Adsorption and reduction of CO_2 on 12-tungstophosphoric and 12-molybdophosphoric acids in the absence of added reductants

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12-tungstophosphoric and 12-molybdophosphoric acids are capable of sorbing and reducing CO_2 without the presence of added reductants. The adsorbed CO_2 (physisorbed as CO_2) desorbs from the acids and salts at low temperatures (50–200 °C). Carbon dioxide also desorbs only from the acids at high temperatures (500–600 °C), suggesting the direct or indirect involvement of the protons in the process and the importance of the Keggin unit as well. Raman and DRIFTS results show that the species responsible for the evolution of CO_2 (at high temperatures) are carbonaceous in nature. Carbon deposits extract the anionic oxygen atoms from the Keggin units during the high-temperature desorption process. The extraction of anionic oxygen atoms by carbon is confirmed using labeled carbon dioxide. The spectroscopic data imply that carbon exists on the surface as such but, additionally, as either carbon or CO_2 bound to the terminal oxygen atoms of the Keggin anion.

Keywords: carbon dioxide, adsorption, reduction, dissociation, 12-tungstophosphoric acid, 12-molybdophosphoric acid

1. Introduction

In the last decade, interest in carbon dioxide has increased markedly as a result of both environmental concerns and industrial applications. As has been frequently noted, CO_2 is the most abundant C1 feedstock [1] and, as such, has considerable importance as a potential reagent in organic chemistry [2]. Additionally, environmentalists and industrialists alike are becoming more aware of the disadvantageous effects of CO_2 on the environment and this has accelerated work on the reduction of CO_2 emissions [3]. Thus the increase in reports on the adsorption of CO_2 is not unexpected. Recent work has examined such disparate adsorbents as carbon in various forms [4–8], zirconium oxide [9], activated carbon and silica gel [10], and soil [11], in some cases for characterization purposes and in others for their capacities for CO_2 removal. The reduction of CO_2 has also been studied on a variety of materials, including Ni–Cu alloys [12] and magnetite [13], and the adsorption and dissociation on polycrystalline molybdenum [14].

Recent work in this laboratory has shown that certain metal–oxygen cluster compounds (also known as heteropoly oxometalates) are capable of the sorption of NO and NO_2, particularly the latter [15–20]. The solid, 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$, abbreviated as HPW) was particularly effective for this purpose, while 12-molybdophosphoric acid ($H_3PMo_{12}O_{40}$, abbreviated as HPMo) was considerably less advantageous. With the former solid acid evidence from a variety of measurements indicated that protons were necessary for the sorption process and furthermore, that the sorbing NO_2 penetrated into the bulk of the solid structure to associate with the protons to form $[HNO_2]^+$, consistent with the results from earlier work from this laboratory which showed that molecules such as those of ammonia, pyridine and methanol were capable of similar penetration into the interior of these solids where interaction with the protons occurred [21–23].

In view of these observations, it appeared to be of interest and importance to examine the sorption and reduction properties of the aforementioned acidic solids for carbon dioxide, a molecule of semi-quantitatively similar structure to that of nitrogen dioxide.

2. Experimental

2.1. Materials

12-tungstophosphoric (HPW) and 12-molybdophosphoric (HPMo) acids were obtained from BDH Chemicals and used without further purification. Carbon dioxide (CO_2) and helium (He) were obtained from Praxair and used as received. Isotopic carbon dioxide ($^{18}OC^{18}O$) was purchased from Isotec, Inc. The $^{18}OC^{18}O$ was diluted with He to give a mixture of approximately 20% $C^{18}O_2$. Sodium carbonate and sodium nitrate were obtained from BDH and were used as received.

2.2. Procedures

Sodium 12-tungstophosphate and sodium 12-molybdophosphate: Stoichiometric quantities of both 12-tungstophosphoric acid, or 12-molybdophosphoric acid, and sodium carbonate were mixed from aqueous solutions. The

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resulting solution was then evaporated to dryness, and the solid formed further dried in vacuum at room temperature.

Pretreatments: All samples were pretreated in helium flow (50 cm^3/min) in the reactor at the desired temperature for 30 min prior to the exposure to pure CO_2 or diluted mixtures.

Reactor system: Aliquots (0.025–0.150 g) of catalyst were loaded into a 4 mm i.d. quartz reactor connected to a gas chromatograph (HP5890) equipped with a 20 m long empty capillary deactivated fused silica column held at 150 °C. The outlet of the capillary column was connected to a mass selective detector (HP-MS5970). The range of masses monitored was set between 10 and 150 amu at a rate of 5.5 scans/s.

For TPD experiments, the effluent of the reactor passed directly into the MS detection system. The samples were pretreated in helium and exposed to the selected gas mixture at the desired temperature(s) in the reactor. After cooling to 30 °C, the reactor was flushed with helium at 15 cm^3/min for 15 min. The temperature of the reactor was then increased linearly from 30 to 650 °C at 10 °C/min with a temperature controller/programmer (Tempstar II, Thermo Electric Instruments, NJ). All data recorded were stored in the computer (IBM750P90) for analysis.

