

Structural and Functional Characterization of Redox Mn and Co Sites in AIPO Materials and Their Role in Alkane Oxidation Catalysis

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The number of redox-active and inactive Mn and Co species in MeAPO-5 and MeAPO-18 (Me = Mn, Co) was measured from H₂ consumption rates during H₂ temperature-programmed reduction (H₂-TPR), and their structure and oxidation state were probed at identical conditions by UV–visible and X-ray absorption spectroscopies. H₂ consumption, loss of Me³⁺ UV–visible features, and a decrease in X-ray absorption edge energy occurred concurrently and at similar rates, indicating excellent agreement between these techniques. No H₂O or CO₂ were detected during treatment in H₂ or CO, respectively, indicating that reduction from Me³⁺ to Me²⁺ occurred by introduction of protons. These protons are fully removed by treatment in O₂ to 773 K, and O₂–H₂ redox cycles involving reversible proton formation suggest that cations reside within AIPO framework positions, in which protons reside as charge balancing cations at Me²⁺–O–P bridges. H₂ consumption rates measured during H₂-TPR could be accurately described by Arrhenius-type behavior, and H₂/Me ratios showed that only a fraction of all Me cations undergo reversible redox cycles. This fraction was 0.86 for MnAPO-18 (atomic Mn/P = 0.05); it decreased from 0.68 to 0.40 for MnAPO-5 as Mn/P ratios increased from 0.028 to 0.10. For CoAPO-18 with 0.028 Co/P and CoAPO-5 with 0.40 Co/P, the fractions of redox sites were 0.64 and 0.40, respectively. UV–visible spectra showed no detectable Me³⁺ features after thermal treatment in H₂. Thus, cations that do not undergo redox cycles remain as permanently divalent cations throughout O₂–H₂ cycles. The redox-active fraction also decreased during repeated H₂–O₂ redox cycles above 773 K, indicating that redox cations convert into permanently divalent sites. This conversion coincides with the evolution of H₂O during H₂ treatments above 773 K. These findings together with the effects of Me/P ratio on the redox fraction are consistent with a mechanism in which OH groups at divalent framework cation sites recombine to form H₂O and an oxygen vacancy. Cyclohexanol and cyclohexanone formation rates during liquid-phase cyclohexane oxidation with O₂ on MnAPO-5 samples increased linearly with the number of redox-active sites, suggesting that elementary steps of cyclohexane oxidation involve cycling between Me²⁺ and Me³⁺, and require cation sites able to reversibly form charge balancing cationic species.

Introduction

Aluminophosphate molecular sieves (AIPO-*n*) consist of Al³⁺ and P⁵⁺ tetrahedra linked by oxygen bridges. Their microporous crystalline structures¹ can accommodate a wide range of substitutional cations within their framework.^{2–4} These materials (MeAPO-*n*) combine the useful catalytic reactivity of transition metal cations (e.g. Co and Mn) with a shape-selective environment provided by small channels. Mn³⁺ and Co³⁺ framework cations have been implicated as active centers in selective oxidation^{5,6} and oxidative dehydrogenation⁷ reactions of alkanes, but direct evidence for specific effects of constraining channels is tenuous. Mechanistic details for these oxidation reactions remain controversial, but framework cations acting as redox centers to form radical-like intermediates are generally consid-

ered,^{6,8} mostly on the basis of heuristic arguments and chemical analogies with homogeneous oxidation processes.

Recent reviews have described spectroscopic data (UV–visible, X-ray absorption, ²⁷Al- and ³¹P NMR, electron-spin resonance) that probe the structure and electronic properties of cations in AIPO materials.^{2–4} Active cations isomorphously substituted in AIPO frameworks have not yet been directly or unequivocally connected with specific structures involved in redox cycles required for oxidation turnovers, even after significant attention and continuing debate. To some extent, the structural complexity arising from multiple cation types and from ubiquitous changes in cation valency during treatment and catalytic turnovers prevent any one spectroscopic method from providing a rigorous assessment of cation speciation and catalytic relevance. Quantitative chemical methods have proven essential to provide such information for cation-modified aluminosilicates,⁹ but they have not been rigorously used for cation-modified aluminophosphate materials.

Here, we combine chemical analysis methods, which measure extents of reduction from the chemical composition of effluent streams during treatment or catalytic reactions, with in situ UV–

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TABLE 1: Elemental Analysis of as Prepared MeAPO Materials

catalyst	atomic fractions X/(Me+Al+P)			atomic fraction			Me Wt%
	X = Me	X = Al	X = P	Me/P	Al/P	(Me+Al)/P	
MnAPO-5-1	0.027	0.482	0.491	0.055	0.982	1.037	2.03
MnAPO-5-2	0.014	0.486	0.500	0.028	0.972	1.000	1.04
MnAPO-5-3	0.049	0.462	0.489	0.100	0.945	1.045	3.61
MnAPO-18	0.025	0.476	0.499	0.050	0.954	1.004	1.83
CoAPO-5	0.020	0.497	0.482	0.041	1.031	1.073	1.65
CoAPO-18	0.014	0.494	0.492	0.028	1.004	1.033	1.08

visible and X-ray absorption spectroscopic methods during treatment in streams containing H₂ or O₂. In the process, we measure the fraction of the Co and Mn atoms present in MeAPO materials that undergo reduction and oxidation in various chemical environments and also the extent to which these cycles are reversible. Concurrent in situ spectroscopic assessments allow unambiguous assignments of specific spectral features to a given species, structure, or oxidation state. Cyclohexane oxidation turnover rates are measured on these materials and related quantitatively to the number of various Mn or Co cation structures in each sample to determine which cation species act as catalytic sites and to confirm the redox requirements for catalytic oxidation sequences.

Experimental Methods

Synthesis and Characterization of MeAPO Samples.

CoAPO-5 and MnAPO-5 samples were prepared using procedures previously described.¹⁰ AlPO-18 and Co- and MnAPO-18 were prepared as described by Chen et al.¹¹ Co and Mn were introduced as divalent cations during synthesis to give Co/P or Mn/P atomic ratios of 0.028–0.10. Thermal treatments were carried out using dry air (Airgas, zero grade), purified using a 13X sieve at ambient temperature, by heating samples to 393 K at 0.167 K s⁻¹, holding for 1 h, and then heating to 823 K at 0.05 K s⁻¹ and holding for 3 h. The chemical composition of the samples was measured by inductively coupled plasma emission spectrometry, and the results are shown in Table 1. (Me+Al)/P atomic ratios differ slightly from the value of unity expected from structurally pure Me_xAl_{1-x}PO₄, although the differences are within the limits of error. All MeAPO-5 and MeAPO-18 samples showed X-ray diffraction patterns for the expected crystal structure.^{12,13} Very weak diffraction lines for trace crystalline impurities were detected only in CoAPO-5; these appear at angles corresponding to the most intense lines for AlPO-18, indicating the presence of ~1% AlPO-18 crystals in this sample.

Temperature-Programmed Reduction and Oxidation Studies. Reduction (TPR) and oxidation (TPO) rates were measured on MeAPO samples (0.1–0.2 g) held within a quartz cell. Temperatures were monitored with K-type thermocouples and set using a Watlow controller (Series 982) and a resistively heated furnace. Reactant mixtures were 1% H₂/Ar (Praxair), 20% H₂/Ar (Matheson), 1% CO/He (Praxair), and several mixtures of O₂ (Airgas, UHP) in He (Airgas, UHP). Each stream was individually purified using a 13X molecular sieve at ambient temperature to remove H₂O and hydrocarbon traces. The effluent was analyzed using a differentially pumped mass spectrometer (MKS Instruments, Orion Compact Residual Gas Analyzer) as the sample temperature was linearly increased while flowing H₂, CO, O₂, or He. H₂ (2 amu), He (4 amu), H₂O (18 amu), CO (28 amu), O₂ (32 amu), Ar (36 and 40 amu), and CO₂ (44 amu) concentrations were measured at 10 s intervals.

Before H₂ or CO reduction experiments, samples were treated within the cell using the protocol described above (except 20%

O₂/He was used instead of air) and then cooled to ambient temperature. The O₂ stream was replaced with He (8.33 cm³ s⁻¹ g⁻¹) in order to remove residual gas phase or physisorbed O₂. Helium was then replaced with 1% H₂/Ar at 3.33 cm³ s⁻¹ g⁻¹ in H₂-TPR studies. After the intensity at 2 amu reached a constant value, the temperature was increased to its final value (773, 823, or 873 K) at 0.167 K s⁻¹. In CO-TPR, He was replaced with 1% CO/He at 3.33 cm³ s⁻¹ g⁻¹ and the sample heated to 773 K at 0.167 K s⁻¹. Detailed H₂ reduction rates were carried out in a 3.33 cm³ s⁻¹ g⁻¹ 20% H₂/Ar stream and measured with a modified Quantasorb apparatus (Quantachrome) equipped with a thermal conductivity detector (TCD). The response was calibrated using known amounts of CuO.

