

OCTANOL DEHYDRATION REACTION OVER γ - Al_2O_3 CATALYST: EFFECT OF PRE-CALCINATION TEMPERATURE

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Abstract: We investigated the effect of pre-calcination temperature of γ - Al_2O_3 catalyst on the catalytic performance in the 1-octanol dehydration reaction for the 1-octene production. The surface area, crystallite phase, and acidic property of γ - Al_2O_3 catalyst depended on the pre-calcination temperature. The pre-calcination at above 500°C showed a change in the surface area and crystallite phase. Furthermore, the pre-calcination temperature had a significant effect on the 1-octanol conversion and 1-octene selectivity of γ - Al_2O_3 catalyst in 1-octanol dehydration. The γ - Al_2O_3 catalysts pre-calcined at 500°C and 750°C showed high 1-octanol conversion and 1-octene selectivity, respectively.

Keywords: Linear alpha olefin (LAO), 1-Octanol dehydration, γ - Al_2O_3 catalyst, 1-Octene.

1. Introduction (11-point boldface)

Linear alpha olefin (LAO), which is olefin locating a double bond at the end of a linear carbon chain, is the source materials of numerous chemical products. Particularly, 1-octene has recently attracted much attention as a commoner of polyolefins, synthetic lubricants (PAO), and plasticizer alcohols, etc. 1-octene can be produced with 1-octanol dehydration reaction, while variable isomers are generated such as cis- and trans-isomers. These isomers have similar properties such as molecular weight, boiling point and density to 1-octene, which results in the difficulties of product separation for 1-octene [1-3]. Hence, the design of catalyst with high conversion and selectivity for 1-octanol dehydration is very important to avoid the formation of by-products, which create separation problems.

Al_2O_3 catalyst is mainly used in alcohol dehydration because it is easily able to control chemophysical characteristics as to acidity, surface area, and crystal phase through calcination at different temperatures. Many researchers have studied the effect of transformation of crystal phase and acidity of Al_2O_3 catalyst on the catalytic performance in alcohol dehydration reaction. Phung et al.[4] investigated the catalytic activity of commercial Al_2O_3 catalysts which had each different crystal phase (γ -, δ -, and θ - Al_2O_3) in ethanol dehydration. The different Al_2O_3 crystal phases affected the acidic property, and the olefin formation depended on the strong Lewis acidity of the Al ion. Moreover, Lee et al.[5] reported that the phase transformation of γ - Al_2O_3 with sequential annealing up to 1100°C influenced the catalytic activity in ethanol dehydration. Increasing the pre-calcination temperature declined catalytic performance in ethanol dehydration. However, there are not many reports concerning the dehydration reaction of higher alcohol like octanol over Al_2O_3 catalysts. Here, we reported the effect of pre-calcination temperature on characteristics and catalytic performance of γ - Al_2O_3 catalyst in 1-octanol dehydration.

2. Experimental

The γ - Al_2O_3 sphere (1.0 mm, Sasol) was used as a catalyst and calcined at different temperatures from 250 to 1000°C in air for 6h. The characteristics of the catalyst as to crystal phase, surface area, pore size distribution, and acidic property were analyzed by XRD, BET, BJH, and pyridine-DRIFT, respectively. The 1-octanol dehydration reaction was carried out at 250-400°C, LHSV = 14 h⁻¹ for 6h in a fixed-bed reactor.

The Al₂O₃ catalyst of 0.2g was loaded into the reactor and heated up to reaction temperatures under N₂ flow. The SiC granule (Goodfellow corp.) was loaded on the upside of the catalyst bed as an inert material to aid vaporization and uniform distribution of 1-octanol. 1-octanol (Aldrich, 99%) was injected using an HPLC pump (NS NP-KX-201) and pre-heated up to 280°C. The product was analyzed using a GC-FID (Agilent7980-B) system equipped with a 30 m HP-5 column (Agilent 19091J-413).

3. Results and discussion

Fig. 1(a) showed XRD patterns of catalyst by influence of pre-calcination temperature. Fresh Al₂O₃ catalyst without calcination had mainly peak of γ -phase which show partially peak of δ -phase. There was no changed in crystal phase up to pre-calcination temperature of 750°C. But XRD pattern of 1000°C was appeared peak of θ -phase and increased intensity of peak. According results of BET (Fig. 1(b)), surface area was declined above pre-calcination temperature of 500°C. Particularly, surface area and pore size of Al₂O₃ catalyst which was calcined at 1000°C sharply decreased.

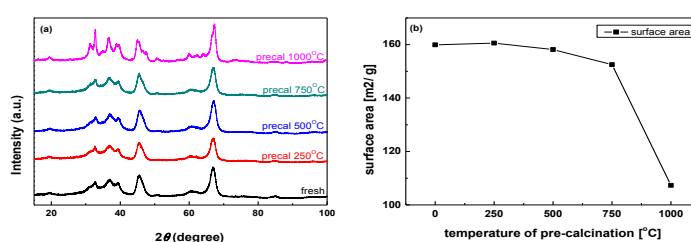


Figure 1 (a) XRD patterns and (b) surface areas of γ -alumina and pre-calcined alumina

Table.1 summarized catalytic performance of 1-octanol dehydration on Al₂O₃ by temperature of pre-calcination. Catalysts which were pre-calcined at 500°C and 750°C showed high 1-octanol conversion and 1-octene selectivity. Catalyst pre-calcined at 1000°C which had dramatically changes of crystal phase and BET surface area had the lowest 1-octanol conversion and 1-octene selectivity, and the highest yield of dioctyl ether which was by-product in 1-octanol dehydration. Furthermore, we investigate change of acidity by pre-calcination temperature and correlation of catalytic performance with effect of pre-calcination temperature.

Table 1 catalyst performance of 1-octanol dehydration with LHSV of 14h⁻¹ at 300°C

Pre-calcination temperature [°C]	1-octanol conversion [%]	1-octene selectivity [%]	1-octene yield [%]	1-octene purity [%]	Dioctyl ether yield [%]
Fresh (Non pre-calcination)	55.7	70.5	39.3	93.9	13.9
250°C	55.4	67.2	37.2	93.4	15.5
500°C	67.8	71.9	48.8	81.8	8.2
750°C	66.8	73.4	49.0	84.7	8.9
1000°C	53.7	57.8	31.1	96.8	21.6

4. Conclusions

Catalytic characterization was changed above pre-calcination temperature of 500°C, and consequentially it was affected catalytic performance. Catalysts calcined at 500°C and 750°C were enhanced 1-octanol conversion and 1-octene selectivity, but catalytic performance was declined on catalyst which was pre-calcined at 1000°C.

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