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Hydrogen Spillover on Silica: Ethylene Hydrogenation and H_2–D_2 Exchange

D. H. LENZ AND W. CURTIS CONNER, JR.

Department of Chemical Engineering, University of Massachusetts, Amherst, Massachusetts 01003

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Using spiltover hydrogen, activation of silica Aerosil has been achieved utilizing a unique reactor similar to one developed in Lyons, France, by Teichner. Activation was achieved without direct contact between the oxide (spillover acceptor phase) and the supported metal (spillover source phase). The induced hydrogenation and exchange activity occurs independent of the metal. This induced catalytic activity is an activated process requiring high temperatures and long time periods. The mechanism of the hydrogenation reaction is similar to that on metal oxides in that the molecular identity of the reacting hydrogen is retained. Thus, dideuteroethane is the primary product in the reaction of deuterium with ethylene. Differences in activity from both metals and metal oxides are noted, such as in ethylene and H_2–D_2 exchange reactions; it is unclear whether these are due to the higher temperatures and/or to changes in the relative rates of the mechanistic steps.

INTRODUCTION

Since the early sixties, when Khoobiar (*1*) and Sinfelt and Lucchesi (*2*) first postulated hydrogen spillover, it has been suggested as a metal–support phenomena many times (*3–5*). However, important parameters, such as the rate and activation energy of spillover, have yet to be adequately determined. Also, the significance of the spillover phenomena in heterogeneous industrial catalysis has only recently been addressed. Barbier *et al.* (*6*) and Parera *et al.* (*7*) both find indications of a strong contribution by the support via hydrogen spillover for catalytic reforming catalysts. Bond (*8*) reports that hydrogen spillover is likely to be an important step in catalyzed coal hydrogenation. Others have begun to address the influence of hydrogen spillover in reactions involving hydrogen, such as cyclohexane dehydrogenation (*9*), benzene hydrogenation (*10*), and ethylene hydrogenation in a fluid bed (*11*). A series of studies by Teichner *et al.* (*12*) have examined hydrogen-spillover-induced catalytic activity on oxide supports without any metal present and have reported unique chemistry on these activated oxides.

The phenomenon of spillover was defined at the First International Congress on Spillover of Absorbed Species as follows (*13*):

> Spillover involves the transport of an active species sorbed or formed on a first phase onto another phase that does not under the same condition sorb or form the active species.

The following comment was also added:

> The result may be the reaction of this species on the second phase with other sorbing gases and/or reaction with and/or activation of the second phase.

Figure 1 depicts schematically the kinetic aspects of these phenomena associated with hydrogen (deuterium) spillover just described. The gas phase species, denoted by *D–D*, sorbs and dissociates into an atomic species on the metal-supported phase. This atomic species then "spills over" from the metal phase across an interface to the support phase. The spiltover species, denoted by D_s, is capable of diffusing across and/or exchanging on the sup-

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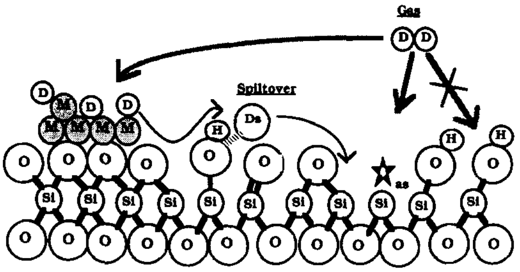

FIG. 1. Schematic representation of the spillover of deuterium (**D**) from a metal (**M**) onto a silica surface containing hydroxyls. If this process occurs at high temperatures (>400°C) for a long time, active sites (☆$_{as}$) are created.

port surface. The nature of the spiltover species has not been established; i.e., it might be a charged, a radical, or a bound species. Coadsorbents, such as water, can promote both the spillover and the transport of the spiltover species. The species can participate in or inhibit reactions. Over a period of time at high temperature, the spiltover species can be involved in the creation of new activity sites on the support, denoted by ☆$_{as}$ in the figure. Whereas previously the support was inert to the gas phase species D–D, with the creation of the active sites, the support *may* now be capable of sorbing and dissociating the molecules from the gas.

