

## Acid Strength of Sulfated Zirconia Inferred from Catalytic Isobutane Conversion

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The kinetics of the catalytic conversion of isobutane under gas-phase fixed-bed flow conditions over sulfated zirconia (SZ), when compared with those of other strong solid acids of known acidity, suggests that SZ may be a very strong solid superacid; this conclusion disagrees with recent reports claiming that SZ is not a superacid, and supports older claims, based on acidity tests with Hammett indicators, that SZ may have  $H_O$  of  $< -16$ .

Sulfated zirconia ( $\text{SO}_4^{2-}/\text{ZrO}_2$ , SZ) was claimed two decades ago<sup>1</sup> a strong solid superacid having Hammett acidity function,  $H_O$  of  $< -16$ , based on the use of Hammett indicators ("the visual method"). The system exhibited high efficiency in the isomerization of small alkanes including isobutane. More recently, some reports have concluded that SZ is not a superacid.<sup>2</sup> In one study, Umansky and Hall, criticizing the use of the visual method in the case of solid acids, presented an alternative method for measuring  $H_O$  in solids, based on spectrophotometry.<sup>3</sup> From that study, involving also silicaluminas and zeolites, the authors concluded that SZ is *not* a strong superacid, and is in fact close in acid strength to sulfuric acid ( $-H_O = \sim 12$ ), hence it should be symbolized by the notation  $\text{H}_2\text{SO}_4/\text{ZrO}_2$ . In another study, Umansky et al. compared many solid catalysts for their performance in the gas phase conversion of isobutane,<sup>4</sup> a reaction considered an appropriate test for strong acid catalysis.<sup>5</sup> The temperature of  $\frac{1}{2}\%$  isobutane conversion, hereinafter denoted  $T_{1/2\%}$ , exhibited an interesting, albeit empirical, correlation with the spectrophotometrically derived  $H_O$ 's. In that correlation, SZ was missing apparently because its isobutane conversion data were unavailable. In view of this and the puzzling fact that the spectrophotometric  $H_O$  value of SZ was found to be some four units higher than the value obtained by the visual method, we have undertaken an investigation on the behavior of SZ under fixed bed flow conditions in the conversion of isobutane. Both the sample and the reaction conditions used by us were very similar to those of Umansky.

Thus, SZ was prepared according to the well established precipitation-sulfation recipe.<sup>1,6</sup> As in the case of Umansky and Hall,<sup>3</sup> the starting salt was zirconyl chloride (Aldrich, >98%) and precipitation with  $\text{NH}_4\text{OH}$  was performed to  $pH 10$ . Sulfation was done in the batch mode, under magnetic stirring for one hour, using 17 ml 1N  $\text{H}_2\text{SO}_4$  per 2 g of the hydrous oxide (Umansky's sample was sulfated with 15 ml acid per 1 g of hydrous). After drying, the sample was calcined at  $650^\circ\text{C}$  for 3 h. It then had 4.3 wt%  $\text{SO}_4^{2-}$  (Umansky's had 4.0%), and a BET surface area of  $74.9 \text{ m}^2/\text{g}$  ( $85 \text{ m}^2/\text{g}$ ).

The isobutane conversion was performed over 0.4 g of 0.2-mm particle size catalyst obtained by pressing, grinding and screening of the calcined SZ powder. The differential fixed-bed flow microreactor used in this study, was equipped with on-line GC (Shimadzu GC-9A) and a sampling arrangement. Gas samples were analyzed over a Supelco Petrocol DH capillary

column. Isobutane (from Matheson; in-house analysis: 0.015 wt% propane, 99.975 wt% isobutane, 0.010 wt% *n*-butane) was mixed with the helium carrier gas, and the gas flow ( $0.05 \text{ ml s}^{-1}$  isobutane,  $0.5 \text{ ml s}^{-1}$  He) was chosen to correspond to a reactant flow rate of  $1.1 \times 10^{-5} \text{ mol g}^{-1} \text{ s}^{-1}$ , as used by Umansky et al.<sup>4</sup> The reaction was carried out at different temperatures, and up to  $180^\circ\text{C}$  it showed no conversion dependency on time on stream (TOS). The same sample was used for all runs and it was activated/reactivated *in situ* at  $500^\circ\text{C}$  under  $\sim 2:1$  air:helium for 1 h, and cooled under pure He. The Arrhenius plot shown in Figure 1 is based on reaction rates as products of conversion and space velocity.<sup>4</sup> The duplicate analyses used to generate the plot were done in the TOS range 60-300 s and had good overall accuracy ( $R^2 = 0.99$ ). The apparent activation energy,  $Ea$  extracted from the Arrhenius plot, is  $8.1 \pm 0.6 \text{ kcal mol}^{-1}$ .

