ZSM-5. Campanella and Harold (2012) investigated the pyrolysis of chlorella under the catalysis of ZSM-5 and the results were found similar to those obtained by Stefanidis *et al.* (2011), in that the CO content was remarkably increased and the CO₂ content changed very little, though H₂O was promoted more distinctly and the alcohol content decreased slightly.

As previous investigations illustrated, the extent of the catalytic effects varied with different biomass resources and with different reaction conditions. Furthermore, the problems of short catalyst life-time and poor reproducibility hindered the industrial applications of zeolites severely, and the reasons for the problems were vague. Thus, it was worthwhile to investigate the working mechanisms of zeolites to improve their effects.

In this paper, the effect of ZSM-5 zeolite on the pyrolysis of four biomass materials of corn cob (CC), corn straw (CS), pine powder (PN), and cellulose (CE) were investigated *via* a thermogravimetric analyzer (TG) coupled with a Fourier transform infrared spectrometer (FTIR). The compounds containing C-O, C=O, and OH groups and

the products of H₂O, CO, and CO₂ evolved with increasing temperature were monitored by FTIR to better understand the catalytic mechanism.

EXPERIMENTAL

An instrument of thermogravimetric analyzer (Netzsch 449C, Germany) coupled with a Fourier transform infrared spectrometer (Bruker Equinox 55, America) was used in this research. Biomass samples were pyrolyzed in the TG analyzer, and the pyrolytic volatiles were carried away by a carrier gas of pure N₂ (60 mL/min) through a transfer line to a gas cell for IR analysis. All samples were heated from 40 °C to 900 °C at 30 °C/min in the pyrolysis zone, and the transfer line and gas cell were kept at 210 °C. In each run, 12 mg of a biomass sample was loaded into a crucible, and the amount of ZSM-5 used was about 3 mg. The IR spectrometer scanned from 400 to 4000 cm⁻¹, and a spectrum was obtained every 32 scans.

RESULTS AND DISCUSSION

TG Analysis

The TG and DTG curves of CC, CS, PN, and CE are shown in Fig. 1. The figure shows that the pyrolysis of CC and CS started at about 200 °C, the initial pyrolytic temperature of PN followed at around 250 °C, and CE started the pyrolytic process at about 300 °C. Consequently, the main pyrolytic processes of CS and CC ended earlier at about 380 °C, and those of PN and CE ended later at around 420 °C. As shown in the DTG curves, two weight loss peaks can be identified in the CC, CS, and PN curves, while only one peak appears in the CE curve.

As previous investigations illustrated (Wang *et al.* 2011; Zhou *et al.* 2013), for biomass materials, the initial pyrolysis of hemicellulose was early, cellulose started the pyrolysis later and proceeded fastest within a narrow temperature range, and lignin pyrolyzed slowly in a broad temperature range with a low initial pyrolytic temperature. Therefore, the first DTG peak was attributed to the pyrolysis of hemicellulose, and the second peak was due to cellulose. The short and broad DTG peak of lignin always overlapped the peaks of hemicellulose and cellulose, influencing the shapes of the first two peaks. Herein, the first peak (Peak 1) of CC was sharpest, the Peak 1 of CS was of average intensity, and the Peak 1 of PN was bluntest. By comparison with the typical TG and DTG curves of these three main biomass components, it could be deduced that hemicellulose was more abundant in CC and CS than in PN, while PN was richer in cellulose and lignin.

Very little difference could be identified in the initial pyrolytic temperatures in the TG curves or the peak positions in the DTG curves between the catalytic and non-catalytic systems. This result indicated that ZSM-5 did not remarkably promote or inhibit the primary pyrolysis of the biomass samples under the experimental conditions and instead might mainly influence the secondary reactions of the pyrolytic products, when the released volatiles contacted the surface of the catalyst. This was similar to the

phenomena as reported by Güngör *et al.* (2012), where the pyrolysis of pine bark under the catalysis of ReUS-Y was conducted by TG analysis.

