Evidence for a cation intermediate during methanol dehydration on Pt(110)

F. Thomas, C. Lu, I.C. Lee, N.S. Chen * and R.I. Masel **

Department of Chemical Engineering, University of Illinois, 600 S. Mathews, Urbana, IL 61801, USA

Received 8 September 2000; accepted 9 January 2001

Cations are thermodynamically stable on certain transition metal surfaces, but so far no one has determined whether cations are catalytic intermediates or merely spectators. In this paper TPD and HREELS are used to determine whether methoxonium cations ($[CH_3OH_2]^+_{(ad)}$) or closely related species are intermediates during the reaction $H_2 + CH_3OH \rightarrow CH_4 + H_2O$ on Pt(110). HREELS shows that the methoxonium cations are produced at the same temperature where reaction starts, and that the methoxonium cations decay in the same temperature range where the reaction stops, suggesting that methoxonium is a likely intermediate during the reaction. Replacement of CH_3OH with CD_3OH produces a 1.8-fold change in the yield of water and methane at 180 K due to a secondary kinetic isotope effect. The strong secondary kinetic isotope effect would be expected only if the reaction occurred via an S_N1 pathway with a fully ionized transition state with the positive charge on the carbon. Together the HREELS and TPD results provide strong evidence that reaction goes via a carbocation pathway, with methoxonium cations or some closely related species as likely intermediates. This paper demonstrates for the first time that carbocations can be reactive intermediates during reactions on metal surfaces.

KEY WORDS: carbocation pathway; cation intermediate; methanol dehydration; Pt(110)

1. Introduction

The purpose of this paper is to provide the first direct evidence that carbocations are catalytic intermediates on metal surfaces. In particular, we will provide data which support the idea that a cationic methoxonium $[CH_3OH_2]^+$-like species is an intermediate during the dehydration of methanol on Pt(110).

In the previous literature, the interaction of methanol with transition metals has been examined in great detail [1–4]. Generally, methanol adsorbs molecularly on most transition metal surfaces at 100 K. Upon heating the methanol usually sequentially dehydrogenates. In previous work, Wang and Masel [2–4] observed the sequential formation of methoxy (CH_3O), formaldehyde (CH_2O), formyl (CHO), and, finally, carbon monoxide (CO) during methanol dehydration on Pt(110). Under certain conditions the methanol can also react with hydrogen to form water and methane:

$$CH_3OH + H_2 \rightarrow CH_4 + H_2O \qquad (1)$$

Reaction (1) is called methanol dehydration, and it is found reproducibly on Pt(110) [5]. Some investigators have also observed reaction (1) on Pd(111) [6,7], but other investigators have not reproduced the findings [8,9].

One of the details is that the rate of methane formation depends on exactly how the layer is prepared, and the details of the pretreatment procedures. Those details make measurements difficult.

At present, the mechanism of reaction (1) is largely known. Years ago, Wang and Masel speculated that the reaction would occur via a simple bond scission, but that mechanism was not consistent with later data [5]. More recently, Chen et al. have speculated that reaction (1) could go via a carbocation pathway [10]. This was an unexpected proposal, because prior to their work, there was little evidence for carbocation intermediates on metal surfaces. A few groups had observed ionic species on metal surfaces [10–12,20–23] and years ago Anderson and Avery [13] had proposed that neopentane isomerization could go via a carbocation intermediate on platinum. Still, at this point, there was no published evidence that ions are catalytic intermediates during hydrocarbon reactions on metal surfaces.

Note, however, that methanol dehydration is known to go via a methoxonium ion intermediate on solid acids [14]. A typical mechanism is

$$CH_3OH + H^+ \rightarrow [CH_3OH_2]^+ \qquad (2)$$

$$[CH_3OH_2]^+ \rightarrow CH_3^+ + H_2O \qquad (3)$$

$$CH_3^+ + H_2 \rightarrow CH_4 + H^+ \qquad (4)$$

One can postulate a similar mechanism on a metal surface:

$$CH_3OH_{(ad)} + H_{(ad)} \rightarrow [CH_3OH_2]^+_{(ad)} + e^-_{(ad)} \qquad (5)$$

$$[CH_3OH_2]^+_{(ad)} \rightarrow [CH_3]^+_{(ad)} + H_2O \qquad (6)$$

$$[CH_3]^+_{(ad)} + e^-_{(ad)} \rightarrow CH_{3(ad)} \qquad (7)$$

$$CH_{3(ad)} + H_{(ad)} \rightarrow CH_4 \qquad (8)$$

where $e^-_{(ad)}$ is an electron deposited in a metal. Years ago, people had thought that reaction (5) was endothermic, so

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[*] Present address: Intel Corporation, Portland Technology Development, RA1-240, 5200 NE Elam Young Parkway, Hillsboro, OR 97124-6497, USA.

[**] To whom correspondence should be addressed.

1011-372X/01/0400-0167$19.50/0

it could not occur. However, several investigators [10–13] have shown that cation formation is thermodynamically feasible on certain faces of platinum. For example, in a previous paper we showed that methoxonium ion formation was about 46 kcal/mol exothermic on (1 × 1)Pt(110) [10]. Consequently, there is no thermodynamic limitation to prevent reactions (5)–(8) from occurring on a metal surface. Therefore, it seems feasible that methanol dehydration on metals could occur via a mechanism similar to that in reactions (5)–(8).

In previous papers we have provided EELS data in support of methoxonium formation [10]. Further, we have also shown that we can explain the available data on the difference in activity of different metal catalysts for methanol dehydration if we assume that the reaction goes via steps (5)–(8).

Of course, the fact that methoxonium exists on Pt(110) and that the data are consistent with a methoxonium ion intermediate does not prove that the methoxonium ion is a catalytic intermediate. The methoxonium ion could be merely a spectator. Therefore, there is a need for further work.

