Hydrogenation of Ethylene on Supported Platinum

The recent publication by Schlatter and Boudart (*1*) concerning the effects of accidental contamination on the rates of ethylene hydrogenation over Pt/SiO_2 catalysts prompts us to communicate some of our results involving the kinetic characterization of a 12% Pt/SiO_2 catalyst being used in an ir study of adsorbed hydrocarbon species.

The apparatus used will be described fully in due course but consisted essentially of a Pyrex static reactor, of 200 ml total volume, connected to a conventional gas handling vacuum line and directly to a glc system via a 2 ml sample valve. High purity cylinder hydrogen was used from a storage bulb maintained at −196°C and high purity ethylene was thoroughly degassed before use but not otherwise purified. Both reactants were shown to be impurity free by glc and mass spectral analysis. The catalyst (12% Pt/SiO_2) was prepared by impregnation of Aerosil SiO_2 with a solution of H_2PtCl_6. After evaporation to dryness and overnight drying at 120°C the catalyst was reduced in flowing hydrogen at 150°C. The ethane produced during the ethylene hydrogenation reaction was separated from unreacted hydrogen and ethylene on a 2 ft silica gel column and the reaction was followed via the recorded signal from a katharometer detector.

Preliminary runs using this catalyst at various dilutions with the support material, in which the reactants were premixed in the desired ratio and expanded into the reaction vessel, showed a noticeable drop in activity after each run and poisoning during the reaction. Fifteen milligrams of a 20 times diluted catalyst were used for a number of runs using 50 Torr of each reactant until the activity fell to a reproducible level. The following kinetic parameters were then determined:

$$\text{Order in } H_2 = 1.0 \pm 0.05 \text{ (at 60°C)}$$
$$\text{Order in } C_2H_4 = -0.2 \pm 0.1 \text{ (at 60°C)}$$
$$E_a = 21 \pm 0.5 \text{ kcal mole}^{-1} \text{ (60–120°C)}$$

Retention of carbidic residues by the metal was thought to be the reason for the observed poisoning. Regeneration treatments with hydrogen at high temperature did not fully restore the catalyst activity and this led us to explore the possibility of burning off these residues with oxygen. Treatment with low pressures of oxygen at 300°C was followed, after evacuation, by exposure to hydrogen to remove any adsorbed oxygen. The catalyst was then allowed to cool to room temperature in fresh hydrogen. A kinetic run under standard conditions (50 Torr of each reactant at 23°C) showed a dramatic increase in activity. This regeneration treatment could fully restore the catalyst activity although reproducibility was not as good as we would have liked for a redetermination of orders of reaction because the activity was so high. However, using 5 mg of a 50 times diluted catalyst, the activation energy was redetermined as 13 ± 2 kcal mole^{-1} (0–50°C) using standard conditions and oxygen regeneration between runs. Unfortunately the metal surface area of the catalyst has not been measured so a value for the turnover number in our system cannot be calculated accurately. However, an approximate minimum value can be estimated assuming 100% dispersion. For the standard pressures used by Schlatter and Boudart (*1*) $N \simeq 4$. This is a very approximate value but it is in the region obtained by these workers for their run after treating the catalyst with air at 300°C.

The marked drop in activation energy noted for the oxygen-treated catalyst is in accord with the conclusions drawn by Schlatter and Boudart concerning the effect of poisons on the catalyst. Whereas a value of 21 kcal mole^{-1} for our deliberately deactivated catalyst compares with 17–20 kcal mole^{-1} reported by Sinfelt and Lucchesi (*2*) for an unintentionally contaminated catalyst the much lower value of 13 kcal mole^{-1} for our "clean" catalyst compares with values ranging from 9 to 11 kcal mole^{-1} quoted in Ref. (*1*). It is worth noting that these latter values were frequently obtained at much lower temperatures (−80 to 0°C) under which conditions poisoning of the metal either by transfer of contaminants from the support or from retention of ethylenic residues would be expected to be reduced. These results lend strong support to the conclusions of Schlatter and Boudart with respect to the effect of inherent carbonaceous contaminants on reaction rates over supported catalysts and the importance of oxygen cleaning treatments. It would also appear that at room temperature poisoning of clean supported platinum by ethylenic residues takes place. This is in agreement with results of Cormack, Thomson and Webb (*3*), Taylor, Thomson and Webb (*4*) and Altham and Webb (*5*) obtained from radiochemical studies on the behavior of ethylenic species retained by supported platinum.

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