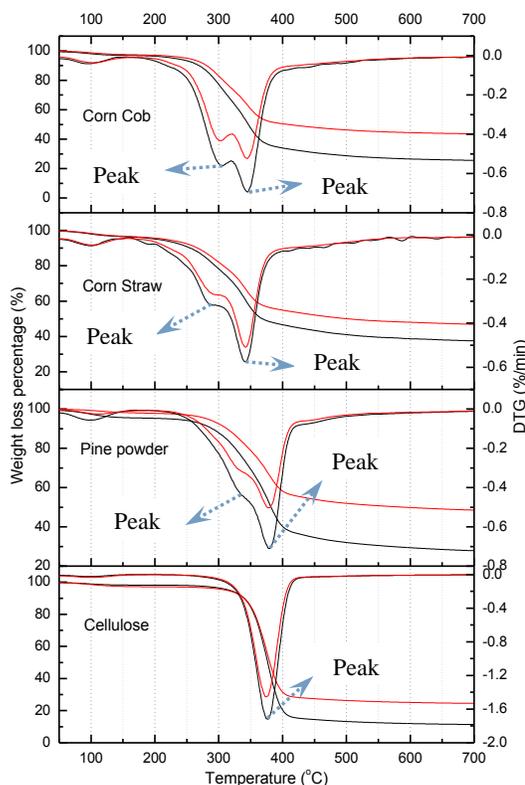


Fig. 1. TG and DTG curves from the pyrolysis of CC, CS, PN, and CE (black curve: non-catalytic pyrolysis of biomass; red curve: catalytic pyrolysis of biomass).

IR Analysis

Spectra from the pyrolysis of pure biomass materials

The IR spectra of the volatiles produced by the pyrolysis of solo biomass materials as pyrolytic temperature increased are shown in Fig. 2. The spectrum bands of major products and chemical groups are listed in Table 1. Figure 2 shows that the products of CO, CO₂, H₂O, and the groups of C-O, C=O, and OH could be accurately identified, and the release of the volatiles began steeply and proceeded rapidly. The carbonyl compounds and CO₂, were two of the most abundant components in all volatile systems. The C=O signal was much stronger than that of CO₂ in the PN and CE systems, while in the CC and CS systems much more CO₂ was generated.

Table 1. Spectral Bands Assigned for Major Products, Chemical Groups (cm⁻¹)

| Chemical groups | CO | CO ₂ | H ₂ O | C-O | C=O | OH |
|-----------------|---------------|-----------------|------------------|---------------|---------------|---------------|
| Spectrum bands | 2090.8~2150.6 | 2285.6~2385.9 | 3801.7~3990.7 | 1024.2~1201.6 | 1697.4~1822.7 | 3230.8~3429.4 |