O₂-TPO and He-TPD studies were carried out by cooling samples in 1% H₂/Ar to ambient temperature after H₂-TPR and using He (8.33 cm³ s⁻¹ g⁻¹) to remove residual gas-phase H₂ or adsorbed species. The sample temperature was then increased to 773 K at 0.167 K s⁻¹, while He was used as the carrier gas (He-TPD). For O₂-TPO, He was replaced with 80% O₂/He (8.33 cm³ s⁻¹ g⁻¹) and the temperature increased at 0.167 K s⁻¹ to 773 K after the O₂ intensity at 32 amu reached constant values. Another H₂-TPR (H₂-TPR-2) measurement was carried out after O₂-TPO to probe the reversibility of oxidation–reduction cycles. These experiments were carried out by cooling samples to ambient temperature after O₂-TPO, replacing the O₂ gas with He and then with 1% H₂/Ar, and finally increasing the temperature as in H₂-TPR experiments.

In Situ UV–Visible Spectroscopy. UV–visible spectra were measured using a Cary 400 Bio spectrophotometer (Varian Corp.) and an in situ flow cell (Harrick, Inc.) with a diffuse reflectance accessory. MgO powders treated in He for 1 h at 393 K (Airgas, UHP, dried on 13X molecular sieve) were used as reference. Reflectance (*R*) data were converted to pseudo-absorbance (*F*(*R*)) using the Kubelka–Munk formalism:¹⁴

$$F(R) = (1 - R)^2/2R \quad (1)$$

Except where noted otherwise, the spectra were measured at ambient temperature between 12 000 and 45 000 cm⁻¹. Fresh and air-treated samples were exposed to He flow (Airgas, UHP, purified by 13X sieve) at 393 K for 1 h to remove weakly adsorbed species. The effect of H₂ treatment was probed by collecting spectra after exposure to H₂ (3.33 cm³ s⁻¹ g⁻¹, Airgas, UHP, purified by 13X sieve) at 773 K for 1 h. Spectra were also collected during temperature-programmed reduction in 3.33 cm³ s⁻¹ g⁻¹ 12.5% H₂/He (mixture of the above H₂ and He gases) as the temperature was raised to 773 K at 0.167 K s⁻¹ after samples were treated in air at 773 K for 1 h (3.33 cm³ s⁻¹ g⁻¹, Airgas, zero grade, purified by 13X sieve). During in situ H₂-TPR measurements, UV–visible spectra were acquired at 180 s intervals in the 12 000–27 000 cm⁻¹ spectral range. These data are reported as the ratio of the intensity for one of the characteristic features at each condition divided by its initial intensity as a function of treatment temperature. These data are also compared to the cumulative consumption of H₂ measured during equivalent H₂-TPR experiments.

In Situ X-ray Absorption Spectroscopy. X-ray absorption (XAS) spectra of CoAPO-18 were measured using beamline 4–1 at the Stanford Synchrotron Radiation Laboratory (SSRL) with a storage ring operating at 30–100 mA and 3.0 GeV. The two-crystal Si(111) monochromator was detuned by 30% in order to minimize harmonics. The definition slit had vertical and horizontal apertures of 0.2 and 15 mm, respectively, leading to a maximum energy resolution of 1 eV at the Co K edge (7709 eV). Ion chambers filled with N₂ were used to detect the

intensities of the incident beam (I_0), the beam after the sample (I_1), and the beam after a reference Co foil located after the sample (I_2). During temperature-programmed experiments, dynamic XANES spectra were acquired in 10 eV increments for 7600–7700 eV, 0.25 eV for 7700–7725 eV, 0.5 eV for 7725–7750 eV, 2 eV for 7750–7790 eV, 8 eV for 7790–7950 eV, and 20 eV for 7950–8050 eV. Absorption intensities were integrated for 0.5 s at each energy to give an acquisition time of 270 s per spectrum.

Samples (10 mg, 125–250 μm pellets) were held within a quartz capillary (0.8 mm inner diameter, 0.1 mm wall thickness).^{15,16} Samples previously treated in air were contacted again with air (Airgas, UHP; $3.33 \text{ cm}^3 \text{ s}^{-1} \text{ g}^{-1}$) as the temperature was increased from ambient to 773 K at 0.167 K s^{-1} and held at 773 K for 1 h. Samples were then cooled to ambient temperature, and the air stream was replaced by He ($3.33 \text{ cm}^3 \text{ s}^{-1} \text{ g}^{-1}$) for 0.5 h. After replacing He with 20% H_2/Ar (Matheson; $3.33 \text{ cm}^3 \text{ s}^{-1} \text{ g}^{-1}$), X-ray absorption spectra were acquired during H_2 -TPR experiments, where the sample temperature was increased to 773 K at 0.067 K s^{-1} . MnAPO samples could not be analyzed in situ because Si atoms in the capillary quartz wall absorb a significant fraction of incident X-rays at the Mn K edge (6539 eV).

Analysis of Near-Edge X-ray Absorption Spectra (XANES). Near-edge and fine structure data were analyzed using WinXAS version 2.1.^{17,18} The energy scale was calibrated by placing the first inflection point in the reference Co foil spectrum at the known Co K edge (7709 eV). A linear regression fit to the preedge region between 7600 and 7680 eV was subtracted from each spectrum, which was then normalized using a third-order polynomial fit for the energy region after the edge (7800–8050 eV). Principal component analysis (PCA)¹⁹ and linear combination methods²⁰ were used to obtain the number and concentration of each structurally distinct Co species contributing to the 7700–7770 eV energy region for each spectrum.

Cyclohexane Oxidation on Mn- and CoAPO-5 Materials. Cyclohexane oxidation was carried out in a shielded high-pressure glass reactor (Andrews Glass; 100 cm^3). Cyclohexane (25 cm^3 ; Aldrich, 99.99%) was added together with $\sim 0.2 \text{ g}$ of catalyst; the catalyst was transferred into this reactor immediately after treatment in air at 773–823 K for 3 h (see Synthesis and Characterization of MeAPO Samples) with minimal intervening exposure to ambient air. The reactor pressure was raised to 0.4 MPa using pure O_2 (Airgas, UHP) while held at ambient temperature before heating to 403 K. Cyclohexanone, cyclohexanol, and cyclohexyl-hydroperoxide products and unreacted cyclohexane were analyzed by gas chromatography (Hewlett-Packard 5890) using a DB-wax column (30 m length, 0.32 mm diameter and 0.5 μm film thickness) and a flame ionization detector. The cyclohexyl hydroperoxide response was calibrated using parallel iodometric titrations of liquid samples extracted from the reactor.

Results and Discussion

Chemical and Structural Changes in Mn- and CoAPO Materials During H_2 Treatment. Reduction of cations in H_2 can occur via either O-atom removal as H_2O or via the formation of protons; both processes consume H_2 , but only the first one forms H_2O . Thus, the amounts of H_2O evolved and H_2 consumed during treatment in H_2 can be used to measure the number and type of reducible cations, including details about the amount of removable lattice oxygens.⁹ Typical H_2 -TPR kinetic data are shown in Figure 1. On MnAPO samples, a H_2 consumption peak appeared at ~ 580 – 600 K ; Co cations

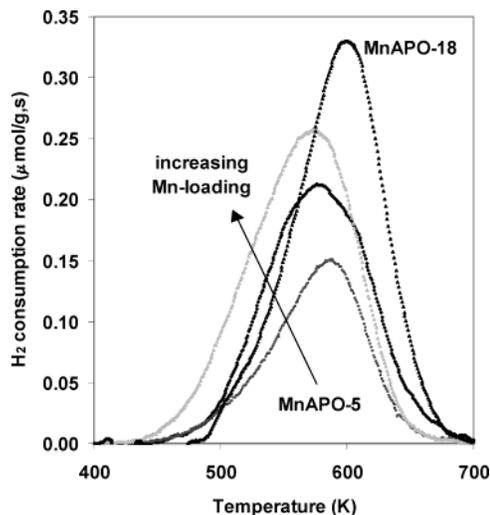
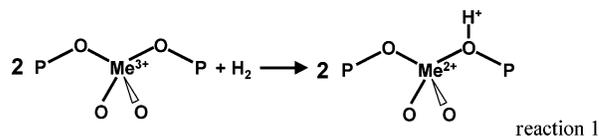


Figure 1. Temperature-programmed reduction of MnAPO-5-1, MnAPO-5-2, MnAPO-5-3, and MnAPO-18 in 20% H_2/Ar [20% H_2/Ar , 0.167 K s^{-1} from 298 to 773 K, hold 0.5 h at 773 K].

reduced at higher temperatures ($\sim 750 \text{ K}$). H_2O was not detected concurrently with H_2 consumption in any of the samples, but small amounts of water appeared at higher temperatures, apparently from condensation of vicinal OH groups at reduced cations to form extraframework cations or distorted cations within the framework.^{21,22} The absence of H_2O during H_2 consumption indicates that reduction occurs exclusively via formation of protons at cation sites (reaction 1) and that O-atom



removal occurs at higher temperatures, if at all. Also, the absence of H_2O confirms the absence of bulk Mn or Co oxides, which reduce to MnO or Co^0 below 773 K with the concurrent removal of lattice oxygens and formation of H_2O . The amount of H_2 consumed reflects the one-electron reduction of Me^{3+} to Me^{2+} shown in reaction 1, as suggested previously from X-ray absorption²² as well as infrared and UV–visible^{23–25} spectra. H_2/Me consumption ratios (0.20–0.43; Table 2) were significantly lower than the value of 0.5 expected from a one-electron reduction of each Mn or Co cation in these samples. Only some of these cations undergo reduction during H_2 treatment up to 773 K; thus, all samples appear to contain a mixture of redox-active (40–86%) and unreactive (14–60%) cations.

