½% Isobutane Conversion as Probe for Acid Strength of Solid Catalysts

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Introduction

The recognition of McVicker et al. [1] that isobutane conversion is especially suitable as a probe for the acid strength of solid catalysts, by virtue of its lack of beta-scission pathways leading to cracking, prompted Umansky et al. [2] to design a special isobutane conversion test (dubbed here the "Hall Acidity Test") based on the temperature at which ½% reaction to total products has occurred under flow conditions. This $T_{½\%}$ was shown to empirically correlate with the Hammett acidity function, H_o. Fraenkel [3] later derived a theoretical kinetic correlation between $T_{½\%}$ and H_o and showed that the apparent activation energy, E_a also plays a role in the above test, since the kinetic development leads to $H_o = E_a/2.303RT_{½\%} - Const.$, where $T_{½\%}$ is in K; from the results of Umansky et al. in the H_o range -10 to -12.5, Fraenkel found that $Const. \approx 23.4$. Applying the Hall Acidity Test for sulfated zirconia (SZ), Fraenkel calculated H_o of SZ to be -17.5±1.5, in agreement with visual Hammett indicator measurements by Hino and Arata [4] that gave $H_o < -16$. Within our ongoing effort to develop better catalysts and processes for skeletal conversion of saturated hydrocarbons, we applied the Hall Acidity Test to four solid acid catalysts varying in acid strength: HY, HZSM-5, nc-HM (nc, nanocrystalline) and SZ. We attempted to find correlation between H_o, based on $T_{½\%}$ and E_a, and the reaction product distribution (reaction network).

Materials and Methods

HY was a calcined NH_4-Y powder from Aldrich. HZSM-5 (Si/Al, 36; SA(m^2/g): BET, 405; t-plot, 120) and nc-HM (~30 nm crystallites, SA(m^2/g): BET, 373; t-plot, 96) were synthesized in-house by proprietary methods. SZ was prepared according to a literature recipe [5]. The Hall Acidity Test was performed in a flow microreactor similar to the one employed previously [3], under identical reaction conditions. The compacted-ground-screened solid acid catalysts were freshly activated *in situ* at 520 °C prior to the acidity test.

Results and Discussion

Figure 1 presents Arrhenius plots near ½% conversion, from which $T_{½\%}$ (°C) and E_a (Kcal/mol) were derived, respectively, as 446.3 and 47.3 for HY, 424.6 and 42.7 for HZSM-5, 256.0 and 23.4 for nc-HM, and 157.5 and 9.54 for SZ. The corresponding H_o values were
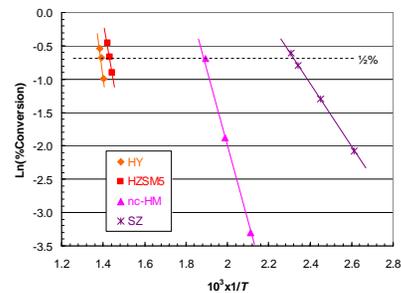
Figure 1. Isobutane conversion near $T_{½\%}$ as a function of temperature: Arrhenius plots.

calculated as -9.0, -10.0, -13.7 and -18.5. The H_o values for the zeolites are within one unit from the values of Umansky et al., measured [2] and/or calculated [3]; the H_o of SZ is within the error margin of the previous test [3]. Figure 2 shows gas chromatograms near $T_{½\%}$. It is clearly seen that the superacidic SZ and nc-HM behave similarly, exhibiting mostly isomerization (to nC_4) and disproportionation (to C_3, iC_5 and iC_6). Trace $nC_4^=$ (butene) and C_2 products are observed with the weaker superacid nc-HM, which also appears to avoid secondary disproportionation to iC_6, unlike SZ. In sharp contrast, the non-superacidic HZSM-5 and HY give as major products $iC_4^=$ and $nC_4^=$, due to dehydrogenation, and C_2, C_3 cracking products. The observed behavior follows the reaction scheme below, in which reaction paths denoted **a** are distinguished from those denoted **b**. With superacids, **a** » **b**, and with non-superacids, **b** » **a**, when **a,b** symbolize kinetic rate constants. We assume that all reactions are "primary," the second step occurring with an intermediate product that has not escaped the catalytic site.
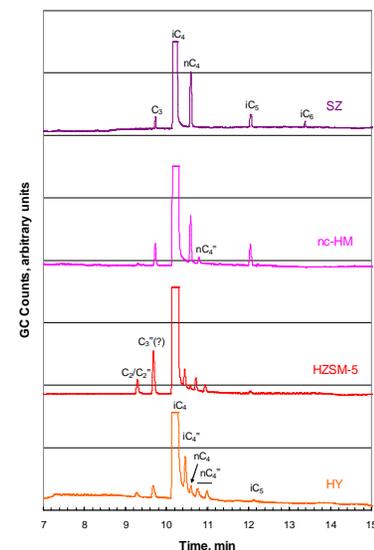
Figure 2. Gas chromatograms of isobutane conversion near $T_{½\%}$.
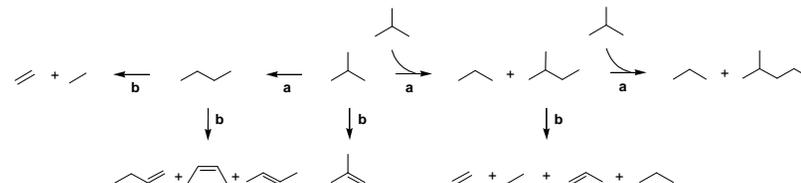
Significance

Our study contributes to the understanding of alkane skeletal transformations under strong acid catalysis; this is important in refinery processing of inferior alkane streams.

References

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