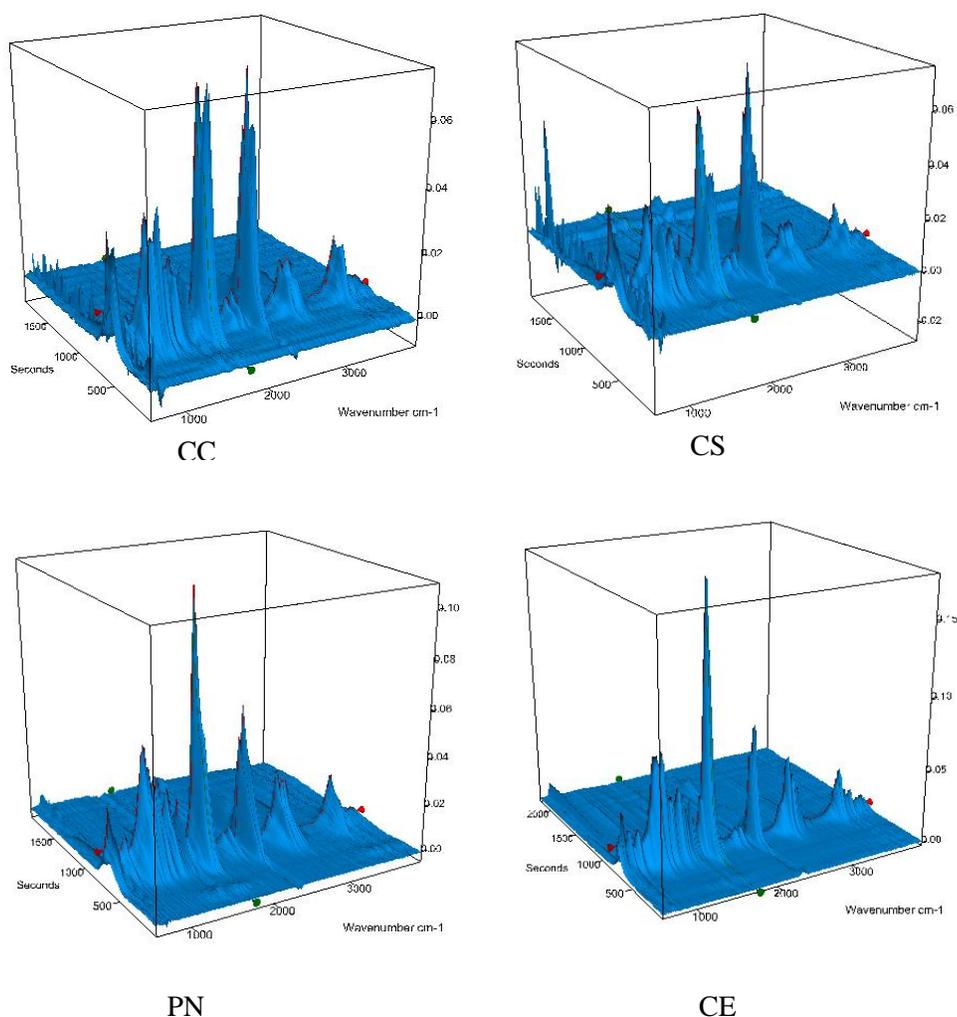


Fig. 2. IR spectra of the pyrolysates evolved from solo biomass materials with increasing pyrolytic temperature

Effect of ZSM-5 catalysis on the pyrolysis reaction

The ratio between the transmission intensity of a certain spectrum band and the total transmission intensity of the whole spectrum band (restricted from 950 cm⁻¹ to 4000 cm⁻¹ to erase the interference of significant noise at wavenumbers lower than 950 cm⁻¹), was used for comparison between the catalytic and non-catalytic systems. Absolute IR values may be influenced by many uncertain factors, such as the differences of the sample amount for TG analysis, baseline drifting of IR signals, variations in the transparency of the glasses (ZnSe and KBr) in the gas cell after a period of usage, *etc.* These factors may cause absolute IR values to vary irregularly, creating difficulties when comparing between systems with tiny changes. Thus, the relative contents of components expressed as transmission percentages are more suitable for comparison between the catalytic and non-catalytic systems. The changes in the transmission percentages with increasing pyrolytic temperature are shown in Fig. 3. In Fig. 3, a lower percentage value

means an increased relative content of the component, as a higher content of a component induces a weaker permeability to its IR signal.

Figure 3 illustrates that, for the four biomass pyrolytic systems, the transmission percentages of the compounds containing C-O and C=O groups under catalysis were all higher than those in the non-catalytic systems, while the percentages of CO, OH, and H₂O were decreased under the catalysis of ZSM-5. The value of CO₂ changed very little between the catalytic and non-catalytic systems. These trends signified that the contents of C-O and C=O groups were decreased under the catalysis of ZSM-5. The formation of CO, H₂O, and the OH containing compounds were promoted, and the CO₂ content remained relatively stable. Considering the relations between the promoted and inhibited components under catalysis, it could be deduced that the compounds containing C-O or C=O groups were partially converted to CO, H₂O, and the OH containing compounds by partial removal of the oxygen atom from the pyrolytic liquid; thus, the oxygen content was decreased under catalysis. The generated water may occupy the active Lewis acid sites on the surface of the catalyst, and the Bronsted acid may be consumed as the reaction proceeds, explaining the deactivation of the catalyst.