Previous H_2 -TPR measurements on CoAPO materials^{8,26–28} have led to H_2/Co consumption ratios of 0.03 for CoAPO-5,²⁶ 0.10 and 0.12 for two different CoAPO-44 samples,²⁶ and 0.385 for CoAPO-11.²⁷ The amounts of H_2O formed were not measured, making it difficult to confirm the exclusive presence of cations at framework positions in these samples. One of these studies proposed that the reduced species resided at extraframework positions and resembled Co oxides,²⁶ a proposal inconsistent with the absence of H_2O evolution during reduction reported here.

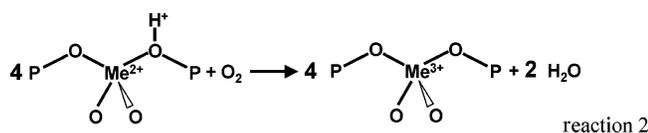
Reversibility of Reduction–Oxidation Cycles. The reversibility of reduction events detected during thermal treatment in H_2 was probed by attempting the removal of adsorbed H atoms during heating in He (He-TPD) after H_2 treatments. The removal of H atoms formed during reduction by reaction with O_2 to form H_2O was also explored (O_2 -TPO).

TABLE 2: Chemical Characterization of MeAPO Materials Using Temperature-Programmed H₂ or O₂ Treatments

sample	T_{\max}^a (K)	H ₂ -TPR-1 ^b (H ₂ /Me)	O ₂ -TPO ^c (H ₂ O/Me)	H ₂ -TPR-2 ^d (H ₂ /Me)	H ₂ -TPR-T ^e (H ₂ /Me)	redox fraction ^f
MnAPO-18	773	0.43	0.42	0.42	0.44	0.86
MnAPO-18	873	0.43	0.39	0.36		
MnAPO-5-1	773	0.31		0.33	0.31	0.62
MnAPO-5-2	773				0.34	0.68
MnAPO-5-3	773				0.20	0.40
CoAPO-18	823	0.32	0.30	0.31		0.64
CoAPO-5	823	0.20		0.23	0.21	0.40

^a Maximum temperature used during treatment. ^b H₂-TPR from 298 to T_{\max} at 0.167 K s⁻¹ [0.2 g, 25 cm³/min 1% H₂/Ar, mass spectrometry]. ^c O₂-TPO after H₂-TPR from 298 to T_{\max} at 0.167 K s⁻¹ [0.2 g, 50 cm³/min 80% O₂/He, mass spectrometry]. ^d H₂-TPR after O₂-TPO from 298 to T_{\max} at 0.167 K s⁻¹ [0.2 g, 25 cm³/min 1% H₂/Ar, mass spectrometry]. ^e H₂-TPR from 298 to T_{\max} at 0.167 K s⁻¹ [0.2 g, 80 cm³/min 20% H₂/Ar, TCD]. ^f Fraction of metal sites that undergo redox cycles. Calculated from the experimental H₂/Me ratio and the reaction stoichiometry of 1/2 H₂/Me_{redox}.

H₂ evolution was not detected (H₂/Me < 0.01) during He-TPD of samples previously reduced during H₂-TPR and cooled in H₂ to ambient temperature, indicating that the microscopic reverse of proton formation during reduction is not kinetically possible; however, H₂O desorbs at temperatures above 773 K indicating the possible recombination of OH groups. In contrast with He, O₂ removes as H₂O all of the H atoms introduced during reduction (reaction 2) and leads to the reoxidation of each of the cations that reduced during the initial H₂-TPR (Figure 2, Table 2).



The amount of H₂O formed during O₂-TPO was similar to the H₂ consumed during H₂-TPR (e.g., 0.42 H₂O/Mn vs 0.43 H₂/Mn for MnAPO-18), indicating that H₂-O₂ redox cycles are fully reversible. Also, a second H₂-TPR gave essentially the same H₂/Me ratio as the initial H₂-TPR (0.42 vs 0.43 H₂/Mn), confirming that these redox cycles are reversible. These conclusions remain valid for thermal treatment temperatures below ~800 K. When H₂-TPR was carried out to 873 K, substantial amounts of H₂O were evolved, apparently via migration and condensation of OH groups to form stable Me-O-Me structures containing divalent Me, which did not oxidize during subsequent treatment in O₂.²¹ H₂-TPR and O₂-TPO cycles on MnAPO-18 with 873 K as the final temperature led to a decrease in the consumed H₂/Mn ratio from 0.43 for the initial H₂-TPR to 0.36 for a subsequent one. Although the number of redox sites decreased after the treatment at 873 K, the XRD pattern and the BET surface area did not change, indicating that the AlPO structure remained intact even though redox sites were made inactive by this treatment. The higher temperature at which H₂O forms on CoAPO-18 (750 K) relative to MnAPO-18 (620 K) during O₂-TPO, as well as the higher temperatures required for H₂ reduction, indicate that Mn cations are more reactive in redox cycles with H₂ and O₂ than Co cations in AlPO structures.

The absence of removable O atoms in CoAPO and MnAPO samples was confirmed by CO-TPR measurements, during which cation reduction must occur with oxygen removal to form CO₂.^{9,29} MnO_x and CoO_x structures (e.g., MnO₂, Mn₂O₃, Co₃O₄, and Co₂O₃) reduce via O-atom removal and lead to CO₂ formation during treatment in CO below 773 K. Neither CO₂ formation nor CO consumption were detected during treatment in CO at temperatures up to 773 K for MnAPO-5 and CoAPO-5 (CO_x/Me < 0.01). These results confirm that H₂ reduction involves only proton formation and is consistent with the exclusive presence of redox sites in framework positions,

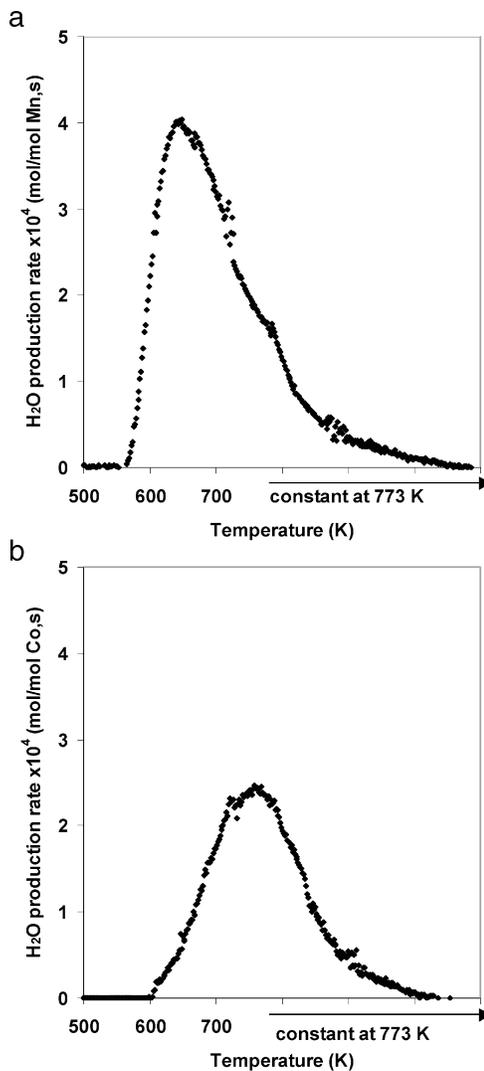


Figure 2. Temperature-programmed oxidation in 80% O₂/He of (a) MnAPO-18 and (b) CoAPO-18 [80% O₂/He, 0.167 K s⁻¹ from 298 to 773 K, hold 1 h at 773 K].

presumably as isomorphous replacements for Al atoms in AlPO crystalline structures.

An analysis of reduction rates during H₂-TPR was used to rigorously assess the relative reduction rates of Mn and Co cations in AlPO-5 and AlPO-18 structures. Reduction profiles were described using a rate constant ($k = Ae^{-E_a/RT}$) for reaction 1 with a first-order dependence of reduction rates on the residual concentration of oxidized metal centers [O*]. H₂ concentrations changed less than 1% during reduction and were assumed to remain constant. Any dependence of reduction rates on H₂ concentration is contained within the pseudo-first-order preex-

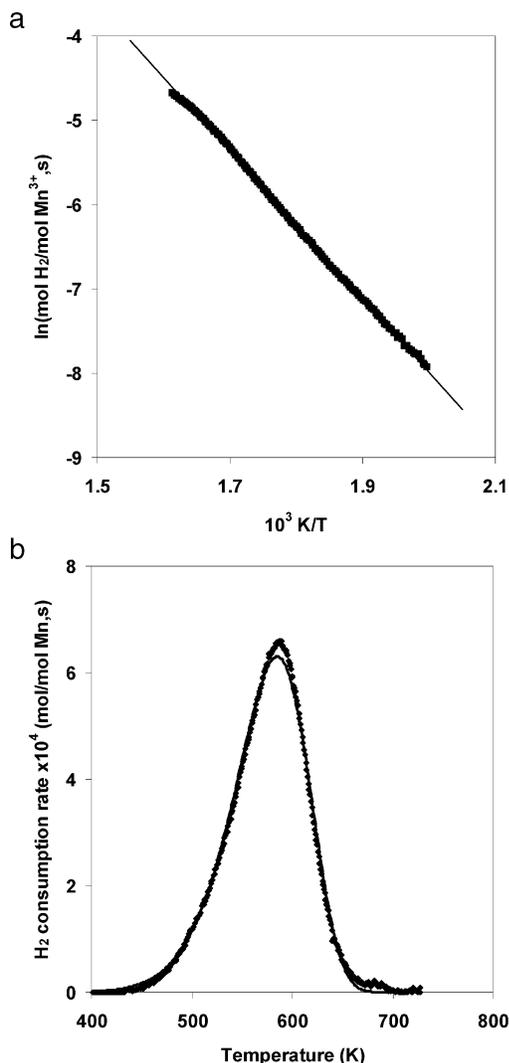


Figure 3. Temperature-programmed reduction of MnAPO-5-2 (a) Arrhenius plot of H₂ consumption rate per remaining Mn³⁺ in the sample (b) experimental (squares) and predicted (solid line) H₂ consumption rates [20% H₂/Ar, 0.167 K s⁻¹ from 298 to 773 K, hold 0.5 h at 773 K].