Temperature-programmed desorption: Two separate continuous-flow systems were also used to analyze the effluent of the reactor during a temperature-programmed desorption (TPD) after exposure of the catalysts to CO_2. The catalysts were exposed to a flow of pure CO_2 (4.7 cm^3/min) at the desired temperature for 5–30 min after pretreatment in helium at the same temperature. The sample was flushed with helium either at the same exposure temperature or at 30 °C. After flushing, the flow of helium was adjusted to 4.5 cm^3/min and the reactor was then heated linearly (10 °C/min) to the desired final temperature (650 °C). An aliquot (0.002003 or 0.00130 dm^3) from the effluent of the reactor was directed to a gas chromatograph equipped with an $8' \times 1/8''$ Porapak R column held at 50 °C for CO_2 analysis. The Porapak R column was replaced with a $3' \times 1/8''$ MS 5A column held at 80 °C for O_2, N_2, and CO analysis and the experiment was repeated. The products desorbing from the chromatographic columns were detected using a TCD. Under the present conditions, the time for analysis of one sample was less than 5 min. A sample could be analyzed from the reactor effluent every 50 °C.

Spectroscopic results: All spectroscopic measurements were obtained from samples pretreated and exposed to CO_2 in the reactor systems.

The samples analyzed by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) were exposed to dry air for 10 min. The samples were ground with KBr, placed in the sample holder and set in the FTIR. The environment was allowed to equilibrate for a few minutes after opening the cell compartment. The FTIR was a Nicolet 510p equipped with Harrick Scientific reaction chamber with ZnS windows and connected to an Omega temperature controller. The reaction chamber was held in a Harrick Scientific DRA-2CO-Praying Mantis-diffuse reflectance attachment. Each spectrum was recorded with a 2 cm^{-1} resolution, and the diffusely reflected radiation was collected at an angle of 120 ° and directed towards an MCT detector.

Raman spectral measurements were obtained on a Renishaw Ramascope using the 632.8 nm line of a He/Ne laser for excitation. The spectrometer was equipped with a microscope attachment.

3. Results and discussion

Temperature-programmed desorption of a sample of HPW not previously intentionally exposed to CO_2 shows the characteristic large water peaks at 100–300 and 400–500 °C, the former of which is due to water existing as such on HPW, the latter of which results from the associative desorption of water formed from the protons and anionic oxygen atoms (figure 1(A) lower) [24]. In addition, a peak of desorbed CO_2 emerges at 580 °C suggesting that strongly held CO_2 or carbon deposits exist on the solid acid (figure 1(A) upper). After saturation of HPW with CO_2 at 30 °C, the water peak again appears (figure 1(B) lower), but the CO_2 peak at 580 °C has now intensified indicating that the desorbing CO_2 results from strongly chemisorbed CO_2 or the oxidation to CO_2 of precursors previously existing on the solid (figure 1(B) upper).

After heating of HPW at 350 °C followed by exposure to CO_2, the lower-temperature water peak has disappeared

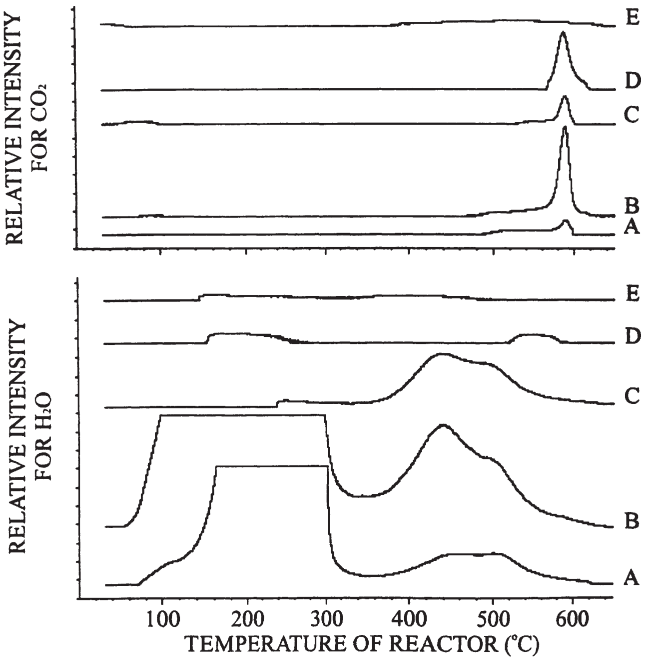

Figure 1. Temperature-programmed desorption (in 15 cm^3/min helium, 10 °C/min) of H_2O and CO_2 from HPW. (A) HPW purged with helium at 25 °C, (B) (A) exposed to pure CO_2 at 30 °C, (C) (A) pretreated at 350 °C and exposed to pure CO_2 at 30 °C, (D) (A) pretreated at 500 °C and exposed to pure CO_2 at 30 °C, (E) (A) pretreated at 650 °C and exposed to pure CO_2 at 30 °C. All samples were exposed to CO_2 (45 cm^3/min) for 30 min before purging with helium at 30 °C.