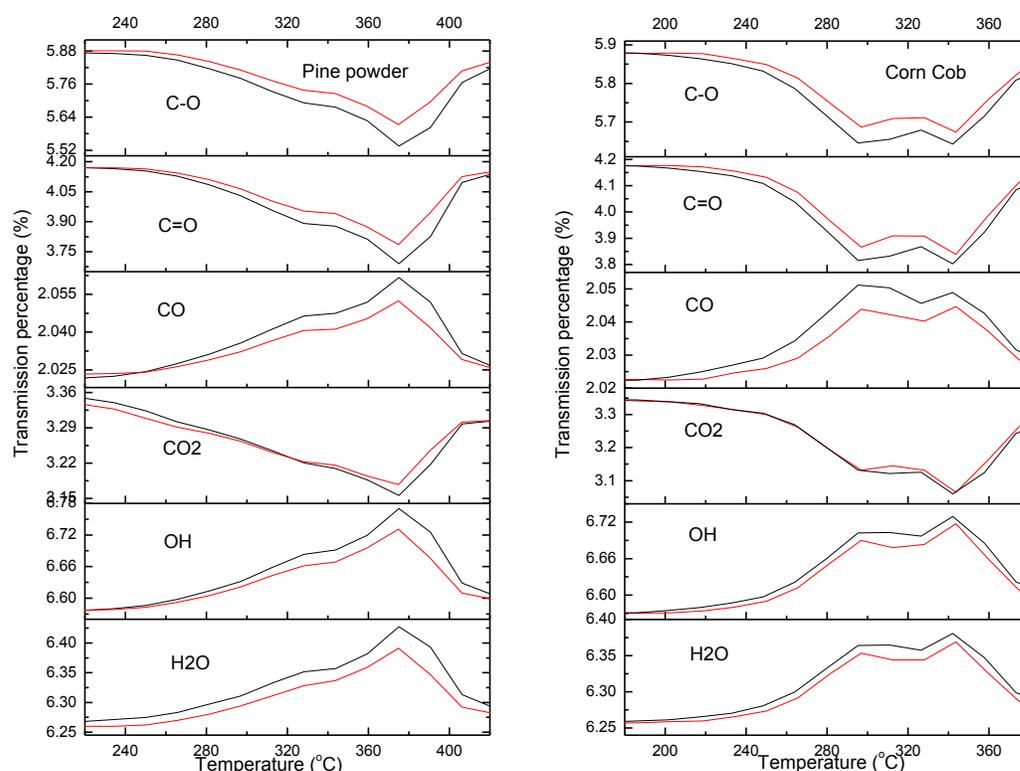


Fig. 3 (Part 1). Transmission percentages of some components changed with increasing temperature (black curve: non-catalytic pyrolysis of biomass; red curve: catalytic pyrolysis of biomass)