ponential factor ($A_1 = A[\text{H}_2]^\alpha$). Equations 2–4 provide the basis for H₂-TPR data analysis

$$r_{\text{H}_2} = k[\text{H}_2]^\alpha[\text{O}^*] = A e^{-E_a/RT}[\text{H}_2]^\alpha[\text{O}^*] = A_1 e^{-E_a/RT}[\text{O}^*] \quad (2)$$

A site balance on oxidized and reduced sites (eq 3) is inserted into eq 2, which is rearranged and shown in Arrhenius-form (eq 4). [L] represents the total concentration of cationic sites that undergo reduction, and [OH*] represents the concentration of reduced sites

$$[\text{L}] = [\text{O}^*] + [\text{OH}^*] \rightarrow [\text{O}^*] = [\text{L}] - [\text{OH}^*] \quad (3)$$

$$\ln\left(\frac{r_{\text{H}_2}}{[\text{L}] - [\text{OH}^*]}\right) = \ln(A_1) - \frac{E_a}{R} \frac{1}{T} \quad (4)$$

The semilogarithmic plot suggested by eq 4 gives a straight line (e.g., Figure 3a for MnAPO-5-2), and Figure 3b demonstrates the excellent agreement between experimental and simulated H₂-TPR results. Table 3 shows preexponential factors (A_1) and activation energies (E_a) for all samples. The data are accurately described using a single kinetic process, which provides additional evidence for the presence of a single type

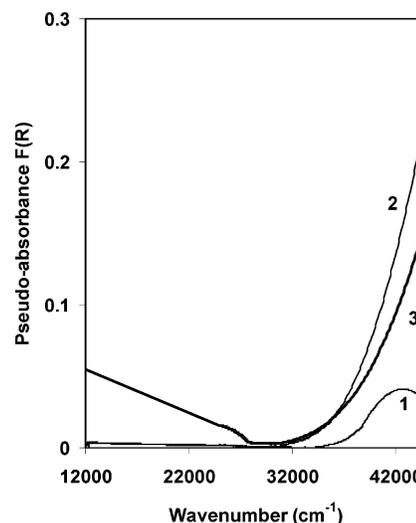


Figure 4. UV-visible spectra of AlPO-18 at 298 K. (1) As prepared, (2) air-treated (air, 0.167 K s⁻¹ to 393 K, 0.05 K s⁻¹ to 823 K, 3 h at 823 K), and (3) in situ H₂-treated (12.5% H₂/He, 0.167 K s⁻¹ to 653 K, 1 h at 653 K).

TABLE 3: Rate Constants and Arrhenius Parameters for H₂ Reduction of Mn- and CoAPO Samples [0.2 G, 80 cm³/min 20% H₂/Ar, 0.167 K s⁻¹ from 298 to 773 K, Hold 0.5 h at 773 K]

sample	A_1 (s ⁻¹)	E_a (kJ/mol)	k (at 500 K) (s ⁻¹)
MnAPO-5-1	22 300	74.9	3.3×10^{-4}
MnAPO-5-2	13 200	72.6	3.4×10^{-4}
MnAPO-5-3	1040	59.5	6.3×10^{-4}
MnAPO-18	37 000	79.8	1.7×10^{-4}
CoAPO-5	329	73.2	7.5×10^{-6}

of reducible cations in these samples. A less equivocal conclusion is precluded by the possibility that minority sites catalyze kinetically relevant H₂ dissociation steps in a unique kinetic process; the resulting H atoms could then spill-over and reduce cation sites at rates unaffected by the relative reduction tendencies of a potentially nonuniform distribution of cation structures. Their lower reduction peak temperatures and larger reduction rate constants (Table 3) indicate that Mn cations are more reducible than Co cations in AlPO structures. Reduction rates per Mn_{redox} also increased slightly with increasing Mn/P ratios in MnAPO-5.

These measurements of the rate and extent of reduction and oxidation in Mn- and CoAPO samples show that these materials contain cations that undergo reversible redox cycles but also cations that do not. The relative amounts of these two cation types can be accurately assessed by these chemical measurements. In parallel, we have probed the structure and electronic properties of Co and Mn sites using UV-visible and X-ray absorption spectroscopies, as described next.

Probing the Redox Behavior of MnAPO and CoAPO Materials Using in Situ UV-Visible Spectroscopy. Figure 4 shows ambient temperature UV-visible spectra for fresh AlPO-18 after treatment in He at 393 K, in dry air at 823 K for 3 h, and then in 12.5% H₂/He at 653 K for 1 h. The corresponding spectra for MnAPO-18 and MnAPO-5-1 are shown in Figure 5 and those for CoAPO-18 and CoAPO-5 in Figure 6. AlPO-18 shows much weaker absorption features in the experimental spectral region (12000–45000 cm⁻¹) than MnAPO-18 or CoAPO-18 after each thermal treatment (Figures 5a and 6a), suggesting that the absorption features in samples containing active cations reflect the electronic spectra of such active Co and Mn cations. The maximum absorption is observed at 41 700

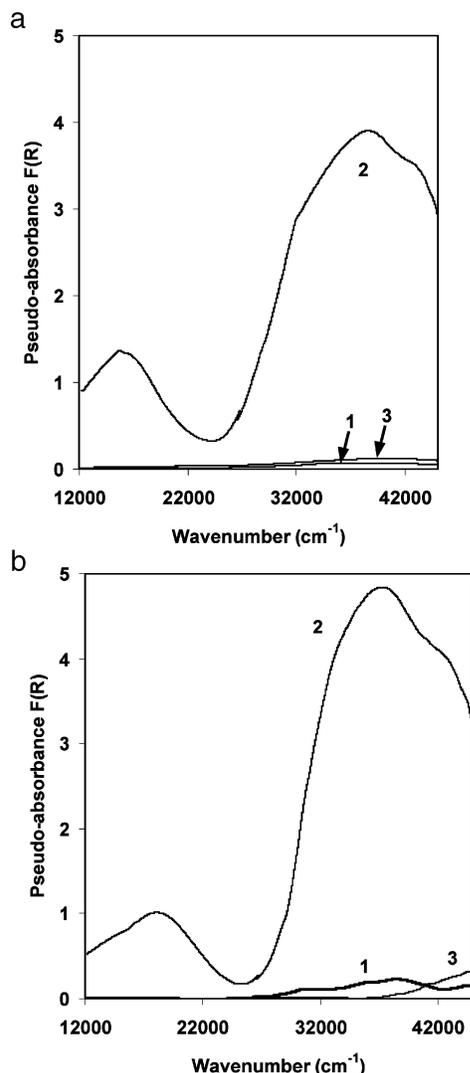


Figure 5. UV-visible spectra at 298 K of (a) MnAPO-18 and (b) MnAPO-5-1. (1) As prepared, (2) air-treated (air, 0.167 K s^{-1} to 393 K, 0.05 K s^{-1} to 823 K, 3 h at 823 K), and (3) in situ H_2 -treated (0.167 K s^{-1} to 773 K, 12.5% H_2/He).

cm^{-1} for the as-synthesized AlPO-18 sample; this maximum shifts to higher wavenumbers (above $45\,000 \text{ cm}^{-1}$) after treatment in air or 12.5% H_2/He at 773 K.

The removal of the organic template from fresh MnAPO-18 by treatment in air leads to two intense broad bands (Figures 5a), which are assigned to the oxidation of Mn^{2+} to Mn^{3+} . The low-energy band ($18\,000 \text{ cm}^{-1}$) corresponds to d-d transitions in Mn^{3+} , which has a d^4 configuration; Mn^{2+} , with a d^5 configuration, does not have an allowed d-d transition for high-spin configurations, in which each d orbital is occupied by one electron. The high-energy band ($37\,000 \text{ cm}^{-1}$ with $42\,000 \text{ cm}^{-1}$ shoulder) is attributed to ligand-to-metal charge transfer from the HOMO in O atoms to the LUMO in Mn^{3+} cations.

