

Pyridine Poisoning of Sulfided Mo-Al₂O₃ Catalyst

Lipsch and Schuit (1) were the first to propose that anion vacancies are the active sites for thiophene hydrogenolysis over molybdena catalysts. Since then, catalytic activity has been related to vacancies in sulfided catalysts in two ways: calculation of vacancy concentration from (i) stoichiometric analysis (2) and (ii) kinetic and adsorption measurements (3). Recently, Verma and Ruthven (4) showed that a catalyst-poisoning technique provides direct information about specific catalyst activities. A Ni catalyst was poisoned with CO during the hydrogenation of cyclopropane. We wish to report a brief study in which a catalyst-poisoning technique has been used to assess the active site vacancy concentration of a sulfided Mo-Al₂O₃ catalyst. In this study, the effects of pyridine poisoning upon catalyst activity were measured during the steady-state desulfurization of benzothiophene.

The experiments were carried out in a stirred-flow microbalance reactor, which allowed simultaneous measurements of catalyst weight change and activity (5). The catalyst was presulfided for 2 hr at 400°C with an H₂S/H₂ mixture of 8% hydrogen sulfide. A solution of benzothiophene and heptane was injected into the reactor via a Sage pump. Pyridine was introduced from a pair of temperature-controlled bubblers in series. The effects of pyridine poisoning on benzothiophene conversion were monitored by gas chromatography using a flame ionization detector. The analytical column consisted of 3% silicone SE-30 on Gas-Chrom Q.

Ethylbenzene was the major product of benzothiophene desulfurization with minor amounts of benzene, toluene, styrene, and dihydrobenzothiophene. Pyridine was introduced at three different levels of concentration under steady-state conditions. The results are given in Table 1. Each increase in pyridine concentration resulted in an increase in catalyst weight and a corresponding decrease in catalyst activity. Neither the weight nor catalyst activity returned to its original value when pyridine was removed from the reaction stream, indicating a permanent poisoning of some sites. It is evident pyridine adsorbs on active desulfurization sites. If this is the case, then a plot of the catalyst activity versus the catalyst weight change, ΔW ,¹ should result in a straight line. This plot is given in Fig. 1. The parameter for catalyst activity, $(C/1 - C)$, where C = percentage conversion/100, is obtained directly from a stirred-flow reactor, and its derivation and use have been discussed previously (5). Extrapolation of the straight line to zero catalyst activity gives a value of 0.047 mmol of pyridine, which corresponds to 0.24 molecules of pyridine per molybdenum atom. This value is in good agreement with the anion vacancies measured by a different method for a thiophene-reacted Mo-Al₂O₃ catalyst (3).

Lipsch and Schuit (1) reported on

¹ Losses in weight due to pyridine partially displacing adsorbed thiophene are small compared to the weight of pyridine adsorbed. A correction for this loss would affect the slope of Fig. 1 by only 10-20%.

TABLE 1
Effects of Pyridine on Benzothiophene Conversion
and Catalyst Weight Change^a

	Run				
	1	2	3	4	5
<i>p</i> ⁰ pyridine (atm)	—	0.00471	0.0149	0.0948	—
Conversion (%)	35.4	19.3	15.4	8.5	21.4
Δ <i>W</i> (mg)	—	2.0	2.6	3.1	1.1

^a Catalyst, 8% Mo/γ-Al₂O₃; catalyst wt., 236.2 mg; reactor flow, 40 ml/min; reactor temperature = 347°C; benzothiophene partial pressure, 0.0032 atm.

pyridine poisoning of a 4% CoO–12% MoO₃ on Al₂O₃ catalyst. They prerduced their catalyst at 500°C in H₂ and measured thiophene conversions at 400°C after successive pulses of pyridine. Thiophene conversion decreased with each pulse to a line-out level, after which no further decrease in conversion occurred with additional pyridine pulses. In the pulse technique, the catalyst only retains irreversibly adsorbed pyridine; therefore, a poisoning decay curve similar to our Fig. 1 would not be obtained by this technique. The amount of adsorbed pyridine taken at their conversion break corresponded to about 0.10 mmol/g, compared to our value of 0.06 mmol/g for Run 5. Their value would be higher if all the pyridine in each pulse was not completely, irreversibly adsorbed, which seems a likely possibility. Hence, both results can be taken to be in good agreement.

One drawback to the poisoning technique is the uncertainty that each adsorbed molecule is effective in poisoning a catalytically active site. This is especially true of catalysts consisting of an acidic-type support when using a basic poison. Therefore, the value obtained here for active sites should be considered a maximum one. However, in view of the linearity of Fig. 1, a significant support contribution to the weight adsorbed would require exactly proportional adsorption–pyridine partial

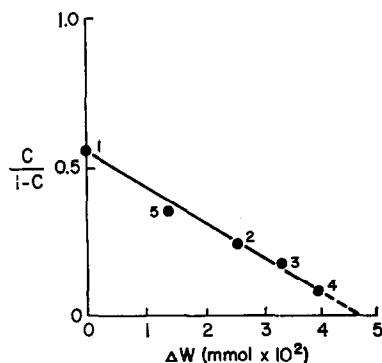


FIG. 1. Effect of pyridine poisoning on catalyst activity.

pressure relationships (including irreversibly retained pyridine) to hold for both thiophene-active and thiophene-inactive (support) sites. One should suppose that a support correction could be made in a separate experiment under identical conditions using only the support. However, this would be of dubious merit in this particular case because of the different character of the alumina portion in the catalyst as compared with the alumina support alone (6) and the uncertainty of the fraction of exposed alumina in the steady-state catalyst which contains carbonaceous deposits on it (2).

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