

Bio-oil upgrading using iron and mesoporous silica-alumina catalysts

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Abstract:

Deoxygenation of bio-oil by mesoporous silica-alumina (MSAl), Fe-loaded mesoporous silica (MSFe) and Fe-loaded mesoporous silica-alumina (MSAl/Fe) catalysts with different Al and Fe contents was studied. The amount of Al and Fe in the prepared catalysts was 1-10 mol% and 1-10 wt%, respectively. Oil yield after catalytic cracking tests by these catalysts was not significantly low (31.2-52.8 wt%) compared to the oil content of the raw bio-oil (67.3 wt%). Water content (32.7 wt% in raw bio-oil) was remarkably lowered to less than 10 wt% by all catalysts. Moreover, calorific value of raw bio-oil (22.5 MJ kg⁻¹) increased to 30-31.8 MJ kg⁻¹ after cracking. Oxygen content in the produced oil decreased with increasing Al content. Although Fe showed a suppressing effect of deoxygenation, an addition of Fe increased H/C ratio of oil. Deoxygenation by MSAl-10/Fe-10, which is the catalyst with the highest Al and Fe contents, produced an oil with the least oxygen content and relatively high H/C ratio among the studied catalysts.

Keywords: bio-oil; calorific value; catalytic upgrading; iron; mesoporous material; deoxygenation

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1. Introduction

These days, replacements of fossil fuels are required because of CO₂ emission and depletion of energy resource. Bio-oil, which is a liquid product obtained by fast pyrolysis of biomass, is a carbon neutral and renewable energy, and is expected to be an alternative to petroleum oil. However, due to high content of oxygen (35-40 wt%) and water (15-30 wt%), the calorific value of bio-oil is significantly lower (17-19 MJ kg⁻¹, HHV) than that of petroleum oil (40-45 MJ kg⁻¹, HHV). In addition, oxygenated compounds in bio-oil (aldehydes, carboxylic acids and phenols) cause poor storage stability and low pH. In order to improve the properties of bio-oil, deoxygenation process is necessary (Zhang et al., 2007).

Catalytic cracking is a well-known method to decompose oxygenated compounds catalytically and produce hydrocarbons. In this method, cracking reaction is triggered by solid acid catalysts. Among them, mesoporous silica-alumina (MSAl) seems to be suitable for bio-oil deoxygenation because its pore size is uniform and enough large (2-10 nm) to incorporate various molecules. On the other hand, iron was proved to be an effective catalyst to decompose tar, which includes oxygenated compounds in large quantities (Murakami, et al., 2011). In this work, to improve the bio-oil properties (water content, oxygen content and calorific value), the effect of catalytic cracking using iron-loaded mesoporous silica (MSFe), MSAl and iron-loaded MSAl (MSAl/Fe) on the properties of bio-oil was investigated.

2. Experiment

2.1 Catalyst preparation

We used three groups of catalysts: MSFe, MSAl and MSAl/Fe. MSFe catalysts were prepared by wet impregnation method. Commercial mesoporous silica (10 g) (MP15300, Nippon Kasei Chemical) was immersed in 100 mL of distilled water containing FeCl₂•4H₂O. The suspension was stirred using a rotary evaporator at 60°C and the water was evaporated to yield the catalysts with a Fe content of 1, 5 and 10 wt% (designated as MSFe-1, MSFe-5 and MSFe-10, respectively). MSAl catalysts were prepared by sol-gel method. The surfactant, hexadecyl trimethyl ammonium bromide (4.8 g) ([CH₃(CH₂)₁₅N(CH₃)₃]Br, CTMABr) was dissolved in 240 mL of distilled water, and then 19.8 mL of 28 wt% NH₃ aqueous solution was added to the solution. A mixture of tetraethyl orthosilicate (TEOS) and aluminum isopropoxide was slowly added to the surfactant solution. The mixture was stirred at 25°C for 1h, and the resulting precipitate was filtered, washed

with distilled water, and dried at 110°C for 24 h. The dried samples were calcined at 300°C for 2 h followed by at 600°C for 8 h. The samples with 1, 5 and 10mol% of Al are labeled as MSAI-1, MSAI-5 and MSAI-10. The MSAI/Fe catalysts were prepared by loading 10 wt% of Fe on the MSAI catalysts in the same way as the case of MSFe (designated as MSAI-1/Fe-10, MSAI-5/Fe-10 and MSAI-10/Fe-10).