Reported band positions for Mn cations in several valences are reported in Table 4.³⁰ Isomorphous substitution of Mn for Al in framework positions would lead to tetrahedral coordination. A few cases of tetrahedral Mn^{2+} compounds have been reported;³¹ however, UV-visible spectra for these compounds (or for Mn^{3+}) are not available. Thus, the nature of the Mn environment on MnAPO samples has remained equivocal even after several literature reports. Octahedral $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$ shows a single absorption at $21\,000 \text{ cm}^{-1}$, assigned to ${}^5\text{E}_g \rightarrow {}^5\text{T}_{2g}$ d-d transitions.³⁰ Wu et al. reported UV-visible spectra for

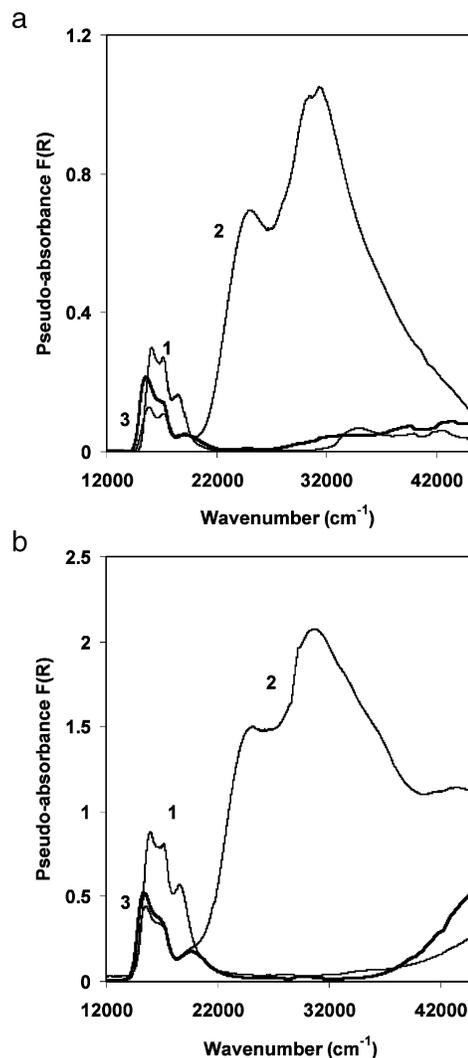


Figure 6. UV-visible spectra at 298 K of (a) CoAPO-18 and (b) CoAPO-5. (1) As prepared, (2) calcined (823 K, air, 0.167 K s^{-1} to 393 K, 0.05 K s^{-1} to 823 K, 3 h), and (3) in situ H_2 -treated (0.167 K s^{-1} to 773 K, 12.5% H_2/He).

TABLE 4: Literature Assignments for Ligand-to-Metal Charge Transfer and d-d Transfer Transitions for Mn Reference Compounds

compound	Mn^{n+}	band position (cm^{-1})	assignment
MnO	Mn^{2+} (octahedral)	23800	${}^6\text{A}_{1g} \rightarrow {}^4\text{A}_{1g}$
		20800	${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}$
		16400	${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}$
Mn_3O_4	Mn^{2+} (spinel)	39125	$\text{O}^{2-} \rightarrow \text{Mn}^{2+}$
	Mn^{3+} (spinel)	31250	$\text{O}^{2-} \rightarrow \text{Mn}^{3+}$
$\alpha\text{-Mn}_2\text{O}_3$	Mn^{3+} (pseudo-octahedral)	27027	${}^5\text{B}_{1g} \rightarrow {}^5\text{B}_{2g}$
		20618	${}^5\text{B}_{1g} \rightarrow {}^5\text{E}_g$
		13245	${}^5\text{B}_{1g} \rightarrow {}^5\text{A}_{1g}$
		23696	${}^6\text{A}_{1g} \rightarrow {}^4\text{A}_{1g}$
Mn-Al ₂ O ₃	Mn^{2+}	18700–20600	${}^5\text{E}_g \rightarrow {}^5\text{T}_{2g}$
	Mn^{3+}		
	Mn^{4+}	21300	${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$

MnAPO-5 treated in air at 823 K for 6 h but then exposed to ambient moisture, which leads to coordination by water and changes in the electronic spectrum of Mn centers.⁷ Nevertheless, their spectra resemble those reported here for samples held within strictly controlled anhydrous environments. Their study reported two ligand-to-metal charge-transfer bands at $45\,450$ and $38\,760 \text{ cm}^{-1}$ and one d-d absorption band at $20\,000 \text{ cm}^{-1}$.⁷

In contrast with air-treated MnAPO-18, UV-visible spectra for fresh and H_2 -treated MnAPO-18 resemble those for pure

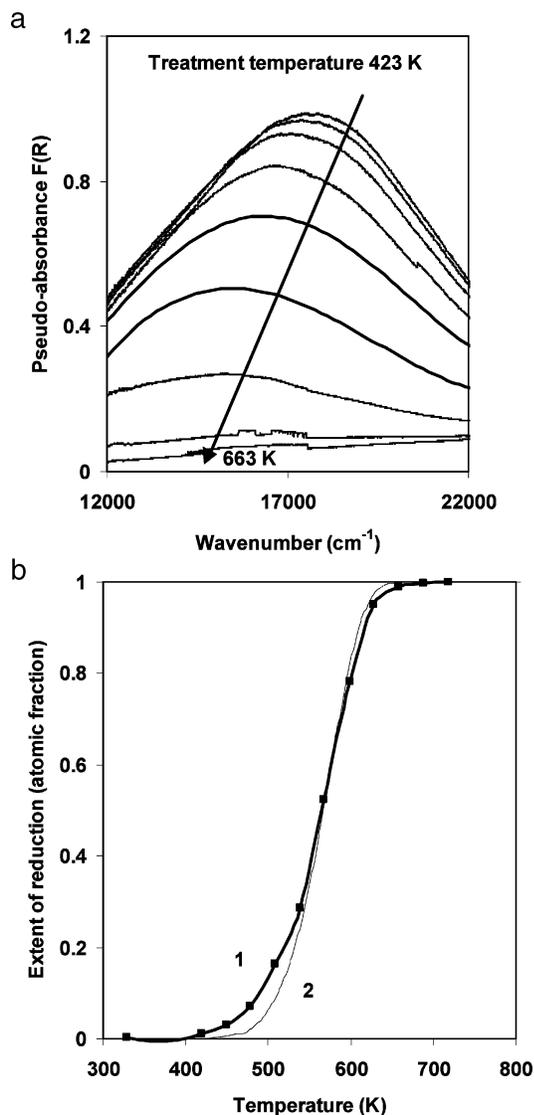


Figure 7. (a) Temperature-programmed reduction of MnAPO-5-1 monitored by UV-visible spectroscopy. (b) Comparison of the extent of reduction of Mn-redox sites detected by (1) UV-visible spectroscopy and (2) H₂ consumption measurements.

AlPO-18 (Figures 4 and 5a). This reflects the predominant presence of Mn²⁺ with a d⁵ configuration. Octahedral [Mn-(H₂O)₆]²⁺ shows broad absorption bands of very low intensity starting at 18 000 cm⁻¹.³⁰ The presence of any Mn³⁺ species in as-synthesized and H₂-treated samples would have led to detectable d-d transitions; thus, we conclude that this H₂-treatment reduces all Mn³⁺ species initially present in the sample to Mn²⁺.

The results of chemical analysis of the effluent during H₂-TPR were compared with the relative amounts of divalent and trivalent cations obtained from UV-visible spectra by carrying out H₂-TPR experiments while continuously monitoring UV-visible spectra (e.g., MnAPO-5-1; Figure 7a). The d-d band for Mn³⁺ (18 000 cm⁻¹) was used as reference as the spectrum changed during TPR; using the band at 37 000 cm⁻¹ led to identical results, because it decreased to the same extent during reduction and corresponds to the same species. Band intensities for air-treated and H₂-treated samples were used to define zero and complete reduction of redox-active cations, respectively, because nonredox sites are not affected and do not contribute to the intensity of absorption features.

TABLE 5: Energies for Absorption Maxima after Various Treatments of CoAPO-5 and CoAPO-18

samples	wavenumber (cm ⁻¹)	
	visible region	UV region
as prepared CoAPO-18	16 000, 17 200, 18 600	none
as prepared CoAPO-5	15 800, 17 200, 18 600	none
calcined CoAPO-18	15 800, 17 200, 19 100	25 100, 30 800
calcined CoAPO-5	15 600, 17 200, 19 400	25 000, 31 100
reduced CoAPO-18	15 600, 17 200, 19 100	none
reduced CoAPO-5	15 400, 17 200, 19 400	none

Figure 7b shows that chemical analysis and UV-visible assessments of the extent of reduction are in excellent agreement. As mentioned earlier, we note that spectral features for Mn³⁺ were absent in UV-visible spectra collected after H₂-TPR to 773 K, indicating that this treatment reduced all Mn³⁺ cations to Mn²⁺. Thus, any Mn cations that do not undergo reduction during this H₂ treatment (as shown from the H₂/Mn ratio below 0.5) must have already been in their divalent state before H₂ treatment. For example, air-treated MnAPO-5-1 contains 62% of the Mn cations as Mn³⁺, all of which reduce to Mn²⁺ during H₂ treatment at 773 K. The remaining 38% of the Mn cations must already be present as Mn²⁺ and they do not reoxidize during subsequent thermal treatment in air up to 823 K. We expect, and indeed find and discuss later, that these permanently divalent cations are not relevant to catalytic oxidation pathways; the structure of these sites and their lack of catalytic implications are discussed in more detail below.

