Preparation of long life indium oxide for conversion of ethanol to propene

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INTRODUCTION

We have reported that In_2O_3 was active for catalytic conversion of ethanol to propene ($C_3^=$), ETP reaction, and its lifetime was greatly improved by additions of Sc onto the catalyst and of water and hydrogen into the reaction system [1]. In this work, effects of a pH value in precipitation of indium hydroxide for properties and catalytic activity of prepared In_2O_3 were investigated to attain longer lifetime of In_2O_3 catalyst.

RESULTS AND DISCUSSION

In_2O_3 was prepared by a precipitation method. An ammonia solution was added to an aqueous indium nitrate solution at 288 K until a predetermined pH (7.3-11.0) was reached. The resulting precipitate was then aged at room temperature for 40 h, washed with deionized water, and calcined at 973 K for 5 h. The prepared In_2O_3 was characterized by SEM and BET methods. Fig. 1 shows SEM images of In_2O_3 aged at various pH values. The higher pH values resulted in the smaller particle sizes and the larger specific surface areas. This would be due to dissolution and re-nucleation of amorphous indium hydroxide at a high pH region [2].

Fig. 2 shows changes in the $C_3^=$ yields with the reaction time on the In_2O_3 catalysts prepared at several pH values. The initial $C_3^=$ yields were all ca. 60%, while the catalyst lifetime increased with increasing pH value. The total amounts of $C_3^=$ produced before the deactivation were found to be roughly proportional to the specific surface areas. A (222) plane is reported to be the most stable surface on an In_2O_3 crystal with bixbyite structure, and the turnover numbers per In atom on the (222) surface were ca. 1600 for the respective catalysts. It was also confirmed in separated experiments that the higher space velocity resulted in the shorter lifetime of the catalyst, but the turnover number was almost the same as those in Fig. 2. It was concluded that the specific surface area of In_2O_3 was largely dependent on the pH value during the precipitation, but the pH value did not cause any changes in the surface structure. Finally it should be added that addition of small particles of polymethyl methacrylate into the precipitation solution and subsequent incineration of PMMA yielded high surface area In_2O_3 samples but their catalytic activity was low.

CONCLUSIONS

The pH values in the preparation of indium hydroxide resulted in the great changes in the surface areas and the lifetimes of In_2O_3. The turnover numbers of In_2O_3 catalysts per surface area, however, were roughly constant, indicating little changes in the surface structure of In_2O_3 with the pH values.

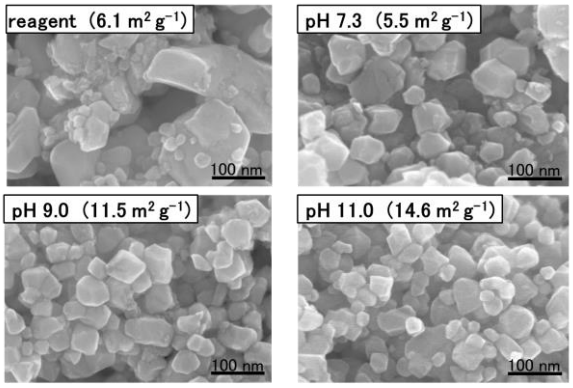

Fig. 1 SEM images of In_2O_3 prepared at various pHs.

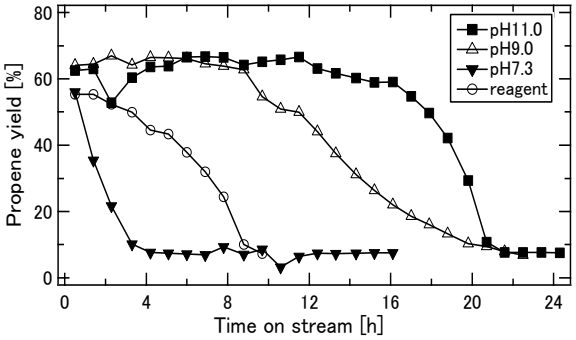

Fig. 2 Catalytic activity of In_2O_3 prepared at various pHs. Conditions: cat. 0.5 g; total flow rate 13.8 ml/min; $P_{ethanol}$ 30 vol%, P_{H2O} 25 vol%, P_{H2} 30 vol%, (N_2 balance).

REFERENCES

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[2] A. Muramatsu *et al.*, Mater. Trans., 50 (2009) 2808.