(figure 1(C) lower), while the higher-temperature water peak and the CO_2 peak remain, although the intensity of the latter appears to have diminished somewhat (figure 1(C) upper). However, after heating of HPW to 500 °C followed by exposure to CO_2 only the high-temperature desorption peak of CO_2 remains (figure 1(D) lower and upper). After heating HPW to 650 °C (at which temperature the Keggin structure is destroyed), followed by exposure to CO_2 at 30 °C, all peaks have vanished (figure 1(E) lower and upper).

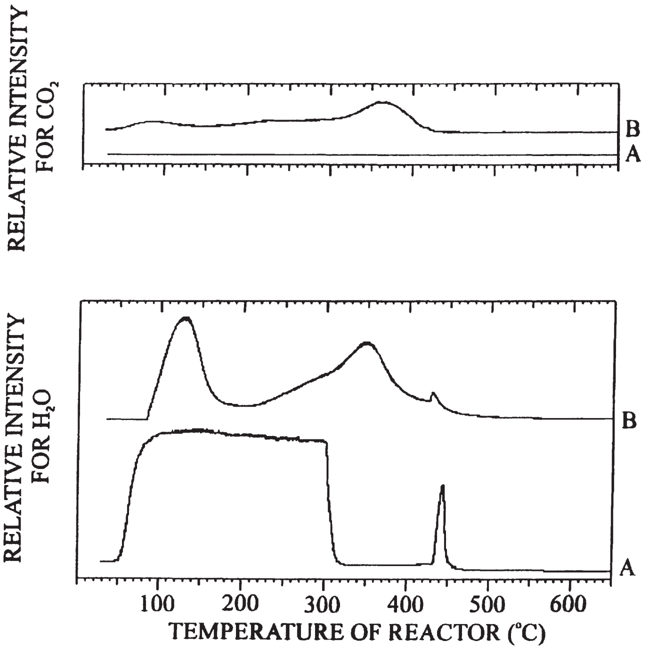

Figure 2. Temperature-programmed desorption (in 15 cm^3/min helium, 10 °C/min) of H_2O and CO_2 from HPMo. (A) HPMo purged with helium at 25 °C, (B) (A) exposed to a 45 cm^3/min flow of CO_2 for 15 h at 30 °C.

In contrast, HPMo, not previously intentionally exposed to CO_2 (figure 2(A) upper), shows no evidence of the desorption of CO_2. After exposure of HPMo to a continuous flow of pure CO_2 at 30 °C for 15 h followed by purging with helium at the same temperature, HPMo desorbs CO_2 at 360 °C (figure 2(B) upper).

Additional TPD measurements of HPW exposed to CO_2 have shown that the sorption and desorption of CO_2 (physisorbed and/or chemisorbed in what form) is dependent upon both the pretreatment temperature and that at which exposure to CO_2 occurs (figure 3). When an aliquot of HPW was pretreated, exposed to pure CO_2 for 10 min, and subsequently flushed with helium at the same temperature (prior cooling to 30 °C), the maximum in the quantity of CO_2 desorbed (at 550 °C) (expressed as the concentration of CO_2 in the gas phase as μmol CO_2 per dm^3) increases with the pretreatment temperature reaching a maximum at 300 °C (figure 3).

The quantity of CO_2 desorbing between 50 and 200 °C is also dependent on the pretreatment and exposure temperatures. With increasing pretreatment temperature, the quantity of CO_2 desorbing in this temperature range increases and also reaches a maximum at 300 °C (figure 4). The similarity of pretreatment temperatures at which both peaks generated by desorbing CO_2 reach maxima (figures 3 and 4) and the temperature at which molecularly bound water has been desorbed (figure 1) suggests that the accessi-

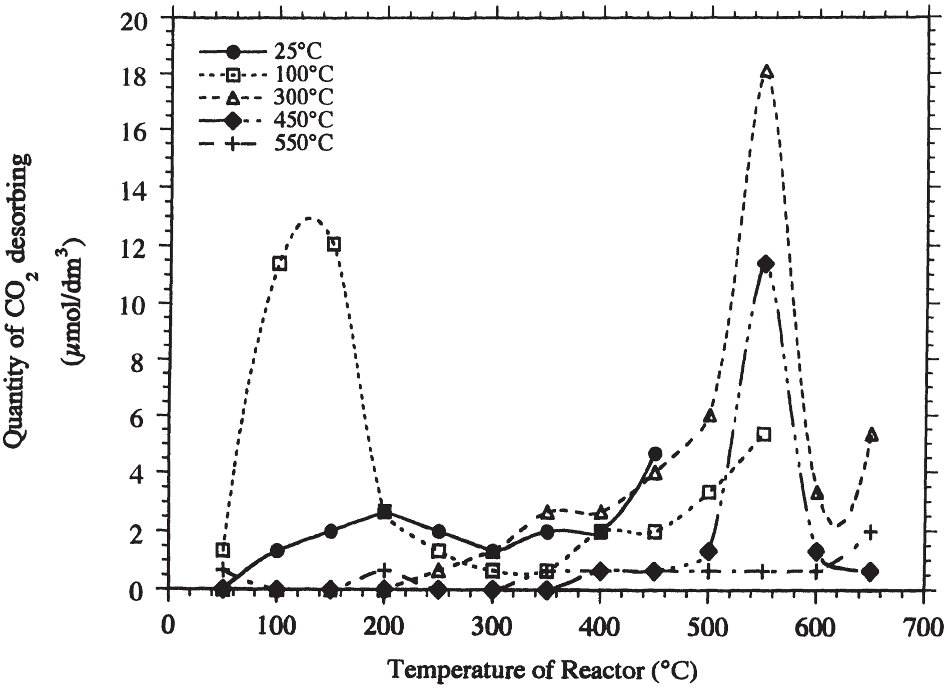

Figure 3. Temperature-programmed desorption (in 4.5 cm^3/min helium, 10 °C/min) of 0.50 g HPW pretreated in helium for 30 min, exposed to pure CO_2 for 10 min at temperatures shown, and subsequently flushed with helium at the same temperature prior to cooling of the sample to 30 °C in a flow of helium.