CoAPO-18 and CoAPO-5 showed three overlapping bands at low energies (15 000–20 000 cm⁻¹) for all treatments, whereas two broad features with maxima at 25 000 and 31 000 cm⁻¹ appeared only during treatment in air (Figure 6, Table 5). The spectra for fresh, air-treated and H₂-treated CoAPO-5 and CoAPO-18 resemble those previously reported for CoAPO-5^{12,13} and CoAPO-18.^{24,25} Low-energy spectral features have been assigned to Co²⁺, but their sensitivity to coordination symmetry remains unclear, because multiple complex electronic transitions are available in both tetrahedral and octahedral Co²⁺ complexes.³⁰ Tetrahedral [CoCl₄]²⁻ shows two bands at 5500 and 14 700 cm⁻¹, which were assigned to ⁴A₂ → ⁴T₁(F) and ⁴A₂ → ⁴T₁(P) transitions, respectively.³¹ A third transition (⁴A₂ → ⁴T₂) at 3500 cm⁻¹ is expected, but it is very weak.³¹ We have assigned the three overlapping bands at 15 000–20 000 cm⁻¹ to ⁴A₂ → ⁴T₁(P) transitions in tetrahedral Co²⁺ structures, consistent with Verberckmoes et al.,¹² who detected a band at 5000–9000 cm⁻¹ for CoAPO-5 (cf. 5500 cm⁻¹ for [CoCl₄]²⁻) and assigned it to these transitions. The splitting of bands between 15000 and 20000 cm⁻¹ reflects significant distortion of tetrahedral Co centers, as suggested previously from spectral changes observed during template removal in CoAPO-36 relative to tetrahedral [CoCl₄]²⁻. The two overlapping bands at higher energies have been assigned to Co³⁺,^{12,24,25,32} but it is unclear whether they arise from d-d or ligand-to-metal transitions. Tetrahedral [Co^{III}W₁₂O₄₀]⁵⁻ gives a single band at 25 700 cm⁻¹ due to ⁵E → ⁵T₂ transitions.³³ The doublet in CoAPO-5 and CoAPO-18 spectra appears to arise, as in Co²⁺, from distorted tetrahedral symmetry. Verberckmoes et al. detected a feature in the near-infrared (9000 cm⁻¹) for CoAPO-5 treated in air and assigned it to d-d transitions, suggesting that the remaining high-energy bands reflect instead ligand-to-metal charge transfer.¹²

As in the case of MnAPO-5, UV-visible spectra of CoAPO-5 during H₂ treatment can be compared with H₂ consumption rates during H₂-TPR (Figure 8). Here, we use the Co³⁺ band at 25 000 cm⁻¹ as reference, but the other absorption band (31 000 cm⁻¹)

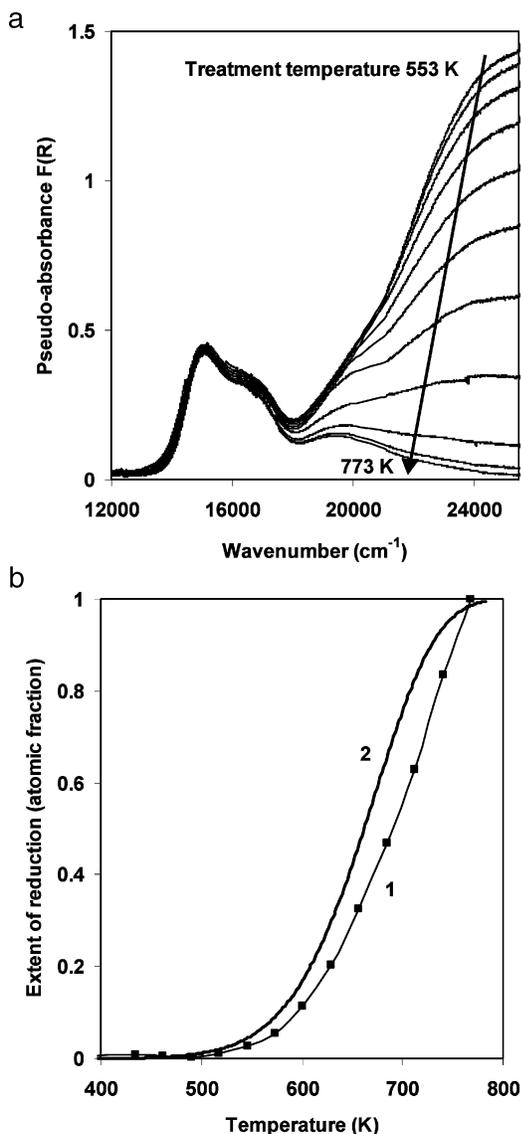


Figure 8. (a) Temperature-programmed reduction of CoAPO-5 monitored by UV-visible spectroscopy. (b) Comparison of the extent of reduction of Co-redox sites detected by (1) UV-visible spectroscopy and (2) H₂ consumption measurements.

follows identical trends, indicating that it arises from other transitions in the same Co cation species. The agreement between these two methods is again excellent, indicating also that the assignment of the high-energy band to Co³⁺ is indeed correct. As for MnAPO-5, we conclude that only some of the Co cations (40%) in CoAPO-5 undergo redox cycles and that all Co species are present as Co²⁺ after treatment in H₂ at 773 K. Thus, redox-inactive species are permanently divalent during all thermal treatments.

In addition to confirming the assignment of the high-energy band to Co³⁺, we also comment on the origins of absorption bands in the low-energy triplet region (15 000–20 000 cm⁻¹). The integrated intensity in this spectral region decreased by 45% for CoAIPO-18 (Figure 6a) and 55% for CoAPO-5 (Figure 6b) after treatment in air at 823 K; this decrease is in quantitative agreement with the results of Peeters et al. (45–55%) for CoAPO-5 at similar conditions.³⁴ The weaker intensity observed after air treatment cannot be recovered after subsequent treatment in H₂ at 773 K; thus, some of the Co²⁺ species initially present cannot be restored to their initial structure by treatment in H₂ at 773 K, and only a small intensity increase (~15%)

was observed, in agreement with previous studies, which provided no interpretation for these results.^{12,13} The partial and irreversible loss of intensity for this triplet band during template removal and during subsequent treatment in H₂ does not reflect irreversible redox processes, because chemical characterization shows that redox cycles are fully reversible. These changes reflect instead some structural distortion of Co²⁺ centers during air treatment. The detailed shape and position of these bands also differ among the various samples (fresh, air-treated, and H₂-treated samples); specifically, the bands shift and the splitting increases after air or H₂ treatments, indicating additional distortion and a consequent decrease in absorption cross-sections during template removal and high-temperature treatments.

We speculate that structural distortion occurs via recombination of hydroxyls associated with reduced Co²⁺ sites initially present in the sample after synthesis. This process requires vicinal or at least mobile Co sites in order to form H₂O and an oxygen vacancy²¹ that must be stabilized by two Co²⁺ atoms. The mere presence of a vacancy site will cause significant distortion of Co centers from the tetrahedral symmetry required by the AIPO framework; Co–O–Co structures within an AIPO crystalline framework would also lead to significant structural distortion.

The partial recovery of the triplet intensity in CoAPO-5 during the H₂-treatment following air-treatment indicates that Co centers that remain divalent throughout both treatments (~60%) account for the triplet intensity. In contrast, the 40% of the Co species that undergo redox cycles only contribute marginally to the triplet absorption bands after reduction in H₂ to Co²⁺. The fraction of Co in CoAPO-18 that is redox-active (64%) is larger than in CoAPO-5 (40%) and the changes in intensity within the Co²⁺ triplet region are commensurately larger. Changes in extinction coefficients arising from structural distortion and the contributions from redox accessible and inaccessible Co²⁺ sites make this spectral region ill-suited for quantitative assessments of the Co oxidation state in these samples. We conclude that valence and structural changes combine to give the observed changes in the UV-visible spectra of CoAPO samples during various thermal treatments. Their unequivocal interpretation and quantitative assessment require parallel chemical and spectroscopic studies, as we have carried out and report here.

X-ray Absorption Spectroscopy During Treatment of CoAPO-18 in H₂. CoAPO materials have been previously studied using X-ray absorption spectroscopy.^{5,22,35–38} Specifically, the fine structure in the absorption spectrum has been used to measure coordination numbers and bond distances;²² recently, Cora et al. extended such methods to MnAPO materials.³⁹ These methods use changes in bond distances between freshly prepared and air-treated samples to determine Mn and Co oxidation states by assuming the exclusive presence of trivalent cations in the samples with shortest Me–O bond distances (Co and Mn in MeAPO-18). This approach assumes a simple (and undemonstrated) linear relation between M–O bond distances and cation oxidation states. Despite the nonrigorous nature of this approach, it gave qualitative trends similar to those in our H₂-TPR measurements, including a lower fraction of the Co as redox-active species in CoAPO-5 than in CoAPO-18. The required assumption that all cations in AIPO-18 are initially their trivalent state, however, is inconsistent with our H₂-TPR data, which show that only 86% and 64% of cations are trivalent after treatment in air in MnAPO-18 and CoAPO-18, respectively. Our UV-visible studies have also shown that misleading conclusions could arise from the comparison of

