

Reactivity of Methoxy Species toward CO on Keggin 12-H₃PW₁₂O₄₀: A Study with Solid State NMR

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By using ¹³C solid-state NMR, monitoring the reactivity of methoxy species with carbon monoxide has been performed on 12-tungstophosphoric acid, H₃PW₁₂O₄₀, at 423–473 K. Surface methoxy species have been selectively prepared from methanol at 293–423 K. Almost quantitative conversion of surface methoxy species into acetyl groups bound to the Keggin anion and acetic acid has been observed at 473 K. These data provide unambiguous evidence for the role of methoxy species as the intermediate of methanol and dimethyl ether carbonylation on solid H₃PW₁₂O₄₀. The formation of a trimethyloxonium ion has been detected on the surface of heteropolyacid for the first time. The carbonylation of trimethyloxonium proceeds via the analogous mechanism through the methoxy species intermediate.

Introduction

Direct monitoring of the evolution of the surface intermediates by spectroscopic methods represents a challenge for heterogeneous catalysis by solid acids. It provides a basis for elucidation of the mechanisms of reactions, including the use of the observed intermediates for justification of theoretical calculations of the reaction pathways.

The formation of methoxy species as a stable intermediate on acidic zeolites^{1–5} and heteropolyacids⁶ has been shown by ¹³C MAS NMR, and its high reactivity toward different probe molecules on acidic zeolite catalysts was clearly demonstrated.⁷

Since the first report by Fujimoto et al.⁸ on vapor phase methanol carbonylation on solid acid catalysts, an intermediate role of surface methoxy species in the methanol carbonylation reaction is generally accepted.^{9–11} According to the mechanism of the classic Koch reaction of olefins (or alcohols), carbonylation with CO, the interaction of methoxy species CH₃O– as a stabilized methyl cation with CO, produces acylium cation CH₃–C⁺=O.¹² An interaction of the latter cation with water gives acetic acid. Alternatively, on solid acid catalysts the interaction of CH₃O– with CO offers the acetyl group bound to the surface of the catalysts, CH₃COO–, implying a direct insertion of CO into the C–O bond of the methoxy species. This hypothesis required experimental verification. Therefore, the mechanism of methanol (or dimethyl ether, DME) carbonylation on acid zeolite catalysts has been studied for the last few years by experimental^{11,13,14} and theoretical methods.¹⁵ Jiang et al.¹⁰ tested the reactivity of DME to CO with solid-state NMR and observed the formation of a final reaction product, acetic acid. Neither the acylium cation nor the acetyl group bonded to the zeolite were identified. Cheung et al.¹¹ tried to follow the elementary steps in DME carbonylation on acidic zeolites by means of kinetic, IR, and desorption experiments. They were

able to detect the formation of some undesorbed species on the zeolite surface. These species were assigned to surface methoxy species and acetyl groups. They further demonstrated a reactivity of acetyl groups toward DME to form methylacetate. However, no evidence was provided for the occurrence of the probable key stage of the carbonylation, the insertion of carbon monoxide into the C–O bond of the surface methoxy species to form an acetyl group bound to the surface of the solid acid catalyst.

Monitoring the reactivity of the methoxy species on zeolites is usually complicated by the impossibility to remove completely the other species from the catalyst surface, which are not chemically bound to the surface, including residual methanol, DME, and water, even at an elevated temperature up to 473 K.⁵ So, the observation of surface methyl or acetyl fragments, which withstand desorption, by IR spectroscopy¹¹ represents debatable evidence for the formation of methyl or acetyl groups attached to the zeolite framework. Indeed, a variety of possible CH₃O– or CH₃COO– species should offer the similar resonance patterns in IR spectra.

In this paper we report that methoxy species can be selectively generated on the surface of a solid acid catalyst, 12-tungstophosphoric acid, 12-H₃PW₁₂O₄₀, from methanol in the absence of other reaction products, DME, and residual CH₃OH. With the use of ¹³C solid-state NMR, we provide the first direct monitoring of the conversion of surface methoxy species into surface acetyl groups under the interaction of MeO– with CO. The rate-determining role of this step in Koch-type methanol carbonylation has been demonstrated. In addition, the formation of the trimethyloxonium ion from methoxy species and dimethyl ether was observed for the first time on heteropolyacid catalyst and its transformation to the carbonylation products was followed with ¹³C MAS NMR.

