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Selective Catalytic Oxidation of Organosulfur Compounds with *tert*-Butyl Hydroperoxide

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Abstract: Rates and selectivities for the oxidation of various organosulfur compounds with *tert*-butyl hydroperoxide were measured on CoAPO-5 (APO = aluminophosphate; Co/P = 0.05), Co/H-Y (Co/Al = 0.15), and MoO_x/Al_2O_3 (15 % wt MoO_3). Rates increased with increasing electron density at the sulfur atom (methyl phenyl sulfide > diphenyl sulfide > 4-methyldibenzothiophene > 2,5-dimethyl thiophene). Rates (per metal atom) were significantly higher on CoAPO-5 than on Co/H-Y, MoO_x/Al_2O_3, or homogeneous Co acetate catalysts. Small amounts of sulfoxides (1-oxide) were detected on all catalysts at low reactant conversions, together with their corresponding sulfones; at higher conversions, only sulfones (1,1-dioxide) were detected, indicating that the oxidation of sulfoxides is much faster than for organosulfur reactants in the sequential oxidation pathways prevalent on these catalysts. Framework Co cations were not leached from CoAPO-5 during the oxidation of 4-methyldibenzothiophene, but most exchanged Co cations in H-Y and > 20 % of Mo cations in MoO_x/Al_2O_3 were extracted during these reactions. The fraction of redox-active Co cations in CoAPO-5 and Co/H-Y was measured by reduction–oxidation cycles using H_2 and O_2 and by UV-visible spectroscopy. This fraction was much larger in CoAPO-5 (0.35) than in Co/H-Y (0.01), consistent with the higher oxidation rates measured on CoAPO-5 and with the involvement of redox-active species in kinetically-relevant steps in catalytic oxidation sequences. Redox-active Co cations at framework positions within accessible channels are required for catalytic activity and structural stability during oxidative desulfurization, whether hydroperoxides are used as reactants or as intermediates (when O_2 is used as the oxidant).

Keywords: aluminophosphates · cobalt · oxidative desulfurization · redox catalysts · zeolites

Introduction

Organosulfur compounds are typically removed from fuel streams by catalytic hydrodesulfurization (HDS). Molecules with sterically-hindered sulfur atoms, such as di-β-substituted dibenzothiophenes, account for most of the residual sulfur after hydrodesulfurization, because of their low reactivity in these processes.[1] Oxidative processes, in contrast, favor reactions of molecules with highly substituted sulfur atoms, because of their high electron density, and can take place at near ambient temperatures with peroxides as oxidants.[2,3] These complementary reactivity trends in reductive and oxidative desulfurization processes can lead to their synergistic deployment to decrease the sulfur content in fuels.

Oxidation of organosulfur compounds occurs by means of electrophilic addition of oxygen at sulfur atoms to form sulfoxides (1-oxides) and sulfones (1,1-dioxides). These compounds can be extracted from hydrocarbon streams by exploiting their polar nature. NO_x, HNO_3, H_2O_2, peracids, organic peroxides, and O_2[4] have been used as oxidants, with peroxides providing a compromise between reactivity and cost.

H_2O_2 reacts with thiophenic compounds at near ambient temperatures with HCOOH, CCl_xCOOH ($x = 1–3$), CF_3COOH,[4,5] methyltrioxorhenium(VII),[6] phosphotung-

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stenic acid,[7] supported metals,[8] and molecular sieves[9,10] as catalysts. Complexes containing transition metals (Ti, Mo, Fe, V, W, Re, or Ru) also catalyze the oxidation of organosulfur compounds with H_2O_2, O_3, or O_2.[11–14] Ti and V cations in zeolite frameworks are also active.[10,15] The structure of the zeolite (MFI, BEA, MEL)[16–18] and the nature of the solvent[19,20] influence oxidation rates. Hulea et al.[21] reported that H_2O_2 reacts with ethylsulfide on Ti-BEA and TS-1 (Ti-MFI), but only Ti-BEA catalyzed the oxidation of larger thiophenic molecules, because of difussional constraints prevalent in TS-1. H_2O_2 reactants, however, require the use of polar co-solvents, because of their low solubility in hydrocarbons.[22] Organic peroxides, such as *tert*-butyl hydroperoxide, dissolve in hydrocarbon liquids and avoid these constraints. *tert*-Butanol, a useful high-octane oxygenate, is formed as the byproduct when *tert*-butyl hydroperoxide is used as the oxidant. Metal-substituted aluminophosphates[23,24] catalyze oxidation[25,26] and oxidative hydrogenation[27] of alkanes, but they have not been reported to catalyze oxidation reactions of organosulfur compounds. Crystalline molecular sieves with relatively large channels [Co/H-Y (FAU, 0.74×0.74 nm, three-dimensional) and CoAPO-5 (AFI, 0.73×0.73 nm, one-dimensional)] were chosen to avoid diffusional constraints that would corrupt kinetic measurements. MoO_x/Al_2O_3 was chosen as a reference material, because it has been reported to be active and stable in the oxidation of thiophenic compounds with *tert*-butyl hydroperoxide.[28,29]

