Article

Catalytic Upgrading of Biomass Fast Pyrolysis Vapors with Nano Metal Oxides: An Analytical Py-GC/MS Study

Qiang Lu [1],*, Zhi-Fei Zhang [1], Chang-Qing Dong [1] and Xi-Feng Zhu [2]

[1] National Engineering Laboratory for Biomass Power Generation Equipment, North China Electric Power University, Beijing 102206, China; E-Mails: fei2190713@sina.com (Z.-F.Z.); cqdong1@163.com (C.-Q.D.)

[2] Key Laboratory for Biomass Clean Energy of Anhui Province, University of Science and Technology of China, Hefei 230026, China; E-Mail: xfzhu@ustc.edu.cn

* Author to whom correspondence should be addressed; E-Mail: qlu@ncepu.edu.cn;
Tel.: +86-10-6177-2032(820); Fax: +86-10-6177-2032(801).

Abstract: Fast pyrolysis of poplar wood followed with catalytic cracking of the pyrolysis vapors was performed using analytical pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). The catalysts applied in this study were nano MgO, CaO, TiO_2, Fe_2O_3, NiO and ZnO. These catalysts displayed different catalytic capabilities towards the pyrolytic products. The catalysis by CaO significantly reduced the levels of phenols and anhydrosugars, and eliminated the acids, while it increased the formation of cyclopentanones, hydrocarbons and several light compounds. ZnO was a mild catalyst, as it only slightly altered the pyrolytic products. The other four catalysts all decreased the linear aldehydes dramatically, while the increased the ketones and cyclopentanones. They also reduced the anhydrosugars, except for NiO. Moreover, the catalysis by Fe_2O_3 resulted in the formation of various hydrocarbons. However, none of these catalysts except CaO were able to greatly reduce the acids.

Keywords: biomass; fast pyrolysis; catalytic cracking; Py-GC/MS; nano metal oxides

1. Introduction

Fast pyrolysis of biomass is one of the most promising technologies to utilize renewable biomass resources, and has attracted extensive interest in recent years. It offers a convenient way to convert biomass mainly into a liquid product, known as bio-oil, which covers a wide applications [1,2].

Bio-oil has been regarded a promising candidate to replace petroleum fuels. However, it is a low-grade liquid fuel, because it is highly oxygenated, acidic and corrosive to common metals, chemically and thermally unstable, as well as non-miscible with petroleum fuels [3,4]. As a result, it is difficult to directly use crude bio-oil in various thermal devices, especially internal combustion engines [5]. These poor fuel properties can be attributed to the presence in bio-oil of large amounts of water, acids, aldehydes and large molecular oligomers, therefore, it is necessary to upgrade bio-oils to eliminate these undesirable compounds or convert them to more desirable ones. Several methods have been applied to upgrade bio-oils, and one of them is the catalytic cracking which can be performed either on liquid bio-oils or on pyrolytic vapors immediately after the pyrolysis process. The key problem for catalytic cracking is the selection of suitable catalysts. In early studies, traditional zeolites (such as HZSM-5, HY, *etc.*) have been widely studied. They were effective to convert the highly oxygenated compounds to hydrocarbons, but many problems were encountered, such as fast deactivation of the catalysts by coke deposition, low organic liquid yield and the formation of polycyclic aromatic hydrocarbons (PAHs) [6,7]. Recently, mesoporous catalysts (such as MCM-41, SBA-15, MSU, *etc.*) have been applied for their potential to upgrade the large molecular oligomers [8–13]. However, due to their poor hydrothermal stability and high production cost, these catalysts cannot be utilized industrially at present.

Chemically, bio-oil contains many valuable compounds, and thus, has the potential for the recovery of useful chemicals. However, most of the compounds in bio-oil are present in low amounts, making the recovery not only technically difficult but also economically unattractive at present [14]. Hence, the commercialization of bio-oil for value-added chemicals requires production of specific bio-oils with high contents of target products. Till now, many special catalysts have been reported to be effective to maximize levels of various chemicals, such as the production of levoglucosenone by using H_3PO_4 [15], 1-hydroxy-3,6-dioxabicyclo[3.2.1]octan-2-one by nano aluminium titanate [16], acetol by NaOH or Na_2CO_3 [17], light furans by sulfated metal oxides [18], and furfural by $MgCl_2$ [19].

In recent years, nano metal oxides have attracted extensive attention in various catalytic processes due to their unique properties, but they are not widely used in catalytic treatment of biomass fast pyrolysis vapors. Li *et al.* prepared nano NiO and tested its activity during biomass pyrolysis using a thermogravimetric analyzer [20]. In our previous study, nano TiO_2 and its modified catalysts were used for experiments and confirmed to have some good catalytic activity [21]. In this study, six nano metal oxides were used as catalysts to test whether they had the capability to upgrade the fuel properties of bio-oil or maximize the formation of some valuable chemicals. The experiments were performed using an analytical Py-GC/MS instrument which allows direct analysis of the pyrolytic products. The catalytic and non-catalytic products were compared to reveal the catalytic capabilities of these catalysts.