Experimental Section

Materials. The sample of pure heteropolyacid H₃PW₁₂O₄₀·15H₂O (HPA) was prepared according to the conventional procedure, including the synthesis of the sodium form, the extraction of H₃PW₁₂O₄₀ with diethyl ether, followed by the

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recrystallization in water for purification. The BET surface area of this sample was $8 \text{ m}^2 \cdot \text{g}^{-1}$.

Methanol- ^{13}C (99 atom % ^{13}C), carbon monoxide ($\geq 99.0\%$), carbon monoxide- ^{13}C (99 atom % ^{13}C), iodomethane- ^{13}C (99 atom % ^{13}C), and acetic acid- I - ^{13}C (99% ^{13}C isotope enrichment) were purchased from Aldrich Chemical Co. Inc. and were used without further purification.

Sample Preparation. The reaction was performed in a sealed glass tube of 3.0 mm outer diameter and 10 mm length, which could be tightly inserted into the 4 mm o.d. zirconia rotor for subsequent in situ NMR analysis of the reaction products. The samples of HPA ($\sim 80 \text{ mg}$) were calcined first in air by increasing the temperature from 300 to 523 K with the rate of 4 K min^{-1} . Further, the samples were maintained at 523 K for 3 h under vacuum with the residual pressure less than 10^{-2} Pa . This procedure offers anhydrous $\text{H}_3\text{PW}_{12}\text{O}_{40}$.

The adsorption of methanol or iodomethane on anhydrous HPA (ca. $150 \mu\text{mol g}^{-1}$) and the loading of carbon monoxide ($25\text{--}90 \mu\text{mol g}^{-1}$) were performed at the temperature of liquid nitrogen. In some cases, the sample with adsorbed methanol was kept at 293–423 K for 20–60 min to allow for the methoxy species to be formed. Further, the sample was evacuated to remove unreacted methanol before CO loading. The glass tube with the sample was then sealed off from the vacuum system at the temperature of liquid nitrogen. Further, the sample was warmed to room temperature and heated at 423–473 K for the reaction to proceed. The reaction products were analyzed in an adsorbed state with ^{13}C MAS NMR.

NMR Experiments. ^{13}C MAS NMR spectra were recorded on a Bruker AVANCE-400 spectrometer (Larmor frequency of 100.613 MHz) at room temperature. ^{13}C MAS NMR spectra with the high power proton decoupling were recorded with or without cross-polarization (CP), denoted below as ^{13}C CP/MAS NMR and ^{13}C MAS NMR. The following conditions were used for recording the spectra with CP: the proton high power decoupling field strength was 11.5 G ($4.9 \mu\text{s}$ length of 90° ^1H pulse), contact time was 4 ms at the Hartmann–Hahn matching condition of 50 kHz, and the delay time between scans was 3 s.

^{13}C CP/MAS NMR spectra with interrupted decoupling were obtained by introducing a $50 \mu\text{s}$ delay without ^1H decoupling prior to the signal acquisition.^{16,17}

^{13}C CP/MAS J -modulated NMR spectra were recorded by the pulse sequence $\pi/2(^1\text{H})\text{--CP}(^1\text{H}\text{--}^{13}\text{C})\text{--}\tau\text{--}\pi(^1\text{H}, ^{13}\text{C})\text{--}\tau\text{--acquisition}$,^{18,19} where τ is equal to $1/J_{\text{C--H}}$; for carbon atoms attached to oxygen in alcohols and ethers, $J_{\text{C--H}} = 140\text{--}150 \text{ Hz}$.²⁰

The single pulse excitation ^{13}C MAS NMR spectra were recorded with 45° flip angle ^{13}C pulses of the $2.5 \mu\text{s}$ duration and 15 s recycle delay, which satisfied the $10T_1$ condition. High power proton decoupling in these experiments was used only during the acquisition time. A few thousand scans were collected for each ^{13}C MAS NMR spectrum. The spinning rate was 5 kHz. ^{13}C chemical shifts were referenced with respect to TMS as an external standard, with accuracy $\pm 0.5 \text{ ppm}$. The precision in the determination of the relative line position was $0.1\text{--}0.15 \text{ ppm}$.

