**TABLE I: Relaxation Parameters for Normal Alkanes** 

	$T_1(\mathbf{H}),$	$T_1(CH_3),$	$T_x(CH_3),$	$T_1(\beta),$	$T_1(\text{main}),$		
	S	S	s .	S	\$	cryst	
C20	8.0	1.5	3.2	51	159	tricl	
C21	5.1	1.6	3.7	14	19	ortho	
C22	8.2	1.4	2.9	33	173	tricl	
C23	7.3	1.2	2.8	16	31	ortho	
C24	10.5	1.3		38	201	tricl	
C31	10.1	1.4		13	183	ortho	
C32	13.9	1.6		17	391	monocl	
U-C20ª	3.4	3.9		11.0	16	hexag	
U-C21	3.4	5.4		8.6	15	hexag	
U-C22	3.4	4.0		10.5	18	hexag	

<sup>a</sup>U indicates urea inclusion complex.

rhombic) has 2-fold axis but there is no symmetry for an even alkane (triclinic). Thus it is expected that the barrier height for the restricted rotation of an odd alkane is considerably lower than that of an adjacent even alkane. Besides, the separation between the lamella of orthorhombic crystal is larger than that of the triclinic crystal and the molecular axis is parallel to the c axis in the case of odd alkanes but not in the case of even alkanes; thus the conformation of the chain end can be altered easier in the case of odd alkanes than in the case of even alkanes. These facts support our conclusion that the methylene chain of an even alkane is held tightly in the triclinic crystal, whereas some conformational change at the chain end or rotational oscillation along the molecular axis is allowed in the case of odd alkane in the ortho-

Schaerer et al. measured the transition enthalpy and the melting enthalpy of a series of purified alkanes<sup>7</sup> and showed that the sum of these two enthalpies changed in an alternating way when the data are plotted as the function of carbon number. This enthalpy change of even alkanes was a little larger (by several hundred calories) than those of adjacent odd alkanes. Because the enthalpy in the liquid state may change regularly as the carbon number, the enthalpy of a *n*-alkane in the triclinic state may be lower than that in the orthorhombic state. This may be related to the alternation of density: i.e., the density of an even alkane is larger than those of adjacent odd alkanes. Therefore, molecules in the triclinic crystal may be packed rather tightly compared with the orthorhombic crystal. This indicates the amplitude of the chain motion in the orthorhombic crystal may be larger than that in the triclinic crystal. This consideration also accords with our conclusion.

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# Evidence for Multiple CO Hydrogenation Pathways on Pt/Al<sub>2</sub>O<sub>3</sub>

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The reactivity of CO toward hydrogen over  $12\% Pt/Al_2O_3$  is examined by temperature-programmed reduction of adsorbed CO (CO TPR) and infrared spectroscopy. The CO TPR spectra show two methane formation rate maxima near 490 and 613 K. The relative intensities of these peaks depend on sample pretreatment temperature with the 490 K peak dominating with higher reduction temperatures. Infrared spectra show the CO chemisorbs molecularly on Pt at 300 K, but some bound CO is converted to alumina-bound methoxy species as the sample is heated to 400 K in H<sub>2</sub>. IR spectra recorded during CO TPR show the 490 K peak reflects hydrogenation of the surface methoxy to methane. The second CO TPR peak is due to methanation of the remaining CO on Pt.