According to Figure 1, under the catalytic test conditions of Umansky et al., SZ has a  $T_{1/2\%}$  value of  $360 \text{ K}$ , in sharp contrast with the  $\sim 520 \text{ K}$  predicted for a SZ with  $H_O = -12$ , based on the  $T_{1/2\%} - H_O$  relation.<sup>4</sup> Furthermore, the experimental  $Ea$  of SZ is  $3\frac{1}{2}$  times smaller than the predicted value ( $\sim 28 \text{ kcal mol}^{-1}$ ). Translating our kinetic results into a  $H_O$  value, using the above relation, is impossible because, being empirical, that relation cannot be extrapolated to accommodate our data. However, a theoretical kinetic expression is developed here, which correlates acidity strength with catalytic activity data obtained under fixed bed flow reactor conditions. The treatment is based on the straightforward assumption that the initial step in isobutane conversion in the presence of strong acids, is reactant protonation. For a reaction of a weak base, B (say, an alkane) under strong Brønsted acid catalysis conditions, governed by initial protonation,

$$\text{Rate} = k_{ef} C_B = k \exp(-2.3H_O) C_B \quad \text{Eq. 1}$$

where  $C_B$  is the concentration of the base,  $k$  is the rate coefficient and  $k_{ef}$  is the effective  $k$ . The dependence of  $k_{ef}$  on  $H_O$  in Eq. 1 is derived from fundamental reaction kinetics considerations.<sup>7</sup> To account for the temperature effect, assuming that  $H_O$  does not vary substantially with temperature, we set  $k_{ef} = k_{ef0} \exp(-\varepsilon)$  where  $\varepsilon$  is the dimensionless Arrhenius exponential factor,  $Ea/RT$ . Since  $k = k_0 \exp(-\varepsilon_0)$ ,  $\varepsilon_0$  being the Arrhenius factor at  $H_O = 0$ , it follows, through substitution into Eq. 1, that  $k_{ef0} \exp(-\varepsilon) = k_0 \exp[-(\varepsilon_0 + 2.3H_O)]$ . Here we compare solid acid catalysts with different  $H_O$  values under gas-phase flow conditions, at a constant reaction rate; since this constant rate is translatable to  $T_x$  – the temperature giving a constant conversion fraction  $x$  ( $x \ll 1$ ) – we may set

$$\text{Rate} = k_{ef} C_B = x (F/W) = k_{efx} = \text{Constant} \quad \text{Eq. 2}$$

$F$  being the gas flow rate,  $W$  the catalyst weight, and  $k_{efx}$  the rate at  $T_x$ . Thus we get  $k_{ef0x} = k_{efx} \exp(\varepsilon_x)$  and  $k_{ox} = k_{efx} \exp(\varepsilon_{ox} + 2.3H_O)$ . Constant  $k_{efx}$  is consistent only with the requirement that  $k_{ef0x} = k_{ox}$  (non-constant for constant  $k_{efx}$ ), and  $\varepsilon_x = \varepsilon_{ox} + 2.3H_O$ . When  $\varepsilon_x$  is plotted against  $H_O$ , it should

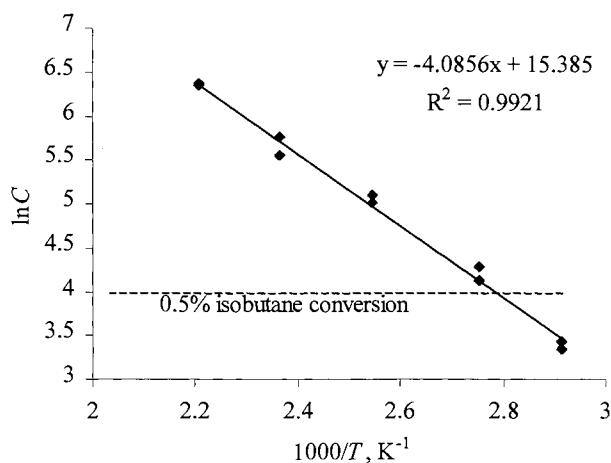


Figure 1. Arrhenius plot for isobutane conversion over SZ ( $C$  given as  $\text{mol g}^{-1} \text{s}^{-1} \times 10^9$ ).

