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Hydrogenation catalysis by thermally activated silica

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Abstract

Conversion of alkenes to alkanes under D_2 or H_2 (5.5 MPa cold pressure) at temperatures as low as 200–350°C is promoted by thermally-activated fumed silica. There is no reaction in the absence of silica and its activity is increased by the thermal pretreatment (330 to 430°C for 16 h under Ar). Stilbene (1,2-diphenylethene) treated as described with D_2 gives 1,2-diphenylethane consisting mainly of molecules containing two atoms of deuterium at aliphatic sites (^{2}H NMR). At 250°C diphenylacetylene is converted to stilbene-d_2 which is predominantly the *cis*-isomer (*cis/trans* > 3) showing that the hydrogenation is stereoselective. Other compounds for which hydrogenation is promoted include 1-nonene and anthracene. In some cases, hydrogenation of isolated aromatic rings is observed. For example, 1,2-diphenylethane in the absence of stilbene gives 1-cyclohexyl-2-phenylethane along with some 1,2-dicyclohexylethane. It is shown that surface OH groups on the silica are converted to OD by D_2 under the reaction conditions.

Keywords: Deuterium; Diphenylacetylene; Hydrogenation stereochemistry; Silica surface

1. Introduction

Recent work by Bittner et al. [1] showed that silica which is thermally activated by heating at 330°C under argon flow catalyzes the reaction, $H_2 + D_2 \rightarrow 2HD$ at temperatures as low as 120°C in a pulse-flow microreactor. Moreover, this material catalyzes the hydrogenation of ethene to ethane at 150°C and produces ethane-d_6 when D_2 is used as a flow gas. We became interested in this phenomenon because it related our ongoing study of the hydrothermolysis of surface-immobilized coal-model compounds [2] to a previous exploration of the uncatalyzed reaction of alkenes and arenes with D_2 and H_2 [3] in which we had shown that temperatures of 400°C and 5.5 MPa (cold pressure) of H_2 were required to convert stilbene (1,2-diphenylethene), STB, α-methylstyrene (2-phenylpropene), MS, and anthracene, AN, to 1,2-diphenylethane, DPE, cumene (2-phenylpropane), and 9,10-dihydroanthracene, respectively.

The results of uncatalyzed reactions for the first two compounds are summarized in Table 1. It will be noted that STB is converted to DPE with an average number of D atoms per molecule approaching 2. Some D was found in recovered STB. We interpreted these results, at least in the case of STB as due to an H-atom propagated kinetic chain, Eq. (1) and Eq. (2), terminated by radical disproportionation, Eq. (3). This mechanistic assignment explained a strong STB con-

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centration dependence of reaction yield. Subsequent kinetic studies, still in progress, have supported this argument by showing that the effective rate constant for the reaction of STB with H_2 increases with increasing conversion, suggesting that the reaction product, DPE, may facilitate the generation of H atoms. The involvement of DPE in the production of H atoms had been explained earlier by us [4] and by Vernon [5]. Further evidence for the involvement of radicals may be adduced from the relatively low levels of D incorporation in cumene produced from MS, a phenomenon explained by H-atom transfer from MS to the intermediate cumyl radical. The formation of molecules thought to be radical dimers also suggested radical involvement in the MS + D_2 reaction (Note h, Table 1).

Table 1
Reaction of unsaturated compounds with D_2 (5.5 MPa cold pressure) at 410°C for 20 min [a]

Compound	Amount [b] (mg)	% H–C–C–H [d]	D atoms in H–C–C–H [c]	D atoms in C = C [c]
STB	25 [e]	22 [g]	1.67	0.23
STB	25 [f]	22 [g]	1.73	0.22
STB	50	8.7 ± 3	1.4 ± 0.1 [i]	< 0.1
STB	100	1.8	1.5 [i]	< 0.05
MS	50	14 [h]	1.34	0.13
MS	150	18 [h]	0.80	0.09
MS	300	27 [h]	0.65	0.16

[a] See [3] for additional details and other substrates. [b] This is the weight of material inside of an approximately 12 ml reaction vessel. [c] Average number of D atoms per molecule as determined by GC/MS analysis. [d] Balance of material is recovered C = C, except as otherwise noted. [e] Commercial material contains 0.7% of DPE. [f] Synthetic material contains < 0.01% DPE. [g] Product mixture also contains 5–10% of products of DPE reaction (benzene, toluene, ethylbenzene, styrene, 1,1-diphenylethane, diphenylmethane, etc. [h] Similar amounts (12, 17 and 21%) of other products, most of which appeared to be dimers and dehydrodimers of expected intermediate radicals. [i] Corrected for DPE in starting STB.