The concept of site transfer has been introduced to explain the results of temperature-programmed experiments where a chemisorbed layer of CO on a supported metal is converted to methane in a H<sub>2</sub> stream.<sup>1</sup> Multiple methanation peaks are occasionally observed in these CO temperature-programmed reaction (CO TPR) experiments.<sup>2</sup> According to the site-transfer model, one or more of these peaks may be due to the hydrogenation of a *support-bound* species formed by reaction of hydrogen with CO originally chemisorbed on the supported metal.<sup>1,3</sup> The Ni/Al<sub>2</sub>O<sub>3</sub> system provides a good example of this process. Gluga et al. found that a Ni/Al<sub>2</sub>O<sub>3</sub> catalyst adsorbed 7 times more CO in H<sub>2</sub> at 385 than at 300 K.<sup>1a</sup> The Ni/Al<sub>2</sub>O<sub>3</sub> catalyst exhibited two CO TPR features near 420 and 520 K, but only the 520 K peak increased in magnitude when CO was adsorbed at the higher temperature. No increased CO adsorption was observed when He was used as a carrier instead of  $H_2$ . They suggested that some of the CO adsorbed on Ni at 300 K is converted to a support-bound species, possibly methoxy, as the sample is heated from 300 to ca. 400 K in  $H_2$ . More of these species form when the CO adsorption is carried out at a higher temperature in  $H_2$ . The lower temperature TPR feature was attributed to hydrogenation of CO bound to Ni while the higher temperature feature was assigned to the hydrogenation of the spilled-over oxygenate species.

Our own studies have focused on supported Pt. We find Pt/ $Al_2O_3$  can also exhibit two CO TPR peaks whose relative intensities depend on the CO adsorption temperature and the extent of surface hydroxylation. FTIR studies of the surface during CO adsorption and CO TPR show that the lower temperature peak corresponds to the hydrogenation of methoxy species spilled over to the support surface, while the higher temperature feature reflects hydrogenation of CO on Pt.

### **Experimental Section**

The sample used in this study is 12.4% Pt on aluminum oxide C (Degussa) prepared by incipient wetness methods using a solution of chloroplatinic acid in acetone. The powder was calcined

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Figure 1. CO TPR spectrum recorded in  $H_2$  at 35 K/min for CO adsorbed on 12% Pt/Al<sub>2</sub>O<sub>3</sub> at 300 K (solid curve) and 380 K (dashed curve).

 $(673 \text{ K}, \text{O}_2, 4 \text{ h})$ , then reduced  $(773 \text{ K}, \text{H}_2, 4 \text{ h})$ , and passivated in air prior to storage. The Pt dispersion is 0.25 according to H<sub>2</sub> chemisorption measurements made using the double-isotherm technique. Pulsed CO chemisorption and temperature-programmed CO hydrogenation studies were carried out in a specially designed unit that will be described in detail in another publication. The pulsing valve delivers 3  $\mu$ L of CO into a 20 cm<sup>3</sup>/min stream of  $H_2$  or He. Samples weighing 10 mg were used in these studies. In situ IR studies of self-supporting wafers were performed in a heated IR cell with CaF<sub>2</sub> windows described previously.<sup>4</sup> Spectra were recorded at a resolution of 4 cm<sup>-1</sup> by a Mattson Sirius 100 FTIR with an MCT detector. Sample spectra were ratioed against background spectra recorded on the clean, H<sub>2</sub>-reduced wafer at the same temperatures as the sample spectra were measured. All IR measurements were made in  $10 \text{ cm}^3/\text{min H}_2$  at atmospheric pressure.

#### **Results and Discussion**

Figure 1 shows the effect of varying the CO adsorption temperature on the temperature-programmed reduction of chemisorbed CO to methane (CO TPR). In this experiment a sample of Pt/Al<sub>2</sub>O<sub>3</sub> was reduced for 1 h at 673 K and saturated with CO at 300 K by introducing 30 CO pulses at 10-s intervals into the  $20 \text{ cm}^3/\text{min H}_2$  stream. No more CO was adsorbed after the 15th pulse, indicating the surface was saturated. Curve a represents the rate of methane production as the sample is ramped at 35 K/min to 840 K in  $H_2$ . This CO TPR curve is reproduced if the sample is next treated with 20 Torr of H<sub>2</sub>O in H<sub>2</sub> for 8 min at 300 K and then reduced at 673 K and saturated with CO as before. The reason for the water introduction step will be discussed later. The CO TPR curve b is generated if the CO is adsorbed at 373 K instead of 300 K. After curve a was measured, the sample was treated with 20 Torr of H<sub>2</sub>O in H<sub>2</sub> at 300 K for 8 min and then reduced at 673 K for 1.5 h. Thirty CO pulses were introduced into the  $H_2$  at 30-s intervals with the reactor at 373 K. The total CO chemisorbed at 373 K is 87.5 µmol/g vs 56.1 µmol/g at 300 K. The TPR peak at 493 K in curve a shifts to 533 K and increases in magnitude. The higher temperature peak near 583 K has not shifted but has grown in apparent intensity. (This may in part be due to increasing overlap with the lower temperature feature.) Hydrogen is required to effect these changes. When CO is adsorbed in He instead of  $H_2$ , the CO uptake and CO TPR curves are insensitive to adsorption temperature in the range 300-373 K. Finally, in  $H_2$  pure alumina adsorbs less than 1% of the CO adsorbed by  $Pt/Al_2O_3$  under these conditions.

