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Reactions of Organosilicon Compounds on Metals

III. Selective Poisoning by Et_3SiH of Catalytic Hydrogenation and Dehydrogenation[1]

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The transformation of Et_3SiH occurring with C—Si bond breaking was studied on Cab-O-Sil-supported Cu, Ni, Rh, Pd, and Pt catalysts by the pulse technique in H_2 and He at 473–673 K. A serious poisoning of the C—Si bond breaking capability of the metals was observed. Cu proved to be much less sensitive to poisoning, and, contrary to the other metals, could be partially reactivated. The poisoning effect of the surface silicon residues was found to be different for the hydrogenation of propene, cyclohexene, and benzene and for the dehydrogenation of 2-propanol and cyclohexene. This new selective poisoning effect may be a new tool for modifying certain metal catalysts.

INTRODUCTION

In earlier papers (*2, 3*) we reported the configurational isomerization of 1,2-dimethylsilacyclopentanes on copper. During this transformation we also observed the formation of C_5 hydrocarbons (pentane and pentenes) as well as the poisoning of configurational isomerization.

C—Si bond breaking has been observed in the ring opening reactions of substituted silacyclobutanes on Pt/C (*4*) and Pd/C (*5*), in the transformations of tetramethylsilane to methane and hydrogen on tungsten and iron films (*6*). Recently Gentle and Muetterties observed the transformation of silacyclobutane on Pd(110) surface indicating C—Si dissociation during adsorption under ultrahigh vacuum conditions (*7*). Detailed studies were made by Wells *et al.*, who investigated the reactions of methylsilane on gold and molybdenum (*8, 9*) and nickel, rhodium, and tungsten (*10*). They also observed that, as a result of bond fission, the exchange with molecular deuterium was poisoned. This poisoning effect was attributed to the formation of strongly triadsorbed alkyl Si species.

Continuing our earlier observation we used triethylsilane as a model compound on different metals to study the effect of C—Si bond fission on the activity of the catalysts in different reactions.

EXPERIMENTAL

Method. The pulse microreactor technique was used (*11*) (1-μl pulses) with hydrogen or helium as the carrier gases. In the measurements 10 or 25 mg of fresh catalyst samples were used.

Catalysts. Cu, 6.8%, on Cab-O-Sil (D_{N_2O} = 4.1%) was prepared according to the literature (*12*). It was activated in a hydrogen stream (25 ml/min) at 473, 523, and 573 K for 1 h at each temperature. All of the other catalysts (Pt, Pd, Rh, and Ni on Cab-O-Sil with 3% loading each) were prepared by wet impregnation, reduced at 473 K (Pt), 673 K (Pd), or 773 K (Ni, Rh), and before every experiment were activated in hydro-

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TABLE 1

Transformation of Et_3SiH[a]

		Ni	Rh	Pd	Pt	Cu
$\frac{C_2 \text{ products formed}^b}{\text{silane converted}}$		2.7	2.7	2.7	2.0	1.6–1.0[c]
$\frac{\text{Ethane}}{\text{ethylene}}$	in H_2	100:0	100:0	80-90:10-20[c]	100:0	50:50
	in He[d]	85:15	89:11[e] 55:45 47:53	52:48 12:88	67:33	3:97
$\frac{\text{Silane converted in five pulses}}{\text{surface metal atom}}$		1.7	1.3	2.2	1.6	4.3
$\frac{C_2 \text{ products formed in five pulses}}{\text{surface metal atoms}}$		4.6	3.5	6.0	3.2	6.0

[a] Catalyst quantity = 25 mg, $T = 523$ K.

[b] Accuracy: ±10%.

[c] Decreasing values by increasing number of pulses.

[d] The high ethane : ethylene ratio in the first pulse is due to incomplete removal of hydrogen after activation.

[e] Several % methane is also formed.

gen at 573 K for 90 min. The dispersion of catalysts measured by oxygen–hydrogen titration is 6.8% for Ni, 27.0% for Rh, 15.4% for Pd, and 11.8% for Pt.