Results and Discussion

Conversion of Methanol- ^{13}C . Figure 1 shows ^{13}C CP/MAS NMR spectra recorded for methanol- ^{13}C adsorbed on solid $\text{H}_3\text{PW}_{12}\text{O}_{40}$. The spectrum of the sample just taken out from liquid nitrogen reveals a new signal that appeared at 59 ppm, which is in addition to the signal at 53 ppm from the initial $^{13}\text{CH}_3\text{OH}$ (Figure 1a). Prolonged standing of the sample with

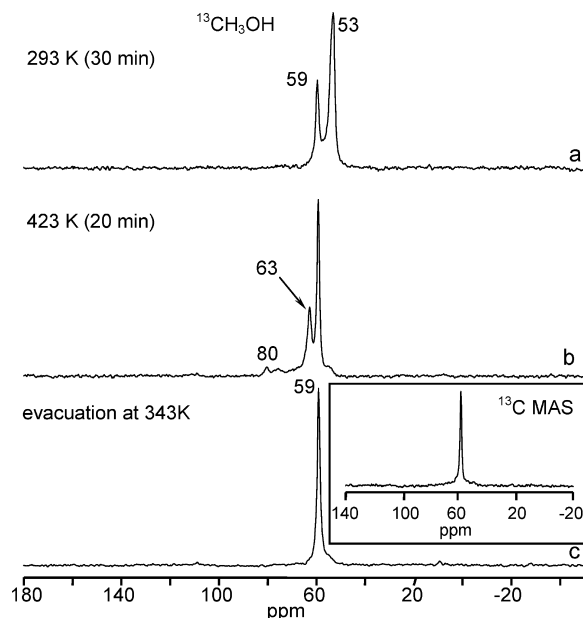


Figure 1. ^{13}C CP/MAS NMR spectra of the products formed from $^{13}\text{CH}_3\text{OH}$ on $\text{H}_3\text{PW}_{12}\text{O}_{40}$: (a) at 293 K; (b) at 423 K; (c) after evacuation of the sample (b) at 343 K for 2 h. Inset: ^{13}C MAS spectrum of the sample (c) is presented.

adsorbed methanol at room temperature or heating it at 423 K for 20 min results in a considerable increase in the intensity of the signal at 59 ppm, and the resonance at 63 ppm also appears in the spectrum (Figure 1b). The residue of the initial methanol is observed as a small right-hand shoulder to the signal at 59 ppm. The resonances of essentially low intensity observed for this sample at about 80 ppm will be discussed later.

According to its position, the signal at 63 ppm belongs to dimethyl ether, DME, whereas that at 59 ppm should be attributed to the $\text{CH}_3\text{--}$ fragment attached to the oxygen of HPA, that is, to the surface methoxy species.⁶ Evacuation of the sample of Figure 1b at 343 K for 2 h leads to a complete disappearance of all signals, excluding that at 59 ppm (Figure 1c). This observation unambiguously proves its assignment to the $\text{CH}_3\text{--}$ group chemically bound to the oxygen of the catalyst surface. Thus, the dehydration of methanol on the Brønsted acid site of the Keggin heteropolyacid, $\text{H}_3\text{PW}_{12}\text{O}_{40}$, occurs with the preferential formation of DME and surface methoxy species. The latter can be prepared on the catalyst surface in the absence of both DME and CH_3OH by evacuation at 343 K. The single pulse excitation ^{13}C MAS NMR spectrum of sample (c) in Figure 1 confirms the formation of the methoxy species as the only species on the surface of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (Figure 1c, inset).

Interaction of the Methoxy Species with Carbon Monoxide: a Carbonylation Reaction. Figure 2a shows the ^{13}C CP/MAS NMR spectrum recorded after loading carbon monoxide on the sample containing surface methoxy species. Heating the sample at 473 K leads to the consumption of the methoxy species; simultaneously, a new signal becomes visible in the spectrum at 21 ppm (Figure 2b). Such a chemical shift is typical for a methyl group of an acetyl fragment of organic compounds both in liquid²⁰ and in the adsorbed state.²¹ Further heating of the sample at 473 K results in an almost quantitative conversion of the surface methoxy group into the acetyl fragment (Figure 2c).