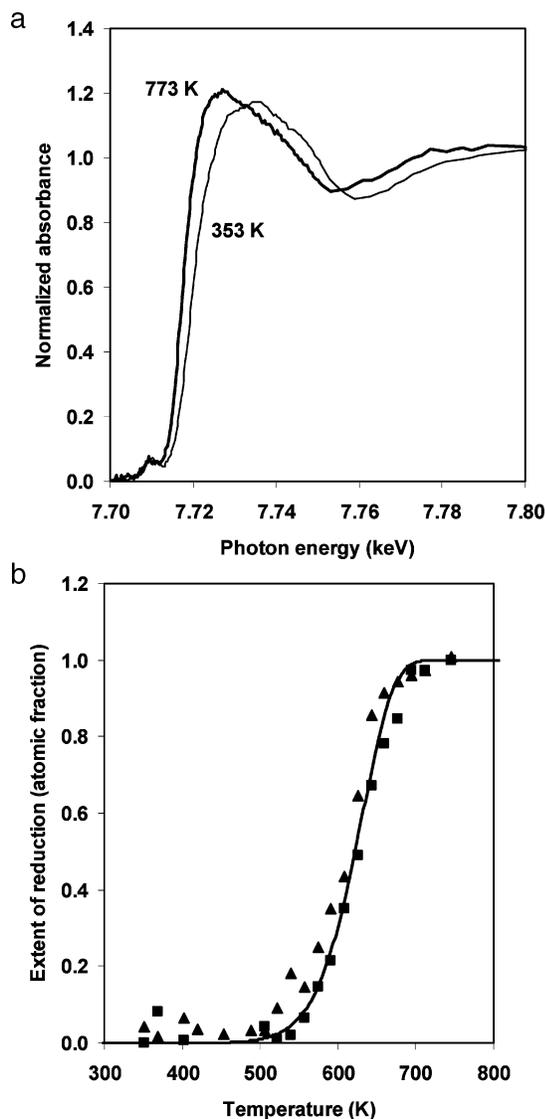


Figure 9. (a) XANES spectra during temperature-programmed reduction in 20% H₂/Ar of CoAPO-18 initially treated in air at 823 K. At 353 K, no reduction has been detected, and at 773 K, the reduction is complete. (b) Comparison of the extent of reduction of Co-redox sites detected by X-ray absorption spectroscopy (linear combination, squares, and edge energy, triangles) and H₂ consumption measurements (solid line). To calculate the extent of reduction, the intermediate spectra during the reduction were fit with a linear combination of the oxidized (353 K) and the reduced (773 K) spectra.

spectral features of as synthesized and subsequent samples. Indeed, Me–O bond distances are not completely restored to their initial values during subsequent reduction in H₂, so relevant comparisons should be made between air-treated and H₂-treated rather than using as synthesized materials, which still contain the template, as standards for divalent cations.²² Finally, the presence of at least two types of metal cations (redox-active and permanently divalent) requires rigorous multiple-shell scattering simulations for analyzing the details of the fine structure; these were carried out only for CoAPO-18 in previous studies.²²

Here, we use the near-edge region, instead of the fine structure, of X-ray absorption spectra to probe changes in oxidation state and coordination symmetry during thermal treatments, and we combine these measurements with H₂-TPR data obtained at identical conditions. Near-edge Co–K spectra for CoAPO-18 are shown in Figure 9a after treatment in air or H₂. They are used as references to define the expected spectra

when redox-active sites are fully oxidized and fully reduced, respectively. Principal component analysis of spectral transients collected during H₂-TPR showed that only two components were required to describe the evolution of the spectra during these treatments. In view of this, we have used the spectra after air and H₂ treatments (Figure 9a) for linear superimposition regressions of the spectral evolution during H₂-TPR. The results are shown in Figure 9b as the extent of reduction as a function of treatment temperature, along with similar data obtained by chemical analysis of the effluent during H₂-TPR. The two methods give very similar extents of reduction.

The edge energy can also be used to estimate the extent of reduction during H₂-TPR; this is done by using edge energies for air-treated (7.7194 keV) and H₂-treated (7.7170 keV) CoAPO-18 as standards. A linear relation between edge energy and extent of reduction is then used to determine the extent of reduction for the intermediate spectra. As seen in Figure 9b, this method gives a larger signal-to-noise ratio than the linear combination fit, but the results follow the same trend as both the linear combination and the H₂ consumption data, indicating the accuracy of this method. The observed decrease in the Co–K edge energy (~2.4 eV) with H₂ treatment at 773 K is significantly larger than reported previously for CoAPO-18 (1.2 eV).³⁶ This shift in edge energy coincided with the H₂ consumption and with the decrease in the intensity of Co³⁺ UV–visible bands during H₂-TPR. A decrease in edge energy is indeed expected upon reduction, as electrons increasingly fill empty orbitals near the vacuum level. For CoAPO-18 (64% reduction), the 2.4 eV energy shift corresponds to 3.75 eV/valence. This shift is in agreement with relations between oxidation state and edge energy for Co and Mn compounds with known valence and structure (3.5–4.5 eV/valence).^{38,40}

Comments about the Nature of Permanently Divalent Cations in AlPO Materials. Chemical characterization and spectroscopic methods led us to the definite conclusion that all MeAPO samples contain some divalent cations that do not undergo redox cycles during subsequent exposure to H₂ or O₂ at high temperatures. The absence of redox processes and of removable O atoms indicates that permanently divalent species are not present as extraframework Mn_xO_y and Co_xO_y clusters, which would undergo redox cycles with O atom removal at the conditions of our treatments. Inert Co or Mn aluminates or phosphates could be present as inert amorphous phases and account for the permanently divalent cations, but we do not detect their crystalline counterparts by X-ray diffraction.

UV–visible spectra showed that irreversible distortion accompanies the formation of permanently divalent sites during initial treatment of template-containing samples in air. This suggests that these sites are likely to form, or at least acquire their structural distortion, during oxidative removal of the organic template. These processes can lead to high local temperatures and to hydrothermal conditions conducive to restructuring of crystalline oxide structures. X-ray absorption spectra, however, detected only a small decrease in Me–O bond distances during treatment in air and a small increase during subsequent treatment in H₂ at 773 K,²² indicating that no significant structural transformations accompany redox cycles. No detectable intensity was observed beyond the first Co–O shell in the radial structure function, suggesting the absence of crystalline phases with Co–Co next nearest neighbors. This conclusion must be treated with caution, because local static disorder in crystalline oxides can lead to weak intensities beyond Me–O bonds in the radial structure functions of materials with Me–O–Me structures.

Taken together, the structural distortion detected in UV–visible spectra and the minor changes in the X-ray absorption radial structure function²² suggest that permanently divalent structures consist of dehydroxylated structures. These structures were first proposed by Peeters et al.²¹ and later supported by infrared and UV–visible spectroscopy.^{23,24} Also, in our H₂-TPR study, less than 0.5 H₂/Me was observed even for samples with the atomic (Me+Al)/P ratio of unity (MnAPO-5-2 and MnAPO-18) expected for MeAPO samples in which all metal ions replace Al within the AIPO framework. This dehydroxylation mechanism is consistent with the observed (Me+Al)/P stoichiometry of unity, because conversion of framework species into permanently divalent species by dehydroxylation would retain this stoichiometry, whereas the presence of extraframework phases would most likely lead to a different stoichiometry. Also, the observed decrease in the redox-active Mn fraction with increasing Mn loading and the loss of redox-active centers as the final temperature in H₂-TPR increases for MnAPO-18 are consistent with a dehydroxylation mechanism forming these permanently divalent sites. If so, the average distance among Me–OH species will critically determine the relative probability that such sites will undergo condensation instead of oxidation at high temperatures. Isolated reduced Me–OH sites can only be oxidized via proton removal to form H₂O in the presence of O₂, but vicinal Me–OH species can also dehydroxylate to form H₂O and an oxygen vacancy. With increasing Mn/P ratio, this would lead to lower average Mn(OH)–Mn(OH) distances, and thus to higher recombination probabilities. A more rigorous analysis of these findings would require theoretical assessments of Me–Me distributions in MeAPO-5 for various Me/P ratios, as recently done for Al–Al distributions in ZSM-5 as a function of Si/Al ratio.⁴¹ The importance of detemplating should also be mentioned here, as inappropriately chosen conditions during detemplating can lead to recombination before oxidation of cations via proton removal occurs.

The relative rates of dehydroxylation and oxidation can also be discussed in the context of comparisons between Mn and Co versions of AIPO structures. CoAPO-5 (or -18) has a lower Me/P ratio than MnAPO-5 (or -18) (Table 1), but the redox-active fraction is lower (Table 2), which seems inconsistent with purely statistical arguments for inactivation of redox sites via bimolecular dehydroxylation. One reason for the greater prevalence of permanently divalent sites in Co samples may be that Co²⁺ to Co³⁺ oxidation in O₂ requires higher temperatures than the corresponding one-electron oxidation of Mn²⁺ (see Figure 2), thus increasing the likelihood of recombination before removal of the proton via reaction with O₂. It is also possible that cation distributions are not random in AIPO frameworks and that cation pairing is more likely for Co than for Mn cations and preferred in some AIPO structures over others. For example, the disappearance of tetrahedral P centers in ³¹P NMR spectra for a series of CoAPO-5 samples with varying Co/P ratios was used to propose that Co-atoms clusters form within AIPO frameworks;⁴² clustering would lead to regions with high local Co contents and shorter Co–Co distances, which would favor dehydroxylation.