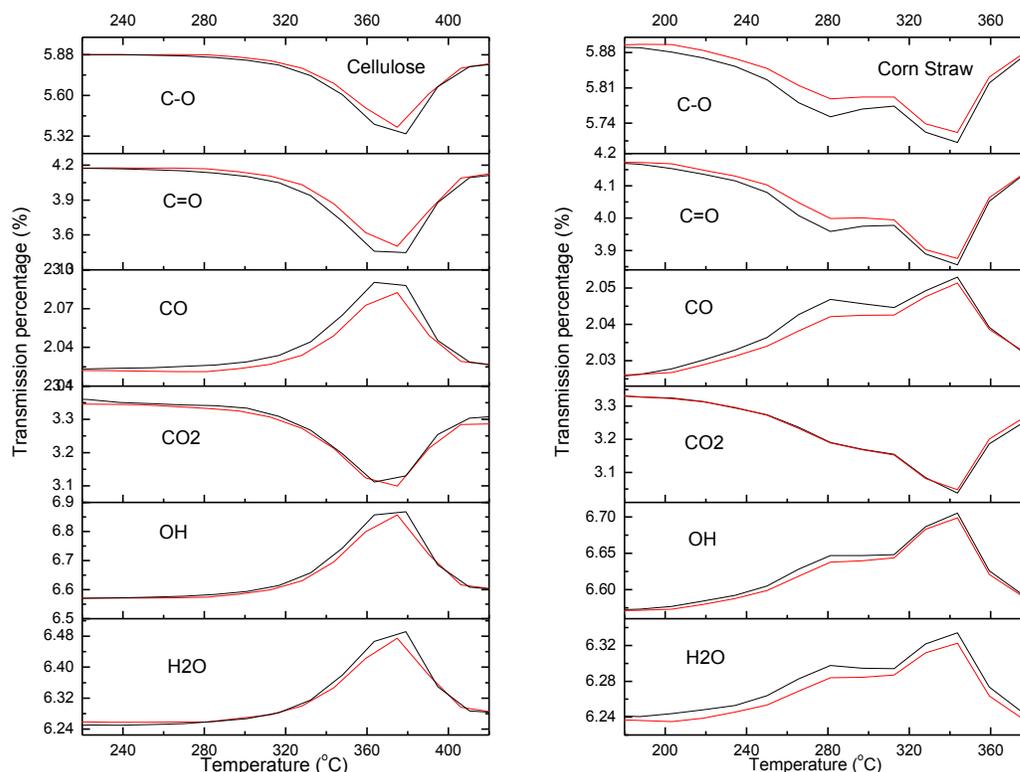


Fig. 3 (Part 2). Transmission percentages of some components changed with increasing temperature (black curve: non-catalytic pyrolysis of biomass; red curve: catalytic pyrolysis of biomass)

Comparison with Literature for Analysis

The effect of ZSM-5 may differ in manner or extent due to different biomass materials or reaction conditions. Thus, some literature results were collected for comparison among each other and with the present results, as listed in Table 2.

Through the comparison among the literature results, the pyrolysis of the biomass materials exhibited a common trend of increased contents of CO, H₂O, and aromatics, and decreased acid, aldehyde, and ketone contents under ZSM-5 catalysis. In general, the sum of acids, aldehydes, and ketones comprised the majority of the C=O containing components, so the C=O content should be decreased under catalysis whether the content of esters was increased or reduced. The effects of ZSM-5 on the contents of CO₂, esters, furans, ethers, and phenols varied with different raw materials and reaction conditions.

In the present work, the increased contents of CO and H₂O and the decreased C=O content were in accordance with the common trends; the CO₂ content changed very little, which was not unusual compared to the decreased, increased, or stable CO₂ contents reported in the literature. The IR analysis can instantaneously provide information on chemical group distribution of a mixture, but it can hardly identify single organic compounds as done by GC/MS, due to the severe overlaps of too many peaks in the complex mixtures. However, it is still possible to deduce some chemical conversions according to the increased and decreased contents of chemical groups. As deduced in formulas (1) and (2), CO₂ is mainly derived from carboxylic acids and CO is mainly

derived from the carbonyl groups of aldehydes and ketones. CO may also be generated from carboxylic acids with the formation of alcohols (or H₂O) as by-products. The promoting effect of ZSM-5 on the conversions of aldehydes or ketones to CO is supported by the increased content of CO for all materials under all conditions. If the promoting effect of ZSM-5 on the conversion of carboxylic acids to CO₂ is more distinct, the content of CO₂ is to be increased; if the conversion of carboxylic acids to CO and OH is more pronounced, the CO₂ content may be reduced and the CO and OH (or H₂O) contents may be increased; if the promoting and inhibiting effect of ZSM-5 on the formation of CO₂ behaves in similar degree, the CO₂ content may change very little.

The products of H₂O and the OH containing compounds may not only be derived from carboxylic acids as mentioned in formula (1) but may also be generated from the C-O containing compounds as showed in formula (3).

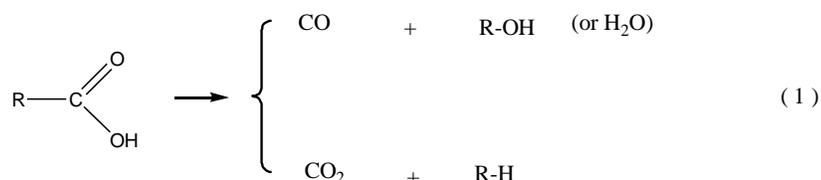


Table 2. Effect of ZSM-5 on Reported Product Distributions

| Ref. | Materials | H ₂ O | CO | CO ₂ | ar | ac | al | ke | es | ah | fu | et | ph |
|------|-----------|------------------|----|-----------------|----|----|----|----|----|----|----|----|----|
| [A] | BW | ↑ | ↑ | ↓ | ↑ | ↓ | ↓ | ↓ | ↓ | ↑ | ↑ | ↑ | ↓ |
| [A] | HTBW | ↑ | ↑ | ↓ | ↑ | ↓ | ↓ | ↓ | ≈ | ↑ | ↑ | ↓ | ↓ |
| [B] | WW | ↑ | ↑ | ↑ | ↑ | | | | | | | | |
| [C] | LC | ↑ | ↑ | ≈ | ↑ | ↓ | ↓ | ↓ | ↑ | ↑ | ↑↓ | ↑ | ↑ |
| [D] | CR | ↑ | ↑ | ≈ | | | | | | ↓ | | | ↑ |