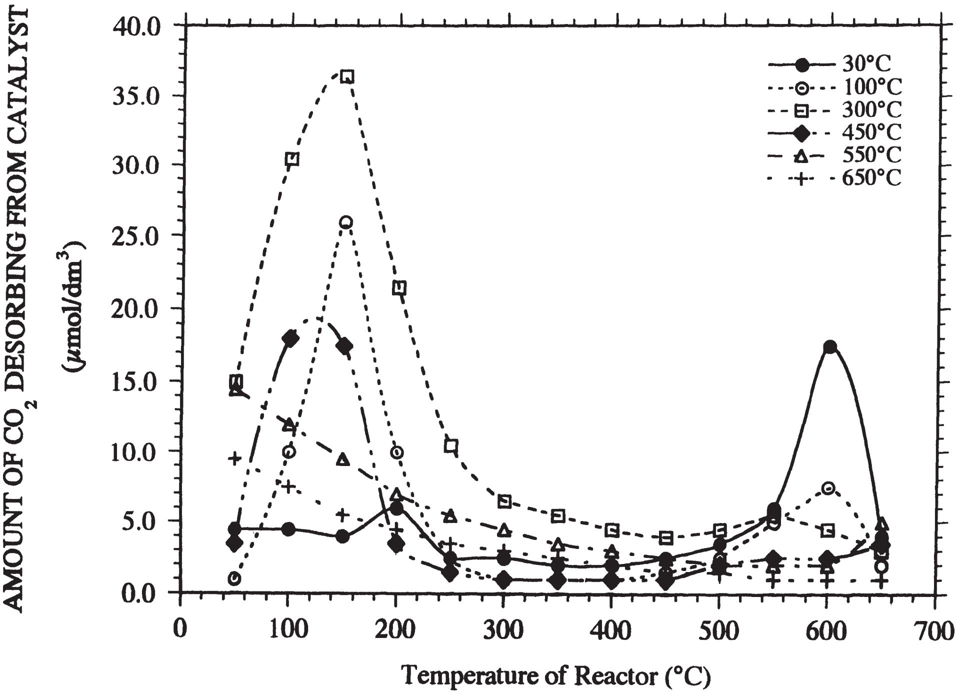

Figure 4. Temperature-programmed desorption (in 4.5 cm^3/min helium, 10 °C/min) of 0.50 g HPW pretreated in helium for 30 min, exposed to pure CO_2 at the temperatures shown, and cooling of the sample to 30 °C in a flow of CO_2. The reactor was purged with helium prior to the TPD measurements.

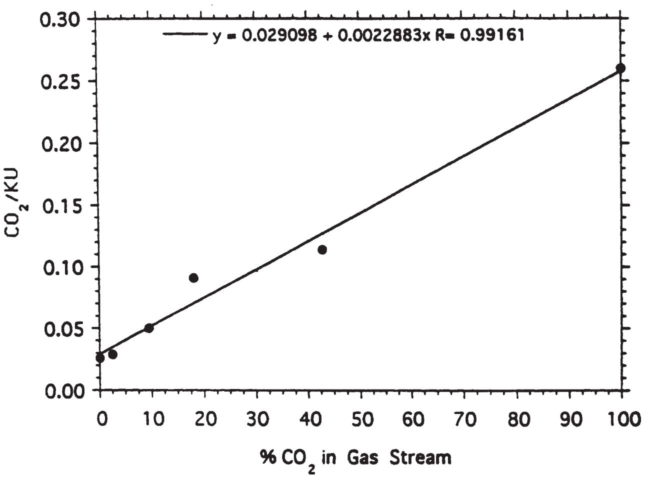

Figure 5. Effect of initial concentration of CO_2 in the gas stream on the sorption of CO_2 (as measured by TPD) on samples of HPW (50 mg) pretreated in helium flow (40 ml/min) and then exposed to pure CO_2 at 450 °C for 30 min.

bility of the protons, which are guarded by water molecules at temperatures below 300 °C, is an important factor in the sorption of CO_2.

The effect of the concentration of CO_2 in the helium gas on its uptake by HPW is illustrated in figure 5 as the number of CO_2 molecules sorbed in 30 min at 450 °C per anion of HPW. It should be noted that the data do not pass through the origin since, as noted earlier in this report, the catalyst was found to contain CO_2 regardless of its intentional exposure to this gas.