Analysis. A Carlo Erba Fractovap Mod. G chromatograph (hot wire detector) was used. The column was 1.5 m 15% Reoplex on Kieselguhr. The gaseous compounds were analyzed by a 1.2-m long silica column. Quantitative evaluation of the results was made by using calibration curves.

Materials. Triethylsilane (Fluka product) was used after distillation (GC purity: 99%). All the other compounds proved to be 100% pure by GC. Hydrogen was generated by a Matheson 8326 hydrogen generator operating with a palladium membrane. Helium had a purity of 99.99%.

RESULTS AND DISCUSSION

By adding 1-μl pulses of Et_3SiH to the catalysts in the presence of hydrogen ethane is formed (Table 1). On Pd and Cu some ethylene is also formed. In helium, the main product is ethylene, indicating that the process is a metal-catalyzed C—Si dissociation rather than hydrogenolysis. The activity of all catalysts in breaking C—Si bonds decreases with increasing pulse number. Copper exhibits different behavior from the other metals. The latter show a drastic activity drop and after several pulses they lose their total initial activity. However, in the case of copper a constant activity is established after the first few pulses (Fig. 1). If the time interval between pulses is increased, a higher constant activity is reached for copper, but for the transition metals no change occurs. Copper can be reactivated to a certain extent by long heat treatments at high temperature in hydrogen

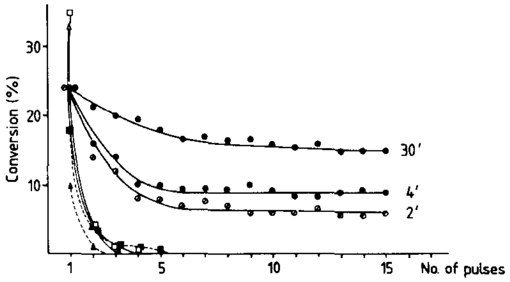


FIG. 1. Transformation of Et_3SiH (catalyst quantity = 25 mg, $T = 523$ K). (⊘ ⊗ ●) Cu with 2-, 4-, and 30-min time intervals between pulses, respectively, (■) Ni, (□) Rh, (△) Pd, (▲) Pt.

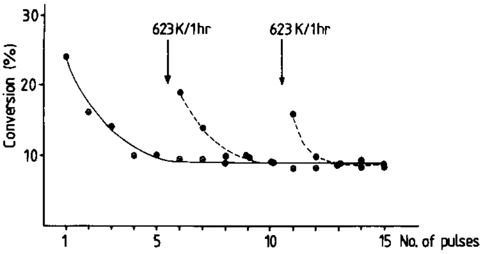


FIG. 2. Reactivation of Cu in the C—Si bond fission reaction (catalyst quantity = 25 mg, T = 523 K). (⊗) Original conversion, (●) conversion after reactivation.

(Fig. 2), but the same treatment does not reactivate the other metals.

The ratio of hydrocarbons (ethane + ethylene) formed to Et_3SiH transformed (Table 1) indicates that Ni, Rh, Pd, and Pt are more capable than Cu for rupturing multiple C—Si bonds in the Et_3SiH molecule. Copper seems to be capable of multiple C—Si bond breaking mainly in the first several pulses but to a smaller extent than the other metals. The results indicate that copper slowly loses this kind of activity upon increasing numbers of pulses and that its multiple bond breaking surface sites are poisoned permanently.

TABLE 2

Hydrogenation of Propene[a]

Catalyst	Conversion (%)	Temperature (K) 423	473	523	573
Ni	Initial	98	100	100	
	After poisoning	76	81	84	
Rh	Initial	100	100	100	
	After poisoning	93	93	100	
Pd	Initial	100	100	97	
	After poisoning	15	17	17	
	After reactivation[b]	40	36	38	
Pt	Initial	98	100	100	
	After poisoning	29	38	34	
	After reactivation[b]	81	89	93	
Cu	Initial		39	56	52
	After poisoning		11	18	23
	After reactivation[c]		28	45	41

[a] Catalyst quantity = 10 mg, except of Cu = 25 mg. Injection of 500 μl of propene, then 5 × 1 μl of Et_3SiH at 523 K, then 500 μl of propene.