In situ FTIR studies reveal the conversion of Pt-CO species to Al-OCH<sub>3</sub> sites as the sample is heated to 380 K in H<sub>2</sub>. They also show that, in contrast to the Ni/Al<sub>2</sub>O<sub>3</sub> case, the spilled-over oxygenate species are more reactive toward H<sub>2</sub> than is most of



Figure 2. (a)  $Pt/Al_2O_3$  saturated with CO in H<sub>2</sub> at 310 K. (b) Spectrum a after heating to 380 K in H<sub>2</sub>. (c) Spectrum b after exposure to CO pulses in H<sub>2</sub> at 380 K.

TABLE I: IR Data for Species Formed from CO +  $H_2$  on  $Pt/Al_2O_3$  at 300–380 K

adsorbate	obsdª	lit.	assignt	ref	
HCO <sub>2</sub>	1596	1597	$v_{as}(CO_2)$	5, 7	
	1380	13//	$v_{s}(CO_{2})$		
CH₃O	2962	2955	$v_{as}(CH_3)$		
	2848	2844	$v_{s}(CH_{3})$	6	
	1480	1472	$v_{as}(CH_3)$		
	1055	1075	(00)		
HCO3	1641	1641		5 10	
	1450	1451		5, 10	
	1220	1250			

<sup>a</sup> All frequencies in wavenumbers for adsorbed <sup>12</sup>C<sup>16</sup>O.

the CO on Pt. Figure 2a shows selected regions of the IR spectrum of  $Pt/Al_2O_3$  reduced in  $H_2$  at 593 K following saturation with pulsed CO in  $H_2$  at 310 K. Figure 2b is the spectrum of the same sample heated to 380 K in flowing  $H_2$ , and Figure 2c is the spectrum recorded after the sample was treated with 30 additional CO pulses delivered at 30-s intervals in  $H_2$  at 380 K. The Pt-CO bands in the 2200–1700-cm<sup>-1</sup> region are hardly affected by the different adsorption temperatures, but significant changes occur in the 3000–2700- and 1700–1000-cm<sup>-1</sup> regions when the sample is heated in  $H_2$  and then treated with CO in  $H_2$ .

In Table I we summarize the observed vibrational bands and our assignments for  ${}^{12}C^{16}O$  adsorbed in H<sub>2</sub> at 310-380 K on Pt/Al<sub>2</sub>O<sub>3</sub>. Bands due to bicarbonate (1641, 1450, and 1228 cm<sup>-1</sup>) and formate (1596 and 1380 cm<sup>-1</sup>) are observed when  ${}^{12}C^{16}O$  is adsorbed on Pt/Al<sub>2</sub>O<sub>3</sub> at 310 K. These species are also observed when thermally activated alumina is contacted with CO near room temperature.<sup>5,8,10</sup> As the sample is heated to 380 K in H<sub>2</sub>, the bicarbonate bands disappear and a new set of bands at 2962, 2848, 1480, and 1093 cm<sup>-1</sup> grow in. These bands are not observed on alumina without Pt. At the same time the integrated intensity of the Pt-CO bands decreases by 10%, suggesting the new species are formed by hydrogenation of CO originally bound to Pt. The intensities of the new IR bands increase further when CO is added in H<sub>2</sub> at 380 K (compare spectra b and c of Figure 2). The frequencies of these bands in  ${}^{12}C^{16}O$  are in good agreement with literature values for methoxy on alumina.<sup>6,7</sup> The methoxy C-O