It should be noted that the signal at 21 ppm represents the superposition of two resonances, at 20 and 22 ppm (Figure 2b). This observation can be rationalized in terms of simultaneous

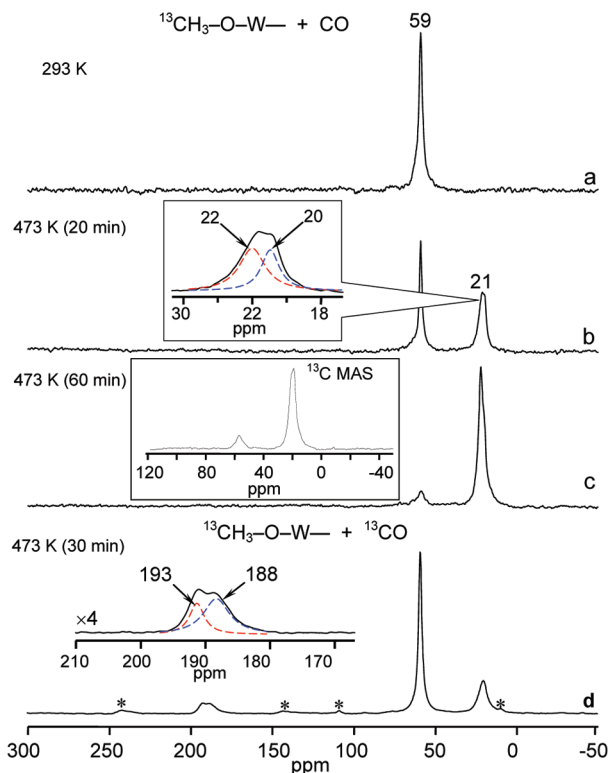
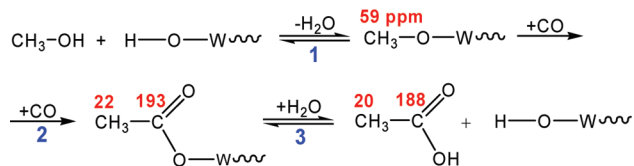


Figure 2. ¹³C CP/MAS NMR spectra of the products formed from surface methoxy species and CO on H₃PW₁₂O₄₀: (a) initial ¹³CH₃-O-W- with coadsorbed unlabeled CO; (b) at 473 K, 20 min; (c) at 473 K, 60 min (with ¹³C MAS spectrum, inset); (d) initial ¹³CH₃-O-W- with coadsorbed ¹³CO at 473 K, 30 min. Asterisks (*) denote spinning side bands.

SCHEME 1: Formation of Methoxy Species on the Brønsted Acid Center of Solid H₃PW₁₂O₄₀ and its Reactivity Towards Carbon Monoxide



formation of both the acetyl group bound to the Keggin anion and acetic acid. Evidently, the surface acetyl group is the result of the attack of nucleophilic CO on the carbon atom of the methoxy species with a partially positive charge, whereas acetic acid is produced by the interaction of the surface acetyl group with a residual water molecule (see Scheme 1). Indeed, being formed at the dehydration of methanol, water molecules are bounded to Brønsted OH-groups of H₃PW₁₂O₄₀ to form H_{2n+1}O_n⁺ (*n* = 1, 2) cations^{22–24} and can not be completely removed from the catalyst by evacuation at 343 K.^{24,25} A total of 0.1–0.5 water molecules per unit cell, which was reported by Filek et al.²⁵ to exist on H₃PW₁₂O₄₀ after dehydration at 373 K (i.e., even at higher temperature than that used in our experiments for generation of methoxy species) is quite sufficient for further partial hydration of surface acetate into acetic acid.

When unlabeled CO was replaced with carbon monoxide-¹³C, ¹³CO, the signals from the carbonyl groups of the acetyl fragment become apparent in the spectrum (Figure 2d). Again, two distinct resonances can be made out at 188 and 193 ppm. This agrees with two signals from methyl carbons at 20 and 22 ppm. To make a conclusive attribution of these two pairs of