Here, we report significant reactivity and selectivity for the oxidation of methyl phenyl sulfide, diphenyl sulfide, 4-methyldibenzothiophene, and 2,5-dimethylthiophene with *tert*-butyl hydroperoxide on CoAPO-5, Co/H-Y, and MoO_x/Al_2O_3. Competitive oxidation of reactant mixtures confirmed that the reactivity of organosulfur compounds increases in parallel with increasing electron density at the sulfur atom on all catalysts, consistent with proposed electrophilic addition pathways. CoAPO-5 catalysts produced the highest reactivity and the greatest stability against the leaching of active cations during the reaction.

Results and Discussion

Temperature-programmed reduction (TPR) of CoAPO-5 and Co/H-Y catalysts in H_2 streams: H_2 consumption rates were measured during thermal treatment to probe the chemical state and redox properties of Co species in CoAPO-5 and Co/H-Y. Co cations can act as reducing agents by O atom removal as H_2O or by proton formation; both processes consume H_2, but only the first reaction forms H_2O. Thus, the amount of H_2O evolved and H_2 consumed can be used to estimate the number and type of reducible cations in each sample.[30]

Reduction was not detected in Co/H-Y between 298 and 823 K, apparently because of the prevalence of exchanged Co^{2+} cations, which interact strongly with Al sites in Y[31–33] and ZSM-5,[34,35] and reduce only above 800 K (Figure 1). These data confirm that crystalline CoO_x species are not present in this sample, because these would reduce below 750 K[36–38] to consume H_2 and form H_2O.

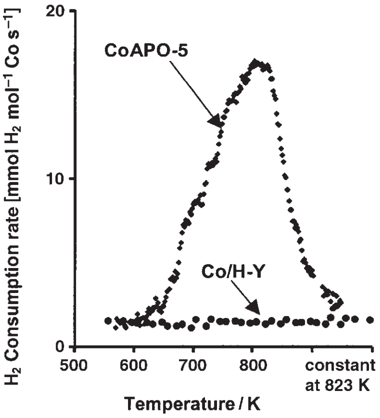
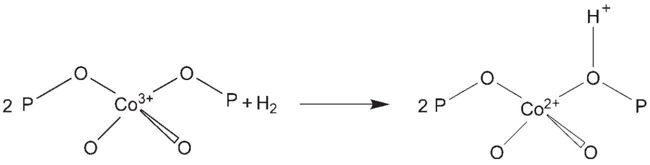


Figure 1. Temperature-programmed reduction of CoAPO-5 and Co/H-Y in 1% H_2/Ar (0.2 g, 0.67 cm^3s^{-1} 1% H_2/Ar, 0.167 Ks^{-1} from 298 to 823 K, hold 0.5 h at 823 K).

CoAPO-5 produces a H_2 consumption peak at ~820 K without detectable formation of H_2O, indicating that proton formation is the prevalent reduction mode, as expected for Co^{3+} framework cations[39,40] (Scheme 1). The amount of H_2 consumed corresponds to one-electron reduction of Co^{3+} of a fraction of all Co atoms present in the sample,[41] consistent with X-ray absorption,[40] IR, and UV-visible[42–44] spectral evidence for some permanently divalent cations. Measured H_2/Co consumption ratios (0.18) were much smaller than expected if all Co atoms in the sample underwent a one-electron reduction (0.5). Thus, CoAPO-5 contains a mixture of redox-active (~36%) and redox-inactive (~64%) Co cations.[45–47] IR of chemisorbed Co at 100 K also indicates that ~35% of the Co atoms in CoAPO-5 are able to undergo one-electron redox cycles. Previous studies have reported similar fractions of redox-active Co cations (40%) in CoAPO-5, similarly prepared.[41]



Scheme 1. Cation reduction mechanism in the CoAPO-5 sample.