yield a straight line with slope +2.3 and intercept  $\varepsilon_{ox}$ . In terms of the measured/calculated reaction parameters, we therefore have

$$Ea/2.3RT_x = \text{Const.} + H_o \quad \text{Eq. 3}$$

In Figure 2, Umansky's results<sup>4</sup> were plotted according to Eq. 3 and a straight line with the predicted slope of -1 (for  $-H_o$ ) was obtained by adjusting the intercept of the least square regression line to 23.428. Even without that adjustment, the slope was very close to -1 (i.e., -0.91). After extrapolating the straight line to the higher  $H_o$  range, the  $Ea/2.3RT_{1/2\%}$  value of SZ was placed on that line and was found to correspond to  $H_o$  of  $-17.5 \pm 1.5$ . This  $H_o$  value<sup>8</sup> is in good accord with literature values based on the visual method (i.e.,  $H_o < -16$ ).<sup>1</sup>

Umansky's inability to measure an  $H_o$  value lower than -12 for SZ, could be rationalized assuming masking of superacidic (Brønsted) sites by non-superacidic sites; being at overwhelmingly higher concentration, the latter sites could spectroscopically 'cover' the former sites. This argument has

been recently used to explain the apparent disagreement between catalytic results<sup>9</sup> (with metal-supported SZ) and HRTEM findings<sup>10</sup> indicating superacidity in SZ, and spectroscopic measurements of SZ suggesting otherwise. Umansky's SZ sample could have also been somewhat rehydrated, perhaps *in situ* and prior to the acid strength measurement. The suggested  $\text{H}_2\text{SO}_4/\text{ZrO}_2$  notation for SZ,<sup>4</sup> could thus adequately represent the casual (rehydration) state of SZ which may have existed in the spectrophotometric cell, since  $\text{SO}_3$  molecules on the SZ surface may have reacted with trace  $\text{H}_2\text{O}$  to form 'surface  $\text{H}_2\text{SO}_4$ ' or related structures. But activated *in situ* in a microreactor at 500 °C, SZ may become a powerful superacid catalyst capable of converting isobutane at very low temperatures. This active system may better be regarded as ' $\text{H}_2\text{SO}_4^n\text{SO}_3/\text{ZrO}_2$  ( $n > \sim 3$ )', or 'zirconia-supported *oleum*'.<sup>6</sup> Oleum is a known superacid which may exhibit  $H_o$  of *ca.* -15.<sup>11</sup>

Even the thermally activated SZ may not be truly 'dry' especially after cooling, and trace rehydration due to ubiquitous water might be unavoidable in most catalytic runs. In fact, that could even 'promote' the catalytic activity of SZ. Supporting this idea is our recent report<sup>12</sup> that deliberate *in situ* moisture addition to SZ makes this solid acid powerful enough to convert methane to a hydrocarbon mixture similar in composition to product mixtures obtained when methane is reacted over known strong superacids, e.g., Magic Acid. The present paper further emphasizes careful catalytic investigations as an effective tool in distinguishing superacidity in solids, and the inadequacy of relying merely on negative spectroscopic measurements in elucidating the nature of catalytic sites.

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#### References and Notes

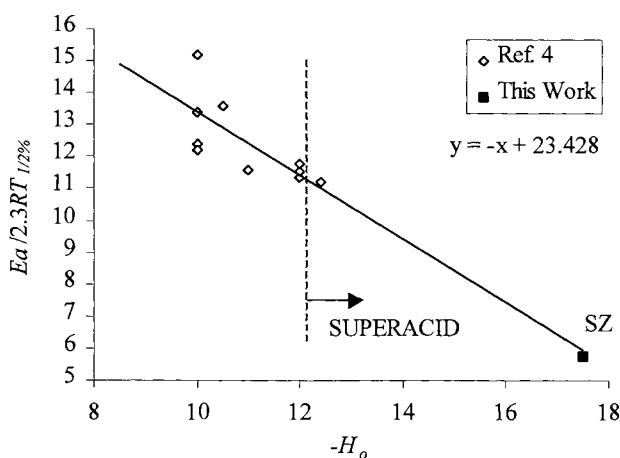


Figure 2. Activity-acidity correlation in isobutane conversion over H-zeolites (Ref. 4) and SZ (This Work).

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