2.2 Catalytic cracking

Catalytic cracking of bio-oil by the catalysts were carried out in the vertical fixed-bed reactor (Fig. 1). Bio-oil [H: 6.6wt%, C: 51.6wt%, O (diff.): 41.8 wt%] was received from Azumasansho, Japan. The catalyst (0.5 g) was put on the quartz wool (0.2 g) in the reactor. Career gas (He) and bio-oil were fed from the top of the reactor. Prior to the reaction, the reactor was purged by 150 mL min⁻¹ of He flow for 10 min and then the temperature was raised to 450°C. The bio-oil was fed dropwise by syringe pump at the rate of 0.01 mL min⁻¹ and reacted at 450°C for 300 min under 30 mL min⁻¹ of He flow. The liquid product was collected by the cold ethanol trap (-50 °C) at the downstream of the reactor. The amount of produced gases (CO, CO₂ and CH₄) was determined by gas chromatography (GC-2014, Shimadzu).

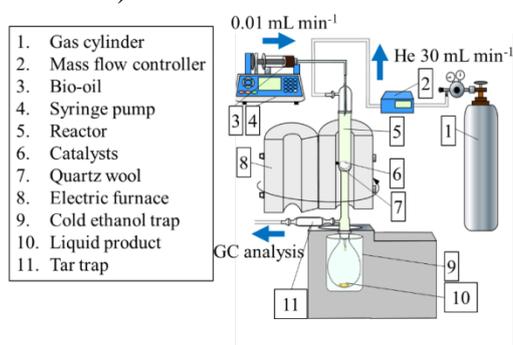


Fig. 1 The experimental apparatus for catalytic cracking of bio-oil.

2.3 Analysis of bio-oil

The liquid product was separated in two phase: oil phase and water phase. Yield of oil phase was determined by weighing after removal of water phase. Water content was determined by Karl Fischer moisture titrator (MKA-610, Kyoto Electronics Manufacturing). Calorific value of oil was measured by calorimeter (CA-4PJ, Shimadzu). Ultimate analysis was carried out by HCN corder (MT-700HCNS, Yanaco) and deoxygenation ratio, H/C and O/C were calculated. Deoxygenation ratio (D) was defined by following equation.

$$D = \frac{O_i - O_f}{O_i} \times 100 \quad (1)$$

where O_i is oxygen content of the raw bio-oil [mol%] and O_f is oxygen content of reacted bio-oil [mol%].

3. Results and discussion

3.1 Oil yield

Yields of oil phase after catalytic upgrading were shown in Fig. 2 together with oil content in the raw bio-oil. Because the water content of the raw bio-oil was determined by Karl Fischer method to be 32.7 wt%, residual 67.3 wt% was oil fraction. After upgrading, the yields of oil phase were 31.2-52.8 wt%, indicating that the catalytic upgrading performed in this study did not reduce oil yields significantly.

3.2 Water content

As shown in Fig.3, water content of bio-oil (32.7 wt%) reduced to less than 10 wt% after catalytic upgrading. Although the difference in water content of oil phase among these catalysts was not

clear, the water was substantially removed to concentrate oil components independent of Al or Fe content in the catalysts.

