Characterization and catalytic activity of zirconia synthesized by using amines as precipitant

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Abstract: Zirconia catalysts were synthesized via a precipitation method, and various physico-chemical characterization were performed depending on precipitants and aging conditions. In particular, BET surface area and acidic properties were largely influenced by the type of amine precipitant. The BET surface area and peak temperature of DTA simultaneously decreased as the carbon number was increased, and also the results of IPA-TPD was well correlated with BET surface area and DTA peak temperature.

Keywords: Zirconia, Precipitant, Amines

1. Introduction

Zirconia has been extensively studied for various acid-catalyzed reactions such as dehydration of alcohols and formic acid, and Fischer-Tropsch. For these applications, the BET surface area is an important factor for improving catalytic activity. For increasing BET surface area, it is known that the surface area of precipitated ZrO_2 is largely influenced by aging condition and precipitant [1]. In particular, the use of NaOH and KOH as precipitants can synthesize the ZrO_2 having relatively high BET surface area [2]. However, because the acid sites of ZrO_2 precipitated by NaOH or KOH were partially blocked by residual Na^+ and K^+ ions, it is not proper to synthesize the ZrO_2 for acid-catalyzed reactions.

In this study, ZrO_2 was synthesized via a chemical precipitation method using various amine precipitants as the alternatives of NaOH or KOH precipitant, because the residue from amine precipitants can be easily removed by calcination procedure. In addition variations in physico-chemical and surface acid properties depending on precipitant and aging condition were deeply investigated.

2. Experimental

The ZrO_2 catalyst was prepared by precipitation method of 0.5 M $ZrOCl_2 \cdot 8H_2O$ aqueous solution using various basic nitrogen compounds, such as monoethylamine (MEA), diethylamine (DEA), triethylamine (TEA) and NH_4OH. The zirconium solution was adjusted to pH 10.0 and the suspension was aged at 100 ℃ for 72 h. The obtained zirconium hydroxides were washed and dried. Finally, the catalysts were calcined at 700 ℃ for 6 h under flowing air. The characterization tools, such as N_2-sorption, IPA-TPD, and TG-DTA were used. The catalytic properties were examined for the dehydration of IPA to propylene at atmospheric pressure.

3. Results and discussion

From the N_2-sorption isotherms, the BET surface area increased in following order: TEA, DEA, MEA, NH_4OH (59.1 < 100.1 < 139.2 < 197.9 m^2 g^{-1}). As shown in Fig. 1A, the BET surface area of catalysts calcined at 700 ℃ for 6 h gradually decreased as the carbon number was increased in chemical structure of precipitant. This result is consistent with the tendency of crystallization temperature obtained from the DTA. The variation in BET surface area is therefore strongly dependent on crystal growth. Fig. 1B shows the IPA-TPD profiles of zirconia used. In the IPA-TPD profile, it is generally accepted that the quantity and strength of acid sites were correlated to peak area and desorption temperature of IPA fragment, respectively [1]. Thus, the results exhibited the increasing quantity and strength as the carbon number of precipitant was decreased, and also correlated with the trend of BET surface area. In addition, increasing of aging time also resulted in an increase of the BET surface area. Consequently, it is considered that ZrO_2, synthesized by small carbon number precipitant with long aging period, exhibited the excellent acid properties, and thus it can be effectively applied to various acid-catalyzed reactions.

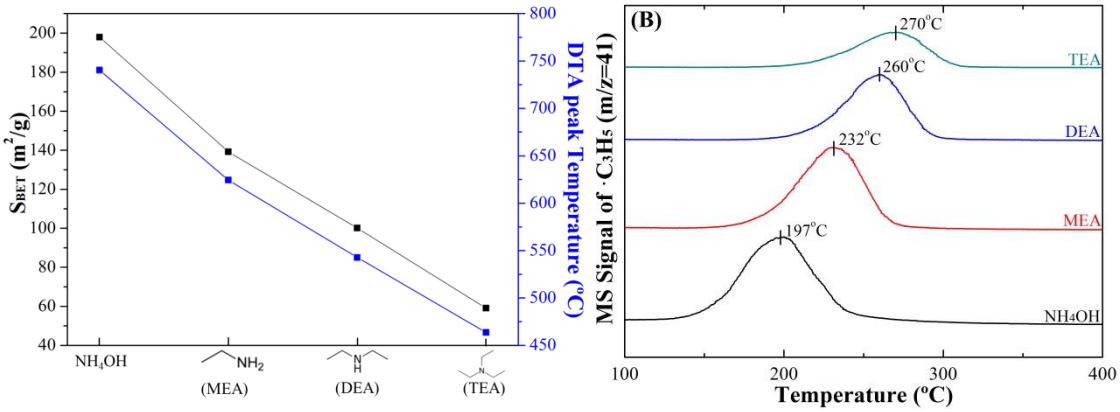

Fig. 1. (A) BET surface area and crystallization temperature of zirconia using amines, and (B) IPA-TPD profiles of zirconia catalysts synthesized with different amine precipitants.

4. Conclusions

Zirconia catalysts with high BET surface areas were synthesized by using various amine precipitants. As a result, the BET surface area, and surface acidic properties were largely influenced by the type of precipitant. The BET surface area gradually decreased with increasing carbon number in chemical structure of precipitant, and it was also correlated with the quantity of acid sites. Furthermore, the acid strength was also consistent with the tendencies of acid site quantity and BET surface area. In addition, increased aging time resulted in increased BET surface area and improved acid strength. Therefore, the ZrO_2, synthesized using NH_4OH precipitant with long aging time, exhibited the most superior acidic properties in terms of quantity and strength.

References

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