$$\mathrm{PhCH = CHPh\,(STB) + H^{\cdot} \rightarrow Ph\dot{C}H - CH_2Ph} \tag{1}$$

$$\mathrm{Ph\dot{C}H - CH_2Ph + H_2 \rightarrow PhCH_2 - CH_2Ph\,(DPE) + H^{\cdot}} \tag{2}$$

$$\mathrm{2Ph\dot{C} - CH_2Ph \rightarrow STB + DPE} \tag{3}$$

We chose STB for our initial look at the silica catalyzed reaction. The results of Table 1 suggested that there should be no significant radical chemistry taking place below 400°C so we began our study by testing the effect of thermally activated silica on the hydrogenation of this compound at 350°C.

2. Experimental

Fumed silica placed in a ca. 10 cm section of 12 mm i.d. glass tubing between glass wool plugs constituted the catalyst bed. The experiments in this paper and most of those described by Bittner utilized Cab-O-Sil M-5, a grade of fumed silica manufactured by Cabot Corporation, having a surface area of 200 m^2/g. A constriction was formed in the tubing at one end of the bed and a ca. 15 cm section of open 1–2 mm capillary tubing was sealed to the other. Activation was carried out in a tube furnace under argon flow, the catalyst bed was cooled and reagents introduced by syringe or funnel while the bed was maintained under argon. The reactor was sealed at the constriction under argon and the vessel thus produced placed inside of a steel reactor housing, subjected to 5.5 MPa of D_2 at 25°C, and then heated in a fluidized sandbath. Workup and analytical procedures have been described in previous publications [2].

3. Results

In Bittner's experiments, silica was packed in a Vicor tube and activated by allowing argon to flow through for 16 h at 320°C. Pulses of reactants were then introduced into the gas stream and their fates determined by mass spectrometry after passage through the catalyst bed. In our case silica and reactant alkenes were placed in a glass-lined vessel under H_2 or D_2 pressure as described in the Experimental section. Table 2 shows results of experiments carried out in this way. It can be seen that the hydrogenation of STB is clearly catalyzed by the silica. Entries 4 to 6 show that no significant reaction occurs at 350°C in the absence of silica. Entries 1 and 2 show that significant conversion of STB to DPE occurs at 300°C and that prior thermal activation of the silica by the argon-flow method significantly increases the conversion. There is nearly complete hydrogenation to DPE after 90 min in the presence of activated silica. For the three runs carried out in the presence of silica, the deuterium distribution in the DPE produced was $d_2 = 85.4\%$, $d_3 = 6.0\%$ $d_4 = 3.5\%$ in the first run, $d_2 = 83.7\%$, $d_3 = 10.6\%$ $d_4 = 2.0\%$ in the second run, and $d_2 = 63.3\%$, $d_3 = 25.4\%$ $d_4 = 7.2\%$ in the third run. The balance was a small amount of DPE-d_0 present as an impurity in the STB. Thus, the product was mainly DPE-d_2 material. The molecules containing higher numbers of D atoms resulted at least partially from the reaction of D_2 with exchanged stilbene. As will be shown below, there exists an exchange process between D_2 and surface SiOH groups producing SiOD groups which can undergo slow exchange with stilbene at 350°C. ^2H NMR showed that neither the DPE nor the STB remaining contained any significant amount of aromatic D whereas there was a prominent signal for the aliphatic D in the DPE produced. It will be noted that unactivated silica does catalyze the reaction to some extent, but this might be expected in view of the fact that reaction temperatures are similar to activation temperatures.

An experiment similar to those of Table 2 was carried out exposing the silica to D_2 and STB sequentially. The silica (300 mg) was activated in the usual way and heated with D_2 at 350°C. Following this, D_2 was removed from the reactor under vacuum and STB (50 mg) was added. The reactor was then placed under N_2 pressure (5.5 MPa) and heated at 350°C for 90 min. A very small amount of DPE-d_2 was detected after this process, ca. 0.2% of the starting STB. In contrast to experiments carried out under a D_2 atmosphere, there was a nearly equal amount of DPE-d_1 However, the recovered STB contained a significant amount of D (average 0.19 atoms/molecule, mainly as STB-d_1). These observations suggest that the sites on or in the silica matrix where hydrogenation

Table 2
Reaction of unsaturated compounds with D_2 or H_2 in the presence and absence of thermally-activated silica