In contrast, it was found that both NaPW and NaPMo were capable of physisorbing significantly larger quantities of CO_2 than their parent acids (figures 6 and 7, respectively). A maximum in the quantity of CO_2 desorbed between 100 and 350 °C was found for samples which had been subjected to pretreatment at 100 °C. In the absence of protons, it is not unexpected that the molecularly bound water would be desorbed at lower temperatures. Since no high-temperature (600 °C) CO_2 peaks are found with the salts, all of the CO_2 taken up by NaPW or NaPMo evidently exists in relatively loosely bound form, resulting in the substantially increased quantities of CO_2 desorbed at the lower temperatures.

The presence of the high-temperature CO_2-desorption peaks with the acids but their absence from the results of similar experiments with the salts suggests that protons are directly or indirectly involved in the production of this peak. That the high-temperature peak is observed at a temperature at which desorption of water resulting from the extraction of anionic oxygen by protons is complete [24] adds further evidence for the participation of the protons. Of course, the presence of the protons and their properties is a consequence of the existence of the Keggin structure of the anions. The absence of a high-temperature peak due to CO_2 desorption in those samples pretreated at 600 °C (figures 1 and 2) provides further evidence for the requirement of both protons and the Keggin structure. This is further illustrated from the results of TPD experiments on samples of NaPW exposed to CO_2 at 30 °C for 22 h (figure 8). Vanishingly small quantities of CO_2 were observed at 580 °C with either this sample or one which had no previous intentional exposure to CO_2.

The nature of the species chemisorbed on the solids and which are precursors to the CO_2 desorbing at high temper-

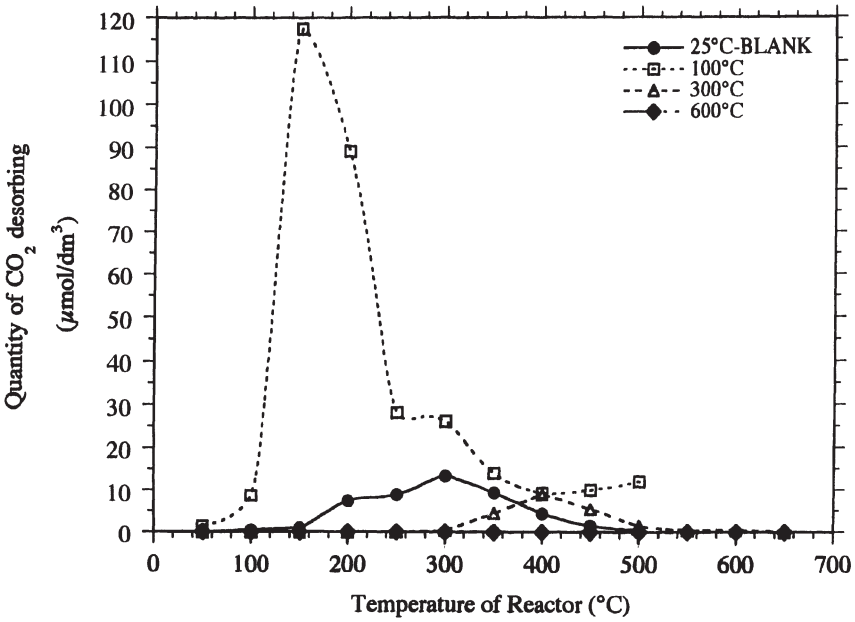

Figure 6. Temperature-programmed desorption (in 4.5 cm^3/min helium, 10 °C/min) of 0.60 g NaPW pretreated in helium for 30 min, exposed to pure CO_2 at the temperatures shown, and subsequently flushed with helium at the same temperature prior to cooling of the sample to 30 °C in a flow of helium.

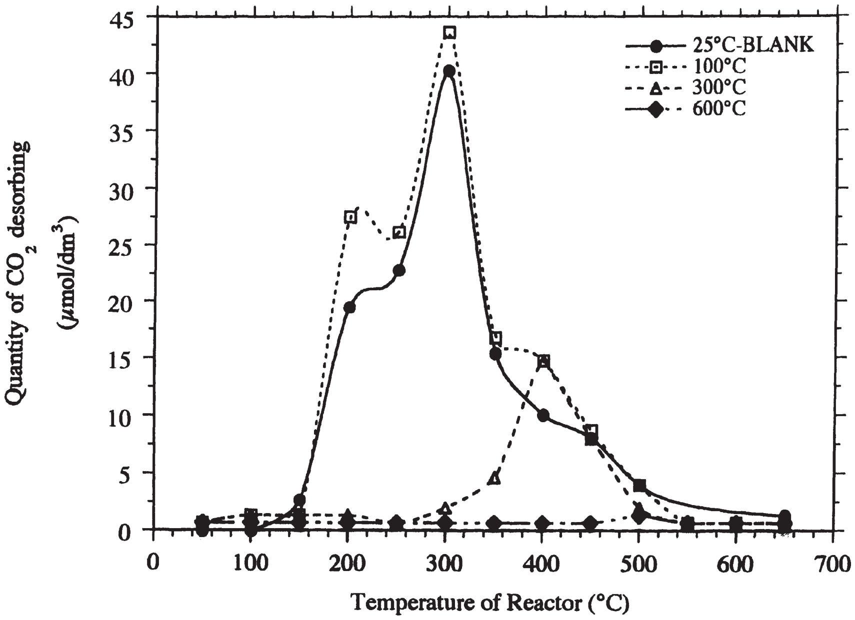

Figure 7. Temperature-programmed desorption (in 4.5 cm^3/min helium, 10 °C/min) of 0.45 g NaPMo pretreated in helium for 30 min, exposed to pure CO_2 at the temperatures shown, and subsequently flushed with helium at the same temperature prior to cooling of the sample to 30 °C in a flow of helium.