2. Experimental

2.1. Materials

The biomass material used in the study was poplar wood. Prior to the experiments, the wood was dried and ground in a high speed rotary cutting mill. Particles of 0.125–0.3 mm size were selected for experiments. Its component composition was analyzed according to the method proposed by Ranganathan *et al.* [22], and the results were cellulose 49.70 wt%, hemicellulose 24.10 wt%, lignin 23.55 wt%, extractive 2.22 wt% and ash 0.43 wt%. The nano MgO, CaO, TiO_2, Fe_2O_3, NiO and ZnO tested in this study, were all purchased from Sigma Aldrich.

2.2. Analytical Py-GC/MS Experiments

Pyrolysis was performed using a CDS Pyroprobe 5250 pyrolyser (Chemical Data Systems). During the preparation of experimental samples, the pyrolysis tube was successively filled with a quartz rod, some quartz wool, 0.50 mg catalyst, some quartz wool, 0.50 mg poplar wood, some quartz wool, 0.50 mg catalyst and some quartz wool. The placement of the catalyst and the poplar wood in the quartz filler tube is shown in Figure 1. An analytical balance with a readability of 0.01 mg was used, and the weighing process of the poplar wood and the catalyst (a layer) was strictly controlled to be exactly 0.50 mg. The catalyst was placed at both sides of the poplar wood and functioned as a fixed bed, so that all the pyrolysis vapors would pass through the catalyst layer. The poplar wood and catalyst were separated by the quartz wool, to ensure that the pyrolysis of the poplar wood would not be influenced by the catalysts. The pyrolysis temperature was set at 600 °C and held for 10 s, with the heating rate of 20 °C/ms. Due to poor thermal conductivity of biomass materials, the actual biomass pyrolysis temperature should be lower than 600 °C, reported as about 500 °C [11].

Figure 1. The placement of the catalyst and poplar wood in the pyrolysis tube.
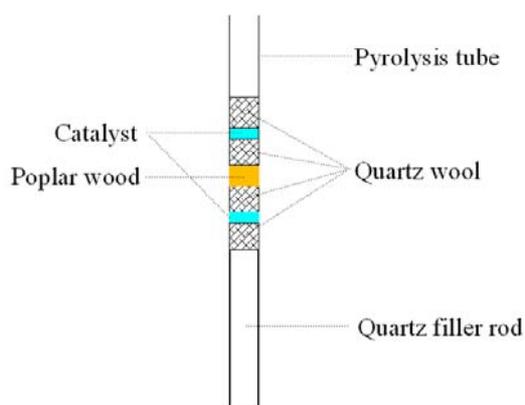
The pyrolysis vapors were analyzed by GC/MS (Thermo Scientific, Trace DSQ II). The injector temperature was kept at 300 °C. The chromatographic separation was performed using a TR-5MS capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness). Helium (99.999%) was used as the carrier gas with a constant flow rate of 1 mL/min and a 1:80 split ratio. The oven temperature was programmed from 40 °C (3 min) to 280 °C (3 min) with the heating rate of 4 °C/min. The temperature

of the GC/MS interface was held at 280 °C, and the mass spectrometer was operated in EI mode at 70 eV. The mass spectra were obtained from m/z 20 to 400 with the scan rate of 500 amu/s. Identification of chromatographic peaks were achieved according to the NIST MS library and the literature data of bio-oils. For each catalyst, the experiments were conducted at least three times to confirm the reproducibility of the reported procedures.

It is known that the GC/MS technique cannot provide a quantitative analysis of the compounds. However, the chromatographic peak area of a compound is considered linear with its quantity, and the peak area% is linear with its content. During each experiment, the mass of the poplar wood was same. Therefore, the corresponding chromatographic peak area of the compound obtained from different reaction conditions can be compared to reveal the changing of its yields, and the peak area% can be compared to show the changing of its relative content among the detected compounds.

3. Results and Discussion

3.1. Catalytic Effects on the Distribution of the Pyrolytic Products

Biomass fast pyrolysis vapors were composed of volatile compounds and non-volatile oligomers. GC/MS was only able to determine the volatile organic compounds. Based on the ion chromatogram from the non-catalytic pyrolysis of the poplar wood, a total of 86 major compounds were identified, as given in Table 1. The identified products were similar to literature data of the chemical composition of bio-oils [23–25], and also agreed well with previous Py-GC/MS studies [8,11–13,21,26].

Table 1. Identified pyrolytic products from non-catalytic fast pyrolysis of the poplar wood.