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<sup>(9)</sup> The CH deformation (ca. 1390 cm<sup>-1</sup>) and the symmetric COO stretch (ca. 1375 cm<sup>-1</sup>) of formate are not always resolved when formate is generated from CO and  $H_2$  on alumina (see ref 8 and 10).

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0.6



Figure 3. Integrated intensities of the 2960-cm<sup>-1</sup> ( $\blacksquare$ ), 2848-cm<sup>-1</sup> (+), 1093-cm<sup>-1</sup> ( $\Delta$ ), and 2100-1900-cm<sup>-1</sup> ( $\diamond$ ) IR bands plotted vs temperature during CO TPR at 10 K/min from 390 to 580 K. For clarity, the areas of the first three bands have been multiplied by 10.

stretch (1093 cm<sup>-1</sup>) red shifts 21 cm<sup>-1</sup> when <sup>13</sup>C<sup>16</sup>O is adsorbed and 31 cm<sup>-1</sup> when <sup>12</sup>C<sup>18</sup>O is adsorbed. Those values are in excellent agreement with the shifts predicted by using the Redlich-Teller rule, 20 and 32 cm<sup>-1</sup>, respectively. The <sup>18</sup>O-labeling experiment also shows the C-O bond remains intact as carbon monoxide is converted to surface methoxy species.

Infrared spectra recorded during CO TPR show the methoxy species are the most reactive form of C on Pt/Al<sub>2</sub>O<sub>3</sub>. The sample whose spectrum is shown in Figure 2a was heated at 10 K/min in 10 cm<sup>3</sup>/min H<sub>2</sub> while 17 vibrational spectra (100 scans each) were averaged over 10-deg temperature intervals. The sample was then cooled at 10 K/min, and background spectra were averaged over the same temperature intervals. In Figure 3 we plot the integrated intensities of the CO/Pt manifold, the symmetric and asymmetric CH stretches, and the CO stretch for methoxy. That the methoxy IR bands do not appear to decline with parallel slopes is related to the difficulties in accurately integrating such weak absorption bands. However, it is clear from the plot that the CO/Pt bands are hardly attenuated until the methoxy species are exhausted near 485 K. The temperature where the methoxy bands become extinct closely correlates with the minimum observed in the CO TPR under these experimental conditions (i.e., at a heating rate of 10 K/min where the first CO TPR peak occurs at 455 K). This firmly establishes that the first CO TPR peak is due to the hydrogenation of surface methoxy groups. GC analyses of the gases evolved during CO TPR show no methanol is formed.

The formate bands first observed at room temperature are among the most stable surface species during CO TPR. These bands are observed up to 573 K in H<sub>2</sub> and disappear after the CO on Pt hydrogenates. They may in fact be responsible for the apparent growth observed in the second TPR peak when CO is adsorbed at 380 K vs 300 K. Very stable formate species have been observed by others in analogous experiments on Ni/Al<sub>2</sub>O<sub>3</sub> and during steady-state CO hydrogenation over alumina-supported Pd, Ru, and Rh.<sup>3,8,11-13</sup> We similarly find that formate species accumulate during steady-state CO hydrogenation over Pt/Al<sub>2</sub>O<sub>3</sub>. These species respond only over periods of hours to transient changes in the isotopic composition of the synthesis gas, indicating they are not particularly reactive under CO hydrogenation conditions.