Due to studies of spillover phenomena, it is apparent that the support can no longer be termed "inert" with respect to heterogenous, catalytic reactions. One question this raises to be addressed in this paper is, "Are the rates of reaction on the activated support similar to or different from those on the metal?" Understanding the kinetics and mechanism of hydrogenation on the activated silica should also provide additional clues as to the nature of the active site.

The possibility of uncoupling the interactions of metal and support in catalytic reactions can be accomplished using the technique developed by Teichner *et al.* to isolate an oxide support from the metal after contact with molecular hydrogen at high temperatures. Any resulting activity is then due solely to the newly created sites on the oxide. Relative rates of catalysis and reaction rates for each surface can be assessed. These studies could yield information as to the relative significance of spillover-activated sites in the presence of supported metal catalysts.

For platinum-on-alumina or -silica catalysts, it has been implied that direct addition of molecular hydrogen to ethylene occurred primarily on the oxide support (*14*). Using the deuteration of ethylene as a test reaction in Teichner's reactor, the reaction mechanism on activated oxides alone can be investigated and the possibility of the essentially direct addition of molecular hydrogen to adsorbed ethylene can be addressed. This reaction was chosen because there is a striking difference in the product distribution on metals from that on metal oxides. The product distribution of ethylene deuteration on nickel metal plotted as the partial pressure of the ethanes and ethylenes versus the extent of reaction, or conversion, shows that the whole range of deuterated ethanes (d_1–d_6) and ethylenes (d_1–d_4) are formed at low temperatures (25°C) (*15*). The product distribution of the deuterated ethylenes implies the possibility of an alkyl reversal step in the mechanism as well, as represented by Ozaki (*16*):

$$C_2H_4(a) + D(a) \Rightarrow C_2H_4D(a) + H(a).$$

The product distribution for the deuteration of ethylene on oxides (e.g., Cr_2O_3 (*17*), Co_3O_4 (*18*), and ZnO (*19*)) would contain predominantly dideuteroethane and no deuterated ethylenes. The essentially direct addition of gaseous molecular hydrogen to adsorbed ethylene is emphasized by the product distribution of ethylene hydrogenation with an equimolar mixture of H_2 and D_2 over various oxide catalysts (*20*). At low temperatures, the direct addition of the hydrogen or deuterium molecules results in the predominance of perhydroethane and dideuteroethane, respectively. Some monodeuteroethane is formed primarily

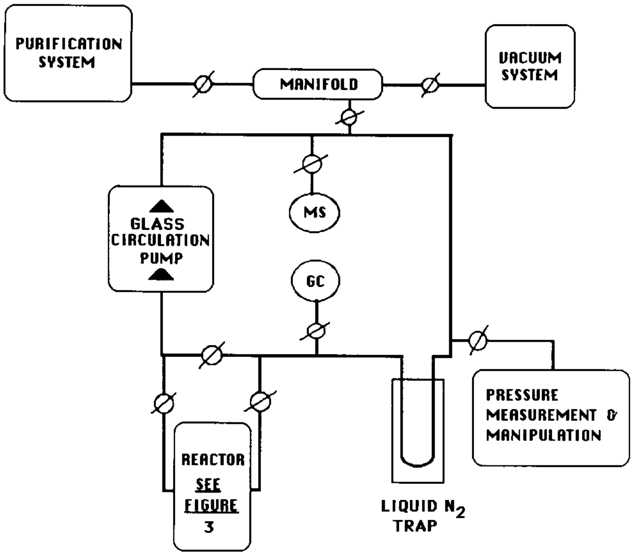

FIG. 2. Schematic of the reactor system used in these studies.

from the direct addition of small amounts of HD in the gas phase. Also, adsorbed ethylene generally inhibits the H_2–D_2 exchange reaction on the catalysts' surface, be it metal or oxide. Using hydrogen-spillover-activated silica Aerosil, we anticipate mechanistic behavior similar to that on the oxide catalysts rather than that on the metal catalysts.