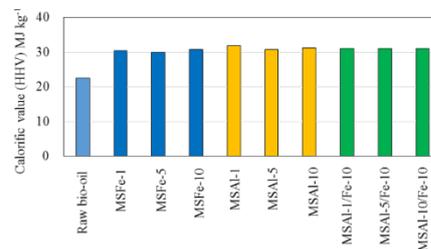
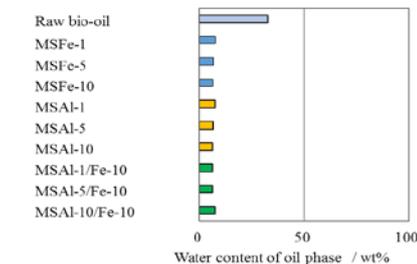
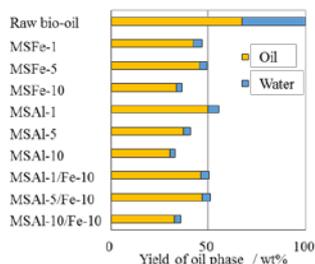


Fig. 2 Yield of oil phase. **Fig. 3** Water content of oil phase. **Fig. 4** Calorific value of oil phase.

3.3 Calorific value

Calorific values of oil after catalytic upgrading were shown in Fig.4. Comparing with the calorific value of the raw bio-oil (22.5 MJ kg^{-1}), the calorific values remarkably increased to $30.0\text{-}31.8 \text{ MJ kg}^{-1}$ by upgrading of the bio-oil using catalysts, suggesting that the MSFe, MSAl and MSAl/Fe catalysts had the effect of deoxygenation or dewatering. However, the differences in the calorific values were not obvious among the catalytic upgrading using these catalysts. Generally, an activity of acidic sites in silica-aluminas is well-known to increase with increasing Si/Al ratio. However, the systematic change in the calorific value was not seen in this study. It suggests that other factors as well as the activity of acidic sites might influence on the increase in the calorific value.

3.4 Ultimate analysis

Ultimate analyses of bio-oil before and after catalytic upgrading were shown in Table 1. The oxygen content in the raw bio-oil (41.8 wt%) was lowered to 22.5-32.5wt%. Fig. 5 shows the deoxygenation ratio in the catalytic upgrading of bio-oil. Bio-oil after catalytic upgrading by MSAl and MSAl/Fe catalysts gave higher deoxygenation ratio with increasing Al content (MSAl-1: 37.0mol%, MSAl-5: 40.4mol%, MSAl-10: 44.3mol%, MSAl-1/Fe-10: 22.2mol%, MSAl-5/Fe-10: 34.9mol%, and MSAl-10/Fe-10: 46.1 mol%). This might be associated with the increase in Al content in the catalysts, i.e. the increase in the number of acidic sites.

Table 1 Ultimate analysis of oil phase [wt%]

	H	C	O (diff.)		H	C	O (diff.)
Raw bio-oil	6.6	51.6	41.8	MSFe-5	6.4	65.2	28.4
MSAl-1	5.9	67.7	26.3	MSFe-10	6.6	63.5	29.9
MSAl-5	5.7	69.4	24.9	MSAl-1/Fe-10	6	61.5	32.5
MSAl-10	6.4	70.3	23.3	MSAl-5/Fe-10	6.5	66.3	27.2
MSFe-1	6.3	68.6	25.1	MSAl-10/Fe-10	7	70.4	22.5

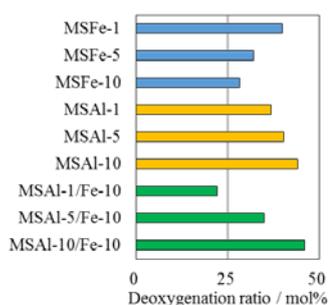


Fig. 5 Deoxygenation ratio in the catalytic upgrading of bio-oil.

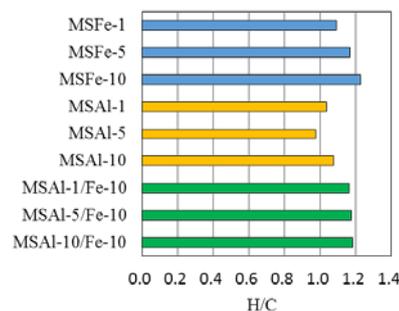


Fig. 6 H/C ratio of upgraded oil.