Diffuse reflectance UV-visible spectroscopy of CoAPO-5 and Co/H-Y samples: UV-visible spectroscopy can be used to determine the valency and coordination of Co cations in AlPO structures. CoAPO-5 is bright blue after synthesis, indicating the presence of tetrahedral Co^{2+} cations. Its UV-visible spectra has been used to confirm that Co^{2+} cations replace Al^{3+} cations in AlPO structures.[42,48,49] Treatment in air at 823 K leads to green-colored solids, suggesting that

Co^{2+} centers undergo one-electron oxidation processes.[42,48–51]

CoAPO-5 and Co/H-Y samples treated in H_2 (“reduced” samples) at 673 K (see Experimental Section for details) show absorptions in the visible (20000–15000 cm^{-1}) and near-IR (10000–4000 cm^{-1}) regions (Figure 2). The two triplet bands in reduced CoAPO-5 have been assigned[42,52–54] to $^4T_1(P) \leftarrow {}^4A_2(F)$ (bands at 19000, 16700, and 15200 cm^{-1}) and to $^4T_1(F) \leftarrow {}^4A_2(F)$ (bands at 5500, 6400, and 8100 cm^{-1}) d–d ligand field transitions in distorted tetrahedral Co^{2+} in AlPO-5 framework. Co-Y treated in H_2 gives absorption bands at 18500, 17100, and 15500 cm^{-1}, as found in other Co-exchanged Y-zeolites, and is assigned to Co^{2+} ions coordinated to three O atoms in sodalite six-ring structures and to an additional H_2O or OH group.[50,55–60]

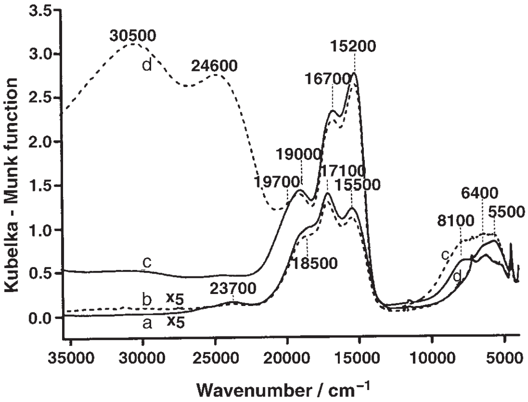


Figure 2. DR-UV-Vis spectra of: a) Co/H-Y after reduction under hydrogen at 623 K; b) Co/H-Y after oxidation at 823 K under oxygen; c) and d) CoAPO-5 after reduction and oxidation, respectively, under similar conditions to those used for Co/H-Y.

The triplet bands for Co^{2+} in CoAPO-5 became slightly weaker upon exposure to O_2 at 823 K (“oxidized” sample; see Experimental Section for details) and a broad absorption band appeared at ~8500 cm^{-1} (Figure 2, curve c). This band arises from $^5T_2 \rightarrow {}^5E$ transitions in tetrahedral Co^{3+} ions at AlPO-5 framework positions.[39,54,61] Strong absorptions at 30500 and 24500 cm^{-1}, arising from ligand-to-metal charge transfer from O atoms to tetrahedral Co^{3+},[41,42] were also detected in CoAPO-5 treated in air (Figure 2, curve c).

The spectrum of oxidized Co/H-Y (treated as CoAPO-5) also shows a weakening of the triplet band at 20000–15000 cm^{-1} upon treatment in air; these results cannot reflect oxidation of Co^{2+} centers, because reduction does not occur upon contact with H_2 at these temperatures (Figure 1). Previous studies have proposed that Co^{2+} ions in faujasite structures can migrate from sodalite cages (tetrahedral species) to hexagonal prisms (octahedral species);[50,57,62,63] this proposal may explain the weaker absorption bands upon exposure to the air.

Recent studies have combined in situ UV-visible and X-ray absorption spectroscopies with measurements of the dynamics of H_2 consumption during H_2 treatments to conclude that the bands at 25000 and 31000 cm^{-1} in samples treated with O_2 correspond to Co^{3+} centers and that redox-inactive Co species are permanently divalent.[41] Thermal treatments of Co/H-Y in streams containing O_2 did not lead to the appearance of ligand-to-metal charge transfer or $^5T_2 \rightarrow {}^5E$ bands, confirming the absence of Co^{3+} cations in these materials in which the prevalent species are redox-inactive Co^{2+} species.