METHODS

Apparatus. The experimental system is shown schematically in Fig. 2. The glass system can be evacuated to $<10^{-6}$ Torr by a vacuum pump connected in series to a three-stage oil diffusion pump and a large liquid nitrogen trap. The reactants are purified and stored in gas bulbs attached to the manifold. The circulation loop (volume approximately 100 cm^3) contains a magnetically driven circulation pump as well as a liquid nitrogen trap for removing any condensable gas phase impurities and water vapor upstream from the reactor. The circulation pump consists of four delicate one-way quartz valves and a glass-coated metal slug surrounded by a coil that generates an alternating magnetic field to pump the gases. System pressure is monitored by a mercury manometer. The system pressure can be manipulated to vary the reactant's partial pressure by a gas burette bulb system. High-vacuum glass stopcocks lubricated by either Apeizon L or H grease are used throughout the system. The glass experimental system has on-line capabilities for mass spectrographic and gas chromatographic analyses.

The glass reactor used is shown in Fig. 3 and is similar to the reactor of Gardes *et al.* (*21*). A porous glass bucket, which is filled with the supported metal catalyst (spillover source), was made from the fritted end of a fritted gas dispersion tube and has a wall thickness of 3 mm and a volume of 0.85 cm^3. The bucket can be lowered by a winch mechanism from the upper compartment (volume approximately 100 cm^3) into the lower compartment (volume approximately 60 cm^3). Here in the lower compartment is the silica support (spillover acceptor). After activation, when the bucket is lifted and the stopcock closed, the activated oxide is effectively isolated from the supported

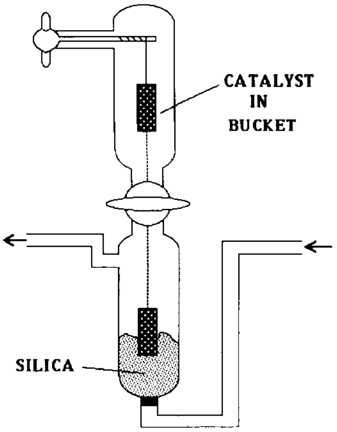

FIG. 3. Depiction of the reactor used to activate the silica (in contact with the lowered Pt containing bucket) and then to remove and isolate the Pt from the reaction system (by raising the bucket and closing the upper stopcock.

metals. The reactor and the inlet and outlet arms are surrounded by an insulated furnace capable of achieving temperatures up to 800°K. The on-line mass spectrometer (MS) was a UTI AGA-100 MUX quadrupole gas analyzer (I.V. 70 eV). The on-line gas chromatograph (GC) was home-built and contains Gow-Mac rhenium/Tungsten TC detector elements. The column used for the ethylene/ethane separation contains Poropak Q, 90/110 mesh. The data from each piece of analytic equipment were collected and stored via an Analog Devices MacSym 350 computer. Programs were developed to calculate the relative MS or GC peak areas. In addition, the mass spectrometer program can perform an isotopic analysis on the spectra to identify the isotopic products formed during the reaction (*22*).

Materials. The support studied for catalytic activity was Degussa Silica Aerosil 200 (+99.8% SiO_2). UOP 0.4% platinum-on-alumina and 4.0% platinum-on-silica, prepared in this lab, were the supported catalysts used as the source of spillover. For the UOP catalysts, γ-alumina spheres were impregnated with chloroplatinic acid. The catalysts had been calcined in air, then prereduced in hydrogen. These catalysts contained 0.4% Pt and 0.57% Cl.

The Pt/SiO_2 catalyst was made by impregnation of the Degussa Aerosil 200 with chloroplatinic acid. First, 4.35 ml of $PtCl_4$ solution was added to 6.36 ml of water. Then 2.82 g of the Aerosil 200 was slowly sifted into the diluted solution, mixing well continuously. The catalyst was calcined at 120°C for 3 h, removed, and finely ground into a powder, then calcined for 3 h more. Before use, the catalyst was also heated at 430°C *in vacuo* for 12 h and then reduced in circulating hydrogen for at least 10 h. The catalyst contained 4.6% Pt and the actual chlorine content was not measured. This catalyst was not used much for this reason. The UOP catalyst was the preferred spillover source.

The hydrogen gas was obtained from Linde Corp. and the deuterium gas was obtained from Aero-Allgas Co. (MG Technology). Both were passed through a heated Pd thimble to assure purity before use. The ethylene gas came from the Aero-Allgas Co. and was dehydrated by flowing through a bed of Davison 3-Å molecular sieves. The ethylene was also distilled in a series of liquid nitrogen traps connected to the vacuum line to remove any remaining contaminants.