We earlier alluded to the fact that the extent of surface hydration/hydroxylation influences the behavior of Pt/Al<sub>2</sub>O<sub>3</sub> in CO TPR. This is illustrated in Figure 4 where we show the CO TPR curves for a single  $Pt/Al_2O_3$  sample as a function of  $H_2$  treatment temperature. To eliminate any possible effects of partial Pt reduction, the sample was first reduced at 723 K. Curve a was



Figure 4. CO TPR curves at 35 K/min in H<sub>2</sub> for Pt/Al<sub>2</sub>O<sub>3</sub> recorded as a function of reduction temperature following exposure to  $H_2O$  vapor at room temperature. Reduction temperatures: (a) 723 K, (b) 523 K, (c) 573 K, (d) 673 K. See text for details of sample pretreatment.

measured after the sample was saturated with CO at 300 K. To rehydrate the sample, it was then treated with a 20 cm<sup>3</sup>/min stream of 20 Torr of H<sub>2</sub>O in H<sub>2</sub> for 8 min at 300 K. The sample was next reduced in  $H_2$  for 1 h at 523 K and then saturated with CO in  $H_2$  as before. The CO TPR curve b was then measured. Curves c and d were recorded following the same rehydration step, a 1-h reduction at 573 or 673 K and saturation with CO in  $H_2$ at 300 K. The total CO uptake did not vary by more than 2% in Figure 4a-d. We do not believe the rehydration/reduction sequences result in Pt oxidation. IR spectra of CO on samples reduced at 523 and 673 K are identical in the CO stretching region. Also, a curve similar to Figure 4a is produced when the sample is hydrated at room temperature, reduced at 523 K, and then dehydrated with He at 723 K.

The two TPR features near 613 and 493 K in Figure 4a-d are respectively referred to as the A and B peaks. The B peak dominates when samples are treated at temperatures greater than 673 K while the A peak dominates when samples are treated at 573 K or less. The IR data show the B peak represents the hydrogenation of surface methoxy species that form from CO on Pt as the sample is heated. The B peak appears at a temperature remarkably close to that observed by Gluga et al. (520 K at a heating rate of 42 K/min) for the hydrogenation of methoxy species during CO TPR on Ni/Al<sub>2</sub>O<sub>3</sub> catalysts.<sup>1</sup> The A peak is due to the hydrogenation of the remaining CO on Pt and formate on the support. We can understand the data in Figure 4 if we assume the formation or stabilization of the reactive methoxy species requires a vacant Al cation site on the surface. This is reasonable because the IR data show the O in CH<sub>3</sub>O comes from CO, not the support surface. The Al cations are formed when the surface dehydroxylates at high temperature. It is generally thought that this process begins to occur on alumina at temperatures greater than 473-523 K. In the extreme case of Figure 4a, there is a sufficient quantity of cation sites to accommodate nearly all the chemisorbed CO as methoxy species. In the case of the most hydroxylated sample (Figure 4b), virtually no Al cations are available so the CO must be hydrogenated via the higher energy A pathway. Due to temperature limitations, our IR/TPR studies were performed under conditions intermediate between those shown in Figure 4c,d. Here a fraction of the CO is first converted to methoxy and then hydrogenated.

This model also helps explain the increase in CO uptake and the accompanying increase in the B peak observed when CO is adsorbed near 373 K vs 300 K. The spectra in Figure 2 show the methoxy species form at a negligible rate at 310 K, but they do grow at the expense of the CO/Pt bands as the sample is heated to 380 K. CO adsorption sites are opened up on Pt as methoxy species spill over onto the support. The methoxy and CO band intensities become constant after 10 min in H<sub>2</sub> at 380 K. Further growth of the methoxy species requires the addition of more CO in H<sub>2</sub>. This may suggest the formation of methoxy on Pt requires

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a particular surface coverage in CO. The rate of methoxy formation in pulsed CO at 380 K may also be related to the rate of methoxy migration on alumina. That migration would generate a new Al cation site in the vicinity of the Pt particle. This site is required to accept newly formed OCH<sub>3</sub>.