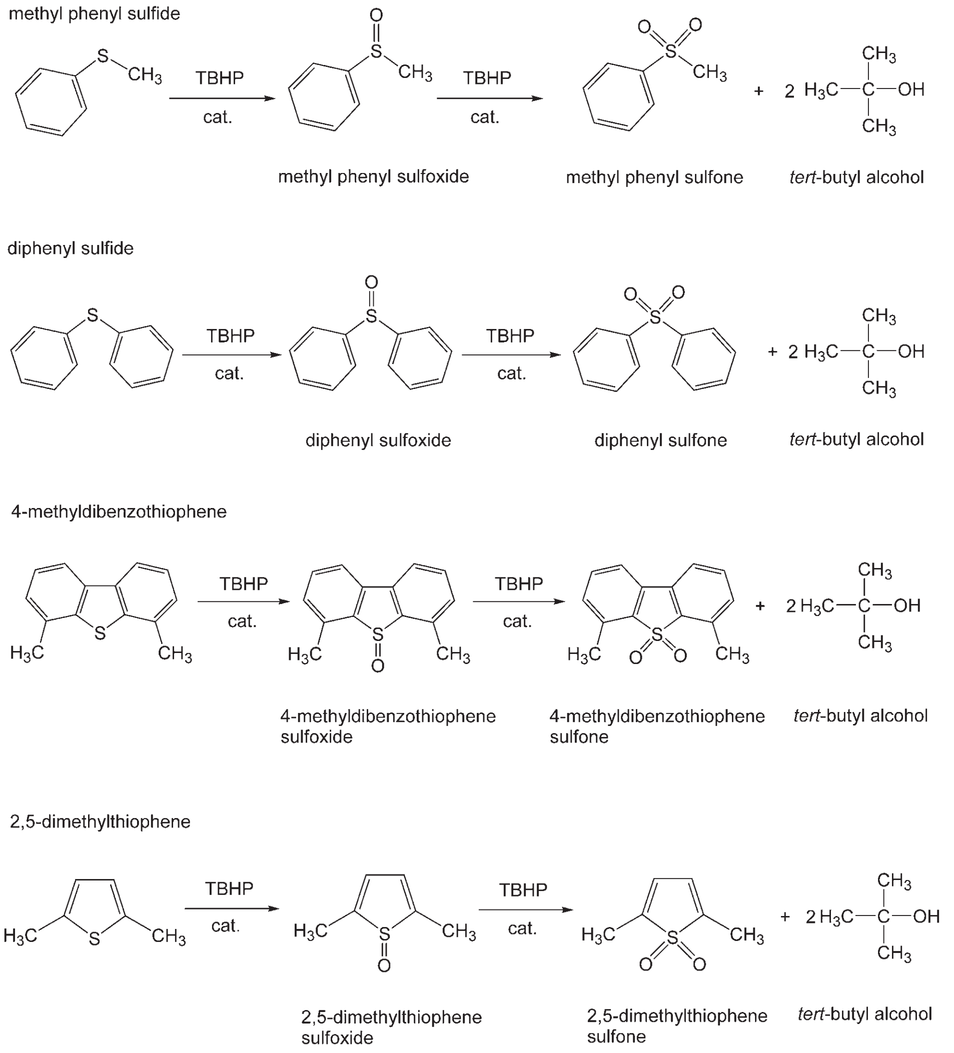
Catalytic oxidation of organosulfur compounds: The oxidation of organosulfur compounds with *tert*-butyl hydroperoxide was carried out by using Co-containing microporous catalysts with large channels [Co/H-Y (FAU, 0.74×0.74 nm, three-dimensional) and CoAPO-5 (AFI, 0.73×0.73 nm, one-dimensional)] and on MoO_x domains supported on mesoporous Al_2O_3. The physicochemical properties of these catalysts are shown in Table 1. Catalytic oxidation reactions formed the corresponding sulfones (1,1-dioxide) as the main products and *tert*-butyl alcohol as the stoichiometric byproduct (Scheme 2). Products of decalin oxidation were detected in trace amounts, while oxidation products of the *n*-decane internal standard were not observed, even at high conversions of organosulfur reactants. The formation of other byproducts, such as SO_x, was ruled out by syringe sampling of the gas phase in hermetically sealed reactors and by detailed sulfur balances, which were typically better than 95%, except at very low conversions. Chromatographic analysis of gas samples extracted after 1.8 and 3.6 ks reaction times showed tetralin in trace amounts, but no other molecules. One sulfoxide or sulfone molecule formed for each organosulfur reactant consumed (1.00±0.05).