Procedure. The activation procedure for the silica Aerosil consists of two steps: high-temperature degassing, i.e., "calcination" *in vacuo,* and reduction/spillover, i.e., "activation" of the silica. At the beginning of the calcination step, the bucket with the catalyst is lowered onto the silica. There is no direct contact between the Aerosil and catalyst, in contrast to the studies of Teichner *et al.* (*12*); however, there is a continuous surface (the porous bucket) connecting the source and the support to be activated. The temperature is raised to the calcination temperature, generally 430°C under vacuum, $<10^{-6}$ Torr, for 8 h or more. Next, 200–300 Torr of hydrogen is admitted into the reactor, at the desired activation temperature (400–500°C), for 6 h or more.

The liquid nitrogen trap is kept at −196°C (77°K) at this point to ensure that only hydrogen stays in the gas phase during activation and to trap out any gaseous products, such as water, formed. With the liquid nitrogen trap in place, the reactor temperature is then lowered to the desired reaction temperature and the bucket with the catalyst is raised and isolated in the upper chamber. The hydrogen can be evacuated and the reactants, fresh hydrogen and/or deuterium plus ethylene, are admitted. The reactants are circulated continuously over the silica in a constant-volume reactor. Unless stated, the supported metal catalyst is never present in the reactor during reaction.

RESULTS AND DISCUSSION

The silica Aerosil becomes catalytically active for the hydrogenation/deuterogenation of ethylene after completing the described activation procedure. In the following discussion, experimental runs are denoted by a number followed by a letter. The numbers indicate different activation procedures and the letters indicate the sequence of hydrogenation and/or exchange reactions on the activated silica. Runs marked 6 used the Pt/SiO_2 catalyst as the spillover source and 9.8 g of silica was first pressed in a die to 10 kpsig, broken into pieces, and placed in the reactor. All other runs utilized the Pt/Al_2O_3 catalyst as the spillover source and 1.5 g of silica as the spillover acceptor to be activated. The amount of either Pt-containing catalyst in the bucket was always 0.09 g. Below we refer to the Pt-containing source of spillover as the "activator" and the silica as the "accepting oxide."

Blank Runs

Three types of blank runs were done. The first one, without the bucket containing the activator present, involved high-temperature degassing of the silica followed by high-temperature exposure to hydrogen. Following this treatment, ethylene is not adsorbed on the isolated oxide in any appreciable amount at 200°C. At this reaction temperature no hydrogenation of ethylene and very minimal H_2–D_2 exchange are evident.

For the second type of blank run, the bucket with the activator was suspended approximately 4 cm above the silica initially used during most of the activation procedure. Finally, for the third type, the bucket with the activator was in full contact with the silica during the calcination step and the reduction/spillover step, which only lasted 6 h in this case. For both of the latter blank runs, after removal of the activator, no appreciable ethylene was adsorbed and no reaction was apparent when the reactants were circulated through the reactor. Teichner and co-workers have shown by neutron activation studies (*23*) that no platinum migrated onto the silica, the accepting oxide with this type of reactor system being subject to similar activation procedures.

Hydrogenation/Deuterogenation

The product distribution as a function of conversion is shown in Table 1, runs 6 b–j, for the reaction of a 1 : 1 reactant mixture of deuterium and ethylene. It is apparent that dideuteroethane is the only initial product. However, with successive reactions over the same catalyst, trideuteroethane begins to form. Some exchange with the ethylene is occurring, as monodeuteroethylene is formed during the reaction. Direct addition of deuterium would then yield the observed ethane products. HD is also being formed, unexpectedly as hydrogen is not a reactant and hydrogen–deuterium exchange is suppressed in the presence of ethylene on metal oxides at lower temperatures.