atures was investigated with Raman spectroscopy. Since samples previously exposed to CO_2 showed visual evidence for the deposition of carbonaceous species, Raman spectra were obtained for several samples of HPW (figure 9). As with infrared measurements [22], the Raman spectrum of HPW shows a series of bands between 500 and 1200 cm^{-1} characteristic of the Keggin anion. After exposure to CO_2 at 450 °C, black particles from the HPW samples were selected for examination (figure 9(B)). Three new bands at 784, 1350 and 1590 cm^{-1} were observed, the latter being attributed to the degenerate E_{2g} mode of graphite, while that at 1350 cm^{-1} is characteristic of the A_{1g} mode of small crystallites of graphite [25,26]. Although the majority of the particles exposed to CO_2 at 450 °C were discoloured, a small portion remained white, at least to the naked eye. It is not clear, at least at this time, why this is occurring, but differences in particle size and, hence, surface areas available to the CO_2 may be playing a role. The white particles selected for examination (figure 9(A)) did not show the two latter bands, but only the band at 784 cm^{-1}. The bands associated with the Keggin units have somewhat diminished after exposure to CO_2. It would appear that the vibrational bands of HPW are convoluted with those associated with the carbon deposits. The HPW sample which was pretreated and exposed to CO_2 at 100 °C showed little or no evidence of darkening (not shown). With a separate sample of HPW, which was exposed to CO_2 at 300 °C and subsequently heated to 400 °C in a helium flow, the bands associated with the carbon deposits have diminished somewhat and the characteristic bands of the Keggin units have shifted. When a HPW sample pretreated and exposed to CO_2 at 300 °C was heated to 600 °C (in helium), the bands associated with the carbon deposits and the characteristic bands for the Keggin units have vanished (not shown).

Further evidence for the presence of carbon species was obtained using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) (figure 10). The series of bands associated with the Keggin units can be seen at 500–1200 cm^{-1}. A weak band attributed to the C–O vibrational mode is observed at 1600 cm^{-1} with HPW pretreated at

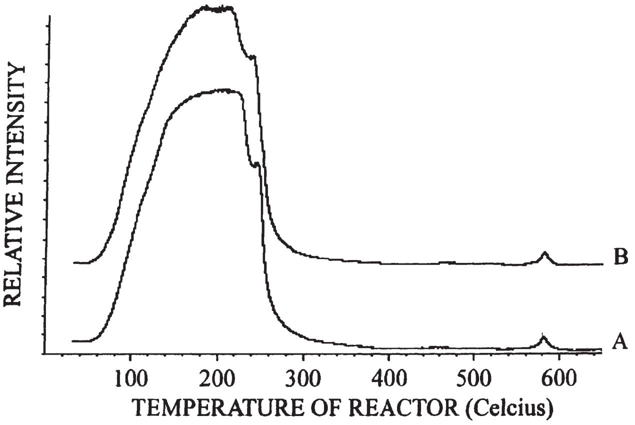

Figure 8. (A) TPD (15 cm^3/min helium, 10 °C/min) of NaPW purged with helium at 25 °C, (B) (A) after exposure to pure CO_2 at 30 °C for 22 h.