Table 1. Properties of the catalytic materials used in this study.

Catalyst	Co or Mo [wt%]	BET area [$m^2 g^{-1}$]	Micropore volume [$cm^3 g^{-1}$]
Co/H-Y	3.74	750	0.250
MoO_x/Al_2O_3	9.38	90	–
CoAPO-5	4.00	400	0.140

With methyl phenyl and diphenyl sulphide reactants, sulfoxides (1-oxide) formed initially in low yields (<3% reactant conversion) together with the corresponding sulfones. At 0.18 ks, the sulfoxide/sulfone ratio was 0.13 and 0.08 for methyl phenyl and diphenyl sulfide, respectively, on CoAPO-5; these ratios decreased sharply with reaction time and sulfones (1,1-dioxide) became the only detectable products at higher reactant conversions (Figure 3). These data show that oxidation occurs by the stepwise addition of a single oxygen atom (Scheme 2) and that oxygen addition to sulfoxides is much faster than for organosulfur reactants.

tert-Butyl hydroperoxide oxidized organosulfur molecules with very high selectivity (>96%), even though such molecules are present as minority species in the reaction liquids.



Scheme 2. Oxidation reactions of the different sulfur compounds studied in this work (TBHP = *tert*-butyl hydroperoxide, cat. = catalyst).

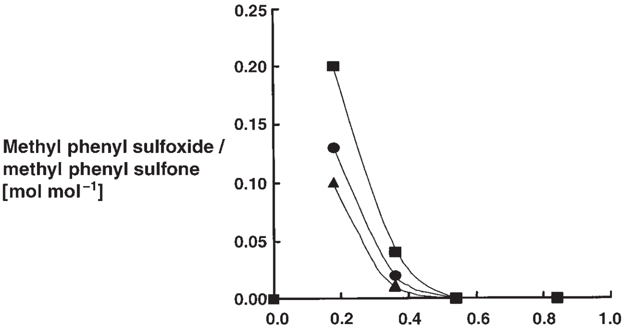


Figure 3. Variation of the methyl phenyl sulfoxide/methyl phenyl sulfone ratio during the oxidation of methyl phenyl sulfide as a function of reaction time over Co/H-Y, MoO_x/Al_2O_3, and CoAPO-5 catalysts at a reaction temperature of 353 K.

Neither the decomposition of *tert*-butyl hydroperoxide or the oxidation of organosulfur species were detected without a catalyst, except for methyl phenyl sulfide and diphenyl sulphide, which formed traces of methyl phenyl and diphenyl sulfones, respectively (<5 and <3% reactant conversion after 7 ks) after reaction times that led to complete conversion of organosulfur compounds on CoAPO-5.

The extent to which each organosulfur compound converts after a given reaction time is reported in Table 2. Oxidation turnovers [TON; organosulfur molecules converted per atom of active metal (Co, Mo)] are shown in Figure 4 as a function of contact time for each organosulfur reactant. Turnovers were significantly higher on CoAPO-5 catalyst than on Co/H-Y, as expected from the larger number of redox-active cations present in CoAPO-5, as shown in the previous section.

At 353 K, methyl phenyl and diphenyl sulfides react faster than thiophenic compounds (4-methyldibenzothiophene and 2,5-dimethylthiophene) on all catalysts. The reactivity of these organosulfur compounds increased with increasing electron density and accessibility of their sulfur atom. Figure 5 shows that fractional reactant conversions (X), plotted as $\ln(1-X)$, varied linearly with time at all conversions, as expected for first-order reactions without inhibition byproducts. Pseudo-first order rate constants (per Co or Mo), given by the slope of these lines (Figure 5), were constant with time, indicating the absence of catalytic deactivation or of any kinetic inhibition by sulfoxides and sulfones formed in these oxidation reactions.

The relative reactivity of these various organosulfur compounds was similar on CoAPO-5, Co/H-Y, and MoO_x/Al_2O_3 catalysts and the observed reactivity sequence (phenyl sulfide > diphenyl sulfide > 4-methyldibenzothiophene > 2,5-dimethyl thiophene) parallels the electron density at the sulfur atom in each of these compounds.[2] This relation (shown in Figure 6) indicates that molecules with more electron-rich sulfur atoms oxidize more rapidly on all catalysts; these reactivity trends are not influenced significantly by the modest steric constraints imposed by the various porous structures within which active sites reside.