The results for the deuterogenation of ethylene at various temperature and partial pressures of deuterium and ethylene are also shown in Table 1. The principle product for each of the deuterogenations is di-

TABLE 1

Hydrogenation and Deuterogenation of Ethylene on Activated Silica

Run	Partial pressure (Torr)			Temperature (°C)	Conversion (%)	Relative concentration of product ethanes				% Ethylene reacted/min	TOF (C_2H_4/site/sec)
	D_2	H_2	C_2H_4			d_0	d_1	d_2	d_3		
Activation at 430°C for 10 h											
6b	237	—	237	200	14	—	0.01	0.99	—	1.12	0.003
6h	242	—	242	135	11	—	0.01	0.62	0.37	0.8	0.002
6j	166	—	166	200	14	—	0.01	0.71	0.28	2.3	0.005
7c	12	—	115	200	10	0.01	—	0.99	—	0.15	0.003
7b	108	—	108	200	34	—	0.01	0.99	—	1.6	0.034
7d	129	—	13	200	65	0.02	—	0.98	—	16.3	0.038
Activation at 400°C for 10 h											
9a	138	—	87	205	15	—	0.01	0.99	—	0.03	0.0005
9b	135	—	90	211	8	—	0.01	0.99	—	0.04	0.0009
9e	—	349	45	174	16	1.0	—	—	—	0.029	0.0003
9g	—	309	31	208	94	1.0	—	—	—	0.28	0.0018

deuteroethane. This is particularly true for freshly activated silica and perhaps lower ethylene partial pressures, as shown in runs 6b and 7b–7d. The initial reaction rate (% ethylene reacted/min) is shown in the next to last column and the estimated turnover frequency (TOF) is shown in the last column. Note that this activity is created by hydrogen spillover activation at 430°C for 10 h. A lower activation temperature of 400°C for 10 h or more results in a marked decrease in overall rate and TOF, as shown in the lower half of Table 1. Silica activated at 480°C exhibited no hydrogenation activity at all. Note that the turnover frequency is based on an estimate of 10^{12} hydrogenation sites per cm^2 created by spillover, a point to be discussed.

It is evident that the reaction is approximately zero order in ethylene (runs 7b and 7d) and first order in hydrogen (runs 7c and 7b). However, at higher ethylene partial pressures the reaction seems to become inhibited or slightly negative in ethylene at these temperatures (run 6j). Further, at higher ethylene partial pressures or at lower temperatures (runs 6h–6j), trideuteroethane becomes a significant product. There are two possible explanations for this behavior. First, it is possible due to the enhanced possibility for exchange with an increased residence time for ethyl intermediates on the surface under these conditions (lower temperature, higher reactant pressure). By slow alkyl reversal, ethylene exchange might be enhanced. Second, these runs were done with activated silica that had been used for about 2 weeks. The possibility of a deuterated alkyl species being left on the surface at the beginning of each run cannot be discounted. Run 6b shows the initial product distribution on a freshly activated silica. Little d_3 ethane is found.

Two other points are of interest. There appears to be a slight induction period during the first experimental hydrogenation run for most samples (compare 9a and 9b). As the turnover frequency is calculated based on the total ethane formed at the time the reaction was stopped, the initial reaction on a fresh catalyst will have a lower average TOF. The induction period may be due to spillover hydrogen or ethylene adsorbed on the active sites. It has been suggested that initially spiltover hydrogen will inhibit the hydrogenation reaction until it is used up by the initial dose of coreactant (*23*). Spiltover hydrogen can be removed either by reverse spillover (via the metal) if the catalyst remains present while the temperature is lowered from the activation to the reaction temperature or by recombination and desorption during evacuation at the reaction temperature before admittance or reactants. This was done successfully prior to runs numbered 6 where no induction period was found.

The other point deals with the differences in TOF under similar reaction conditions on the activated silica for runs of the 6 and 7 series. Several differences exist between these runs. The source of spillover was Pt/Al_2O_3 for run 6 and the amount of silica activated in run 6 was almost an order of magnitude greater than that in run 7. As the rate of activation of the support is very slow (requiring over 6 h to achieve measurable activity) and platinum supported on silica or alumina readily exchanges all the surface hydroxyls via spillover, the differences in the source of spillover would not seem to account for the differences. The 10 g of silica assembled from pressed pieces in run 6 formed, at best, a loose agglomerate. This poor contact between adjoining pieces could have substantially impeded the activation procedure and fewer sites were actually created. The differences in the turnover frequencies are, we believe, due to an inaccurate estimation of the number of active sites created in run 6.