No.	RT	Compound	No.	RT	Compound
1	2.22	methanol	44	18.23	1-(2-furanyl)-2-hydroxyethanone
2	2.30	acetaldehyde	45	18.30	2-methoxyphenol
3	2.54	2-propenal	46	18.36	2,5-dimethyl-4-hydroxy-3(2*H*)-furanone
4	2.58	acetone	47	19.32	maltol
5	2.61	furan	48	19.43	3-ethyl-2-hydroxy-2-cyclopentenone
6	2.79	1,3-cyclopentadiene	49	19.50	levoglucosenone
7	2.85	2-propen-1-ol	50	20.44	3-methyl-2,4(3*H*,5*H*)-furandione
8	3.06	hydroxyacetaldehyde	51	20.52	3,5-dihydroxy-6-methyl-2,3-dihydro-4*H*-pyran-4-one
9	3.22	2,3-butanedione	52	20.60	2,4-dimethylphenol
10	3.35	2-methylfuran	53	21.43	2,3-dihydrobenzaldehyde
11	3.50	acetic acid	54	21.93	3,5-dihydroxy-2-methyl-4-pyrone
12	4.12	2-butenal	55	22.13	2-methoxy-4-methylphenol
13	4.32	1-hydroxy-2-propanone	56	23.28	2,3-dihydrobenzofruan
14	4.99	1,2-ethanediol	57	23.39	1,4:3,6-dianhydro-D-glucopyranose
15	5.08	2,5-dimethylfuran	58	23.74	5-(hydroxymethyl)-2-furaldehyde
16	5.55	vinylfuran	59	23.85	3,4-anhydro-D-galactosan
17	6.62	toluene	60	24.61	3-methoxy-1,2-benzenediol
18	6.73	1-hydroxy-2-butanone	61	25.12	4-ethyl-2-methoxyphenol

Table 1. *Cont.*

19	6.83	acetoxyacetic acid	62	25.70	4-methyl-1,2-benzenediol
20	7.28	butanedial	63	26.53	2-methoxy-4-vinylphenol
21	7.39	methyl pyruvate	64	26.85	3-methoxy-5-methylphenol
22	8.74	furfural	65	27.76	2,6-dimethoxyphenol
23	9.39	2-furanmethanol	66	28.10	2-methoxy-4-propylphenol
24	9.91	1-(acetyloxy)-2-propanone	67	29.54	4-hydroxy-3-methoxybenzaldehyde
25	9.97	5-methyl-2(3*H*)-furanone	68	30.79	1,2,4-trimethoxybenzene
26	10.19	4-hydroxydihydro-2(3*H*)-furanone	69	30.99	2-methoxy-4-propenylphenol
27	10.58	2-cyclopentene-1,4-dione	70	31.31	2-methoxy-4-propylphenol
28	11.07	1,3-dihydroxy-2-propanone	71	32.02	6-methoxy-3-methylbenzofuran
29	11.14	5-(hydroxymethyl)dihydro-2(3*H*)-furanone	72	32.22	1-(4-hydroxy-3-methoxyphenyl)-ethanone
30	11.31	2-methyl-2-cyclopentenone	73	33.14	levoglucosan
31	11.46	1-(2-furanyl)-ethanone	74	33.42	1-(4-hydroxy-3-methoxyphenyl)-2-propanone
32	12.10	1,2-cyclopentanedione	75	34.46	3,5-dimethoxyacetophenone
33	12.69	5-methyl-2(5*H*)-furanone	76	34.86	4-((1*E*)-3-hydroxy-1-propenyl)-2-methoxyphenol
34	13.01	3-methyl-2,5-furandione	77	35.14	1-(2,4-dihydroxy-3-methylphenyl)-1-propanone
35	13.51	5-methylfurfural	78	35.22	3-hydroxy-1-(4-hydroxy-3-methoxy-phenyl)-1-propanone
36	13.99	5-acetyldihydro-2(3*H*)-furanone	79	35.72	1,6-anhydro-D-galactofuranose
37	14.15	phenol	80	37.37	4-hydroxy-3,5-dimethoxybenzaldehyde
38	14.79	2H-pyran-2,6-3(*H*)-dione	81	38.41	4-allyl-2,6-dimethoxyphenol
39	14.88	3-hydroxydihydro-2(3*H*)-furanone	82	39.31	1-(4-hydroxy-3,5-dimethoxyphenyl)-ethanone
40	15.93	2-hydroxy-3-methyl-2-cyclopentenone	83	39.55	4-hydroxy-2-methoxycinnamaldehyde
41	16.35	2,3-dimethyl-2-cyclopentenone	84	40.18	1-(2,6-dihydroxy-4-methoxyphenyl)-1-butanone
42	17.00	2-methylphenol	85	41.73	4-biphenyl ethyl ketone
43	17.83	4-methylphenol	86	45.85	3,5-dimethoxy-4-hydroxycinnamaldehyde

RT: Retention time on the ion chromatograms.

After catalysis, the distribution of the pyrolytic products was altered differently by these catalysts. Many new compounds were formed, and the results are shown in Table 2. Among the tested catalysts, ZnO seemed to be a mild catalyst, as most of the primary pyrolytic products were unaltered. Only six new compounds were formed after catalysis, and these new compounds were all in low amounts. The results agreed well with the previous study which confirmed that the catalytic cracking of biomass pyrolysis vapors by ZnO only slightly altered the properties of the catalytic bio-oil [27]. However, the catalysis by CaO significantly decreased or completely eliminated most of the primary pyrolytic products, and meanwhile, promoted the formation of many new products, mainly linear ketones, cyclopentanones and hydrocarbons. Fe_2O_3 was also effective to alter the pyrolytic products by

increasing the formation of hydrocarbons and aromatic products. In regard to the catalysts MgO, TiO$_2$ and NiO, their catalytic activity to alter the pyrolytic products was between that of ZnO and Fe$_2$O$_3$. In addition, all the detected products were classified into ten groups, with the purpose of clearly showing their compositional changes, and the results are presented in Table 3. The changes of each product group, in terms of the specific compounds, will be discussed in details in the following sections to reveal the catalytic activity of these nano metal oxides.