In this paper we will attempt to determine whether the methoxonium species observed spectroscopically is an intermediate during the dehydration of methanol. Our strategy will be to do careful EELS measurements to try to correlate the presence of methoxonium to rate data. We will also look carefully for a secondary kinetic isotope effect during the dehydration process since in the previous literature, the presence of a secondary kinetic isotope effect is often taken to be strong evidence for a fully charged carbocation intermediate [15–19].

There is an important detail in this experiment: we will actually be looking for methanol dehydration on (2 × 1) Pt(110). In previous papers we found that (2 × 1)Pt(110) is much less active than (1 × 1)Pt(110) for methanol dehydration [2–4]. One would not expect to observe a secondary kinetic isotope effect on (1 × 1)Pt(110) because the dehydration reaction is desorption limited but there is a chance of seeing a secondary kinetic isotope effect on (2 × 1)Pt(110). Generally, a clean (2 × 1)Pt(110) surface is inactive for dehydration [2,24] but some dehydration activity is seen when the surface is saturated with hydrogen. The dehydration process is reaction limited on the hydrogen saturated (2 × 1)Pt(110) surface. Consequently, if the dehydration process goes via a methoxonium intermediate, a secondary kinetic isotope effect should be seen on a hydrogen saturated (2 × 1)Pt(110) surface.

2. Methods

The apparatus and procedures have been described elsewhere [2–5,10]. The HREELS experiments were performed in a UHV chamber pumped by a diffusion pump and an ion pump. Its base pressure was 1×10^{-10} Torr. An LK2000 EELS spectrometer was used to make the HREELS measurements.

The TPD experiments were performed in a UHV chamber having a base pressure of 1×10^{-10} Torr. The chamber was pumped by a turbomolecular pump and was equipped with a PHI 4-161 sputter gun system, a PHI 10-155 Auger electron spectroscopy (AES) system, a Princeton reverse-view LEED, and a UTI-100C quadrupole mass spectrometer. The Pt(110) sample was the same sample used for the work in Wang et al. [2–5]. Prior to the experiments reported here, the sample was repolished with diamond paste and was oxidized in flowing oxygen and washed in dilute HF to remove residual calcium and silicon. The sample was then mounted in a tantalum wire and placed in the vacuum system. The sample was cleaned by heating in oxygen at 800 °C, annealing to 1000 °C, and sputtering with argon ions until no impurities could be detected in AES. In a TPD experiment, the sample was first cleaned by oxidizing and sputtering at 800 °C. The sample was then annealed for 3 min at 1000 °C, to repair sputtering damage, and put into a (2 × 1) reconstruction. The sample showed a hydrogen TPD spectrum characteristic of a well ordered (2 × 1)Pt(110) sample at this stage. The sample was cooled to 110 K and dosed with hydrogen and methanol by backfilling the chamber. Exposures were calculated using uncorrected ion gauge readings. The TPD heating rate was 15 K/s. Typically, the samples showed a mixture of (2 × 1) and (1 × 1) LEED patterns at the end of the TPD runs. However, the samples went back to (2 × 1) after cleaning and annealing.

3. Results

3.1. Further evidence for methoxonium ion formation

In a previous paper we provided evidence for methoxonium ion formation [10]. First it is useful to review those findings and expand on them so we can provide a basis for the current work. Figure 1(A) shows an EELS spectrum taken by exposing a clean (2 × 1)Pt(110) surface to 5 L of hydrogen at 273 K, cooling to 100 K, adsorbing 0.5 L of methanol, and scanning an EELS spectrum. There are peaks at 965, 1100, 1420, and 2980 cm^{-1}, smaller peaks at 790, 1950, 2560, and 3310 cm^{-1}, and shoulders at 1550 and 3190 cm^{-1}. Figure 1(B) shows a subsequent spectrum taken by flashing the surface in figure 1(A) to 180 K for 1 min and cooling back to 100 K and then scanning an EELS spectrum. There are new peaks at 450, 1550, 2060, 3320, and 3420 cm^{-1}, and minor shifts in the other peak positions. The shoulders at 1740, 1300, 2850, and 3110 cm^{-1} also become separate peaks. Note, however, that the scale is a factor of 10 different in figure 1 (A) and (B). The peaks at 1740 and 2060 cm^{-1} are probably associated with production of CO and have been enhanced because the scale was increased by a factor of 10.

The presence of extra peaks at 450, 1550, 3320, and 3420 cm^{-1}, however, is strong evidence that some new species is forming during methanol and hydrogen coadsorption on (2 × 1)Pt(110).

Table 1 compares the peak positions in figure 1 to those expected for methanol, methoxonium cations, and several other species. Notice that the 100 K spectrum in figure 1(A) is similar to that expected for methanol, except that there is an unexpected shoulder at 1550 cm^{-1}. However, the spectrum in figure 1(B) contains peaks not expected for methanol.