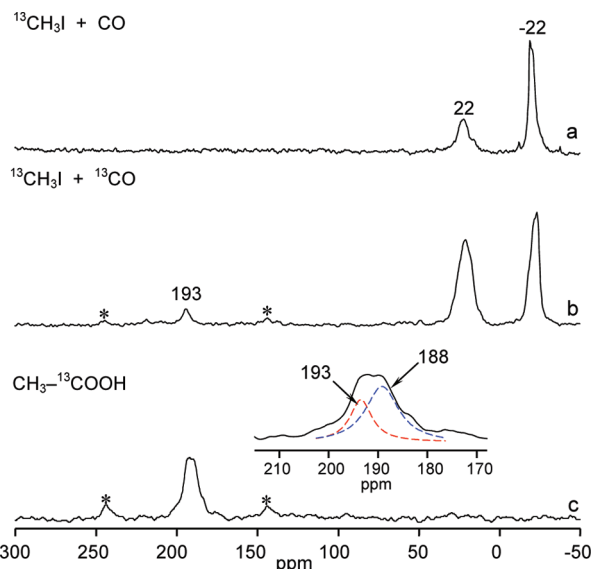
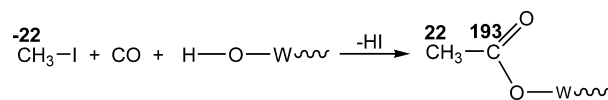


Figure 3. ¹³C CP/MAS spectra for the products formed on H₃PW₁₂O₄₀: (a) from ¹³CH₃I and CO at 473 K for 2 h; (b) from ¹³CH₃I and ¹³CO at 473 K for 4 h; (c) from acetic acid-*l*-¹³C at 293 K. Asterisks (*) denote spinning side bands.

resonances, we have tried to generate an acetyl group bound to the surface of H₃PW₁₂O₄₀ in the absence of acetic acid, from iodomethane and CO. In addition, we adsorbed acetic acid labeled selectively with ¹³C in carboxyl group, CH₃-¹³COOH, on HPA.

Figure 3a,b displays ¹³C CP/MAS NMR spectra obtained when the samples, containing HPA with a coadsorbed iodomethane-¹³C and CO (or ¹³CO), were heated at 473 K for 2 h. Unreacted ¹³CH₃I is identified at -22 ppm.²⁰ The product of the reaction of CH₃I with CO shows two signals at 22 ppm from the methyl group (Figure 3a) and at 193 ppm from the carbonyl carbon (Figure 3b). In principle, the carbonylation of iodomethane with carbon monoxide can produce acetyl iodide. The latter, however, should give rise to the signals at about 47 ppm from the methyl and 158 ppm from the carbonyl group, respectively.²⁶ So, acetyl iodide can not be responsible for the signals observed at 22 and 193 ppm (Figure 3a,b). Another and the only alternative product of the iodomethane carbonylation is the acetyl group bound to the Keggin anion:



Thus, despite the fact that the formation of surface methoxy species from CH₃I was not observed, the signals at 22 and 193 ppm should be unequivocally attributed to the surface acetyl group, which is formed from intermediate methoxy species and CO. A complete coincidence of these resonances with those observed for the product of the interaction between the methoxy species and CO (Figure 2b–d) clearly indicates that the surface acetyl fragment is indeed formed from methoxy species and CO on H₃PW₁₂O₄₀.

Similar to the products of methoxy species and CO interaction, acetic acid-*l*-¹³C adsorbed on H₃PW₁₂O₄₀ exhibits two signals at 188 and 193 ppm from ¹³C-labeled carboxyl group in ¹³C CP/MAS NMR spectrum (Figure 3c). This implies that acetic acid undergoes a dehydration at room temperature to give a surface acetyl group with the resonance at 193 ppm. The signal

at 188 ppm should be assigned to adsorbed acetic acid. This is consistent with the fact that the resonance from the carbonyl group of the surface acetyl fragment is usually shifted to a lower field in comparison with adsorbed acetic acid.^{21,27} These data indicate that stage 3 in Scheme 1 is reversible and acetic acid does present another product of the methoxy species carbonylation (cf. Figures 2d and 3c). Evidently, the acid is formed by the interaction of the surface acetyl group with water left on HPA after selective formation of methoxy species from CH₃OH at evacuation of the HPA sample at 343 K. The formation of the surface acetyl group CH₃COO[−] rather than the acylium cation CH₃–C⁺=O on the interaction of CH₃I with CO provides unequivocal evidence that the acylium cation is not stabilized on the surface of the Keggin anion as it is on solid aluminum halides.^{28,29}

Thus, under the interaction with CO, methoxy species convert into an acetyl group attached to the surface of the solid heteropolyacid. The acetyl group reacts further with water to produce acetic acid (Scheme 1). A direct observation of methyl-to-acetyl group transformation provides the unambiguous evidence for the intermediary role of the methoxy species, generated on H₃PW₁₂O₄₀, in the carbonylation of methanol and its ether on solid heteropolyacid catalyst.