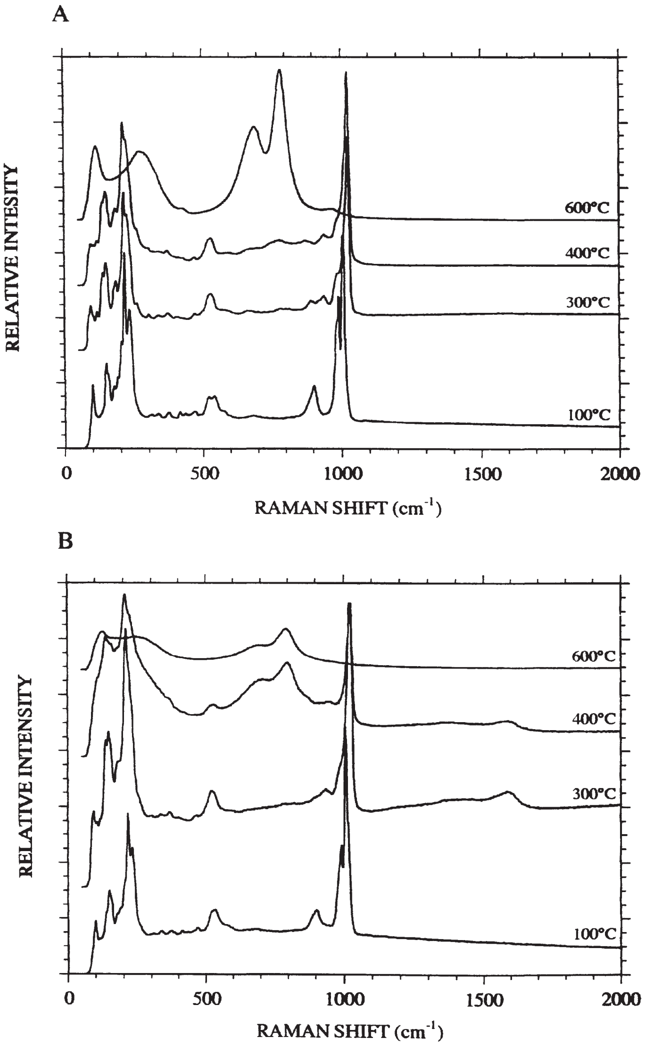

Figure 9. Raman spectra (taken at 25 °C) of HPW exposed to pure CO_2 for 22 h at the temperatures shown. (A) White particles, (B) black particles.

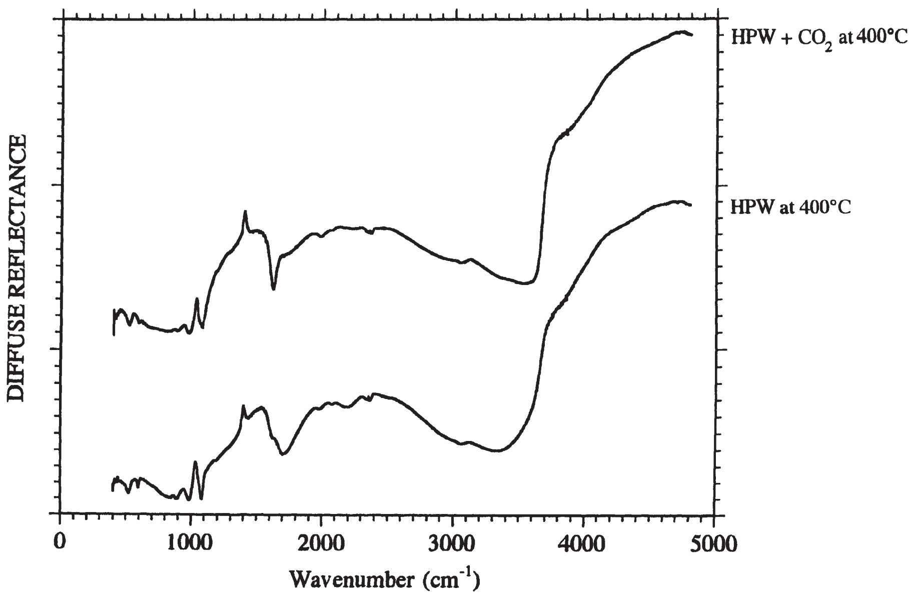

Figure 10. DRIFTS spectra of HPW pretreated at 400 °C and of HPW exposed to CO_2 at 400 °C for 30 min.

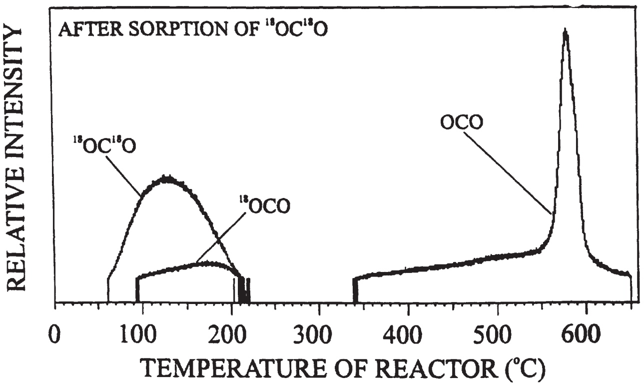

Figure 11. Temperature-programmed desorption of 0.20 g HPW pretreated in helium for 30 min, exposed to $^{13}CO_2$ or $^{18}OC^{18}O$ at 450 °C, and subsequently flushed with helium at 30 °C after cooling of the sample in the presence of labeled CO$_2$.

400 °C. After exposure of the catalyst to CO$_2$, this band has significantly intensified. This suggests that at least a portion of the carbon on the surface is associated with oxygen atoms of the anion. The data from the two spectroscopies imply that carbon exists on the surface as such, as well as in a form in which it is bound to oxygen, presumably the terminal oxygen atoms of the anion. Whether the carbon is bound directly to the anionic oxygen atoms or as CO$_2$ in the form of a carbonate is not clear at this time, but the former appears more probable in view of the high temperatures at which the CO$_2$ emerges. A fresh sample of HPW, after exposure to $^{18}OC^{18}O$ at 450 °C, shows a TPD peak at 50–200 °C as well as a peak due to ^{18}OCO (figure 11). However, the high-temperature peak is due entirely to OCO. Evidently, the CO$_2$ emerging at high temperature results from the bonding interaction between the anionic oxygen atoms and carbon. The relatively high temperatures at which the CO$_2$ is desorbed ($\approx$580 °C) are presumably sufficient to enhance the lability of the terminal oxygen atoms of the anions, thereby promoting their interaction with and bonding to the carbon atoms deposited on the surface.