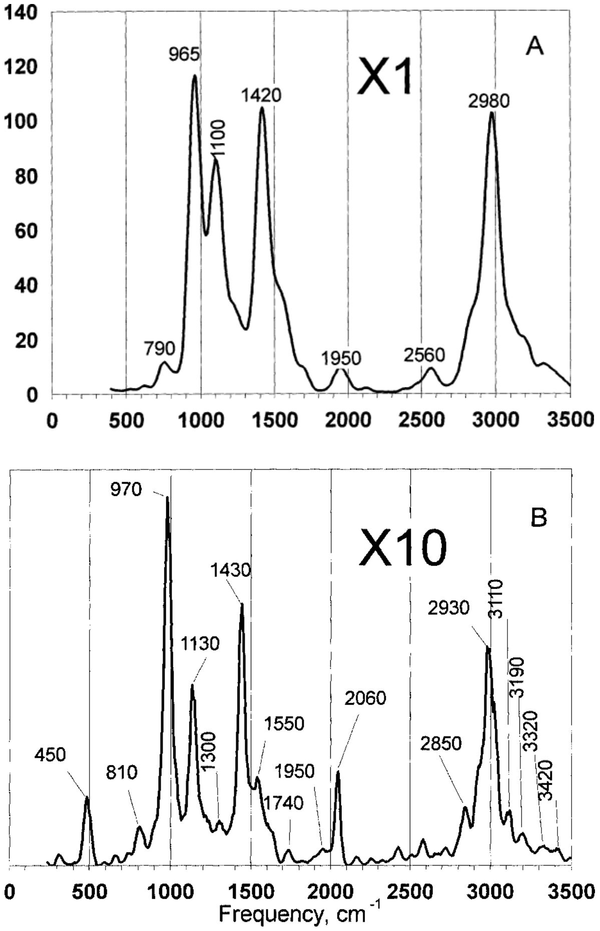

Figure 1. (A) An EELS spectrum taken by adsorbing 3 L of hydrogen on a 273 K Pt(110) sharply cooling to 100 K, adding 1 L of methanol and scanning. (B) An EELS spectrum taken by flashing the sample in a 180 K and cooling to 100 K.

Table 1 shows the expected spectrum for several other species. Of the species considered, only methoxonium cations show the peaks at 810 and 1600 cm^{-1}. In previous work [10], we have also carefully examined the shifts in the peak positions with deuteration, and found good agreement between our measured spectra and those calculated for methoxonium ions. We also considered dozens of other species and did not find good agreement with the HREELS spectra. There are a series of carbocations of the form $[(CH_3OH)_nCH_3OH_2]^+$ all of which would be expected to have HREELS spectra similar to those of methoxonium. Consequently, we cannot tell whether we are observing methoxonium cations or a species of the form $[(CH_3OH)_nCH_3OH_2]^+$. Still, the spectroscopic evidence suggests that a methoxonium cation, or some other closely related species forms during methanol and hydrogen coadsorption on (2 × 1)Pt(110).

3.2. TPD of methanol and hydrogen on Pt(110)(2 × 1)

Next we want to use TPD to see if the methoxonium ions are important intermediates during methanol dehydration on Pt(110) or merely spectators. The experiment will compare the dehydration of methanol and CD_3OH to look for a secondary kinetic isotope effect.

Consider the two overall reactions:

$$CH_3OH + H_2 \rightarrow CH_4 + H_2O \quad (1)$$

$$CD_3OH + H_2 \rightarrow CD_3H + H_2O \quad (9)$$

If reactions (1) and (9) go via reactions (5)–(8) with reaction (6) rate determining, the hybridization of the carbon atom will change from sp^3 to sp^2 during the rate-determining step. The change in hybridization shifts the wagging modes

Table 1
A comparison of the vibrational features observed here to those in previous papers.

Methanol and H_2 on Pt(110)		Solid methanol	Methanol		$[CH_3OH_2]^+$	CH_3OH_2	CH_2O	CH_3O	HCO	HCOH
Figure 1(A)	Figure 1(B)	[25]	On Pt(110) [5]	On Pt(111) [26]	[27]	radical [27]	[27]	[27]	[27]	[27]
–	450	–	–	–	–	–	–	–	–	–
790	810	730	740	680	810	860	–	653	–	–
965	970	1032	1060	970	914	944	–	1047	–	1003
1100	1130	1124	1135	–	1125	1077	1187	–	1087	1188
–	1300	–	–	–	1258	–	1249	1362	–	1286
1420	1430	1453	1470	1830	1438	1388, 1490	1500	1497	–	1436
–	1550	–	–	–	1616	–	1748	–	–	–
1950	1950	–	–	–	–	–	–	–	1868	–
2560	2850	2822	2590	–	–	2875	2840	2840	2435	2745
2980	2930	2928	2960	2930	3006	2990, 2957	2953	–	–	–
–	3110	–	3275	–	3137	–	–	–	–	–
3190	3190	3187	–	–	3191	–	–	–	–	–
3310	3320	3284	3320	3320	3499	–	–	–	–	–
–	3420	–	–	–	3585	–	–	–	–	3495
–	–	–	–	–	–	4259	–	–	–	–

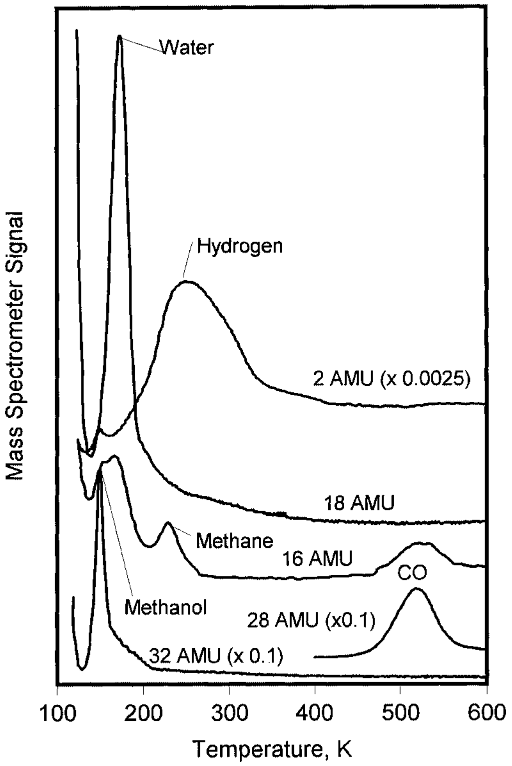

Figure 2. A composite TPD spectrum taken by exposing a clean 110 K (2 × 1)Pt(110) sample to 5 L of hydrogen, adding 1 L of methanol and then heating at 15 K/s. The scale factors in the figure are the raw scale factors, uncorrected for differences in mass spectrometer sensitivity.