Notes: [A]- Stephanidis *et al.* 2011; [B]- Williams *et al.* 1995; [C]- Stefanidis *et al.* 2011; [D]- Campanella and Harold 2012; BW- beech wood; HTBW- hydrothermal treated beech wood; WW- wood waste; LC- Lignocel HBS 150-500; CR- chlorella; ar- aromatics; ac- acids; al- aldehydes; ke- ketones; es- esters; ah- alcohols; fu- furans; et- ethers; ph- phenols; ↑- increased; ↓- reduced; ↑↓ -increased or reduced depends on surface area of catalyst; ≈- in similar level.

The decreasing extents of C-O and C=O in the CC, CS, and PN systems were much more significant than those in the CE system, indicating a poor catalytic activity of ZSM-5 on pure cellulose. The enhanced conversions of the CC, CS, and PN samples could be attributed to the inherent catalytic effects of ash materials (Bridgwater 2012) and the interactions among the various components.

Mechanism Discussion

A possible catalytic mechanism for the conversion from C=O to CO and from C-O to OH (or H₂O) was speculated, as shown in Fig. 4 and Fig. 5. In the two figures, the model formula of zeolite was a simplified form of the one used in the book of *Industrial Catalysis* (Tang *et al.* 2010). In the conversion route from C=O to CO, the C=O group first adsorbs onto the surface of ZSM-5 *via* the interaction between the O atom of the C=O group and the Lewis acid site on Al atom. Then, some electrons from the O atom may move close to the C atom, which may promote the scission of the C-C bond to form an adsorbed R₁⁻ on the surface of ZSM-5 that is stabilized by the Lewis acid site. In the following steps, some electrons from R₂ may shift to the C atom of the C=O group, which causes the release of CO and forms an adsorbed R₂⁺ on the O atom of ZSM-5. The adsorbed R₁⁻ and R₂⁺ may combine together further and generate a new R₁-R₂ compound, or they may react with any other free radicals to form other products.

