Metal-modified zeolite catalysts for production of phenolic compounds by fast pyrolysis of eucalyptus

Megumu Inaba*, Kazuhisa Murata, Isao Takahara, Yanyong Liu
National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8565 Japan
**corresponding author: mg.inaba@aist.go.jp*

Introduction

Recently, fast pyrolysis of biomass using zeolite catalysts has been many reported. In our laboratory, fast pyrolysis of eucalyptus had been studied: main products were non-oxygenated aromatic compounds [1]. On the other hand, phenolic compounds are important materials as chemicals. Conversion of biomass to phenolic compounds had also been reported [2-3]. Nilsen et al. reported pyrolysis of wooden based biomass using metal-modified Al-MCM-41 catalysts [2]. Bu et al. reported production of phenolic compounds by catalytic microwave pyrolysis using activated carbon catalysts [3]. In this study, fast pyrolysis of eucalyptus was carried out using metal-modified zeolite catalysts.

Materials and Methods

Metal-modified zeolite catalysts were prepared by impregnation method. As zeolite support, USY (Si/Al_2 = 80) was used after calcination at 500 ºC for 6 h in muffle furnace. Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Sr, Y, Zr, Mo, Ru, Rh, Pd, Ag, In, Sn, La, Ce, Re, Ir, Pt and Au were added to zeolites. Loading was 1 wt.%. After impregnation, the wet catalysts were dried at 110 ºC in an oven, followed by calcination at 600 ºC in air for 3 h. For reference, H-Beta (Si/Al_2 = 27, 350), H-ZSM-5 (30, 190), H-mordenite (18.3), and USY (80) with no metal loaded were used for reaction: these were calcined at 500 ºC for 6 h, followed by calcination at 600 ºC for 3 h before use. Reaction was carried out in quartz tube reactor at 550 ºC in flow of N_2 (50 ml min^{-1}). Catalyst (1 g) was already set in reactor. Solid of eucalyptus (0.5 g) was dropped from the top of reactor. Liquid products were collected by two glass tubes: one was next to reactor, cooled by ice water, and the other was cooled by mixture of toluene and liquid N_2. Gaseous products were collected by gas bag next to two cooled glass tubes, followed by GC analysis. After cooling the reactor to room temperature, inner wall of reactor and two glass tubes were washed with acetone. Obtained mixture of acetone solution of liquid products was analyzed by GC/MS apparatus. Product selectivity was evaluated by area % of each peak. TG analyses of catalysts after reaction were carried out to evaluate the amount of deposited carbon after reaction. From the result, mole number of carbon atoms was calculated. Carbon selectivity was calculated from mole number of carbon atoms. Mole number of carbon atoms in liquid products was calculated as follows: carbon atoms in liquid products = (total carbon atoms in used eucalyptus (19482 µmol)) − (carbon atoms in gaseous products) − (carbon atoms in deposited carbon). Yield of each liquid product was calculated as follows: yield of each liquid product = (carbon atoms in total liquid product) × (selectivity of each liquid product).

Results and Discussion

In the case of no catalyst used, 1-ring oxygenated aromatic compounds other than phenols were exclusively obtained. H-ZSM-5 (Si/Al_2 = 30) rarely yielded oxygenated aromatic compounds due to high yield of non-oxygenated aromatics. H-Beta showed relatively low yield of oxygenated aromatics independent of Si/Al_2 ratio due to high yield of non-oxygenated aromatics. H-ZSM-5 (190), H-mordenite and USY exhibited high yield of oxygenated aromatics. In the case of USY, phenol and methylphenols were obtained in especially high yield. From these results, moderate solid acidity is essential for formation of phenolic compounds, since strong solid acidity enhances the formation of non-oxygenated aromatics [2]. **Figure 1** shows the plots of yield of total phenolic products (phenol + methylphenols + dimethylphenols) vs. yield of phenol over USY and metal-modified USY catalysts. Order of yield of phenol was as follows: Cr > Ag > Re > Mo > Pt > Fe > Zn > Mn > Cu > USY. Order of yield of total phenolic products was as follows: Ag > Pt > Fe = USY. From these results, only Ag and Pt enhanced the formation of both of phenol and total phenolic products. Other kind of metals-addition led to decrease in yield of both of phenol and total phenolic products. In most cases, metal-addition led to increase in carbon deposition. Factor affecting catalytic performance (for example, solid acidity) is under investigation.

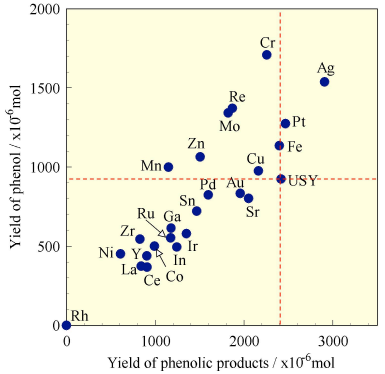

Figure 1. Plots of yield of phenolic products (phenol + methylphenols + dimethylphenols) vs. yield of phenol over USY and metal-modified USY catalysts.

Significance

USY zeolite is effective for production of phenolic compounds by fast pyrolysis of eucalyptus, suggesting that moderate solid acidity is essential for the formation of phenolic products. Addition of Cr, Mn, Fe, Cu, Zn, Mo, Ag, Re or Pt to USY improved the yield of phenol. Ag- or Pt-modification improved the yield of total phenolic compounds (phenol + methylphenols + dimethylphenols). Other metals inhibited the formation of phenolic products.

References

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