[b] 723 K, 1 h.

[c] 623 K, 1 h.

Wells *et al.* (*10*) proposed that a strongly adsorbed

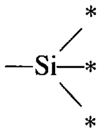


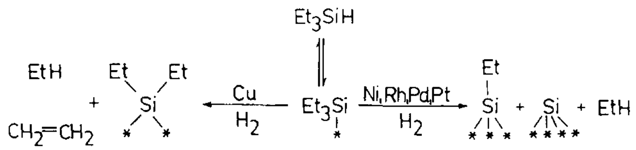
TABLE 3

Transformations of Cyclohexene[a]

Temp. (K):		423		473		523		573	
Catalyst		Composition of reaction mixture[b] (mol%)							
		I	P	I	P	I	P	I	P
	Cyclohexane	95	25	75	24	38	20	11	17
Ni	Cyclohexene	0	75	5	71	3	63	1	49
	Benzene	5	0	20	5	59	17	88	34
	Cyclohexane	100	44	95	42	64	33	24	36
Rh	Cyclohexene	0	56	0	57	0	61	0	43
	Benzene	0	0	5	1	36	6	76	21
	Cyclohexane	96	5	90	7	68	4	35	3
Pd	Cyclohexene	2	95	5	93	5	95	5	95
	Benzene	2	0	5	0	27	1	60	2

[a] Catalyst quantity = 25 mg. Injection of 1 μl of cyclohexene, then 5 × 1 μl of Et_3SiH at 523 K, then 1 μl of cyclohexene.

[b] I = initial composition, P = composition after poisoning.



SCHEME 1

species is responsible for the poisoning effect. They suggest that the last step of its formation is irreversible and it cannot be removed from the surface.

Our results indicate that on Ni, Rh, Pd, and Pt one exposed surface metal atom is capable of transforming between 1.3 and 2.2 silane molecules (Table 1). As a result of the multiple bond fission, multiple bond surface silicon residues are formed. On the other hand, on copper mainly singly and doubly bound surface species are formed (Scheme 1) which block the surface more slowly than the triply bound species. To interpret the special activity of copper in C—Si bond fission we tried to detect compounds, which desorb from the catalysts during heat treatment in hydrogen. The only compound desorbing from the catalysts was ethane. On the basis of this and the fact that no Si-containing compounds desorb from copper during reactivation we suppose that its reactivation is connected with some kind of rearrangement of silicon residues on the surface. This rearrangement results in regeneration of sites active for the reaction.

The effect of C—Si bond fission on the transformation of other organic compounds was also studied. On all metals we examined the hydrogenation of propene, on Cu and Ni the dehydrogenation of 2-propanol, on Ni, Rh, and Pd the transformations of cyclohexene, and on Ni, Rh, and Pt the hydrogenation of benzene. During these measurements, first the activity of the catalysts for the specific reaction was determined, then 5 × 1 μl of Et_3SiH was injected at a certain temperature (indicated in figures and tables) and the activity was checked again. In this way the effect of Si poisoning could be evaluated.

In the hydrogenation of propene, Rh and Ni are least sensitive to poisoning (Fig. 3). It is worth emphasizing that although these two metals are totally inactive for C—Si bond breaking after treatment with 5 μl of Et_3SiH at 523 K, they are still very active for hydrogenation of olefinic bonds. Under the same conditions Cu exhibits a large activity drop, but can be partially reactivated by heat treatment in hydrogen. Surpris-

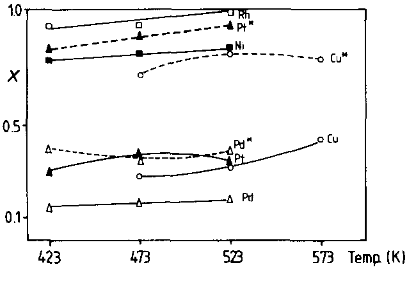


FIG. 3. Effect of poisoning on hydrogenation of propene (catalyst quantity = 10 mg, except of Cu = 25 mg, poisoning by 5 × 1 μl of Et_3SiH at 523 K): x = conversion after poisoning/initial conversion or conversion after reactivation/initial conversion. (—) After poisoning, (---) after reactivation in hydrogen (Cu,* 623 K, 1 h; Pd,* 723 K, 1 h; Pt,* 723 K, 1 h).

