Conversion of isobutanol into isobutylene by dehydration over alumina catalysts

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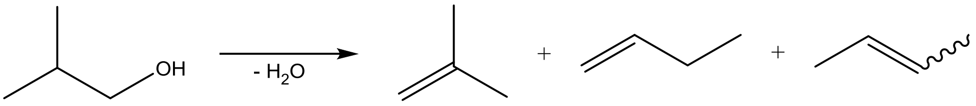
Abstract: Isobutanol was dehydrated over alumina catalysts and converted into isobutylene. Reaction conditions including reaction temperature and concentration of isobutanol were investigated. Reaction temperatures were varied from 220 to 380°C and the conversion of isobutanol started increasing around 300°C with a slight decrease of selectivity of isobutylene. The conversion of isobutanol reached 85% at 340°C. Reactions at 340°C were executed under different isobutanol concentration. The selectivity of isobutylene increased according to an increase in the concentration and showed 95% selectivity of isobutylene. Alumina catalysts with different specific surface areas were also examined and showed changes in isobutylene selectivity.

Keywords: Isobutanol, Dehydration, Alumina.

1. Introduction

Dehydration of alcohols is one of very useful reactions to obtain the corresponding olefins. As a typical example, dehydration of ethanol (EtOH) to ethylene (C_2') is widely known and has been actively investigated in the field of bio-EtOH conversion.[1] This reaction is generally conducted over zeolite, silica alumina and alumina (Al_2O_3) catalysts with pretty high selectivity of C_2' and, in this reaction, moderately acidic sites on the catalysts would work very well as active sites.[2]

Recently much attention has been paid to the production of isobutanol (iBuOH) from biomass feedstock, which can be utilised as biofuels and chemicals.[3] As a biofuel, iBuOH has higher energy density, lower water solubility and less aggressiveness to elastomers and plastics than EtOH and, therefore, its demand is gradually increasing.[4] As well as EtOH, iBuOH can be dehydrated and converted into olefin, preferably isobutylene (iC_4') (Eq. 1). iC_4' is an useful building block and raw material for solvents, fuel additives, plastics and rubbers such as alkyl *t*-butyl ethers, isooctane, *p*-xylene, terephthalic acid, methyl methacrylate (MMA), butyl rubber and so on.[5] Catalytic dehydration of iBuOH into iC_4' has been reported by using Al_2O_3.[6] Reaction pathway of iBuOH dehydration is more complicated compared to that of EtOH. In the case of iBuOH dehydration, linear butenes such as 1-butene, *trans*- and *cis*-2-butenes form as a result of isomerisation, which should be separated from iC_4'. Therefore, it is necessary to reduce the isomerisation and achieve high selectivity of iC_4'.



Isobutanol (iBuOH) Isobutylene (iC_4') 1-Butene *trans/cis*-2-Butenes (1)

The dehydration of iBuOH can be an alternative route to produce iC_4' and the aim of our research is to enhance the selectivity of iC_4'. Therefore, Al_2O_3 catalysts and reaction conditions for the catalytic dehydration of iBuOH were widely investigated.

2. Experimental

Commercially available Al_2O_3 samples were used as dehydration catalysts. The samples were characterised by XRD, N_2 adsorption, NH_3-TPD and FTIR. The reaction procedure has been thoroughly shown elsewhere in the published material.[7] Roughly, Al_2O_3 pellets were crushed and sieved. The sieved Al_2O_3 was charged into a tubular reactor and heated up to a reaction temperature. Commercially available iBuOH was fed by a pump and mixed with nitrogen at vaporiser. The mixture was then introduced into the reactor. The concentration of iBuOH in the reaction gas was changed by changing the ratio of iBuOH and N_2. Reaction gas from the outlet was introduced into ice/water-cooled acetonitrile traps and the off-gas was collected by a gas bag. Liquid and gas components were both analysed by GC and GC/MS.