It should be emphasized that the methoxy fragment is the only species generated on the surface of H₃PW₁₂O₄₀ at 293–443 K. At these temperatures, the surface methoxy group is stable and is not involved in the interaction with carbon monoxide. A noticeable conversion of surface methoxy species into an acetyl fragment begins only at 473 K. Thus, as was expected earlier,^{11,30} the interaction between the surface methyl group and carbon monoxide does represent the rate-determining stage of carbonylation on solid acid catalysts.

Interaction of Methoxy Species with DME: the Observation of the Trimethyloxonium Ion (TMOI). As has been mentioned above, the signals of small intensity were observed at 77–82 ppm when the sample of H₃PW₁₂O₄₀ with adsorbed methanol-¹³C was heated at 423 K (see Figure 1b). Evacuation of such a sample at 423 K, rather than at 343 K used for the generation of methoxy species, leads to a considerable increase in the intensity of these signals (Figure 4a). At the same time, the resonances from both the methoxy species at 59 ppm and DME at 63 ppm decrease (cf. Figures 1b and 4a). Being typical for carbon atoms adjacent to oxygen in alcohols and ethers,²⁰ the chemical shift of 77–82 ppm is nevertheless unusual for the CH₃O[−] group. To make a careful attribution of these resonances, the ¹³C CP/MAS spectra with *J*-modulation, as well as with interrupted decoupling, were recorded.

In the *J*-modulated spectrum, the pulse sequence $\pi/2(^1\text{H})\text{-CP}(^1\text{H}\text{-}^{13}\text{C})\text{-}\tau\text{-}\pi(^1\text{H}\text{-}^{13}\text{C})\text{-}\tau\text{-acquisition}$ ¹⁹ allows one to distinguish CH₃ or CH groups from the CH₂ groups. Application of τ -delay, which is equal to $1/J_{\text{C-H}}$, inverts the phase of signals from either CH₃ or CH groups, whereas the intensity of the CH₂ resonances remains positive.¹⁸ The use of $\tau = 7$ ms, which is a reciprocal value to $J_{\text{C-H}} \sim 140\text{--}150$ Hz for C–O carbons, results in a negative intensity of the signals concerned (Figure 4b). So, the resonances at 77–82 ppm can be attributed to either CH₃ or CH groups.

To make a final conclusion on the origin of the signals at 77–82 ppm, the ¹³C CP/MAS experiment with interrupted decoupling was performed. The interrupted-decoupling (or dipolar-dephasing) experiment easily differentiates resonances of nonprotonated and methyl carbons from those of CH or CH₂ by introducing a short delay without ¹H decoupling prior to the signal acquisition.^{16,17} Usually, the delay of 40–50 μs is

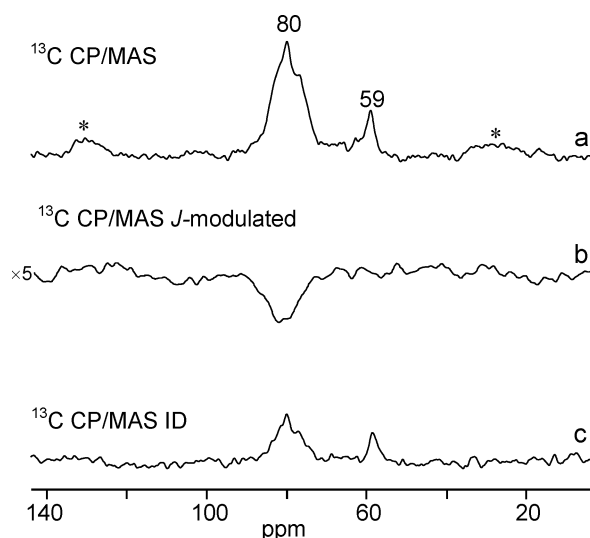
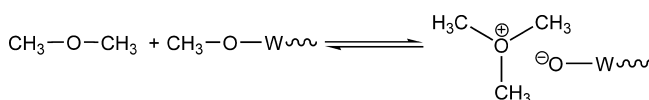