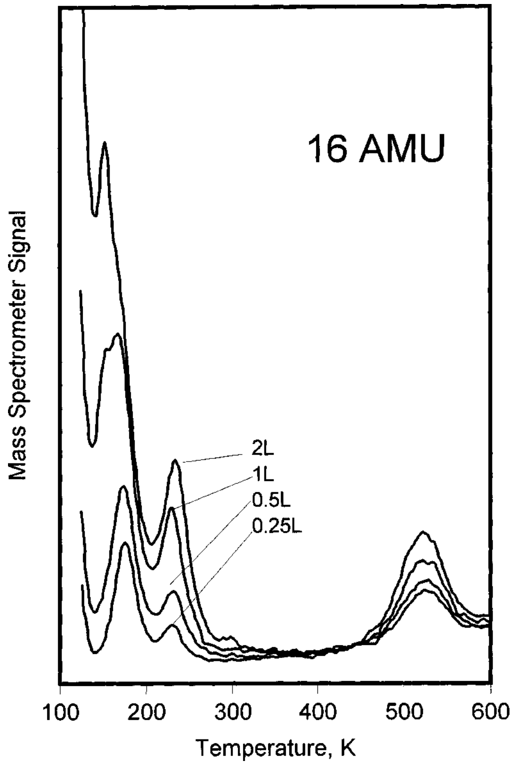

Figure 3. A series of 16 AMU TPD spectrum taken by exposing a clean 110 K (2 × 1)Pt(110) sample to 5 L of hydrogen, adding various amounts of methanol and then heating at 15 K/s.

of the hydrogen. This lowers the barrier. The lowering of the barrier is smaller with deuterated species. Consequently, if reactions (1) and (9) occur via steps (5)–(8) with reaction (6) rate determining, one would expect reaction (9) to be slower than reaction (1). In contrast, if reaction (6) is not rate determining, or if the overall reaction goes via a CH_3 radical or some other species where the hybridization of the CH_3 is preserved, one would not expect to observe a secondary kinetic isotope effect.

Experimentally Maskill finds that reactions which go via an S_N1 pathway through a fully-charged transition state show a secondary kinetic isotope effect of a factor of 1.2–1.3 at 300 K and a factor of 1.4–1.8 at 150 K [15]. In contrast, reactions going via an S_N2 pathway, or those involving neutral species usually show a rate which changes by at most a factor of 1.05 [15–17]. Consequently, one can use the presence of a secondary kinetic isotope effect as strong evidence for an S_N1 reaction.

Figure 2 shows TPD spectra taken by exposing a clean (2 × 1)Pt(110) surface at 110 K to 5 L hydrogen, adding 1 L of methanol, and then heating at 15 K/s. There is a methanol desorption peak at 150 K, a hydrogen desorption peak at 250 K, a water desorption peak at 180 K, a methane desorption peak at 230 K, and a carbon monoxide desorption peak at 520 K. We only show a small fraction of our data in figure 2, but the identities have been confirmed by carefully examining the cracking patterns as a function of coverage at each temperature.

We have also carefully searched for other species. Under some conditions we can also detect a small amount of dimethyl ether desorption.

Analysis of the data in figure 2 indicates that the hydrogen-covered (2 × 1)Pt(110) surface is only mildly active for methanol decomposition. We observe about 9% as much methane on the hydrogen covered sample (2 × 1)Pt(110) as we observed previously on (1 × 1)Pt(110). Still this is enough that we can do meaningful measurements. There is one other detail of note: the LEED pattern shows considerable disorder after adsorption of hydrogen and heating. Consequently, it is unclear that the methane is being produced on a true (2 × 1) layer. Instead the methane might be formed on a disordered area of the sample. We have also done experiments for methanol alone. In that case, we only observe CO and H_2 desorption in agreement with our previous work [2–5].

Figure 3 shows the evolution of the 16 AMU peak with coverage. At an exposure of 0.25 L, we observe distinct peaks in the 16 AMU spectrum at 180 and 230 K corresponding to desorption of water and methane. The peaks grow with increasing coverage but the ratio of the peaks does not change. Then at higher exposures, another small peak appears at 150 K corresponding to a cracking fraction of methanol. That peak grows with exposure and is exceptionally sharp.

Figure 4 shows the corresponding 18 AMU peaks. A single peak that shifts from 180 to 160 K with increasing methanol exposure is seen.

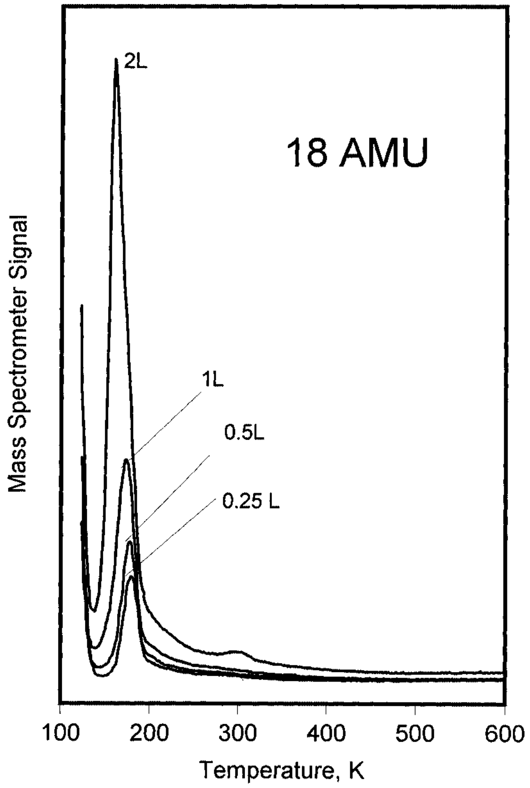

Figure 4. A series of 18 AMU TPD spectrum taken by exposing a clean 110 K (2 × 1)Pt(110) sample to 5 L of hydrogen, adding various amounts of methanol and then heating at 15 K/s.