On the other hand, the MSFe catalysts gave higher deoxygenation ratio with decreasing in Fe content (MSFe-10: 28.4mol%, MSFe-5: 32.1mol%, MSFe-1: 40.0mol%). Furthermore, the deoxygenation ratios in the catalytic upgrading using MSAI catalysts were higher than those using MSAI/Fe catalysts with the same Al content, except for Al-10. This result suggests that iron has a suppressive effect of the deoxygenation. However, the deoxygenation ratio in the catalytic upgrading using MSAI-10/Fe-10 slightly higher than that using MSAI-10, suggesting that there is a synergetic effect of Al and Fe. As shown in Fig.6, the H/C of the upgraded oil increased with increasing Fe content (MSFe-1: 1.09, MSFe-5: 1.17, and MSFe-10: 1.23). Also, Fig. 6 reveals that MSAI/Fe catalysts produced oil with slightly higher H/C (1.17-1.19) than MSAI catalysts (0.98-1.08) did. Since the H/C of heavy oil is about 1.8, an increase in H/C means desirable change. In order to clarify the route of deoxygenation in the catalytic upgrading using the catalysts prepared in this study, Van Krevelen diagram was used (Fig. 7). In MSFe and MSAI, both H/C and O/C ratios shifted to the lower side when Fe content decreased and Al content increased in the catalysts. Also, this change in H/C and O/C ratios indicates that the deoxygenation might mainly proceed with the removal of water. On the other hand, in the case of MSAI/Fe catalyst, the O/C ratio decreased with increasing Al content, while the H/C ratio did not change independent of Al content, unlike in the catalytic upgrading by MSAI catalysts. This change means more decarbonation has occurred comparing with the use of MSAI catalysts.

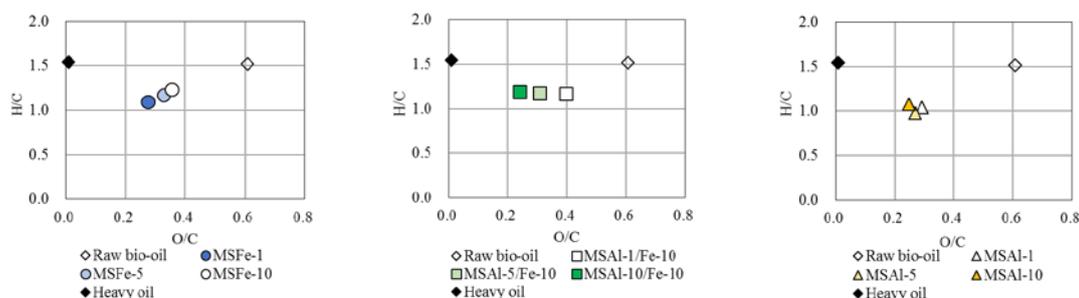


Fig. 7 Relationship between O/C and H/C ratios of the upgraded oils.

4. Conclusion

The catalytic upgrading of bio-oil was performed by using mesoporous silica-alumina (MSAI), iron-loaded mesoporous silica (MSFe) and iron-loaded mesoporous silica-alumina (MSAI/Fe) catalysts. The oil yields were 32.7-67.3 wt% and did not decrease significantly. The calorific value of bio-oil increased from 22.5 MJ kg⁻¹ up to 30.0-31.8 MJ kg⁻¹ by catalytic upgrading using all the catalysts used in this study. Deoxygenation ratio (calculated from ultimate analysis) increased with increasing Al content. Although the iron had a suppressive effect on deoxygenation, it caused the increase in H/C ratio of upgraded oil. In the catalytic upgrading by MSAI-10/Fe-10 catalyst, a synergetic effect between Al and Fe was observed and the deoxygenation ratio was superior to MSAI-10. Moreover, the H/C ratio of the oil upgraded by MSAI-10/Fe-10 was slightly higher than that of the oil upgraded by MSAI-10 catalyst.

5. Acknowledgement

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6. References

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