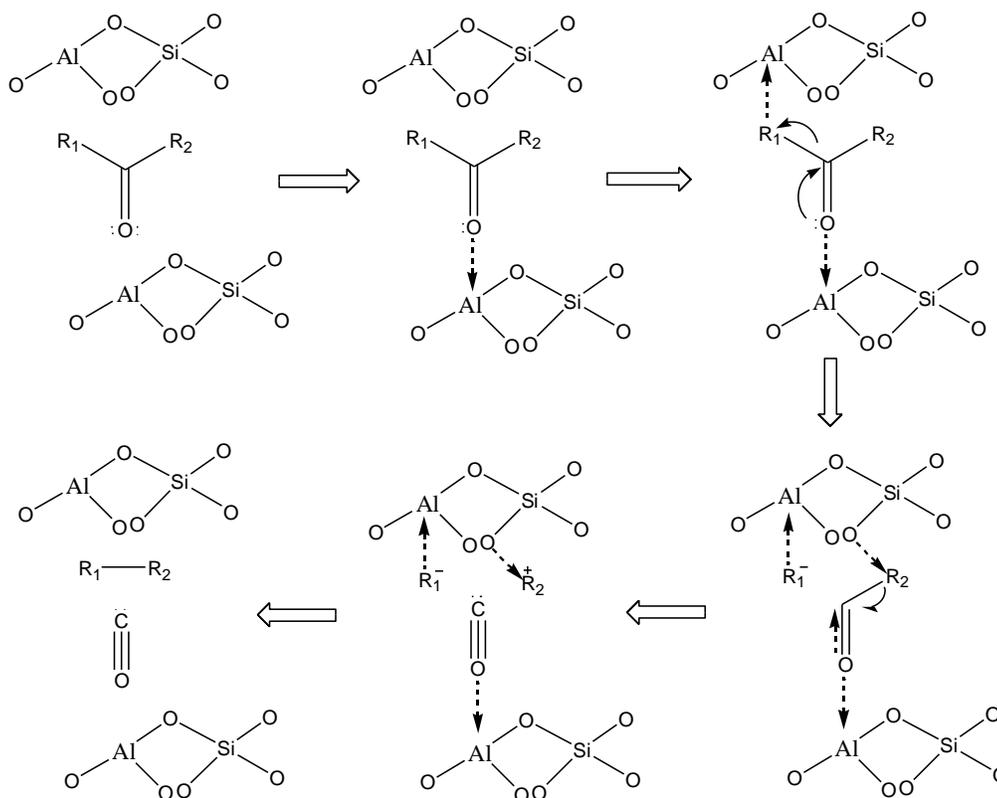


Fig. 4. Catalytic reaction routes from C=O to CO

In the route from C-O to OH or to H₂O, the O atom of the C-O-C(H) group may first adsorb onto the surface of ZSM-5 at the Lewis acid site, and a hydrogen bond may be generated between the O atom of ZSM-5 and the β-H of the organic compound. The ethers or alcohols are then converted to alkenes by the β-H elimination reaction.

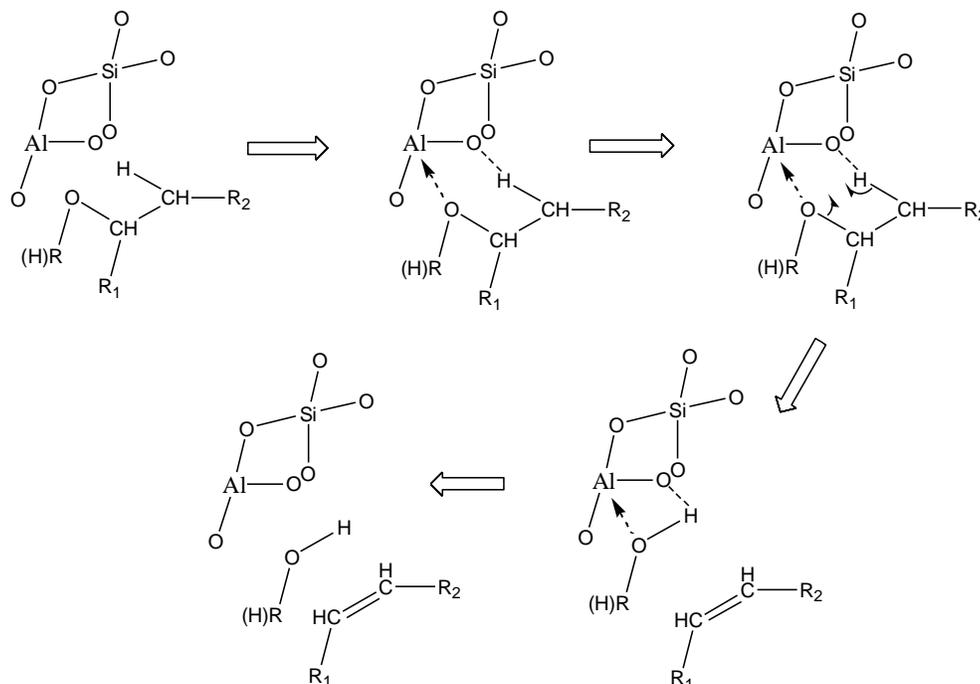


Fig. 5. Catalytic reaction routes from C-O to OH (or H₂O)

CONCLUSIONS

1. The C=O signal was much stronger than that of CO₂ in the pyrolysates of PN and CE, while in the CC and CS systems much more CO₂ was generated.
2. The contents of the C-O and C=O containing components were decreased under the catalysis of ZSM-5, the formations of CO, H₂O, and the OH containing compounds were promoted, and the content of CO₂ remained relatively stable.
3. It was deduced that carboxylic acids may be converted to CO₂, or to CO and alcohols (or H₂O). CO may also be derived from aldehydes or ketones. The C-O-C(H) group may be converted to H-O-C(H) to generate alcohols or H₂O during ZSM-5 catalysis.
4. In the conversion route from C=O to CO, the adsorption of C=O onto the surface of ZSM-5 *via* the interaction between the O atom of the C=O group and the Lewis acid site on Al atom, is probably the first catalytic activation step.
5. In the route from C-O to OH or to H₂O, the adsorption of the O atom of the C-O-C(H) group onto the surface of ZSM-5 at the Lewis acid site and the formation of a hydrogen bond between the O atom of ZSM-5 and the β-H of the organic compound may be the key activation steps.

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