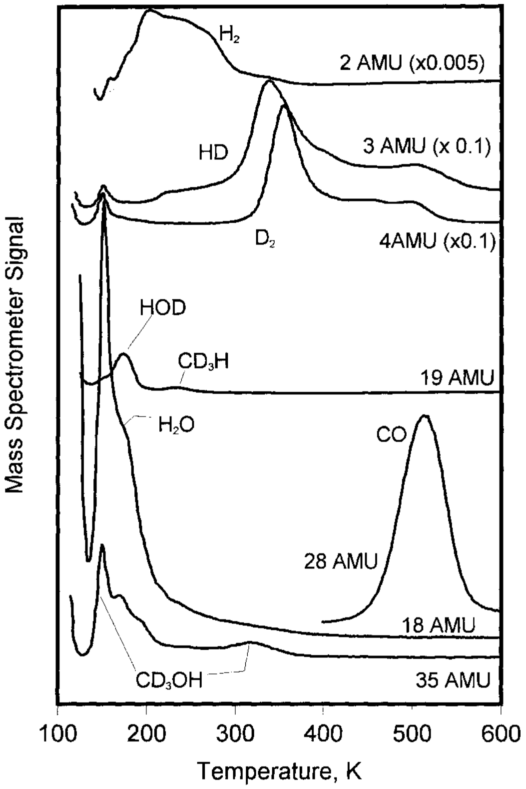

Figure 5. A composite TPD spectrum taken by exposing a clean 110 K (2 × 1)Pt(110) sample to 5 L of hydrogen, adding 1 L of CD_3OH and then heating at 15 K/s.

Figure 5 is a series of TPD spectra taken by dosing 5 L of H_2 then 1 L of CD_3OH onto a clean (2 × 1)Pt(110) surface, and then heating at 15 K/s. The 35 AMU spectrum contains a sharp peak at 150 K, a shoulder extending up to 240 K and a second peak at 320 K. The 18 AMU spectrum shows a peak at 150 K corresponding to a cracking fragment of CD_3OH, and a smaller peak at 180 K associated with water desorption. Analysis on an expanded scale shows that a tiny peak is present at about 220 K corresponding to a cracking fraction of CD_3H. The 19 AMU spectrum shows a peak at 180 K corresponding to HOD desorption and a feature at 230 K corresponding to CD_3H desorption.

Figure 6 compares the 19 AMU spectrum produced by dosing 5 L of H_2 then 1 L of CD_3OH onto a clean (2 × 1)Pt(110) surface and then heating at 15 K/s to the 16 AMU spectrum taken by dosing by dosing 5 L of H_2 then 1 L of CH_3OH onto a clean 2 × 1)Pt(110) surface, and then heating at 15 K/s. There is clearly much less methane desorption in the former case than the latter. Comparing the peak areas subtracting off our measured cracking pattern for CH_3OH and CD_3OH, and making a small adjustment for the difference in the reported cracking patterns of CH_4 and CD_3H shows that about a factor of 1.8–2.0 more methane is produced during the dehydration of CH_3OH than during the dehydration of CD_3OH. We have also performed similar calculations at several coverages and always find that there is about a factor of two less methane with CD_3OH than with CH_3OH.

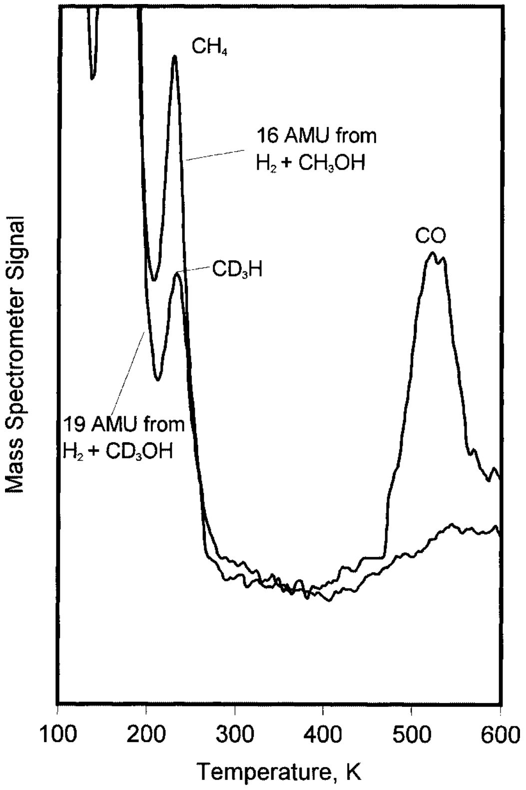

Figure 6. A comparison of the methane peak at 16 AMU produced during the coadsorption of CH_3OH and H_2 to the CD_3H peak at 19 AMU during the coadsorption of CD_3OH and H_2.