At this stage our data do not tell us whether Al cation sites (or other "special" support surface sites) act as catalysts in the formation of methoxy or simply as reservoirs for methoxy species generated on the metal surface. According to one model, exposed cations on the support surface participate in CO hydrogenation catalysis over metals like Pt, Rh, and Pd by coordinating to the oxygen end of CO bound to the metallic particle.<sup>14-17</sup> The relationship of our results to this notion is not clear, because the CO hydrogenation reaction produces water over these metals and we have shown that water strongly inhibits the formation of methoxy by hydroxylating the Al cations. However, the support plays an important role in defining both the CO TPR behavior and steady-state CO hydrogenation rates over Pt. Vannice has shown the rate of CO hydrogenation over Pt/Al<sub>2</sub>O<sub>3</sub> is 20 times higher on a site-time-yield basis than over Pt powder.<sup>15,18</sup> In this context we find it noteworthy that no methanation peak appears in the CO TPR spectrum measured on a high-purity Pt powder characterized by ISS, XPS, and methanation kinetics.<sup>19</sup> In flowing  $H_2$  the adsorbed CO simply desorbs in a 200 K wide peak centered near 670 K. In accord with Vannice's results, the site-time-yield for CO hydrogenation is 40 times higher for the  $Pt/Al_2O_3$  than for the Pt powder at 520 K. From this it is not clear to us whether the higher activity of Pt/Al<sub>2</sub>O<sub>3</sub> should be associated with the CO TPR peak B that dominates on dehydroxylated surfaces or the peak A that dominates on hydroxylated surfaces. This issue is being addressed by comparing the CO TPR behavior of Pt on other supports as well as oxide-modified Pt powders.

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# Theoretical Studies of Bond Stretch Isomerism in Silabicyclobutanes

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The structures and relative energies of the bond stretch isomers of tetrasilabicyclo[1.1.0]butane (1), 1,2,3-trisilabicyclo-[1:1.0] butane (2), and 1,3-disilabicyclo[1.1.0] butane (3) are predicted at the GVB/3-21G\* level, with the  $\sigma$  and  $\sigma^*$  bridge bond molecular orbitals correlated in the GVB wave function. The transition-state structure and intrinsic reaction coordinate connecting each pair of bond stretch isomers are calculated. Two transition states joining the bond stretch isomers of 3 are located. The more stable isomer in all three molecules is the one with the longer bridge bond.

Tetrasilabicyclo[1.1.0]butane (1), the silicon analogue of bicyclobutane, has been the focus of several recent theoretical studies.<sup>1-6</sup> These studies have predicted the molecular and electronic structure, as well as strain energies<sup>1,2a,3-5</sup> and harmonic vibrational frequencies.<sup>6</sup> There have been several experiments aimed at the synthesis<sup>7</sup> and X-ray structure determination<sup>7c</sup> of derivatives of this molecule. Of particular interest is the recent discovery by Schleyer et al.<sup>1</sup> of the presence of two structures differing primarily in the length of the Si-Si bridge bond (2.485 and 2.974 Å, using a five-configuration MCSCF wave function with a 3-21G pseudopotential basis), the isomer with the longer bridge bond being 17 kcal/mol more stable than the short-bond structure. Subsequent calculations at the RHF/polarized splitvalence (SVP) basis set,<sup>2b</sup> RMP2/SVP-compact effective core potential (CEP-31G\*),<sup>4</sup> and MP4/6-31G(d) levels<sup>5</sup> predict the long bond isomer of 1 to be more stable than the short-bond

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counterpart by 2.9, 2.4, and 8.9 kcal/mol, respectively.

We report here the structures, relative energies, and transition states of the bond-stretch isomers of 1 and its 1,2,3-trisilabicyclo[1.1.0]butane [2] and 1,3-disilabicyclo[1.1.0]butane [3] analogues. (The long-bond isomer of 3 has been reported<sup>4</sup> to be more stable than the short-bond isomer by 24.5 kcal/mol, at the MP2/CEP-31G\* level.) 2 and 3 are derived from 1 by successive replacement of the peripheral silicon atoms with carbon. All structures have been computed at the GVB/3-21G\* level,<sup>8</sup> with

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