Although both 12-tungstophosphoric and 12-molybdophosphoric acids and their salts sorb CO$_2$, only the acids are capable of the reduction of the oxide. With both the acids and their salts, substantial quantities of CO$_2$ are sorbed and held in relatively weakly bound molecular form. In contrast, CO$_2$ is also reduced to carbon on the acids, with the tungsten-based acid being a stronger reductant than that containing molybdenum.

Evidently, the presence of both protons and Keggin anions is required to affect the reduction process. Earlier work from this laboratory has shown that water desorbs from the heteropoly acids at two temperatures, that which emerges at the lower temperature having been hydrogen-bonded to the protons, while the higher-temperature desorption results from water produced from the extraction of anionic oxygen atoms by the protons, leaving oxygen vacancies on the anions [24]. Other work has demonstrated that the proton is required in the partial oxidation of methane on the heteropoly acids, apparently to produce the vacancies necessary for the oxidation process [27]. Exposure of the acid to N$_2$O has been shown to result in the dissociative adsorption of the oxide and the consequent filling of the previously existing oxygen vacancies [28].

In the present work, the acids, but not the salts, contain vacancies as a result of the associative desorption of water at temperatures of approximately 400–500 °C. The dissociation of CO$_2$ on the acids yields oxygen atoms which may desorb as O$_2$ or H$_2$O, the hydrogen being that contained on the solid as protons. Alternatively, the aforementioned vacancies may be occupied by the oxygen atoms resulting from the dissociation of CO$_2$. This would be consistent with the demonstrated requirement that dissociation occurs only on the acids. On heating the coked solid to sufficiently high temperatures, the anionic oxygen atoms become sufficiently labile to re-oxidize the carbon atoms and desorb as CO$_2$. It is to be noted, however, that the desorbing CO$_2$ contains only unlabeled oxygen atoms and consequently the oxygen atoms (from $^{18}OC^{18}O$) which occupied the vacancies do not participate in the reformation of CO$_2$.

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References

[1] M. Freemantle, Chem. Eng. News 11 (1996) 6.
[2] J.R. Babcock and L.R. Sita, J. Am. Chem. Soc. 118 (1996) 10912.
[3] J.H. Krieger, Chem. Eng. News 8 (1996) 8.
[4] D. Cazorlaamoros, J. Alcanizmonge and A. Linaressolano, Langmuir 12 (1996) 2820.
[5] M. Molinasabio, M.A. Munecas, F. Rodriguezreinoso and B. McEnaney, Carbon 33 (1995) 1777.
[6] T. Michida, S. Yatsunami, Y. Kawabuchi and Y. Nakayama, Carbon 33 (1995) 1611.
[7] M. Nakashima, S. Shimada, M. Inagaki and T.A. Centeno, Carbon 33 (1995) 1301.
[8] M.A. Salasperegrin, F. Carrascomar, F.J. Lopergarzon and C. Morenocastilla, Energy Fuels 9 (1995) 390.
[9] C. Morterra, G. Cerrato and L. Ferroni, J. Chem. Soc. Faraday Trans. 91 (1995) 125.
[10] K. Berlier and M. Frere, J. Chem. Eng. Data 42 (1997) 533.
[11] H. Dejonge and M.C. Mittelmesjer Hazeleger, Environ. Sci. Technol. 30 (1996) 408.
[12] Y. Kitayama, Y. Watanabe, K. Muramatsu and T. Kodama, Energy 22 (1997) 177.
[13] C.L. Zhang, Z.Q. Liu, T.H. Wu, H.M. Yang, Y.Z. Jiang and S.Y. Peng, Mater. Chem. Phys. 44 (1996) 194.
[14] L.D. Lopezcarreno, J.M. Heras and L. Viscido, Surf. Sci. 377 (1997) 615.
[15] R. Bélanger and J.B. Moffat, Appl. Catal. B 13 (1997) 167.
[16] R. Bélanger and J.B. Moffat, J. Mol. Catal. A 114 (1996) 319.
[17] R. Bélanger and J.B. Moffat, Langmuir 12 (1996) 2230.
[18] R. Bélanger and J.B. Moffat, Catal. Lett. 32 (1995) 371.

[19] R. Bélanger and J.B. Moffat, Environ. Sci. Technol. 29 (1995) 1681.
[20] R. Bélanger and J.B. Moffat, J. Catal. 152 (1995) 179.
[21] J.G. Highfield and J.B. Moffat, J. Catal. 95 (1985) 108.
[22] J.G. Highfield and J.B. Moffat, J. Catal. 89 (1984) 185.
[23] J.G. Highfield and J.B. Moffat, J. Catal. 88 (1984) 177.
[24] B.K. Hodnett and J.B. Moffat, J. Catal. 88 (1984) 253.
[25] F. Tuinstra and J.L. Doenig, J. Chem. Phys. 53 (1970) 1126.
[26] Y. Wang, D.C. Alsmeyer and R.L. McCreery, Chem. Mater. 2 (1990) 557.
[27] S. Kasztelan and J.B. Moffat, J. Catal. 112 (1988) 54.
[28] S. Kasztelan and J.B. Moffat, J. Catal. 116 (1989) 82.