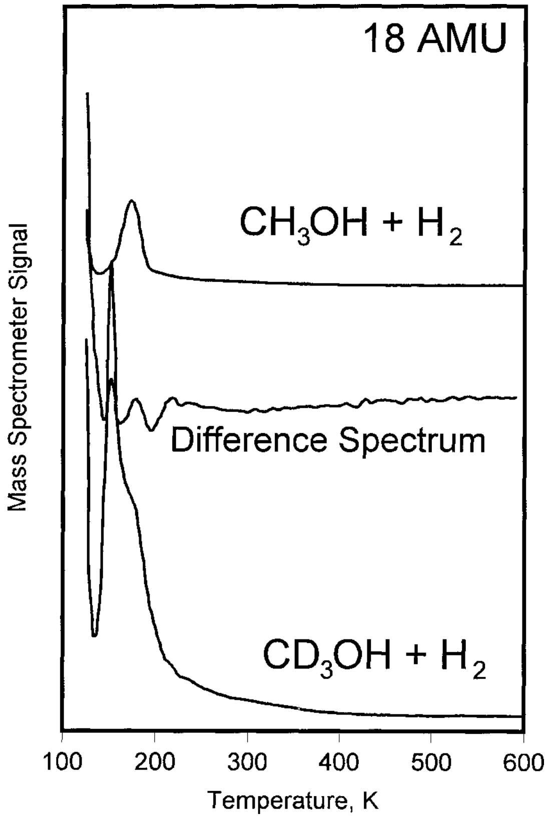

Figure 7. A comparison of the 18 AMU H_2O produced during coadsorption of $CH_3OH + H_2$ and $CD_3OH + H_2$. A difference spectrum taken by starting with the 18 AMU spectrum for $CD_3OH + H_2$, and subtracting away our measured cracking fraction of CD_3OH at 18 AMU is also shown.

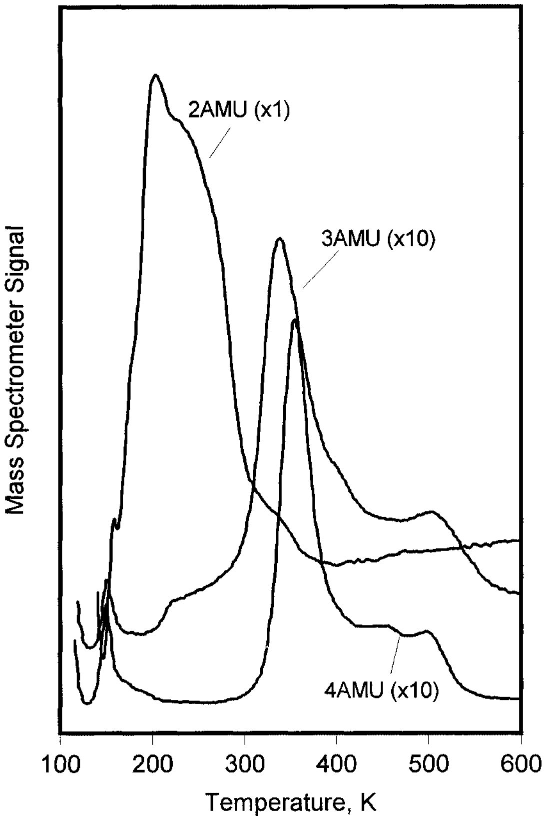

Figure 8. The 2, 3 and 4 AMU spectra taken by exposing a clean 110 K (2 × 1)Pt(110) sample to 5 L of hydrogen, adding 1 L of CD_3OH and then heating at 15 K/s.

Figure 7 compares the 18 AMU (water + CD_3OH cracking) TPD spectrum taken by adsorbing 5 L of H_2, 1 L of CD_3OH and then heating at 15 K/s to the 18 AMU (water) TPD spectrum taken by adsorbing 5 L of H_2, 1 L of CH_3OH and then heating at 15 K/s. The $H_2 + CH_3OH$ spectrum shows a single peak at 180 K associated with water desorption. The $H_2 + CD_3OH$ spectrum shows a peak at 150 K associated with CD_3OH desorption and a shoulder at about 180 K associated with water desorption.

Figure 7 also shows a difference spectrum taken by starting with the 18 AMU spectrum from coadsorbed H_2 and CD_3OH and subtracting away the portion of the 18 AMU spectrum expected for CD_3OH cracking. The difference spectrum was calculated by first measuring the cracking pattern of methanol in our chamber. We then measured an 18 AMU spectrum and a 32 AMU spectrum in sequential runs. The 32 AMU peak was multiplied by the intensity of the methanol cracking pattern at 18 AMU, and the result was subtracted from our 18 AMU spectrum.

There is a small residual peak in the difference spectrum at 150 K, suggesting that we might not have had exactly the same dose on the sample in the two sequential runs used to compute the difference spectrum. However, while the size of the 150 K peak is very sensitive to the dosing conditions, the shoulder near 200 K does not change significantly with coverage in this coverage range. Consequently, a small dosing error does not produce significant error in the size of the D_2O peak. The difference spectrum shows a peak at 150 K, for residual CD_3OH, and a peak at 180 K for H_2O. Notice that the water peak in the difference spectrum is considerably smaller than the water peak from coadsorbed H_2 and CH_3OH. We calculate that the H_2O peak is a factor of 2 to 2.2 smaller with coadsorbed H_2 and CD_3OH than from coadsorbed H_2 and CH_3OH. In the CD_3OH case there is also some HOD formed via an exchange mechanism; we do not detect D_2O. After adding up all the peaks we find that the H_2O peak seen during the dehydration of CH_3OH is about 1.7–1.8 times the sum of the H_2O and HOD formed during the dehydration of CD_3OH. There is considerable uncertainty in these numbers because of the uncertainties in computing a difference spectrum. Still, the results show that we produce considerably less H_2O when we coadsorb H_2 and CD_3OH than when we coadsorb H_2 and CH_3OH.