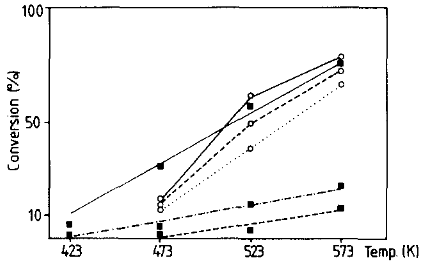


FIG. 4. Effect of poisoning on dehydrogenation of 2-propanol (catalyst quantity = 25 mg). (■) Ni, (○) Cu; (—) initial conversion; conversions after poisoning by 5 × 1 μl of Et_3SiH at (-·-·) 473 K, at (---) 523 K, and at (···) 573 K.

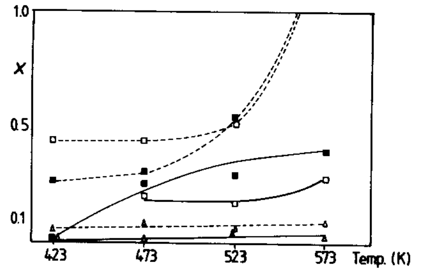


FIG. 5. Effect of poisoning on the transformations of cyclohexene (catalyst quantity = 25 mg, poisoning by 5 × 1 μl of Et_3SiH at 523 K). (■) Ni, (□) Rh, (△) Pd; (---) formation of cyclohexane, (—) formation of benzene.

$$x = \frac{\text{mol\% cyclohexane (or benzene) formed after poisoning}}{\text{mol\% cyclohexane (or benzene) formed before poisoning}}$$

ingly, the activation was successful for both Pd and Pt even though they could not be reactivated for silane hydrogenolysis. Moreover, in the case of Pt, the original activity was almost totally restored as a result of activation.

For the dehydrogenation of 2-propanol Ni and Cu showed opposite behavior to poisoning. The activity of the former decreased drastically, while the latter was almost insensitive to Si poisoning (Fig. 4).

For the transformations of benzene and cyclohexene, the different catalysts exhibited different sensitivities to poisoning (Figs. 5 and 6). Both the formation and hydrogenation of benzene are poisoned more markedly after the same treatment with Et_3SiH. The hydrogenation of cyclohexene, in turn, was less affected. A similar observation was made by Plate (*13*), who found that the cyclohexane ⇌ benzene reaction on Pt/C at 573 K was poisoned by tetrasubstituted silanes but that the catalyst was still active in the hydrogenation of the double bond. On the other hand, Paál *et al.* (*14*) observed an enhanced aromatization of *n*-heptane in a static system on a Pt/SiO_2 catalyst, supposedly partially siliconized with Me_4Si. Our efforts to reactivate the poisoned Ni, Rh, and Pt for the hydrogenation of benzene failed in the case of Ni and Pt and were only partially successful for Rh.

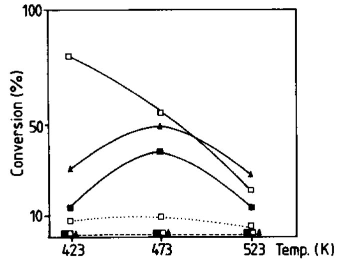


FIG. 6. Effect of poisoning on hydrogenation of benzene (catalyst quantity = 25 mg). (■) Ni, (□) Rh, (▲) Pt; (—) initial conversion, (---) conversion after poisoning by 5 × 1 μl of Et_3SiH at 523 K, (···) conversion after reactivation in H_2 (723 K, 1 h).

The above results show that the poisoning effect of surface silicon residues resulting from C—Si bond fission is different on the different catalysts and depends on the transformations involved. This treatment seems to be promising for the selective poisoning of catalysts in different reactions and may be useful for the characterization of the surfaces of metal catalysts.

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