Table 2. New compounds formed after catalytic cracking of the pyrolysis vapors.

No.	RT	Compound	MgO	CaO	TiO$_2$	Fe$_2$O$_3$	NiO	ZnO
1	2.72	methyl acetate	*	*	*	*	*	*
2	2.96	2-methylpropanal		*				
3	3.27	2-butanone	*	*	*	*	*	*
4	3.70	methyl propionate		*				
5	3.88	4-methylene-1-cyclopentene	*	*	*	*		
6	4.31	benzene		*		*		
7	4.70	2-pentanone		*				
8	4.94	3-pentanone		*				
9	4.98	propanoic acid			*	*		
10	5.29	3-hydroxy-2-butanone	*	*			*	
11	5.91	1-methylcyclohexa-1,3-diene	*	*	*	*		
12	5.97	1-methyl-1,4-cyclohexadiene		*				
13	5.98	(*E*)-3-penten-2-one	*		*	*		
14	6.07	1,2-dimethyl-1,3-cyclopentadiene				*		
15	7.06	3-hexanone		*				
16	7.19	2-hexanone		*				
17	7.40	cyclopentanone	*	*				
18	7.61	4-hydroxy-3-hexanone		*				
19	8.76	2-cyclopentenone	*	*	*	*	*	*
20	8.98	2-methylcyclopentanone	*	*			*	
21	9.29	3-methylcyclopentanone		*				
22	9.51	ethylbenzene	*			*		
23	9.52	1,5-dimethyl-1,4-cyclohexadiene		*				
24	9.86	*p*-xylene		*				
25	9.95	2-ethylfuran		*				
26	10.33	2,3-dimethyl-1,3-pentadiene		*				
27	10.68	*o*-xylene		*				
28	10.8	2,5-dimethylcyclopentanone		*				
29	10.96	4-methyl-cyclohexanone		*				
30	11.02	3-methyl-cyclohexanone		*				
31	11.67	methoxybenzene		*				
32	11.91	3-methyl-3-cyclohexenone		*				
33	12.44	3,4-dimethyl-2-cyclopentenone		*			*	
34	12.59	2-ethylcyclopentanone		*				
35	13.41	3-ethylcyclopentanone		*				
36	14.57	1,3,5-trimethylbenzene		*				

Table 2. *Cont.*

| No.	RT	Compound	MgO	CaO	TiO_2	Fe_2O_3	NiO	ZnO
37	15.77	3-methyl-3-cyclohexenone					*	
38	16.68	indene	*	*	*		*	*
39	17.64	acetophenone					*	
40	18.29	2,3,4-trimethyl-2-cyclopentenone			*			
41	18.64	methyl benzoate	*				*	*
42	19.13	2-methylbenzofuran					*	
43	20.13	4-ethylphenol			*			
44	20.94	1-methyl-4-(1-propynyl)-benzene			*			
45	23.11	2,3,4,5-tetramethyl-2-cyclopentenone			*			
46	23.13	4,7-dimethylbenzofuran					*	
47	23.83	2,6-dimethoxytoluene			*			
48	24.08	2(3*H*)-benzofuranone	*				*	
49	24.57	3-propyl-phenol			*			
50	24.68	4,7-dimethyl-1*H*-indene			*			
51	24.90	3,5-dimethoxytoluene	*				*	
52	25.67	1-indanone	*	*				
53	26.11	1-methylnaphthalene			*		*	
54	26.34	1,2,3-trimethoxybenzene			*			
55	26.64	2-methylnaphthalene					*	
56	27.47	3-methoxy-2,4,5-trimethylphenol			*			
57	27.97	7-methyl-1-indanone			*			
58	28.69	methyl 3-methoxybenzoate	*				*	*
59	28.90	biphenyl					*	
60	31.32	4-hydroxybenzamide					*	
61	33.12	3,4,5-trimethoxytoluene			*		*	
62	32.01	6-methoxy-3-methylbenzofuran	*				*	*
63	32.44	1,2-dimethoxy-4-propenylbenzene			*			
64	36.83	1,2,3-trimethoxy-5-[(1*E*)-1-propenyl]benzene			*			
65	41.04	phenanthrene					*	
66	41.34	anthracene					*	
67	43.43	3,5-dimethoxy-4-hydroxyphenylacetic acid	*			*	*	*
68	47.92	5-hydroxy-3,4'-dimethoxy-1,1'-biphenyl	*			*	*	*
69	48.09	pyrene					*	

*: detected in the catalytic products.