If our hypothesis is correct, redox-active and permanently divalent sites arise from Me–OH species, which lose their redox capability by forming permanently divalent structures via dehydroxylation. A rigorous evaluation of the active sites required for catalytic oxidation reactions and estimates of rigorous turnover rates require accurate measurements of the number of each type of site for each composition and thermal treatment procedure. Chemical analysis of the effluent during

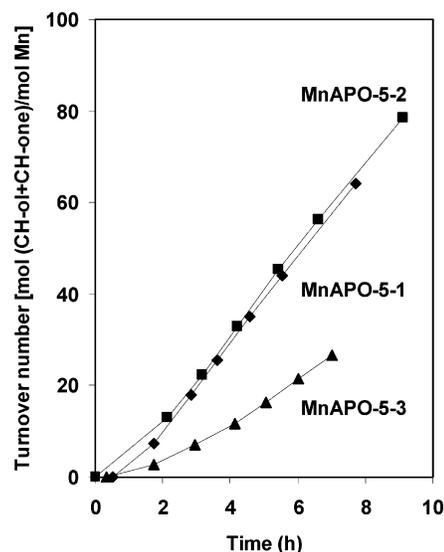


Figure 10. Cyclohexanol + cyclohexanone formation turnover number per total Mn vs contact time during cyclohexane oxidation on MnAPO-5-1, MnAPO-5-2, and MnAPO-5-3 [403 K, 25 mL cyclohexane, 4 atm O₂ (at 298 K), 0.2 g catalyst].

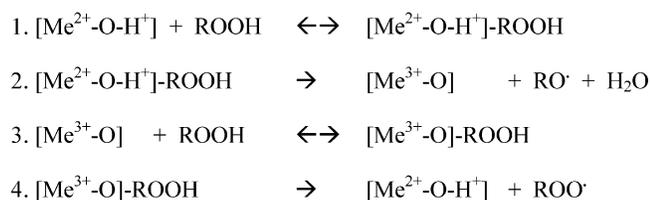
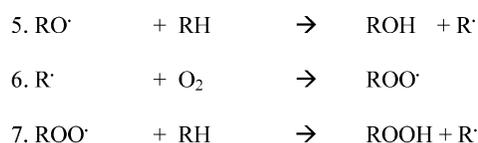
TABLE 6: Cyclohexanol + Cyclohexanone Formation Rate Normalized by Mn_j (Mn_j = Mn_{total}, Mn_{redox} or Mn_{non-redox})

catalyst	turnover rate [mol (ROH + R=O)/mol Mn _j h]		
	Mn _{total}	Mn _{redox}	Mn _{non-redox}
MnAPO-5-1	9.11	14.7	24.0
MnAPO-5-2	9.30	13.1	32.1
MnAPO-5-3	5.74	13.4	10.0

H₂-TPR provides a simple and accurate method for this required site speciation, which can then be used to assign catalytic relevance to the various forms of Co and Mn cations in MeAPO materials.

Involvement of Redox-Active and Permanent Sites in Catalytic Oxidation of Cyclohexane on MnAPO and CoAPO Materials. Cyclohexane oxidation has previously been studied on MeAPO materials,^{5,8,43–45} frequently without detailed time-resolved kinetic studies or well-characterized materials. Here, cyclohexane oxidation rates and selectivities were measured on three MnAPO-5 catalysts (Mn/P = 0.028–0.10) to assess the effect of Mn content and of reversible redox sites. Cyclohexanol (ROH) and cyclohexanone (R=O) turnovers (per Mn atom) are shown in Figure 10. The relatively low conversions (<5%) allow kinetic studies of the formation of initial products; at higher conversions, esters and acids form via secondary reactions, which introduce analytical complexities and can cause leaching of cations from inorganic structures. Cyclohexanol and cyclohexanone turnover rates (slope in Figure 10) reached constant values after 2–4 h. These steady-state rates increased in parallel with the number of redox-active Mn atoms measured during reduction studies for these MnAPO-5 samples (Table 6). They were not influenced by the number of permanently divalent Mn centers, indicating that redox sites, determined from H₂-TPR, UV–visible, and X-ray absorption measurements, are the only active structures for cyclohexane oxidation on these samples.

By inference from other low-temperature catalytic oxidations with homogeneous Mn and Co complexes and O₂, reactions are assumed to occur on MeAPO materials via initial formation of cyclohexyl hydroperoxide (ROOH), which in the case of homogeneous complexes decomposes using cations in solution to form solvated ROO[•] and RO[•] radicals in initiation steps. More specifically, ROOH decomposition is proposed to involve Me-

SCHEME 1: Cyclohexane (RH) Oxidation Pathways on Me Sites (Me = Mn or Co)InitiationPropagationTermination

ROOH complexes and one-electron redox cycles (steps 1–4 in Scheme 1). Scheme 1 is adapted from previous proposals⁴⁶ by replacing homogeneous Me centers with active framework Me_{redox} species; $[\text{Me}^{2+}\text{-O-H}^+]$ and $[\text{Me}^{3+}\text{-O}]$ represent reduced and oxidized species in reaction 1. Pathways resembling those in Scheme 1 are likely to be involved on heterogeneous catalysts, but radical-type intermediates are likely to remain adsorbed at cation sites, or at least react within microporous channels, which lack a well-defined liquid phase. Thus, it seems inappropriate to describe this oxidation as free radical-like, because alternate pathways of surface-bound intermediates may offer opportunities for specific regioselectivity in oxygen insertion steps. However, homolytic bond activation steps follow trends similar to those in radical reactions, so we use the radical-like steps proposed for homogeneous systems (Scheme 1) as a starting point in analyzing the kinetic results of this study.

Constant cyclohexanol and cyclohexanone formation rates were observed after an initial induction period indicating that all kinetically relevant intermediates reached steady-state concentrations; thus, initiation and termination rates become equal and catalyst surface coverages also reach steady-state. Rates of cyclohexanol and cyclohexanone formation initially increased with increasing ROOH concentration, but further increases in ROOH concentration did not influence reaction rates, indicating that ROOH-derived intermediates required for product formation reached saturation coverages at active sites and that all cations form $\text{Me}\text{-ROOH}$ complexes. The divalent state $[\text{Me}^{2+}\text{-O-H}^+]\text{-ROOH}$ was inferred kinetically to decompose more slowly than the trivalent state $[\text{Me}^{3+}\text{-O}]\text{-ROOH}$,⁴⁶ but no direct evidence was provided. In this case, we expect that $[\text{Me}^{2+}\text{-O-H}^+]\text{-ROOH}$ is the most abundant reactive intermediate (MARI) when the rates of steps 2 and 4 become equal after the induction period. Then, we can extract k_2 values (k_2 is the rate constant for step 2 in Scheme 1) from measurements of initiation rates (which equal cyclohexane conversion rates at steady-state) and the number of redox-active sites. These k_2 values are then used for rigorous comparisons of intrinsic reactivity for redox-active cations on different catalysts. It should be noted that the analysis is not limited to the case of step 2 as the slowest step. If radicals remain adsorbed, another step may be slower, for example the decomposition of adsorbed ROO^\cdot (step 8). Then, the nature of the rate constant would change (because it

represents a different step), but the value would be the same, as the slowest decomposing intermediate would be at saturation coverage on the active Mn_{redox} sites. At saturation coverage, the k_2 values for MnAPO-5-1, MnAPO-5-2, and MnAPO-5-3 are the same value as the rate per Mn_{redox} site, i.e., 14.7, 13.1, and 13.4 mol $(\text{ROH} + \text{R=O}) (\text{mol Mn}_{\text{redox}})^{-1} \text{h}^{-1}$, showing an essentially constant k_2 value and, thus, a constant Mn_{redox} activity for these three samples.

Conclusions

During H_2 -TPR on MeAPO catalysts, H_2 consumption, loss of Me^{3+} UV-visible features, and a decrease in X-ray absorption edge energy occurred concurrently and at similar rates, indicating excellent agreement between these three techniques. No H_2O or CO_2 were detected during treatment in H_2 or CO , respectively, indicating that reduction from Me^{3+} to Me^{2+} occurred by introduction of protons rather than removal of oxygen atoms. These protons are fully removed by treatment in O_2 to 773 K.

H_2 consumption rates measured during H_2 -TPR could be accurately described by Arrhenius-type behavior, and integrated H_2/Me ratios showed that all samples contain a mixture of sites that can undergo reversible redox cycles and redox-inactive sites that cannot. After thermal treatment in H_2 , UV-visible spectra showed no detectable Me^{3+} features indicating that cations that do not undergo redox cycles remain as permanently divalent cations.

The fraction of redox cations decreased during repeated $\text{H}_2\text{-O}_2$ redox cycles above 773 K, indicating that redox cations can be converted into permanently divalent sites. This conversion coincides with the evolution of H_2O during H_2 treatments above 773 K. These findings together with the decrease in the redox fraction with increasing Me/P ratio are consistent with a mechanism in which OH-groups at divalent framework sites recombine to form H_2O and an oxygen vacancy.

Cyclohexanol and cyclohexanone formation rates during liquid-phase cyclohexane oxidation with O_2 on MnAPO-5 samples increased linearly with the number of Mn_{redox} sites determined from the H_2 -TPR, suggesting that Mn_{redox} sites are the active sites for cyclohexane oxidation, and that elementary steps of this reaction require cycling between Me^{2+} and Me^{3+} .

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