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NOTES

Sulfate as a Precursor of Catalyst Poisoning

INTRODUCTION

Sulfate is not generally considered a poison for noble metal catalysts employed in hydrogenation reactions. Over 50 years ago Maxted (Ref. (*1*) and following papers in this series) showed that electron-rich, lower valent sulfur compounds [H_2S, sulfur(0), mercaptans, disulfides, sulfites] were poisons; electronically saturated, high-valent sulfur compounds [sulfate, sulfonic acids, sulfones] were innocuous.

These findings are correct, but incomplete. They ignore the fact that 6+ sulfur is reducible to lower valencies with dihydrogen and a catalyst. Consideration of a Latimer-type diagram for the reduction of sulfur compounds in acid solution,

$$\underset{\text{(VI)}}{SO_4^{2-}} \rightarrow \underset{\text{(IV)}}{SO_3^{2-} \text{ or } SO_2} \rightarrow \underset{\text{("IV")}}{S_2O_3^{2-}} \rightarrow \underset{(0)}{S} \rightarrow \underset{(-II)}{H_2S}$$

shows that the complete reduction has a $\Delta G^\circ_{298\,K}$ of −49.0 kcal, and that each separate step in the cascade is thermodynamically allowed. The reduction of other oxyacids, notably nitrate (*2*) and perchlorate (*3*), is similarly favorable, being driven by coproduction of water. Catalysts for these reductions include noble metals and tungsten carbide, respectively.

RESULTS AND DISCUSSION

It is readily demonstrated that, on doping of 0.1% Pd-on-carbon with H_2SO_4, passage of H_2 over the catalyst produces SO_2 in the exit stream at temperatures as low as 100°C. Doping with a weaker acid such as $NaHSO_4$ produces H_2S at 100°C, and additionally SO_2 and S at higher temperatures. $NaHSO_4$ and argon in place of H_2 yields a small amount of SO_2 at 225°C thus showing that the thermal decomposition is minimal. No products are evolved even at 300°C with a Na_2SO_4 doped catalyst and H_2. If a weak acid (adipic acid) is used as a co-dopant (2 mole/mole Na_2SO_4), then H_2S is observed starting at 185°C. Doping with $NaHSO_3$ yields SO_2 with H_2 at room temperature and H_2S at 210°C; Na_2SO_3 produces H_2S starting at 275°C. Similar results are obtained with other noble metal catalysts including Pd/Al_2O_3, Pt/C, and Pd-sulfided/C. It is noteworthy that presulfided materials are active. The order of activity for sulfuric acid reduction is Pd/C > Pt/C > Pd(S)/C > Pd/Al_2O_3.

We have not mapped out in detail the relationship between the various low-valent sulfur products. It is not known whether they are formed directly or sequentially produced. It is possible that other chemistry such as the Claus reaction intervenes.

Several instances are reported of catalyzed reduction of sulfur compounds. In connection with the removal of SO_2 from flue gas, its reduction by H_2 is reportedly catalyzed by Ru/Al_2O_3 (*4*). Very high conversions to sulfur were obtained with no measurable amounts of H_2S. SO_2 in flue gas may be absorbed on carbon, and in the presence of O_2 and H_2O is oxidized to H_2SO_4. $CuSO_4$ was shown to be a catalyst for the reduction of H_2SO_4 by H_2 in the range of 190 to 270°C (*5*). In further work, Pt, Pd, and Ag were catalytically active; Co, Ni, and Zn, inactive (*6*). It was noted that the sulfate salts of the active metals all had negative free energy changes for reduction to the metals.

Sulfuric acid as an additive is known to be an inhibitor for C_5H_{10} hydrogenolysis (*7*)

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or C_6H_6 hydrogenation (*8*), a promoter for NO reduction (*9, 10*) or a necessary ingredient in partial hydrogenation of nitroaromatics (*11*). It is possible in some instances that the acidity *per se* is a contributing factor. However, in the context of this note, the chemistry of the sulfate reduction is controlling.

Where carbon is used as a catalyst support, there is another mode of reduction of sulfuric acid that does not require H_2. Reduction by carbon is thermodynamically feasible, $\Delta G^\circ_{298\,K} = -43.4$ kcal/mole, and is evidenced by CO_2 in the exit gas. The relative rates for reduction by H_2 and carbon are approximately 10/1.

Illustrative of the results encountered in catalyst poisoning, the hydrogenation of phenol to cyclohexanone in a batch liquid–phase reaction at 90°C using a Pd/C catalyst was investigated. Addition of 1000 ppm $NaHSO_4$, based on the amount of phenol, resulted in a decrease of the reaction rate to one-third of that in the absence of the added $NaHSO_4$. If the $NaHSO_4$-doped catalyst was pretreated with H_2 at 170°C prior to introduction of the phenol, the resultant catalyst was practically inactive. Use of He instead of H_2 in the pretreatment gave the reduced rate. Doping with Na_2SO_4 instead of $NaHSO_4$ had no effect on the rate. $PdSO_4$ doping resulted in an inactive catalyst. The poisoning was transferable in that an admixture of a poisoned catalyst, known to carry surface sulfate, to active catalyst resulted in decreased activity despite increased metal charged.

A similar pattern of results was found for olefin hydrogenation in a vapor-phase flow system. Thus while Pd/C promotes complete saturation of 1-octene at 25°C, pretreatment with $NaHSO_4$ (3 mole/mole Pd) at 150°C results in catalyst requiring elevated temperature for partial conversion. This catalyst was subsequently determined to carry 90% of the charged "sulfate" sulfur as sulfide.

The structure of the poisoned catalysts produced by reduction of sulfate-containing materials appears to be different from that of commercially available "sulfided" catalysts. The latter are believed to be made by treatment with H_2S (*12*). They show no crystalline patterns by XRD and are seemingly amorphous or else carry small-particle metal sulfide. In contrast, materials produced by reduction of sulfate show reflections at 2θ values of 39.3 and 40.7° characteristic of Pd_4S (*13*). These appear as shoulders on the Pd^0 peak at 40.0°. At higher S/Pd ratios other structures appear corresponding to $Pd_{2.8}S$ and $Pd_{2.2}S$. By XPS these sulfides evidence a S_{2p} signal at 163.8 eV, characteristic of coordinated low-valent sulfur (*14–16*) and distinct from surface sulfur. Sulfiding by H_2S often leads to deposition of elemental sulfur (*12*) (recently Me_2S_2 has been cited as a promising sulfiding agent, see Ref. (*17*)). Hydrogen reduction of unsupported $PdSO_4$ also provides Pd_4S. The complete sulfiding to PdS is not observed in this case or that of supported material. In view of the reported thermodynamic relationship between the various Pd sulfides (*18*), partial sulfiding as reported here is kinetically controlled. In any case, catalyst activity is dramatically altered through sulfate conversion, suggesting pronounced electronic effects (*19*).

Reductions of sulfate are ubiquitous, encompassing flue gas scrubbing, coal liquefaction, cleanup of Portland cement, and bacterial metabolic processes. As this note emphasizes, it may also play a role in catalytic hydrogenations where sulfate may enter as an impurity in the feedstock or in the catalyst preparative method, or in any of the other mysterious ways in which catalyst poisoning tests our sanity.

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