Table 3. The composition of the pyrolytic products before and after catalysis (peak area%).

Catalyst	—	MgO	CaO	TiO_2	Fe_2O_3	NiO	ZnO
Anhydrosugars	10.1	8.4	1.2	4.0	7.5	13.6	7.2
Furans	7.0	7.4	5.2	9.2	6.8	6.4	8.2
Aldehydes	14.5	8.6	15.1	12.0	9.4	9.0	12.6
Ketones	3.8	8.5	20.9	5.3	7.4	4.8	4.5
Phenols	26.5	30.2	13.0	27.3	28.1	32.6	28.3
Acids	11.0	10.2	0.0	11.5	12.9	9.3	11.4
Alcohols	2.5	3.4	8.6	2.1	2.0	2.2	2.8
Hydrocarbons	0.2	0.8	4.2	0.9	3.1	0.3	0.3
Cyclopentenones	2.4	4.7	16.7	6.9	4.6	3.3	3.6
Others	3.3	3.5	1.6	3.9	3.2	2.7	2.9

The analytical Py-GC/MS experiments did not allow product collection, and thus, the exact bio-oil yield could not be determined. However, it is able to have a primary estimate of the yield changes of the total organic volatile products, through the comparison of the total chromatographic peak areas, and the results are shown in Figure 2.

**Figure 2.** The total chromatographic peak areas from catalytic and non-catalytic experiments.
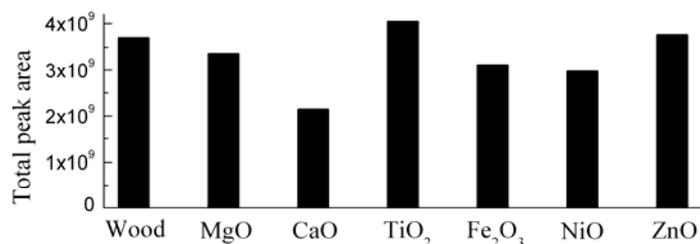
During the catalytic process, the volatile product yield would be influenced by catalysts in the following two ways: on the one hand, the catalysts would cause the cracking of the products to permanent gases or polymerizing them to form cokes or chars, which reduced the volatiles. On the other hand, the catalysts would promote the cracking of the non-volatile oligomers into monomeric ones, which increased the volatiles. The final volatile yield was determined by the above two ways. According to Figure 2, the total chromatographic peak areas were slightly increased after catalysis by TiO_2 and ZnO, slightly decreased by MgO, Fe_2O_3 and NiO, and greatly decreased by CaO. The reduction of the volatile product indicated the formation of some other products which could not be determined in this study. Further studies are required to reveal the conversion ways of the primary pyrolytic products during the catalytic process.

3.2. Catalytic Effects on the Levoglucosan and Furan Compounds

During fast pyrolysis of holocellulose (cellulose and hemicellulose), two competing pyrolytic pathways are mainly responsible for its primary decomposition: depolymerization and ring scission [28–30]. The depolymerization process formed various anhydrosugars (mainly levoglucosan), furans and other products. The catalytic effects on the peak area% of the levoglucosan are shown in Figure 3 (the peak area results are not shown in detail here).

Figure 3. The catalytic effects on the levoglucosan.
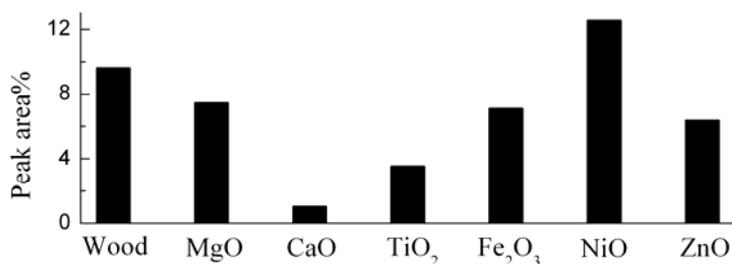
It is seen that the levoglucosan was reduced by all the catalysts except the NiO, especially by the CaO, agreed well with previous studies that levoglucosan was easy to be converted by catalysts [8,12]. In regard to the NiO, the peak area of the levoglucosan, representing its yield, was not reduced by NiO,

while the peak area%, representing its content, was increased due to the reduction of total product yield. A lot of furan compounds were detected in the non-catalytic pyrolytic products, and they are known to be formed from dehydration of carbohydrates [18,31]. The catalytic effects on the peak area% of major furans are given in Figure 4.