Compound	T (°C)	Time (min)	D_2/H_2	Silica [a]	% H-C-C-H	% C = C
trans-STB	300	30	D_2	A	31	65
	300	50	D_2	NA	7.2	90
	350	90	D_2	A	91.2	7.3
	350	60	D_2	none	1	98
	350	15	H_2	none	< 1	99 [b]
	350	100	H_2	none	< 1	99 [c]
Naphthalene	300	30	D_2	A	1.2 [d]	98.5
	350	90	D_2	A	1.5 [d]	98.5
1-Nonene	300	30	D_2	A	36.3 [e]	35.3 [e]
Anthracene	350	80	D_2	A	30	61
	350	60	D_2	none	0.5	99.5
DPA [f]	350	40	D_2	A	3.3 + 38.9 [g]	57.5 [g]
	300	90	D_2	A	29 + 69 [h]	< 1 [h]

[a] A = activated, NA = not activated. [b] *cis/trans* = 0.085. [c] *cis/trans* = 0.087. [d] Product appears to be mixture of dihydronaphthalene-d_2 and tetralin-d_4. [e] Remainder appears to be alkene isomers. [f] DPA = diphenylacetylene. [g] Product contains 3.3% diphenylethane, DPE, and 38.8% mixed *cis*- and *trans*-STB, *cis/trans* = 0.26. This run was carried out with a different procedure, however, and it is not certain that all of the DPA was available for reaction. [h] Product is a mixture of DPE (29%) and STB with no significant amount of residual DPA. The STB shows *cis/trans* = 0.18.

takes place are relatively few in number, ca. 0.5% of OH pairs on the silica surface are involved in formation of active sites [1].

Nonene was picked as a prototypical nonaromatic alkene and it shows hydrogenation to nonane. The saturated material produced under these conditions is a mixture of ca. 64% nonane-d_2 and 36% nonane-d_3. The unreacted 1-nonene is mainly undeuterated, but the precision required to determine small amounts of D was unavailable due to extensive mass spectral fragmentation. Both of the nonene isomers, presumably *cis*- and *trans*-2-nonene are mainly d_1 material but contain about 30% d_0 material. It thus seems likely that 1-nonene can isomerize under these circumstances and that at least part of the process does not involve the intermediacy of nonane-d_2.

The reaction is not limited to alkenes as anthracene can be reduced to dihydroanthracene, mainly with two atoms of D. Diphenylacetylene (DPA) is also hydrogenated. At 350°C, the STB produced is largely converted to DPE-d_4. At 300°C, a substantial amount of intermediate STB is observed, mainly d_2. The STB from these experiments seemed to be slightly enriched in the *cis*-isomer but the analysis was inherently imprecise due to the GC overlap between *cis*-STB and DPE. In order to provide more convincing evidence that the initial product of hydrogenation of DPA is *cis*-STB, the reaction temperature was lowered to 250°C. Data for hydrogenation of DPA (with H_2) under these conditions is presented in Table 3.

It is clear from the data in Table 3 that the predominant product of hydrogenation of DPA at 250°C is *cis*-STB by a ratio of at least 3 to 1. The equilibrium ratio of *cis*-/*trans*-STB has not been established at 250°C, but the 5th and 6th runs of Table 1 show that at 350°C the ratio is 0.086 and a lower value might be expected at 250°C. Thus there seems little doubt that *cis*-STB is the kinetic product of DPA hydrogenation. It seems likely that the *trans*-STB produced in this reaction results from the thermal isomerization of the *cis*-isomer.

Table 3
Yields of products from reaction of diphenylacetylene with H_2 at 250°C over thermally-activated Cab-O-Sil

	Time (min)				
	5	15	30 [f]	60 [e,f]	60 (*trans*-STB [b])
DPA [a]	98.8	87.7	55.8	35.1	
cis-STB [b]	0.9	5.5	20.3	47.9	1.5
*trans*Ŧ>-STB	0.3	1.7	3.5	10.9	52.8
cis / *trans* [c]	3	3.3	5.8	4.4	
DPE [d]	< 0.3	5.1	20.3	6.0	45.7

[a] DPA = diphenylacetylene. [b] STB = stilbene. [c] Thermal equilibration gives a ratio of 0.1 at 350°C. [d] DPE = diphenylethane. [e] Reasons for the dramatic decrease in DPE formation in the 60 min run are uncertain. But, for this run the silica was activated at 430°C rather than the 330°C used for all of the other runs. This result is being checked. [f] Two other runs at somewhat lower bath temperatures gave lower conversions and *cis* / *trans* ratios of 7.1 and 8.5 for 30 min and 60 min, respectively.

