JOURNAL OF CATALYSIS **82**, 493–494 (1983)

LETTERS TO THE EDITORS

Comment on "The Kinetics of the Catalytic Hydrogenolysis of Ethane over Ni/SO_2"

The above paper by Martin (*1*), presents evidence for identification of the rate-controlling step based on careful measurement of the order of reaction with respect to each of the reactants. The procedure is classical. In this case the partial pressure of hydrogen was fixed and the partial pressure of ethane was varied over a decade. Total pressure and contact time were held constant by adding or removing a diluent, helium. Diluent partial pressure varied by up to 70%. In some experiments of this type the variation could be two- or threefold.

It is tacitly assumed in experiments to determine reaction order that the diluent is truly inert so that the rate is independent of diluent partial pressure (of course, the kinetics must be free of transport interference; this is the case in the above paper). This assumption may not be justified in all cases. It has been found (*2–4*) that diluents, even noble gases such as helium and argon, influence the rate of catalytic reactions. Silva *et al.* (*5*) demonstrated that the rate of oxidation of CO over V_2O_5/SiO_2 depends on the diluent concentration even when the reaction is chemically controlled (rather than diffusionally).

Because of the importance of the order in the paper by Martin, his reaction system was chosen for an investigation of the influence of the diluent on the rate of hydrogenolysis. Instead of varying diluent partial pressure as was done in the original experiment, a constant diluent partial pressure was used and diluents—N_2, Ar, He—were substituted in the reaction mixture. Much larger diluent effects are observed when substitution is used so this is a more sensitive test (*4*). Our purpose in this letter is to discuss the results of our search for a diluent gas effect on ethane hydrogenolysis reaction because our results bear on the identification of the rate-controlling step in this reaction.

The experimental conditions and the catalyst used in our investigation are essentially those used by Martin. The only differences were our special precautions to avoid transport interference, namely high space velocities, the use of a bed of inert quartz grains just above the catalyst to insure the reactant mixture reached the desired temperature before reaching the catalyst, and placement of a thermocouple in the bed to detect temperature change.

The search for a diluent gas effect was made using both ultrapure and technical grades of helium, argon, and nitrogen. Ultra pure grades contained less than 5 ppm of each of water and oxygen, whereas specifications for the technical grades were less than 50 ppm of water and oxygen. The water specification for the ultrapure grades was checked by hygrometer and found to be between 5 and 6 ppm for helium and argon. Typical compositions were: 80% diluent, 3% ethane, and 17% hydrogen. Space velocity and temperature were chosen to give ethane conversions of 1 to 4%. Experiments were performed by running for 30 min to several hours with one diluent (He) and then switching to the other (argon) for a period of equal length. The original diluent (He) was then used for the same period. This permitted compensation for a slow deactivation of the catalyst. Hydrogenolysis was measured by the rate of methane formation. Uncertainty in the rate measurements was within 5%.

No diluent effect was found. Measurements made at 205°C gave virtually identical rates of methane formation with ultrapure grades of helium and argon. The largest difference between the means of successive sets was about 3% after adjust-

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ing for catalyst deactivation. No trends were observed. Replacing ultrapure Ar by technical grade Ar changed the measured rates by less than 2%. However, when technical grade nitrogen was used as a diluent, hydrogenolysis rates were consistently below those found with the ultrapure grades of He and Ar as diluents. The difference, less than 5%, may be due to traces of O_2 or H_2O in the N_2. We suggest this because in initial experiments, a significant diluent effect of the order of 15% on rate was observed. This was ultimately traced to the use of a rubber diaphragm rather than a steel diaphragm in a reducing valve on a gas cylinder. Oxygen and water vapor passed through the rubber diaphragm contaminating the diluent and thereby reversibly lowering catalyst activity. Hygrometer measurements indicated 130 ppm water in argon leaving the reducing valve instead of 6 ppm found when the valve was equipped with a steel diaphragm.

Although a diluent effect on the hydrogenolysis rate was *not* found, varying the amount of diluent in a feed stream alters the transport properties of the reacting gas stream. This can affect heat and mass transfer and thereby influence the observed rate. For example, in this work a space velocity of about 4.5×10^{-4} m^3/s g catalyst was needed to insure that heat transfer from the catalyst particles to the flowing gas did not increase the particle temperature and thus the observed rate of reaction. If the space velocity was kept above this value, temperature measured in the bed remained constant when argon was substituted for the helium diluent. Space velocities above 4.5×10^{-4} m^3/s g catalyst required the use of a 2-cm-deep layer of quartz placed above the catalyst bed to bring the reacting gas to 205°C before reaching the catalyst. Without preheat, space velocity had a significant influence on hydrogenolysis rate even though the system functioned as a differential reactor.

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Received February 26, 1983