Additional information on the reaction mechanisms is obtained by reacting a hydrogen/deuterium mixture with ethylene at various temperatures. Table 2 shows the results. The product distribution of ethanes that would be formed assuming molecular addition of the hydrogen/HD/deuterium present in the gas phase at the indicated conversion is shown, as is the distribution calculated for random addition of H and D. At lower temperatures the molecular addition mechanism seems to predict the ethane

TABLE 2

Hydrogenation of Ethylene with H_2–D_2 Mixtures

	Partial pressure (Torr)			Temperature (°C)	Conversion (%)	Relative partial pressure ethanes				TOF (C_2H_4 reacted/site · sec^{-1})	Relative patial pressure			TOF (HD formed/site · sec^{-1})
	H_2	D_2	C_2H_4			d_0	d_1	d_2	d_3		H_2	HD	D_2	
	132	108	240	135	67	0.46	0.34	0.15	0.05	0.004	0.56	0.31	0.13	0.002
With molecular addition						0.52	0.33	0.14	0.01					
With random addition						0.27	0.48	0.23	0.01					
	189	105	300	174	64	0.59	0.26	0.12	0.03	0.014	0.53	0.32	0.15	0.005
With molecular addition						0.50	0.33	0.16	0.01					
With random addition						0.41	0.48	0.16	0.01					
	162	112	280	206	54	0.40	0.42	0.18	—	0.011	0.58	0.23	0.17	0.005
With random addition						0.34	0.48	0.17	0.01					
With molecular addition						0.57	0.23	0.17	0.01					

product distribution well, but at higher reaction temperatures the results are mixed at best. Neither mechanism (molecular or random addition) predicts better results at the highest reaction temperature (>200°C). As the presence of trideuteroethane decreases with increasing temperature, this suggests that the ethylene exchange reaction is more favorable at the lower temperatures. At higher temperatures where the coverage of the reacting sites would be reduced, H_2–D_2 exchange rates seem to be increasingly important.

The results in Table 2 as discussed above imply that the surface hydrogen and deuterium atoms continue to mix rapidly as the temperature is increased, although desorption of HD may not be increasing as rapidly. This is seen in the limited increase in the TOF for HD formation (Table 2, last column) compared to the more random addition at higher reaction temperatures shown in the center of the table.

Note, however, that whereas the activities of these catalysts are fairly good (TOF $= 10^{-1}$ to 10^{-3}), slight variations are evident in the activity when comparing various runs. Indeed, in Table 2 the expected increase in rate, reflected in the turnover numbers, was not evident with an increase in the reaction temperature from 174 to 200°C. Due to the sensitivity of the activity to variations in pretreatment conditions giving rise to spillover-induced activity, a detailed kinetic analysis (i.e., determining specific reaction order and activation energy of each reaction) of the hydrogenation of ethylene on activated silica was not the major focus of these studies. Though the reactant concentrations were not maintained exactly constant from run to run, estimation of the apparent activation energy for the hydrogenation reaction was performed. The rate constant, k, is approximated by dividing the initial rate by the hydrogen partial pressure. From the slope of $\ln k$ versus $1/T$, the activation energy was calculated to be around 6 kcal/mol on silica activated at 430°C and approximately twice that on silica activated at 400°C. These results are generally in agreement with other studies of the hydrogenation of ethylene (*17, 18, 23, 24*).

Hydrogen–Deuterium Exchange

The isotopic exchange of H_2–D_2 was also studied on activated silica. The rate increased with increasing reaction temperature but was independent of the total pressure. The kinetics appear to be zero order for the hydrogen exchange on activated silica. Also, the activity is less for the lower activation temperature (400°C) and nonexistent at very high activation temperatures (greater than 480°C).

The TOFs for the H_2–D_2 exchange reaction increase dramatically in the absence of ethylene from 0.002 to 0.02 at 135°C, 0.005 to 0.241 at 174°C, and 0.005 to 0.621 at 206°C. This suggests competitive adsorption between ethylene and hydrogen (or deuterium) for the active sites with ethylene the more strongly adsorbed. If, alternatively, two types of site exist, the number or activity of the exchange sites is small or both types of sites are blocked by ethylene but only one is active for hydrogenation. It seems that a single type of site is more probable. Approximate activation energies for the exchange reaction were calculated to be about 15 kcal/mol, independent of the temperature of silica activation.

