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On the Superacidity of Sulfated Zirconia Catalysts for Low-Temperature Isomerization of Butane

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Sulfated zirconia catalysts for low-temperature butane isomerization reportedly possess acid sites with a Hammett acidity, H_o, of less than -16.[1] Since 100% sulfuric acid has an H_o value of -12, sulfated zirconia is classified as a solid superacid catalyst with acid strength 10 000 times greater than that of pure sulfuric acid. However, determination of solid acid strength by a color change of adsorbed indicators is fraught with experimental difficulty. More recently, acidity measurements for sulfated zirconia using spectroscopic evaluations of adsorbed indicators are consistent with strengths not exceeding that of 100% sulfuric acid.[2] Thus, some researchers propose that sulfated zirconia is essentially mounted sulfuric acid instead of a strong superacid.[3] Catalytic test reactions are also used to probe surface acidity. The high activity of sulfated zirconia for butane isomerization has been used to establish its superacidity since sulfuric acid does not catalyze isomerization of *n*-alkanes.[4] In this communication, we show that butane isomerization on sulfated zirconia occurs exclusively through the participation of trace butenes, present in the feed or generated in situ, and not through alkane activation via superacid protolysis reactions. Thus, previous rankings of acidity derived from the activity level of sulfated zirconia catalysts are highly suspect.

The promotional effect of trace amounts of butenes on the acid-catalyzed butane isomerization was first reported by Pines and Wackher.[5] Recent work in our lab and elsewhere has shown that trace butenes play an important role in the isomerization of *n*-butane to isobutane over sulfated zirconia catalysts.[6−8] We demonstrated that transition metal promoters like Fe, Mn, and Pt supported on sulfated zirconia facilitate the low-temperature isomerization reaction by increasing the surface concentration of olefins.[6] These active olefinic intermediates either react with acid sites to form carbenium ions or alkylate surface carbenium ions to form octyl (C_8) intermediates. Butane isomerization occurs by methyl shifts and β-scissions of C_8 intermediates followed by hydride transfers according to classical acid catalysis.[9] In all of these steps, superacidity of the catalyst is not required.

The bimolecular chain reaction for butane isomerization discussed above occurs over transition metal-promoted and unpromoted sulfated zirconia.[6−8] The role of promoters is easily rationalized in terms of olefin formation since transition metals and metal oxides are recognized as dehydrogenation catalysts. However, the mechanism of butene or carbenium ion formation on unpromoted sulfated zirconia is less clear. Superacids form classical carbenium ions by protonating alkanes to give nonclassical carbonium ions which subsequently release dihydrogen.[4,9] Carbenium ions are also formed by reactions of trace olefins with acids of moderate strength.[4,9] In this study, we attempted to eliminate all of the trace butenes in the butane feed in order to test the intrinsic activity of the acidic sites on sulfated zirconia for butane isomerization.

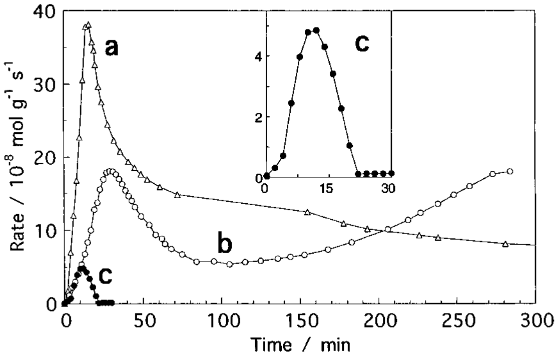

Figure 1. Effect of a butene adsorption bed on the *n*-butane isomerization activity of sulfated zirconia: (a) (triangles) no adsorption bed, (b) (open circles) adsorption bed of 0.5 g, and (c) (filled circles) adsorption bed of 2.0 g. The inset shows run (c) on expanded axes. Reaction conditions: 0.4 g of catalyst, $T = 373$ K, $Y_{C4} = 0.1$, He flow 9 cm^3 min^{-1} STP.

One way to reduce the trace butene concentration in the butane is to pass the feed stream over a platinum catalyst in the presence of dihydrogen to hydrogenate the butenes to butanes. Liu et al. attempted to lower the butene concentration with this method and showed that the butane isomerization rate was lowered, but the catalyst was still active.[8] Catalytic hydrogenation does not completely eliminate the trace butenes, but instead lowers their concentration to the equilibrium value. In this work, an adsorption method was used to eliminate butenes from the feed. An adsorption bed of calcined sulfated zirconia, maintained at room temperature, was placed prior to an active catalyst bed containing sulfated zirconia at 373 K. The trace butenes adsorbed irreversibly on surface acid sites since the adsorption bed temperature was too low for significant reaction and desorption.

