Continuous Hydrogenation of Ethene using Spilt-over Hydrogen

By Mariana S. W. Lau and Paul A. Sermon*
(*School of Chemistry, Brunel University, Uxbridge, Middlesex,* UB8 3PH)

Summary The ability of fluidised powders of SiO_2–Al_2O_3, γ-Al_2O_3, and MoO_3 to catalyse the hydrogenation of C_2H_4 continuously at 400–550 K is greatly increased when they receive H atoms spilling over from Pt/γ-Al_2O_3 pellets.

Hydrogen[1] and other adsorbed species[2] may spill over from metal particles and adsorb, absorb, or react with the supporting or adjacent oxide. Hydrogen spilt over from Pt/γ-Al_2O_3 to additional γ-Al_2O_3 may hydrogenate alkenes, and other unsaturated hydrocarbons, adsorbed thereon.[1,3] However, spilt-over hydrogen reacts more slowly than metal-held hydrogen[4] and, after separation of metallic and oxide phases, it cannot sustain continuous hydrogenation reactions.[3] We now report that the apparently conflicting requirements for continuous hydrogenation by spilt-over hydrogen (*i.e.* separation of highly reactive sites and high rates of spillover) have been fulfilled.

A sample (0·4 g) of Al_2O_3 pellets (3 mm diameter), impregnated with H_2PtCl_6 to give 1·7% Pt after reduction in H_2, was placed in the reactor shown in the Figure and was covered with γ-Al_2O_3 (3 g), SiO_3 (3 g), SiO_2–Al_2O_3 (3 g), or MoO_3 (8 g). After flushing with N_2, each sample was treated at 473 or 573 K with H_2 (101 kPa, 0·40 $dm^3\ min^{-1}$) for 1 h, which entered at the base of the reactor, fluidising the oxide powders, but leaving the pellets stationary on the sinter. Then, with the sample at 473 K, C_2H_4 in N_2 (101 kPa, 60 $cm^3\ min^{-1}$, N_2:C_2H_4 = 1000:1) was also introduced 3 cm above the pellets. C_2H_4 (final concentration 130 p.p.m.) was therefore only in contact with the oxide powders but H_2 was in contact with both pellets and the oxide powders. The extent of C_2H_4 hydrogenation was monitored by g.l.c. and some results are given in the Table.

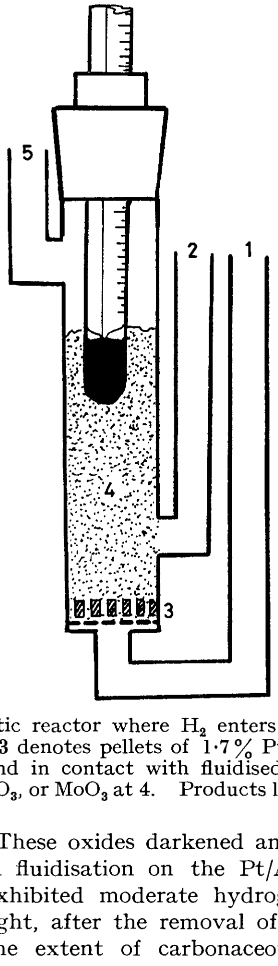

Figure. Catalytic reactor where H_2 enters at 1 and C_2H_4 in N_2 enters at 2. 3 denotes pellets of 1·7% Pt/Al_2O_3 at the base of the reactor and in contact with fluidised powders of SiO_2, γ-Al_2O_3, SiO_2–Al_2O_3, or MoO_3 at 4. Products left the reactor at 5.