Mechanism on the Active Sites

To summarize the main results, one can say that initially the product of the deuterogenation of ethylene on the spillover-activated sites of the silica Aerosil is dideuteroethane. Also, the molecular identity of the deuterium/hydrogen gas phase species is retained for the most part during the reaction at temperatures below 200°C. However, unlike oxide catalysts, which are active at lower temperatures, partial ethylene exchange and H_2–D_2 exchange are promoted. Therefore, the reaction mechanism may include an alkyl reversal type step at this temperature. The sites must also be ca-

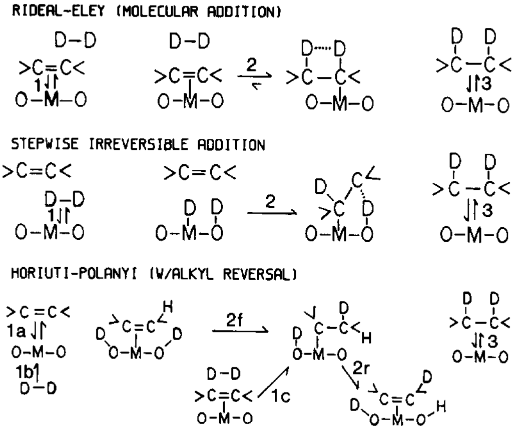

FIG. 4. Representation of the mechanisms proposed for ethylene hydrogenation.

pable of adsorbing and dissociating, or at least exchanging, the gas phase hydrogen species.

With this in mind, certain mechanisms for the hydrogenation reaction can be assessed. Figure 4 shows the three mechanisms most often suggested in the literature. The Rideal–Eley gas phase molecular addition mechanism alone does not allow for the H_2–D_2 exchange reaction to occur. The stepwise irreversible addition cannot account for the partial ethylene exchange which occurs. Both of these mechanisms have been used to interpret the activity of oxide catalysts (*18*). Unless there are separate sites activated for the exchange and hydrogenation reactions (discussed above), these mechanisms do not seem operable.

For supported metal or metal catalysts, the Horiuti–Polanyi mechanism, with an alkyl reversal step, is suggested in the literature. In step 1b becomes reversible and the reversibility of step 2 decreases so that the forward rate is promoted and/or the reverse rate inhibited, this mechanism will now describe the activity of the spillover-activated silica sites. If this does occur, then the more general Horiuti–Polanyi mechanism can be used for both metal and activated oxides; only the relative rates of some of the reaction steps on the activated oxides change. It should be reiterated that these reactions are now occurring on previously "inert" silica Aerosil without any metal present.

Deuterogenation on Activated Silica and Metal Catalyst

The deuterogenation reaction was also performed in the presence of both the supported metal and the activated silica to attempt to gauge the influence or independence of one from the other. The bucket with the catalyst was relowered into the lower chamber and suspended over the silica after it was assured that the silica had been activated. No direct contact was made, in contrast to the activation procedure but similiar to the second blank run. The standard reaction performed was with a 10 : 1 deuterium to ethylene reactant ratio at 200°C.

First, the deuterogenation of ethylene with both the activator (UOP Pt/Al_2O_3) and the silica and with the activator alone are shown in Table 3. Bond's results for this reaction at 0°C on a platinum-on-alumina catalyst (although prepared differently) are shown for comparison (from ref. (*1*)). As expected, no H_2–D_2 exchange is noted for the Pt/Al_2O_3 alone. Clearly there is a smear of deuterated ethane products for each type of experiment.