To determine whether surface SiOH groups are directly involved in a reaction with H_2 (D_2), we carried out a series of experiments in which silica was activated then heated with D_2 followed by removal of the D_2 under vacuum and heating with phenol. Earlier work had shown that the *ortho*- and *para*-positions of phenol undergo exchange with OH groups on the silica surface at temperatures above 140°C [2]. After recovery from an aqueous workup the deuterium content of the phenol was determined by GC/MS analysis. Typical data are presented in Table 4. It is clear that at temperatures of 250°C or above, Cab-O-Sil undergoes exchange with D_2 to give SiOD groups on the surface. Calculations based on the expected [2] 4.5 SiOH groups per nm^2 of surface area suggest that roughly 75% of the surface SiOH groups are replaced by SiOD groups in the high temperature runs. The threshold temperature for the exchange reaction

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[1] A calculational error in the preprint led to this being reported earlier as 10%.

[2] Information provided in product bulletin by Cabot Corporation for Cab-O-Sil M-5.

Table 4
Deuterium content of phenol exchanged[a] with Cab-O-Sil (300 mg) previously treated with D_2 at 5.5 MPa (cold pressure) at various temperatures

Run	Activation?	Reaction time (min)	Reaction temperature (°C)	mg PhOH	D/molecule
1	yes	20	350	40	0.30
2	yes	60	350	45	0.27
3	yes	120	350	42	0.38
4	yes	180	350	43	0.23
5	no	20	350	40	0.29
6	no	60	350	33	0.26
7	no	180	350	37	0.45
8	yes	60	250	16 (12)	0.31 (0.34)
9	no	60	250	19 (11)	0.18 (0.18)
12	yes	60	200	22	0.03
13	no	60	200	21	0.06

with D_2 appears to be between 200 and 250°C. In the four runs carried out at 250°C, the exchange with D_2 seemed about twice as great with silica which had undergone prior activation, however, the effect of activation on exchange was not as great as on the STB reduction and of questionable significance considering the scatter in the data.

We find in some experiments that the thermally activated silica also is capable of catalyzing the hydrogenation of aromatic rings. As shown in Table 2, a small amount of naphthalene is hydrogenated under the conditions described. To our astonishment, DPE was more extensively hydrogenated than naphthalene provided that the silica was thermally activated either for several days at 330°C or at 430°C for 16 h. Representative experiments are listed in Table 5. The reaction gives two products with gas chromatographic retention times which are very similar to DPE. With H_2 these products have mass spectra which match 1-cyclohexyl-2-phenylethane, CPE, and 1,2-dicyclohexylethane, DCE. Using D_2, each is extensively deuterated and the ^2H NMR spectrum of the mixture shows an envelope of purely aliphatic D atoms in the range of 1 to 1.5 ppm from TMS. The D content of the two reduction products suggests that much of the material arises from the replacement of the four benzylic H atoms in DPE as well as the addition of three D_2 molecules r reduced benzene ring. However, evidence for exchange at the aliphatic sites of the saturated rings is provided by the presence of up to CPE-d_{18} and up to DCE-d_{26}. The DPE which is recovered is mainly DPE-d_4 but there

Table 5
Yields of products from reaction of diphenylethane (DPE) with D_2 in the presence of thermally-activated Cab-O-Sil

	Run 1	Run 2	Run 3	Run 4 [h]
Activation time (h)	42	16	16	16
Activation temperature (°C)	330	430	430	430
Run time (h)	1	1	7	7
Run temperature (°C)	350	350	350	350
Yield CPE [a] (%)	30.4	22.6 [e]	37 [e]	< 1
Yield DCE [b] (%)	5	5 [f]	13 [f]	< 1
Recovery DPE [c] (%)	64	72 [g]	50 [g]	> 99

[a] CPE = 1-cyclohexyl-2-phenylethane. [b] DCE = 1,2-dicyclohexylethane. [c] DPE = 1,2-diphenylethane. [e] This was not completely resolved from DPE by GC, but its presence was clearly indicated by an envelope of ions in the mass spectrum ranging from d_6 to d_{18} with maximum intensity at d_{11}. The relative intensities of the ions in this envelope were similar for runs 2 and 3. [f] DCE was well resolved from DPE and CPE. Its mass spectrum showed an envelope of ions from d_{12} to d_{26} with maximum intensity at d_{19}. Again, relative intensities were similar for runs 2 and 3. [g] Recovered DPE showed an envelope of ions ranging from d_0 to d_{12} with maximum intensity at d_4. In run 2, a substantial amount of d_0 material remained (slightly more than d_4). In run 3, the d_0 material had been largely consumed. However, the D distribution in the d_4 to d_{12} material was similar in the two runs. [h] In run 4, an equal weight (50 mg) of naphthalene was added. Recovered DPE in this experiment contained very little D, > 96% d_0.

is evidence for some exchange in the aromatic rings as well.