**Figure 4.** The catalytic effects on the furan compounds.
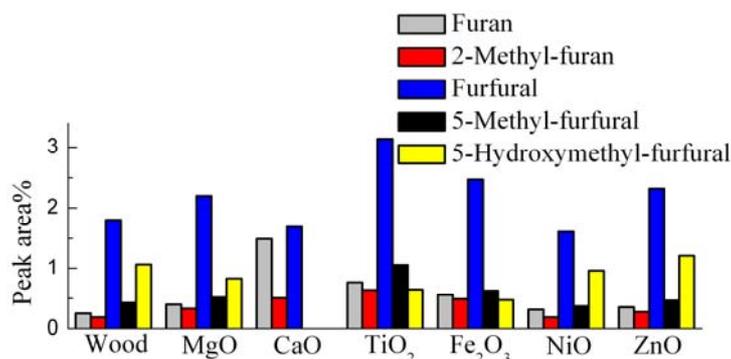
In general, all the catalysts exhibited cracking capabilities, increasing the light furans while decreasing the heavy ones. To be more specific, CaO was the most effective in increasing the two lightest furans (furan and 2-methylfuran), while it decreased the furfural and eliminated all the heavy furans, such as 5-hydroxymethylfurfural and 3-methyl-2,4-(3*H*,5*H*)-furandione. NiO was the least effective in increasing the two lightest furans, while it decreased the other furans. The other four catalysts increased not only the two lightest furans, but also the furfural and 5-methylfurfural. On the whole, the TiO$_2$catalysis gave the highest furan yield.

3.3. Catalytic Effects on the Linear Carbonyl Compounds

The pyrolytic ring scission of holocellulose formed various light products, mainly linear carbonyls. The catalytic effects on major carbonyl products are given in Figure 5. Hydroxyacetaldehyde and 1-hydroxy-2-propanone were the most abundant aldehyde and ketone in the non-catalytic pyrolytic products, respectively. After catalysis, the hydroxyacetaldehyde was significantly reduced or completely eliminated, while the 1-hydroxy-2-propanone was also decreased by all the catalysts except MgO and ZnO. Meanwhile, some light carbonyls, such as acetaldehyde, acetone and 2-butanone were increased considerably by most of the catalysts. CaO was the most effective one to produce these species, with a relative content as high as 12.1% for acetaldehyde, 9.4% for acetone and 7.3% for 2-butanone. Hence, the catalytic bio-oil might be used for the recovery of these three compounds. The results were similar to one of our previous studies using nano ZrO$_2$ and TiO$_2$ as catalyst [21].

Particular attention should be paid to the aldehydes, because they are mainly responsible for the ageing reactions and instability of bio-oils. According to Table 1, the content of the linear aldehydes was reduced by all the catalysts except CaO. Besides the linear aldehydes, some furan or phenolic compounds also contain an aldehyde group were formed, such as furfural, 5-hydroxymethylfurfural, 4-hydroxy-3,5-dimethoxybenzaldehyde, *etc*. On the whole, the relative content of the total aldehydes was decreased after catalysis, which is beneficial for improving the stability of the catalytic bio-oils.

Figure 5. The catalytic effects on the linear carbonyls.
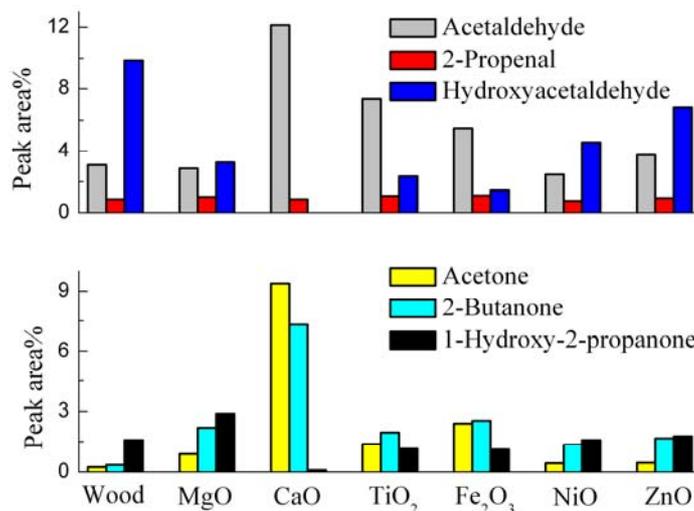

3.4. Catalytic Effects on the Phenolic Compounds

Fast pyrolysis of the lignin produced monomeric phenolic compounds and oligomers with different degrees of polymerization [32–35]. It is believed that the lignin-derived products are mainly responsible for the high molecular weight and viscosity of bio-oils, and thus, one of the aims of using catalysts in the pyrolysis process is to crack these products into lighter ones. The catalytic effects on major monomeric phenols are shown in Figure 6. According to the results, CaO differed greatly from the other catalysts in altering the phenolic compounds. It only increased several light phenols (phenol, 2-methylphenol, 4-methylphenol, 2,4-dimethylphenol, *etc.*), while it significantly reduced or completely eliminated the other phenols (Figures 6b and 6c), resulting in the low overall phenol content after catalysis. The light phenols are thought to be derived from the secondary cracking of the other phenols, and their increased yield indicated the cracking capability of CaO. However, most of the other phenols were reduced greatly after catalysis. Since only some of them were cracked to form lighter phenols, the others must be converted to other products. During the catalytic process, it is impossible that the phenols were significantly cracked to gases or deoxygenated to form aromatic hydrocarbons. Therefore, it is very likely that CaO catalyzed the polymerization of phenols to form cokes or chars. Further studies are required to reveal the catalytic conversion pathways of the phenols.