3. Results and discussion

As shown in Figure 1, the dehydration reaction of iBuOH was carried out at various temperatures from 220 to 380°C. iBuOH conversion gradually increased with an increase in reaction temperature and reached 85% at 340°C. However, iC_4' selectivity slightly decreased at high reaction temperature due to isomerisation reaction. The correlation between iBuOH concentration and iC_4' selectivity at 340°C is shown in Figure 2. iC_4' selectivity with similar iBuOH conversion increased at high iBuOH concentration. According to analysis of products, in the case of high iBuOH concentration, the formation of diisobutyl ether, which could be decomposed into iBuOH and isobutylene, by intramolecular dehydration of iBuOH was enhanced. This result indicated that dehydration became more preferable via the ether formation and decomposition and, as a result, isomerisation was suppressed under high iBuOH concentration. Various Al_2O_3 catalysts having different surface area between ca. 70 and 270 m^2/g were examined at 340°C. As shown in Figure 3, Al_2O_3 having 200 m^2/g surface area showed the lowest iC_4' selectivity. There were differences in those crystal structures, which might have influences on catalytic performances.

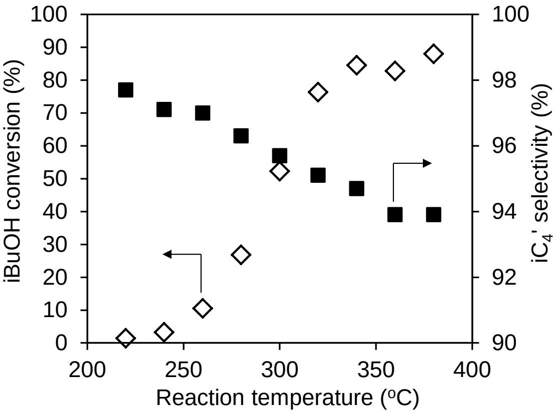


Figure 1. Correlations between reaction temperature and catalytic performances.

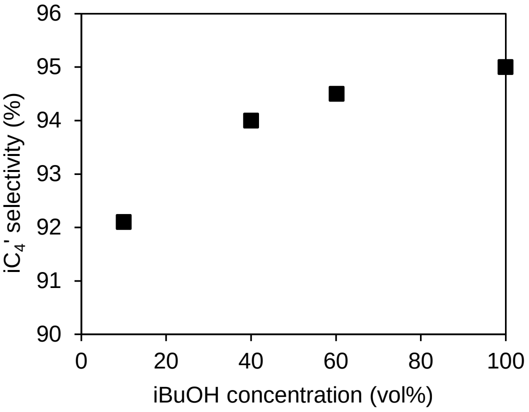


Figure 2. Correlation between iBuOH concentration and iC_4' selectivity.

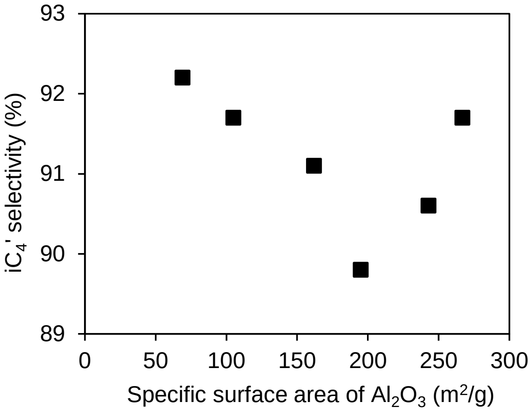


Figure 3. Correlation between Al_2O_3 surface area and iC_4' selectivity.

4. Conclusions

The dehydration of iBuOH to iC_4' was well demonstrated over Al_2O_3 catalysts. This reaction required more than 340°C to increase iBuOH conversion. To enhance iC_4' selectivity, high iBuOH concentration was advantageous. iC_4' selectivity was also influenced by surface area and crystal structure of Al_2O_3 catalysts.

References

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