Figure 4. ¹³C CP/MAS spectra after ¹³C-methanol reaction on H₃PW₁₂O₄₀ at 423 K followed by evacuation at 423 K: (a) ordinary ¹³C CP/MAS spectrum; (b) ¹³C CP/MAS spectrum with *J*-modulation; (c) ¹³C CP/MAS spectrum with interrupted decoupling (CP/MAS ID). All spectra were recorded under identical conditions and presented in the same scale. Asterisks (*) denote spinning side bands.

sufficient to completely suppress the signals from CH or CH₂ groups in ¹³C CP/MAS NMR spectrum. Under these conditions, the resonances from the methyl carbons decrease but can still be detected. The interrupted-decoupling spectrum of the sample in Figure 4a revealed that the signals at 77–82 ppm were decreased in intensity but did not completely disappear from the spectrum (Figure 4c). Thus, we conclude that the signals at 77–82 ppm arise from the methyl groups.

The lower-field shift of the signals at 77–82 ppm in comparison with the typical region for CH₃–O– fragment, 50–60 ppm, is indicative of the decrease of electron density around the methyl carbon atom, which can be rationalized by the formation of some positively charged species containing the CH₃–O– group. Among all such species, the ¹³C chemical shift of 80 ppm is characteristic of trimethyloxonium ion (TMOI) both in superacid solution³¹ and on the surface of acidic zeolites.^{32,33} Thus, we have concluded that TMOI is formed on H₃PW₁₂O₄₀. The possible pathway for the TMOI formation is the interaction between DME and the methoxy species:^{15,33}



Three signals, distinguished at 77–82 ppm (Figure 5a) can be attributed to TMOI adjacent to three nonequivalent external oxygen atoms of the Keggin anion.³⁴ Note, however, that we have identified only one signal for the surface methoxy group. Contrary to our data, Zhang et al.⁶ have recently reported that two types of surface methoxy groups, CH₃–O_c and CH₃–O_d, are formed on H₃PW₁₂O₄₀ from methanol, with the signals at 59 and 55 ppm, respectively. In principle, the signal at 54 ppm observed in Figure 1b as a right-hand shoulder to the resonance at 59 ppm can be tentatively assigned to the second type of surface methoxide, CH₃–O_d. However, we presume this signal arises from the unreacted methanol. In our opinion, the evolution of ¹³C NMR spectrum described in ref 6 for methanol adsorbed on H₃PW₁₂O₄₀ within the temperature range 223–293 K can

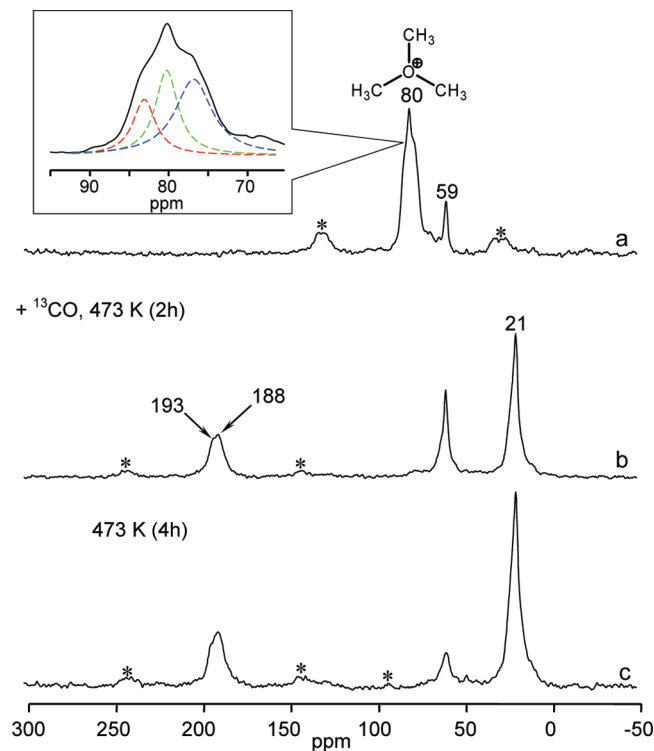


Figure 5. ^{13}C CP/MAS NMR spectra of the products formed from trimethyloxonium ion and CO on $\text{H}_3\text{PW}_{12}\text{O}_{40}$: (a) initial TMOI with coadsorbed ^{13}C O; (b) at 473 K for 2 h; (c) at 473 K for 4 h. Asterisks (*) denote spinning side bands.