There also is some evidence for H/D exchange. Figure 8 shows a series of 2, 3, and 4 AMU spectra taken by dosing 5 L of H_2 and then 1 L of CD_3OH and heating at 15 K/s. Generally, the 2 AMU peak is about a factor of 10 larger than the 3 and 4 AMU peaks. The 2 AMU spectrum shows a broad H_2 desorption peak centered at about 200 K and a shoulder at about 280 K. The 3 AMU spectrum shows HD desorption peaks at 240, 340, and 500 K. The 4 AMU spectrum shows D_2 desorption peaks at 353 and 500 K. Note that if H/D exchange was rapid, the 2, 3, and 4 AMU peaks should all track each other. However, the 2 AMU peak does not track the 3 or 4 AMU peak below 240 K. Consequently, it does not appear that there is significant H/D exchange below 240 K. The 3 and 4 AMU peaks track each other above 270 K, and there are smaller 2 AMU peaks in the same temperature range. Consequently, the implication of figure 7 is that the H/D exchange is slow at temperatures up to 240 K, but the exchange process becomes more rapid at higher temperatures.

4. Discussion

The results here provide strong evidence that methoxonium cations are key intermediates during methanol dehydration on Pt(110). We observe a factor of 1.8 reduction in the dehydration rate when we change from CH_3OH to CD_3OH. Such a change is characteristic of a secondary kinetic isotope effect, of the type often used to prove that the rate-determining step in a reaction is an S_N1 process with a fully ionized carbocation intermediate [16]. Further, in previous work [10], we observed formation and decay of methoxonium in just the same temperature range that dehydration occurs. Together, these two measurements provide strong evidence that methoxonium is an intermediate during methanol dehydration on platinum.

Next, it is useful to focus on our observation that the yield of methanol dehydration is reduced by a factor of 1.8 when we change from CH_3OH to CD_3OH. We observe a factor of 1.8 reduction in the net water production and a factor of 1.9 reduction in the net methane production when we switch from CH_3OH to CD_3OH. In the latter case, our main products are H_2O and CD_3H. We do not detect CD_4 and detect only a small amount of HOD. Therefore, we are changing the rate by deuterating the methyl group. Such a change is characteristic of a secondary kinetic isotope effect.

It is also important to check that deuterium is not a direct participant in the reaction. Recall that if there was significant amount of H/D exchange, then one could form HOD via an S_N2 reaction:

$$CD_3OH_{(ad)} + D_{(ad)} \rightarrow [CD_3OHD]^+_{(ad)} \tag{10}$$

$$[CD_3OHD]^+_{(ad)} + e^-{}_{(ad)} \rightarrow CD_{3(ad)} + HOD \tag{11}$$

Reaction (10) could show a primary isotope effect. Further, if a significant amount of methanol reacted via reaction (10), there would be less methanol to react via reaction (9), so the rate of reaction (9) would be reduced.

The data show, however, that reactions (10) and (11) do not occur at a substantial rate. Figure 5 shows that the HOD formation is only a small fraction of the total water production, so reaction (10) could not be depleting a significant amount of the methanol. Further, figure 7 shows that little HD desorbs below 210 K (i.e., in the temperature range where water forms) even though H_2 desorbs so the H/D exchange rate is likely to be small. Reaction (10) does not appear to be occurring at a substantial rate. Therefore, the difference in rate that we observe when we switch from CH_3OH to CD_3OH must be associated with a secondary kinetic isotope effect.

Next we want to consider the implications of a secondary kinetic isotope effect of a factor of 1.8. Secondary kinetic isotope effects are subtle. When we switch from CH_3OH to CD_3OH we are not changing the molecule significantly. According to Maskill [15] and Collins and Bowman [16], S_N1 reactions with fully charged transition states with the charge on the carbon show large secondary kinetic isotope effects, but other reactions do not show large secondary isotope effects. At room temperature, Banks et al. measure a factor of 1.2–1.3 change in rate for a series of S_N1 reactions where a fully ionized carbocation forms [18]. In contrast, S_N2 reactions and reactions involving an uncharged species show at most a factor of 1.05 in rate due to a secondary kinetic isotope effect [16–18]. Banks et al. do not present any measurements below 274 K, so one does not know how large an effect will occur. However, if we extrapolate their data using the model in Maskill [15], we find that one would expect a factor of 1.4–1.8 change in rate if the dehydration process goes via an S_N1 reaction with a fully ionized carbocation intermediate. In contrast, the rate should change by at most a factor of 1.1 if the reaction goes via an S_N2 pathway or an uncharged intermediate [16–18]. We observe a factor of 1.8 change in rate. Therefore, it is clear that the rate-determining step in methanol dehydration on Pt(110) is an S_N1 process with a cationic transition state starting with a cationic intermediate. Further, even if there is an error in our measurements and the change in rate were only a factor of 1.4, we would still conclude that the rate-determining step in methanol decomposition on Pt(110) is an S_N1 process with a cationic transition state.

Further we note that the secondary isotope effect occurs upon deuterating the carbon. Therefore, the transition state must have a positive charge on the carbon. Consequently, we conclude that the transition state is a true carbocation and not simply a cation with charge elsewhere on the molecule.

Next we want to consider the likely intermediates during the reaction. Note that the rate-determining step in the dehydration process must produce methyl cations. We observe a factor of 1.8 change in the rate of water formation upon deuteration of the methyl groups. That would only occur if CH_3^+ was forming during the rate-determining step of the dehydration process [16,17]. Similarly, we suggest that water is probably produced in the rate-determining step of the dehydration process. We observe water desorption at 180 K. In contrast, when we coadsorb water and methanol, the water desorbs at about 170 K. Consequently, the formation of water in the data in figure 2 must be largely reaction limited. Therefore, it seems likely that water is being produced in the rate-determining step of the methanol dehydration process.

One can imagine a series of possible S_N1 reactions forming water, methyl cations, and possibly other species. All of the reactions must be of the form $(CH_3)(OH_2)R \rightarrow CH_3^+ + H_2O + R$ in order to yield CH_3^+ and H_2O. Only water, methanol, and a trace of dimethyl ether desorb below 200 K. Consequently, there are not very many possible reactions.