Some typical results for the differences in reaction rates of ethylene deuteration on activated silica, on supported metal (the activator), and on the combination of both are shown in Figs. 5 and 6. The activated silica in Fig. 6 has a better activity than that in Fig. 5, due to differences in the activation procedure. It can be seen that the rate of reaction on the silica alone approaches that due to the combined sites as the activity on the silica improves. However, the activity on the combined sites is always less than that due to the supported platinum catalyst alone. When not directly coupled, it appears that the two types of catalysts are now competing for the reactants. It should be noted that the amount of Pt in the reac-

TABLE 3

Deuteration of Ethylene in the Presence of Pt "Activator" at 200°C

Run	% Conversion	Relative partial pressures														
		Ethanes							Ethylenes					Hydrogen		
		d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_0	d_1	d_2	d_3	d_4	H_2	HD	D_2
		Combination of Pt "activator" and active silica.														
12d	2.2	—	0	1	—	—	—	—	1	—	—	—	—	0	0.1	0.9
	17.4	—	—	0.8	0.2	—	—	—	1	—	—	—	—	0	0.1	0.9
	48	—	—	0.5	0.2	0.3	0.1	—	0.9	0.1	—	—	—	0	0.2	0.8
	52.8	—	—	0.4	0.3	0.4	—	—	0.8	0.2	—	—	—	0	0.2	0.8
13d	66.3	0.3	0	0.1	0.2	0.2	0.1	0.1	0.5	—	—	—	—	0	0.2	0.8
	89.1	—	0.4	0	0.1	0.2	0.2	0.1	0.2	—	—	—	—	0	0.1	0.9
	100	—	—	0.2	0.4	0.2	0.1	0.1	—	—	—	—	—	0.1	0.2	0.7
		Reaction of Pt "activator" alone														
17a	54	0	0	0.6	0.2	0.1	0.1	0	1	0	0			None formed		
	73	0	0	0.4	0.2	0.2	0.1	0.1	0.8	0.2	0					
	94		0	0.3	0.3	0.2	0.1	0.1	0	1	0					
	98	0	0	0.3	0.3	0.2	0.1	0.1	0	1	0					
Ref. (*1*)	100	0.1	0.2	0.4	0.1	0.1	0	0	?	?	?					

tor in any case was several orders of magnitude less than the amount of silica. Indeed we believe that the activity on the sites created by spiltover hydrogen on silica are inherently less active than the Pt, by at least an order of magnitude.

The isotopic product distribution for the deuterogenation of ethylene in these specific studies is summarized in Table 3. The high initial fraction of dideuteroethane and the formation of HD are probably due to contributions from the activated silica. However, the isotopic product smear typical of the supported metal catalyst predominates as the reaction goes to completion. At this point in the reaction, it seems the main contribution from the activated silica are the H_2–D_2 exchange reaction products.

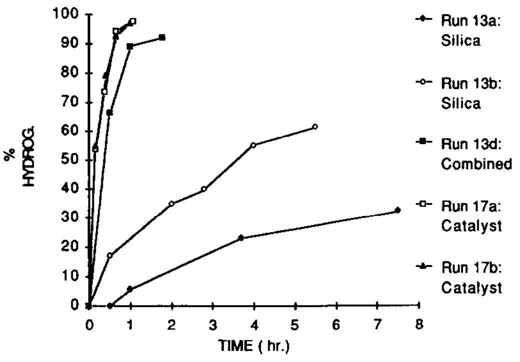

FIG. 5. Reaction rate comparison for Experiments 13 and 17. Progress of the deuteration of ethylene comparing the reaction over activated silica, over the Pt containing spillover source, and over a combination of both the source and the activated silica.

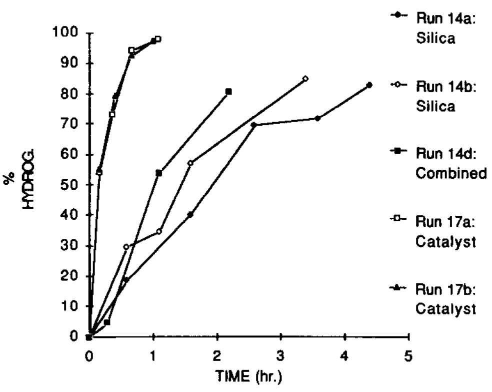

FIG. 6. Reaction rate comparison for Experiments 14 and 17. Progress of the deuteration of ethylene as in Fig. 5 with a more active, spillover-activated silica.

As these studies were only exploratory, not much more can be said now.

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