The sulfated zirconia for both the adsorption bed and the reactor was generated from calcination of sulfate-doped zirconium hydroxide (Magnesium Electron Inc.) at 825−900 K in flowing air, cooled to room temperature, and stored before use. The calcined sulfated zirconia was reactivated in situ in the the adsorption bed and the reactor by heating in flowing air to 773 K. These treatments yield sulfated zirconia with about 100 m^2 g^{-1} specific surface area.[10] We also prepared a Pt-promoted sulfated zirconia catalyst by incipient wetness impregnation of MEI sulfate-doped zirconium hydroxide with an aqueous solution of hexachloroplatinic acid (Aldrich, ACS Reagent) followed by calcination in air at 873 K. Elemental analysis by Galbraith Laboratories (Knoxville, TN) showed S and Pt loadings to be 2.0 and 1.8 wt %, respectively. The specific surface area of the platinum-promoted sample was measured at 98 m^2 g^{-1}. In the absence of an adsorption bed, the butene impurity level in the *n*-butane feed (Aldrich, 98%) was measured by capillary column gas chromatography and found to be ~0.4%, present mostly as *trans*-2-butene and isobutene. When butene impurities were removed from the reactant feed, the trace concentration fell below the detection limit estimated as <0.001%.

Figure 1 shows the results from reactions carried out in the absence of an adsorption bed (butenes present in the feed), and with adsorption beds of two different sizes. The reaction

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conditions were $T = 373$ K, $Y_{\text{butane}} = 0.1$, and He flow 9 cm^3 min^{-1} STP. For the run with no adsorption bed (Figure 1a), the reaction proceeded through an induction period of increasing activity followed by deactivation. The rate of reaction was in the range of values reported in the literature for sulfated zirconia catalysts. When an adsorption bed of 0.5 g is used (Figure 1b), the level of butene impurities drops below the sensitivity of our detector. Interestingly, the initial maximum in activity of the catalyst at 373 K is reduced from 38×10^{-8} to 18×10^{-8} mol g^{-1} s^{-1}, presumably because of the lower butene concentration in the feed. However, at times later than 100 min, the rate of *n*-butane isomerization starts to increase considerably. This puzzling behavior was observed repeatedly when attempts were made to eliminate the impurity level of butenes from the reactant feed with moderately sized adsorption beds. Evidently, the increase in rate after 100 min results from leakage or breakthrough of butenes from the adsorption bed. When a relatively large adsorption bed of 2 g was used (Figure 1c and inset), sulfated zirconia exhibited an extremely low activity maximum of 5×10^{-8} mol g^{-1} s^{-1} for a short initial period before becoming totally inactive. Two possibilities can account for the results in Figure 1. Either sulfated zirconia does not catalyze butane isomerization in the absence of butene, or the adsorption bed alters the intrinsic activity of the catalyst.

A recent report by Ng and Horvat showed that small amounts of dihydrogen sulfide are evolved from sulfated zirconia during butane isomerization.[11] Thus, small amounts of H_2S may be evolving from the large adsorption bed and poisoning the active sites in the reaction zone. In order to disprove this hypothesis, we tested a Pt-doped sulfated zirconia catalyst with a 2 g adsorption bed. Since Pt enhances the butane isomerization reaction by generating butene in situ,[6,8] we expect that the Pt-promoted catalyst will be active as long as the acid sites are not poisoned. Indeed, the activity of our Pt-promoted catalyst with purified butane was very high. The rate of butane isomerization was 29×10^{-8} mol g^{-1} s^{-1} after 100 min on stream. High conversions at earlier times prevented calculations of rates. Apparently, the acid sites of the catalysts are not significantly affected by trace amounts of H_2S that may be evolving from the adsorption bed.

The selectivity to isobutane exceeded 92% in all of the runs with sustained activity. The formation rates of disproportionation products propane and pentanes (normal and iso) correlated with the formation rate of isobutane, indicating that the bimolecular pathway of isobutane formation described above is relevant to all the cases. No disproportionation products were detected during the run in Figure 1c due to the low conversion level of butane.

The small initial activity observed in Figure 1c could result from trace amounts of olefins produced from oxidative dehydrogenation on sulfated zirconia. Farcasiu *et al.* suggest that oxidation plays an important role in the initial catalysis of hydrocarbons on sulfated zirconia.[12]

The high sensitivity of sulfated zirconia to trace amounts of olefins is probably responsible for the relatively poor agreement in catalytic activity reported in the literature since the impurity level of butenes is seldom, if ever, reported along with reactivity data. More importantly, we find little evidence for superacidic sites on sulfated zirconia. The lack of significant butane isomerization activity at 373 K with a purified feed is consistent with negligible carbenium ion formation via superacidic protolysis of butane. Even though the very small initial activity of sulfated zirconia in Figure 1c may result from superacidic sites, a more likely explanation is that redox sites initiate carbenium ion formation. Regardless of the initiation mechanism, the butane isomerization reaction is not sustained in the absence of butenes.

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