The only feasible possibilities that we have been able to find are:

$$[CH_3OH_2]^+ \rightarrow CH_3^+ + H_2O \quad (3)$$

$$[(CH_3OH)_n(CH_3)(OH_2)]^+ \rightarrow CH_3^+ + H_2O + nCH_3OH \quad (12)$$

Both reactions start with methoxonium-like intermediates. Therefore, the TPD data provide strong evidence that the rate-determining step during methanol dehydration on Pt(110) is an S_N1 process starting with a methoxium intermediate or some closely related species.

The spectroscopic evidence is consistent with this view. Figure 1 and table 1 summarize our results. We observe a species in EELS which has a vibrational spectrum consistent with that expected for methoxonium cations. The spectra are not consistent with methoxonium radicals or, for example, a mixture of formaldehyde and water. In a previous paper we also compared to 23 other species and found good agreement only with methoxonium cations or some closely related species, e.g. $[(CH_3OH)_nCH_3OH_2]^+$. The data in figure 1 provide spectroscopic evidence that methoxonium ions form at the same conditions where methanol dehydration occurs on Pt(110).

In other data [10], we found that the methoxonium ions start to form at 110 K and decay between 150 and 200 K. That is the same temperature range where we observe water formation. Our evidence, therefore, is that methoxonium ions start to form below where water production starts and the methoxonium ions decay when the water production stops. Thus our EELS data is largely consistent with the idea that the reaction goes via a methoxonium intermediate.

There is a detail that might be inconsistent with the idea that methoxonium is an intermediate in the dehydration process: in unpublished work, we have observed a small amount of methoxonium after heating the surface to 210 K, and then cooling back to 100 K, even though most of the water desorbs below 200 K. Still, there is some water desorbing at 210 K. The majority of the methoxonium disappears over the same temperature range where water forms. This coupled with the observation of a strong secondary kinetic isotope effect is strong evidence that the methoxonium is an intermediate during methanol dehydration.

Our conclusion, therefore, is that methanol dehydration goes via a methoxonium carbocation intermediate or some closely related species on Pt(110). We observe a secondary kinetic isotope effect, characteristic of an S_N1 reaction with a carbocationic transition state. We also observe a species in HREELS whose spectrum matches that expected for methoxonium cations, and the species forms and decays in the right temperature range. Given this evidence, it seems that the dehydration process must occur via a methoxonium intermediate or some closely related species. These results are strong evidence that cations, and in particular carbocations can be intermediates during reactions on metal surfaces.

5. Implications

Next we want to change topics, and look at the bigger implications of the findings here. The data here provide the first strong evidence that a cation is an intermediate during a reaction on a metal surface. Previous investigators [10–12,20,21] had observed ionic species on metal surfaces, but no one had shown that the ionic species were important catalytically. This paper provides the first evidence that a cation is an intermediate during an important catalytic reaction. Clearly this is an important finding.

The question, then, is whether it is a general finding, or this is just a special case. At this point we do not know. Years ago, Anderson and Avery proposed that carbocations are important intermediates during hydrocarbon isomerization [13]. In particular, they could explain why platinum behaves differently than palladium, based on the presumption that carbocations could form on platinum and the theoretical finding that carbocations should be more stable on platinum than on any other metal.

Our work shows that cations do form on platinum, and the cations can be intermediates during reactions on metal surfaces. We show that the transition state for methanol dehydration is a carbocation. Consequently, Anderson and Avery may have been right that carbocations can be important intermediates on metal surfaces.

Before we follow this reasoning too far, we want to note that we chose the case where we thought there was the highest probability of detecting a carbocation intermediate. Carbocations would be expected to be more stable on platinum than on almost any other transition metal. Platinum has the highest electronegativity of all of the transition metals, and one of the lowest binding energies for hydrogen. Consequently, the thermodynamics of carbocation formation are more favorable on platinum than on any other metal. (1×1)Pt(110) is special in that it is the most electronegative face of platinum, and it also has one of the lowest binding energies for hydrogen. As a result the thermodynamics of cation formation are especially favorable on Pt(110).

There is nothing special about the stability of methoxyonium, though. Many carbocations are much more thermodynamically stable than methoxonium. Methoxonium is one of the few cations that has a distinct vibrational spectrum so it is easier to detect than other possible cations. Still, methoxonium is not particularly stable. Consequently, one might expect carbocations to be stable on platinum and other closely related metals, e.g., iridium.

6. Conclusions

In summary then, in this paper TPD and HREELS were used to determine whether methoxonium is an intermediate during methanol dehydration on Pt(110). We find that the rate of water and methane production is reduced by about a factor of 1.8 when we switch from CH_3OH to CD_3OH due to a secondary kinetic isotope effect. Previous literature shows that secondary kinetic isotope effects this large are seen only in S_N1 reactions with fully ionized transition states. The data show that water desorption is reaction rate limited, so the rate-determining step must involve water formation. The presence of the secondary kinetic isotope effect upon deuteration of the methyl groups shows that methyl cations are also produced in the rate-determining step. From a mass balance we need to start with a moiety with a stoichiometry of $[CH_3OH_2]^+$ to end up with CH_3^+ and H_2O. Consequently, our TPD data provide strong evidence for a methoxonium-cation intermediate during the methanol decomposition process.

The EELS data are consistent with this view. We observe a species with an EELS spectrum consistent with that expected for methoxonium cations and the species forms and decays in the right temperature range.

Together, the TPD and HREELS data provides strong evidence that methanol dehydration occurs via a methoxonium-cation intermediate or closely related species on Pt(110).

Acknowledgement

This work was supported by The Department Of Energy under grant DEGF-02–99ER14993.

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