After catalysis by the other catalysts, except NiO, the light phenols were also increased considerably (Figure 3a), indicative of the catalytic capability of these catalysts. In regard to the other phenolic compounds, the changes of each specific compound appeared to be small, so that it is necessary to focus on the overall changes of all the phenols. According to Table 1, the phenol content was slightly increased after catalysis, with the highest phenol content of 32.6% in the NiO-catalyzed products compared with 26.5% in the non-catalytic products. In previous Py-GC/MS studies, it was found that most of the catalysts such as ZSM-5, Al-MCM-41, Al-SBA-15, Al-MSU-F, MI-575 or HY altered the phenolic compounds by increasing the light phenols while decreasing the heavy ones [8,11,12,26], but the overall phenol yield was decreased by these catalysts. As indicated above, the reduction of the phenols suggested that the phenols might be catalyzed to form cokes or chars. Hence, it is seen that the utilization of these nano metal oxides might avoid the polymerization of the

phenols. Phenols are valuable and useful chemicals. They can be easily separated from bio-oils, and used for the production of adhesives, pharmaceutical, dyes, food additives and other products [36,37]. Hence, the increased phenol content enables the use of catalytic bio-oils for the recovery of phenols.

Figure 6. The catalytic effects on phenolic compounds.
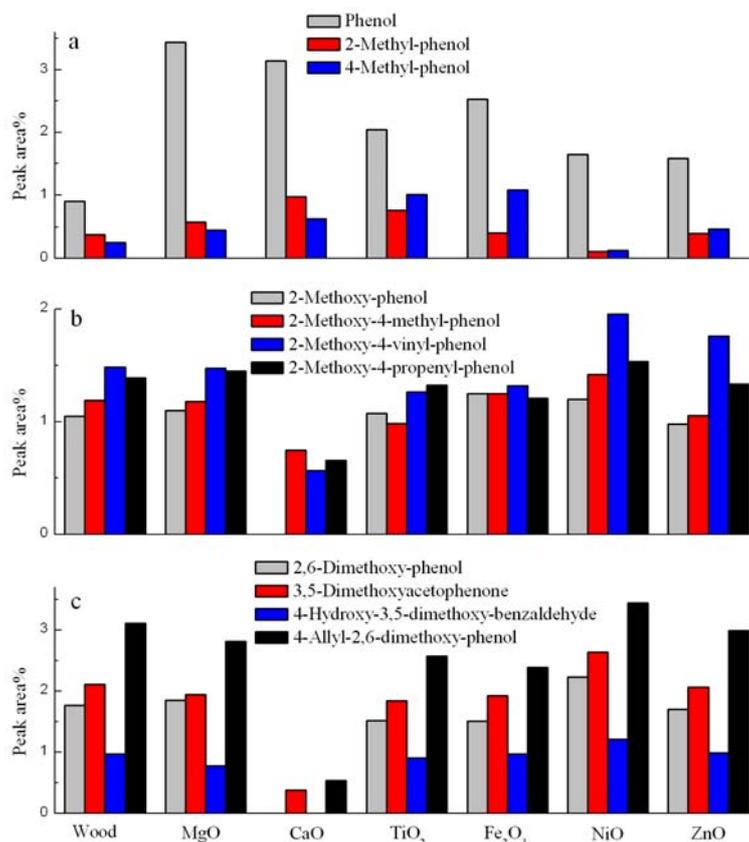
3.5. Catalytic Effects on the Acid and Alcohol Compounds

Fast pyrolysis of poplar wood gave some acids, especially acetic acid which was mainly derived from the deacetylation of hemicellulose. The presence of acids will bring about negative effects on the properties of bio-oils, due to their corrosiveness and effects in accelerating the ageing of bio-oils.

Figure 7. The catalytic effects on the acids.
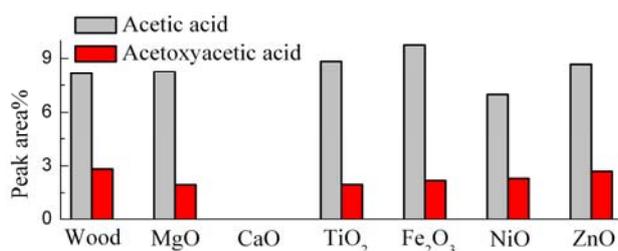
According to Figure 7, the acids were completely eliminated by CaO, which might be linked to its strong alkalinity. Moreover, the acids were slightly reduced by NiO and MgO, but increased by the other catalysts. It was confirmed in previous studies that the catalytic cracking by most of catalysts

could promote acid formation [8,11,12]. The high acid content is definitely unfavorable for the use of catalytic bio-oils as liquid fuels.

Fast pyrolysis of poplar wood also produced some alcohol compounds, mainly methanol, together with small amounts of 2-propenol and 1,2-ethanediol. The 1,2-ethanediol was completely eliminated by all the catalysts except ZnO. The catalytic effects on methanol are given in Figure 8. The methanol was increased by all the catalysts, especially by CaO (8.0%), which is beneficial for the stability of the catalytic bio-oils, because methanol is able to stabilize bio-oils, even at low levels [38].