The original oxides were inactive in C_2H_4 hydrogenation at 473 and 573 K. Since SiO_2 (of similar surface area, porosity, and particle size to the other oxides) fluidised upon the 1·7% Pt/Al_2O_3 pellets was also inactive, we infer that direct C_2H_4 hydrogenation upon the pellets is insignificant under these conditions. However, γ-Al_2O_3, SiO_2–Al_2O_3, and MoO_3 were active when fluidised upon these pellets. These oxides darkened and gained slightly in weight upon fluidisation on the Pt/Al_2O_3 pellets and subsequently exhibited moderate hydrogenation activity in their own right, after the removal of the pellets, proportional to the extent of carbonaceous deposit. The oxides then lost weight and returned to their original colour on heating in air or O_2 to 773 K with removal of carbonaceous residues. No Pt was detected in any of the powders after contact with Pt/Al_2O_3 pellets using

Table. Hydrogenation activities of various oxides

		Molecules C_2H_4 hydrogenated × $10^{13}\ g^{-1}\ s^{-1}$ at 473 K[a]	
Sample[b]	Reduction temp./K	Oxide activated by 1·7% Pt/Al_2O_3 pellets	Oxide after removal of 1·7% Pt/Al_2O_3 pellets and reduction in H_2
SiO_2	573	0	0
SiO_2–Al_2O_3 (13%)	573	80	25
SiO_2–Al_2O_3 (25%)	573	275	127
MoO_3	473	153	45
γ-Al_2O_3 calcined at 843 K	473	51	

[a] No molecules of C_2H_4 were hydrogenated with oxide alone. [b] Porosities (SiO_2: 1·3 $cm^3\ g^{-1}$; SiO_2–13% Al_2O_3: 1·5 $cm^3\ g^{-1}$; SiO_2–25% Al_2O_3: 1·4 $cm^3\ g^{-1}$; γ-Al_2O_3: 0·8 $cm^3\ g^{-1}$) and surface areas (SiO_2: 270 $m^2\ g^{-1}$; SiO_2–13% Al_2O_3: 450 $m^2\ g^{-1}$; SiO_2–25% Al_2O_3: 550 $m^2\ g^{-1}$).

atomic absorption, and its concentration must have been <10 p.p.m. The SiO_2 results confirm the insignificance of Pt transfer. The insignificance of C_2H_4 hydrogenation on Pt/Al_2O_3 pellets was confirmed when a probe in the operating reactor adjacent to the pellets, and sampling the gas phase at 2 $cm^3 min^{-1}$, detected only 0·4 p.p.m. of both C_2H_4 and C_2H_6. This could have contributed only 1·5% of the observed hydrogenation (*i.e.*, 98·5% of the observed hydrogenation on SiO_2–Al_2O_3 fluidised upon Pt/Al_2O_3 occurred upon the fluidised oxide powder).

It appears that hydrogen spills over on to the oxide powders from the Pt/Al_2O_3 pellets where it participates in C_2H_4 hydrogenation and induces the formation of sites active in their own right thereafter, which are subject to further study. After replacement of H_2 by N_2 (0·35 dm^3 min^{-1}) the quantity of C_2H_4 hydrogenated fell to zero rapidly indicating that the concentration of active sites onto which H_2 spilt over was $<2 \times 10^{20}$ g^{-1} for all oxide samples.

The activity of SiO_2–Al_2O_3 upon Pt/Al_2O_3 pellets was (i) almost constant with an increase in reactant flow rate, indicating the benefits of increased fluidisation, (ii) was a maximum at a reaction temperature of 473 K, (iii) increased slightly in the presence of O_2 (25 p.p.m.), (iv) decreased by a factor of 3·4 at 473 K when the amount of Al_2O_3 in SiO_2–Al_2O_3 decreased from 25 to 13%, (v) was not affected when the concentration of Pt on the Al_2O_3 pellets decreased from 1·7 to 0·5%, (vi) increased linearly as the weight of Pt/Al_2O_3 pellets increased, and (vii) increased slowly with repeated reductions.

The novel manner in which hydrogen spilled over from Pt/Al_2O_3 pellets to various oxide powders inducing continuous hydrogenations thereon may find more widespread use.

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