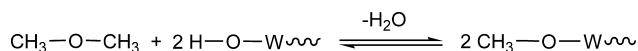
be alternatively rationalized. The observed increase of the chemical shift from 53.7 to 55.3 ppm (or from 53 to 54 ppm in our study) with simultaneous growth of the signal at 59 ppm can be caused by two parallel processes. The first one represents the redistribution of methanol molecules over the surface of HPA. The second process is the dehydration toward the methoxy group at 59 ppm. Being initially in the frozen state after the preparation of the NMR sample, methanol undergoes consecutive transitions from frozen to liquid state and finally to the uniformly adsorbed state during the registration of the spectrum. It is well-known that the interaction of organic adsorbates with Brønsted acid sites usually results in an increase of ^{13}C chemical shift, particularly in the case of C–O carbon atoms.^{35–38} The effect observed can also be reinforced by the inherent increasing chemical shift of methanol with temperature.³⁹ Thus, in contrast to ref 6, we suppose that either only one kind of surface methoxy group, $\text{CH}_3\text{—O}_\text{e}$, is generated on the surface of HPA or all types of methoxy species possess similar chemical shifts at 59 ppm.

Again, as to the observation of three signals of trimethyloxonium ion is concerned, we believe that the rather bulky TMOI as compared to the methoxy species makes its chemical shift more sensitive to the local environment. Therefore, TMOI adjacent to three nonequivalent oxygen atoms of HPA exhibits three different signals near 80 ppm.

It should be noted that at the temperatures ≥ 423 K the trimethyloxonium ion exists only as a minor species if the reaction is performed in the sealed tube, that is, without evacuation (see Figure 1b). However, when heating at 423 K is accompanied by the evacuation, TMOI is formed as the dominating species (Figures 4a, 5a). Evacuating the sample at 423 K, rather than the 343 K used for methoxy-species generation, results in the more complete removal of water from $\text{H}_3\text{PW}_{12}\text{O}_{40}$. According to the literature data,³³ TMOI has not been observed on acidic zeolites in the presence of water

molecules. So, the dehydration by evacuation at 423 K may be a conducive factor for the formation of TMOI on $\text{H}_3\text{PW}_{12}\text{O}_{40}$.

Loading of carbon monoxide on the HPA sample with generated TMOI and further heating at 473 K leads to the same products, surface acetyl group and acetic acid, as in the case of the interaction of methoxy species with CO (cf. Figures 2d and 5b). In addition, an extra amount of methoxy species at 59 ppm is formed (Figure 5b). Subsequent heating of the sample leads to further consumption of methoxy species accompanied by the growth of the signals from acetyl fragments, both the surface acetyl group and acetic acid (Figure 5c). Thus, TMOI decomposes at 473 K according to the reverse reaction of its formation from surface methoxy species and DME, and the latter offers some additional amounts of methoxy species:



Finally, the interaction of CO with surface methoxy species results in an acetyl fragment, which is partially hydrolyzed to acetic acid (see Scheme 1).

Conclusion

With the use of ^{13}C solid-state NMR, the principal stage of the carbonylation of methanol and dimethyl ether has been directly studied on a solid acid catalyst, 12-tungstophosphoric acid. It has been demonstrated that methoxy species, which can be selectively produced on the surface of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ at 293–423 K from methanol, react quantitatively with carbon monoxide at 473 K and give rise to an acetyl group bound to the Keggin anion. Under the interaction with water formed at the dehydration of methanol to form methoxy species, the surface acetyl group converts into acetic acid. The reaction observed provides the direct evidence for the intermediary role of surface methoxy species in the carbonylation of methanol and DME on solid acid catalysts. Proceeding at distinctly higher temperature than needed for the formation of methoxy species, the interaction of methoxy species with CO represents the rate-determining step of the reaction under study.

The formation of trimethyloxonium ions on the surface of solid heteropolyacid was observed for the first time. The expected equilibrium of the trimethyloxonium ion with DME and methoxy species provides a similar pathway for trimethyloxonium carbonylation via the intermediate formation of surface methoxy species.

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