Figure 8. The catalytic effects on the methanol.
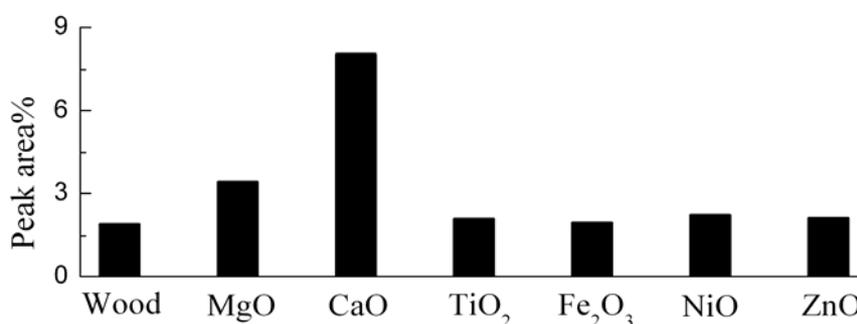
3.6. Catalytic Effects on the Hydrocarbons and Cyclopentanones

In addition to the above products, many other products were detected at low levels in the non-catalytic pyrolytic products, such as hydrocarbons, cyclopentanones and esters. It is necessary to pay attention to the hydrocarbons due to their contribution to the heating values of bio-oils. The non-catalytic pyrolysis of poplar wood only generated small amounts of hydrocarbons (0.2%). After catalysis by MgO, TiO_2, NiO and ZnO, the hydrocarbons were only slightly increased, indicating that these catalysts were not effective in deoxygenating pyrolysis vapors. However, the catalysis by CaO and Fe_2O_3 resulted in the formation of various hydrocarbon products (Table 2), although these hydrocarbons were all produced in low amounts. As a result, the details of the hydrocarbons are not shown here. Moreover, it is noteworthy that Fe_2O_3 catalyzed the formation of many PAHs, including phenanthrene, anthracene, pyrene, and methyl substituted naphthalenes. Due to their toxicity and potential role in the incidence of cancer, the presence of PAHs deserves attention.

Figure 9. The catalytic effects on cyclopentanones.
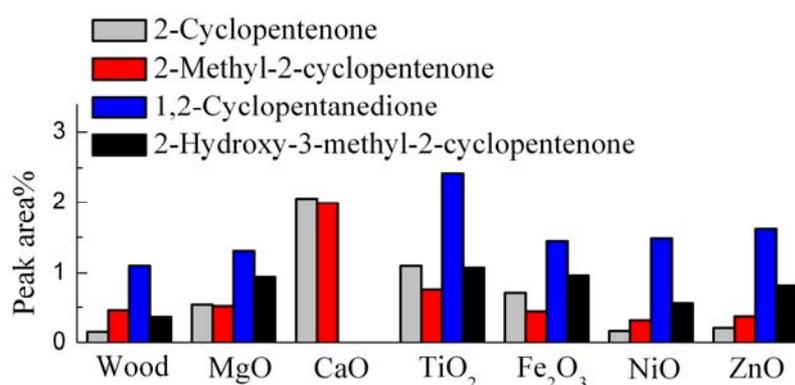
The cyclopentanones were increased greatly by all the catalysts, as shown in Figure 9. CaO mainly catalyzed the formation of various methyl- or ethyl-substituted 2-cyclopentenones, with a total cyclopentanone content as high as 16.7%. TiO_2 favored the formation of 1,2-cyclopentane-dione. The formation of cyclopentanones should improve the heating value of the catalytic oils, due to their low oxygen content.

4. Conclusions

Six nano metal oxides were employed for studying the catalytic cracking of biomass fast pyrolysis vapors through analytical Py-GC/MS experiments. CaO was the most effective catalyst in altering the pyrolytic products. It reduced most of the heavy products (anhydrosugars and phenols), and eliminated the acids, while it increased the formation of hydrocarbons and cyclopentanones. Moreover, it increased four light products (acetaldehyde, acetone, 2-butanone and methanol) greatly, which made the catalytic bio-oil a possible raw material for the recovery of these products.

ZnO was a mild catalyst, because it only slightly altered the distribution of the pyrolytic products. In regard to the other catalysts, they all reduced the linear aldehydes, while the increased the methanol, linear ketones, phenols and cyclopentanones levels. They also reduced the anhydrosugars remarkably, except for NiO. Moreover, the catalysis by Fe_2O_3 was capable of forming various hydrocarbons, but with several PAHs. These catalytic effects suggested a potential for bio-oil quality improvement, due to the enhanced stability promotion due to the reduced aldehyde levels and increased methanol, and the heating value increase by the formation of cyclopentanones and hydrocarbons. In addition, the increased phenol content after catalysis enabled the recovery of the valuable phenols from the catalytic bio-oils. However, none of these catalysts except CaO were able to greatly reduce the acids, which could be a problem for the use of catalytic bio-oils as liquid fuels.

Acknowledgements

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