Study of the Resistance to Nitrogen Poison of Pt/SAPO-11 Catalyst by the Devised NH_3-TPD Characterizations

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Introduction

Hydroisomerization of normal paraffins is carried out on the bifunctional catalysts, i.e., platinum supported on acidic carriers such as silica-alumina doped with chlorine or fluorine and molecular sieves. These catalysts are sensitive to sulfur and nitrogen compounds, with N likely to be mostly detrimental to acidity and S most detrimental to the metal hydrogenation component [1]. These issues have been investigated by a few authors aiming at developing new poison-resistant catalysts [2,3]. Many works have manifested that a Pt/SAPO-11 catalyst showed some unique features such as pretty good isomerization selectivity and resistant to sulfur and nitrogen [4], and the deactivation of the catalyst was mainly caused by NH_3, which formed by the hydrodenitrogenation on catalyst and poisoned the acidic centers [5,6]. In this work [7], a new phenomenon has been discovered that the catalyst shows improved performance of resistance to nitrogen poison at higher reaction temperature. The origin of this character was studied by the devised characterizations with NH_3-temperature programmed desorption (NH_3-TPD) used thermal conductivity detector (TCD) and mass spectroscopy (MS) as detectors.

Materials and Methods

Catalyst preparation included coextrusion of the SAPO-11 molecular sieve with alumina followed by calcination in air at 813K for 4h. Calcined extrudates were impregnated with H_2PtCl_6 solution targeting 0.6 wt. % platinum of loading, dried and calcined in air at 673K for 4h. Previous to the NH_3-TPD characterization, the catalyst was reduced in situ at 673K for 4h with hydrogen. The products of TPD were detected by TCD or MS alternatively.

Results and Discussion

For TCD as detector, nitrogen was used as carrier gas and two successive NH_3-TPD runs were carried out. With fresh Pt/SAPO-11 catalyst, a pretty high desorption peak was observed in the high temperature range (See figure 1A). However, the acidity, obtained by chemical titration of the desorbed ammonia in aqueous solution, was much less than that in low temperature range. Such a feature of excessive signal with Pt/SAPO-11 was very well confirmed by several repeated tests.

The evolution of desorption peak in the high temperature range was found to be sensitive to catalyst pretreatment conditions. As mentioned before, the Pt/SAPO-11catalyst was activated by oxidation with air at 673K and followed by reduction with H_2 at the same temperature. When the catalyst sample was treated without H_2 reduction, the desorption peak decreased much. Also, a second run after the first TPD test without any treatment gave decreased desorption peak in the high temperature range (See figure 1B). However, the high desorption peak almost restored when the tested sample was re-treated with H_2.

Therefore, the emergence of the strong signal in the high temperature range was not induced by desorption of NH_3, but by a new substance produced in situ by further reaction of NH_3 with catalyst. Considering the ability of the noble metal to decompose NH_3, we speculate that the high desorption signal peak was induced by hydrogen, whose thermal conductivity response is much higher than that of NH_3 at the TCD.

If the signal peak in the high temperature range was induced by hydrogen, then we expect nitrogen should be formed at the same time. To verify this point, another TPD system that had a mass spectroscopy (MS) was used to check the variation of nitrogen in the effluent gas during TPD. In that experiment, Ar instead of N_2 was used as carrier gas. For SAPO-11 free of metal, only a weak signal peak of nitrogen was found in the high temperature range, which maybe induced by catalytic impurities contained in the sample (See figure 1D). For Pt/SAPO-11 catalyst, two strong nitrogen peaks were observed, which centered at 623K and 805K respectively (See figure 1C). This clearly manifested that nitrogen was produced during the process of TPD process.

Therefore it has been suggested that Pt/SAPO-11 catalyst has the ability to decompose ammonia into N_2 and H_2. With increasing temperature, the catalytic ability to decompose nitrogen compounds also increases and that can be reasonably explains the improved resistance to nitrogen poison of Pt/SAPO-11 catalyst at elevated reaction temperatures.

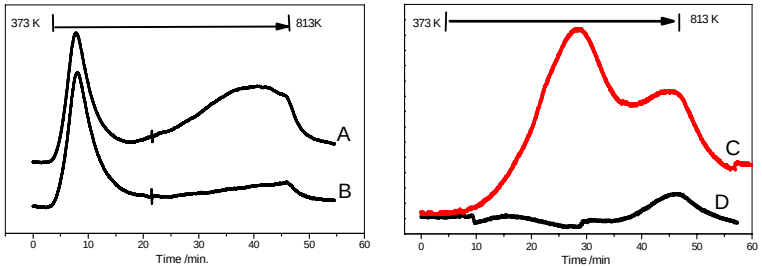

Figure 1. NH_3-TPD profiles of Pt/SAPO-11 and SAPO-11 A) Fresh Pt/SAPO-11, B) After first run Pt/SAPO-11 without any treatment, C) Pt/SAPO-11, D) SAPO-11

Significance

By the devised NH_3-TPD characterizations, the high resistance to nitrogen poison of Pt/SAPO-11 was studied and some new insights may be thrown into the nature of the resistance to nitrogen poison for the platinum loaded catalysts.

References

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