TABLE 1
TIME-TEMPERATURE STUDY

Time (min)	% Conversion		% Selectivity					
			I[a]		Unknown		1,3-COD	
	25°C	50°C	25°C	50°C	25°C	50°C	25°C	50°C
1	10.5	75.6	88.3	92.8	5.1	5.8	6.2	1.5
5	42.2	99+	89.4	92.6	4.1	5.6	1.5	1.8
15	92.2	100	92.5	92.5	6.3	5.9	1.3	1.7
30	100	100	95.9	93.0	2.2	5.5	1.9	1.5

[a] I, bicyclo[3.3.0]oct-2-ene.

reaction. When the conversion of 1,5-COD was attempted using soluble Co(II) and Fe(II) salts with the Al co-catalyst, no reaction was observed.

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On the Question of Hydrogen Spillover in Ethylene Hydrogenation on Supported Platinum

The kinetic evidence of Sinfelt and Lucchesi (*1*) for spillover of hydrogen from platinum in a Pt–SiO_2 catalyst to Al_2O_3 to give enhanced rates of ethylene hydrogenation on the Al_2O_3 has been strongly challenged recently by Schlatter and Boudart (*2*). In a recent letter (*3*) we present evidence which supports the results of Schlatter and Boudart inasmuch as it confirms the importance of achieving clean platinum surfaces through removal of contaminant inherent in the supporting material. By coincidence we have also obtained new information regarding the occurrence or nonoccurrence of hydrogen spillover in the system first described by Sinfelt and Lucchesi, from the deuteration of ethylene on Pt–SiO_2, which we present here.

This investigation arose from a study, as yet incomplete, of the effect of the support on ethylene hydrogenation over supported platinum using the pattern of deuterium addition/exchange as the experimental probe. Early work by Bond (*4*) using this technique indicated differences in the distribution of the deuteroethanes for platinum on different supports. Ethylene exchange was noted to be very low, but variations were found in this process, too, although figures were not quoted.

The experimental set-up was as previously described (*3*). Deuterium (Matheson C. P. Grade) was taken directly from the cylinder and used from a storage bulb maintained at −196°C. All catalysts were subjected to oxygen and deuterium treatment at 300°C before cooling in deuterium to room temperature. After evacuation, the premixed reactants, ethylene and deuterium, were expanded into the reaction vessel to give equal pressures of each (usually 100 Torr). Samples (~1%) were taken at low conversion directly into a glc system. The separated ethane and ethylene components were collected in capillary 'U' tube traps cooled in liquid nitrogen and subsequently expanded through a capillary leak into an Edwards Mass Spectrometer for analysis. 16 V electrons were used for both analyses. Only fragments due to loss of one or two H/D atoms need be considered for ethane analyses while for ethylene only the parent peak need be considered. The fragmentation of C_2H_6 was always checked when analysing deuterated ethane samples.

Results from four catalysts are described:

1. 12% Pt–SiO_2 diluted 20 times with SiO_2. Prepared as described previously (*3*). Aerosil SiO_2.
2. 0.1% Pt–SiO_2. Prepared similarly. Aerosil SiO_2.
3. 0.1% Pt–Al_2O_3. Prepared similarly. Ketjen CK300 Al_2O_3.
4. 50:50 mixture of catalyst 2 and CK300 Al_2O_3. Prepared by grinding the constituents together.

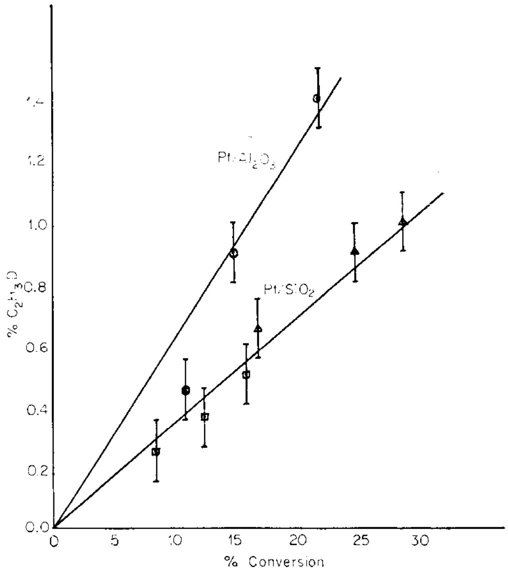

FIG. 1. Variation of C_2H_3D concentration with conversion by the catalysts. ⊗ 12% Pt–SiO_2 diluted 20× with SiO_2, △ 0.1% Pt–SiO_2, ⊡ 50:50 mixture of 0.1% Pt–SiO_2 with Al_2O_3.