We were surprised to find that when naphthalene was mixed with DPE and subjected to the conditions of Table 5, neither compound was hydrogenated and, moreover, the presence of naphthalene prevented even the exchange of the benzylic hydrogens as the DPE recovered contains very little deuterium (see run 4 in Table 5 and footnote h). Naphthalene had no significant effect on the hydrogenation of STB. Ring hydrogenation was also observed with diphenylmethane, DPM, however the hydrogenations of each of these compounds was sensitive to the particular lot of Cab-O-Sil used and in several cases apparently comparable to runs listed in Table 5, much lower conversions were observed. However, all batches of 200 m^2/g material gave some aromatic ring reduction. Only one experiment (with a smaller particle size fumed silica) showed no detectable ring hydrogenation under comparable conditions. Reasons for the variability are being sought.

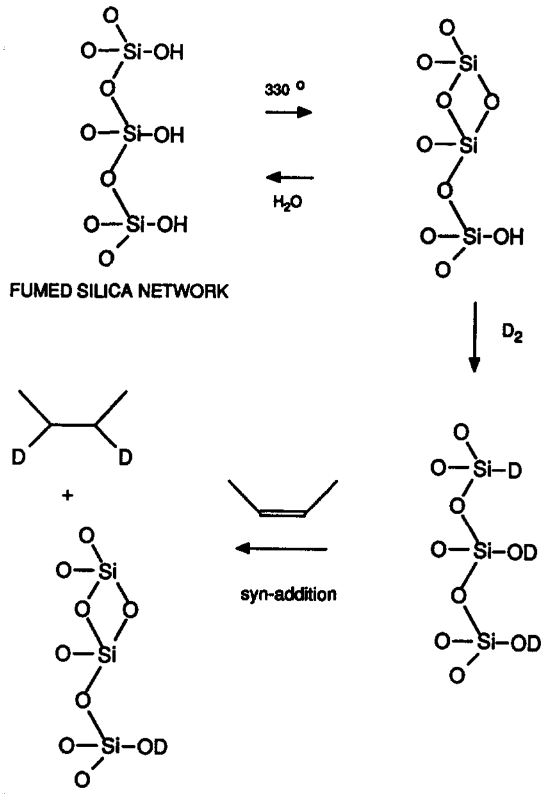

Fig. 1. Possible mechanism for hydrogenation of alkenes by thermally-activated, fumed silica.

4. Conclusions

These studies have shown that thermally-activated, fumed silica is capable of promoting alkene hydrogenation at temperatures below those required for purely thermal (H-atom mediated reactions). When the process is carried out with D_2, the hydrogenated alkenes contain approximately 2 atoms of D with some d_3 product explained by exchange of the starting alkene with SiOD groups on the silica. Silica was shown to undergo exchange of surface SiOH groups with D_2 by using a technique involving heating the exchanged silica with phenol and measuring D incorporation in the recovered phenol. It is believed that the relatively high pressures of D_2 (5.5 MPa cold pressure) used in our experiments account for the fact that this phenomenon was not observed in pulse microreactor experiments [1]. During the silica promoted reaction of arylalkenes with D_2, there is little or no D incorporation at aromatic ring positions. Hydrogenation of an alkyne (DPA) at threshold temperatures produces an amount of *syn*-hydrogenated product (*cis*-STB/*trans*-STB > 3) in great excess of the equilibrium value (*cis*-STB/*trans*-STB ~ 0.1). Thus, the process shows the chemical and stereochemical characteristics usually associated with metal-surface catalyzed hydrogenations. Suggestion of a detailed mechanism is probably premature at this juncture given that there is little evidence regarding the atomic and molecular changes which take place on the silica surface. Nevertheless, the behavior we and Bittner et al. [1] have observed for fumed silica is very similar to that reported for zinc oxide by Dent and Kokes [6], who suggested that H_2 adds to the ZnO bond to give H–Zn–O–H. An analogous mechanism for the silica reaction is shown in Fig. 1. In suggesting this possibility, we do not intend to discount a competing or cooperating mechanism involving adsorption of alkene or arene on the silica surface. Indeed, the competitive influence of naphthalene could be taken as evidence for a surface-arene interaction. Nevertheless, it is also clear from our exchange experiments that D_2 reacts with the surface in the absence of alkene or arene substrates. It is the relationship between these two processes that remains undefined.

The hydrogenation of arenes has proven somewhat less reproducible than the hydrogenation of alkenes, but the evidence is clear that it can be made to occur if conditions are optimal. The effect of naphthalene suggests that this process may be sensitive to small amounts of adventitious impurities. We are trying to search out the experimental variables responsible for the observed changes in efficiency.

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