Experiments on the variation of ethane distributions with conversion (for Pt–SiO_2) showed that there was little change up to ~25% since ethylene exchange was so low. The amount of $CH_2{=}CHD$ rose linearly with conversion over this range. The ethane distributions are summarized in Table I, and Fig. 1 shows the variation of C_2H_3D concentration with conversion for the four catalyst preparations.

The difficulty of obtaining reliable ethane distributions is well known. The results for catalysts 2–4 are very similar but differ slightly from catalyst 1. The reliability of the results from catalyst 1 is less than the rest, however, on the basis of the agreement between calculated and observed peak heights for masses 28 and 29. There is certainly no significant difference between the results from catalysts 2–4. In agreement with Bond (*4*) we find the amount of ethylene exchange over Pt–Al_2O_3 is significantly higher than over Pt–SiO_2, but of more immediate relevance to the present discussion is the lack of detectable difference between Pt–SiO_2, Pt–SiO_2 + SiO_2, and Pt–SiO_2 + Al_2O_3 for ethylene exchange.

The ethylene exchange probe is obviously sensitive enough to detect a support effect (to be discussed in detail in a later report); consequently, if hydrogen spillover from

TABLE I

Catalyst	Ethanes (%) d_0	d_1	d_2	d_3	d_4	d_5	d_6	Conversion (%)
1	14.7	30.1	29.5	12.7	7.4	3.7	1.8	19
2	17.1	23.8	37.2	12.3	5.3	2.9	1.3	25
3	17.2	21.8	40.3	12.2	5.2	2.2	1.1	22
4	21.3	23.3	35.3	11.5	4.4	2.5	1.7	16

metal to support occurs to promote ethylene hyrdogenation on the support then a difference would be expected in the data from Pt–SiO_2 mixed with SiO_2 or Al_2O_3. The absence of this difference, mirrored by the less sensitive ethane distributions, plainly indicates that the reaction takes place only on the metal and is in disagreement with the proposal of Sinfelt and Lucchesi (*1*) concerning hydrogen spillover and reaction on the support. Furthermore, although it was not the object of this work to obtain detailed kinetic data, the estimated initial rates of reaction for catalysts 2–4 when related to unit Pt weight (assuming similar Pt dispersions on SiO_2 and Al_2O_3) are the same to within 20%. The value for catalyst 1 which is very different from the others is still only about half these. Since all catalysts were subjected to oxygen cleaning treatment at 300°C before runs these observations are in complete agreement with the more detailed kinetic data obtained by Schlatter and Boudart on this system (*2*).

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Defect Control in Oxidation Catalysts

Active sites on heterogeneous catalysts have long been suspected to be intimately related to surface defects. However, the control and characterization of such defects is very difficult. We have introduced lattice defects into the bulk structure of scheelite-type catalysts and find that catalytic activity correlates well with total defect concentration. Thus, it appears that we are also controlling surface defects.

The scheelite-structure catalysts for this study were all single-phase, crystalline materials. The scheelite structure[1] (*1*) has the ideal formula AMO_4 and exists for many molybdates and tungstates, e.g., $Ca^{2+}W^{6+}O_4$ and $Pb^{2+}Mo^{6+}O_4$. Substitution on the A site is possible giving scheelite compounds of the type $A^{1+}_{0.5}A^{3+}_{0.5}MO_4$, e.g., $Li_{0.5}La_{0.5}MoO_4$ and $Na_{0.5}Bi_{0.5}WO_4$. We find that defects can be introduced according to the formulas $A^{2+}_{1\text{-}3x}A^{3+}_{2x}\square_xMO_4$ or $A^{1+}_{0.5\text{-}3x}Bi_{0.5+x}\square_{2x}MO_4$

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[1] A description of the scheelite structure and many examples of compounds with this structure may be found in Ref. (*1*).