Table 2. Total conversion of methyl phenyl sulfide, diphenyl sulfide, 4-methyldibenzothiophene, and 2,5-dimethylthiophene at a given reaction time.[a]

	Co/H-Y		MoO_x/Al_2O_3		CoAPO-5	
Sulfur compounds	Reaction time [ks]	Conv. [mol %]	Reaction time [ks]	Conv. [mol %]	Reaction time [ks]	Conv. [mol %]
methyl phenyl sulfide	0.2	38.6	0.2	67.5	0.2	62.1
	1.6	98.8	0.8	98.5	0.84	96.8
diphenyl sulfide	0.2	7.7	0.2	20.2	0.2	17.5
	2.5	67.3	2.7	94.1	0.84	97.6
4-methyldibenzothiophene	0.2	2.6	0.2	9.6	0.2	8.5
	2.5	30.9	2.7	72.5	3.3	70.4
2,5-dimethylthiophene	0.2	0.5	0.2	3.1	0.2	5.1
	2.5	7.2	2.7	29.6	3.3	27.4

[a] Reaction conditions: methyl phenyl sulfide ($0.090\,mol\,L^{-1}$), diphenyl sulfide ($0.080\,mol\,L^{-1}$), 4-methyldibenzothiophene ($0.080\,mol\,L^{-1}$), 2,5-dimethylthiophene ($0.116\,mol\,L^{-1}$), *tert*-butyl hydroperoxide/S ratio of 3 ($mol\,mol^{-1}$), catalyst concentration $20\,g\,L^{-1}$, and a reaction temperature of 353 K.

The stability and leaching tendencies of Co and Mo cations during catalysis were examined for the specific case of 4-methyldibenzothiophene oxidation. This study was carried out at lower temperatures (333 K) to decrease reaction rates and accurately measure rate differences with and without a catalyst. After a reaction time of 0.6 ks, the catalyst was separated from the reaction medium by filtration. The solid-free liquid was held at 333 K for an additional 2.4 ks and liquid samples were extracted for analysis as a function of reaction time before and after removing the solids. Table 3 shows first-order rate constants before and after catalyst removal. The oxidation of 4-methyldibenzothiophene continues after removing Co/H-Y from the reaction medium, indicating that active Co species have leached from Co/H-Y during reaction. Chemical analysis of Co/H-Y samples after reaction confirmed that ~95 % of the Co atoms in the fresh sample were removed after reaction for 0.6 ks (Table 3). 4-Methyldibenzothiophene oxidation was also carried out by using solvated Co acetate as catalyst. Its rate constant (per Co) was very similar to that measured by assuming that all Co atoms in Co/H-Y remained in the filtrate after reaction [2.3×10^{-3} versus $2.1\times10^{-3}\,m^3\,(mol\,Co)^{-1}\,ks^{-1}$, respectively], confirming the nearly complete leaching of Co from H-Y during reaction.

4-Methyldibenzothiophene oxidation rate constants (per liquid volume) decreased from 5.8×10^4 to $0.13\times10^4\,ks^{-1}$ after removing MoO_x/Al_2O_3 from the reaction medium by filtration; this indicates partial leaching of Mo from Al_2O_3 during reaction. In contrast, 4-methyldibenzothiophene oxidation rates were undetectable after removing CoAPO-5 from the reaction mixture, suggesting that Co cations at framework sites in APO-5 structures were not leached during reaction. The Co content of CoAPO-5 was nearly identical to that in the fresh catalyst (Table 3), consistent with the undetectable catalytic rates for the filtrate.

Oxidation rates and leaching data reported here indicate that Co cations in CoAPO-5 samples are active in redox reactions and more stable than exchanged Co cations on Y-zeolite or dispersed MoO_x domains on Al_2O_3 surfaces and more reactive than solvated Co cations. CoAPO-5 is an effective and stable catalyst for the oxidation of organosulfur molecules to the corresponding sulfones with organic hydroperoxides, which in contrast with H_2O_2, do not require cosolvents. The crystalline AlPO-5 structure provides the framework positions required for Co cation stability and resistance to leaching, while its relatively large channels (0.73×0.73 nm) allow organosulfur molecules as large as diphenyl sulfide and 4-dimethyldibenzothiophene to access active sites without significant diffusional constraints.

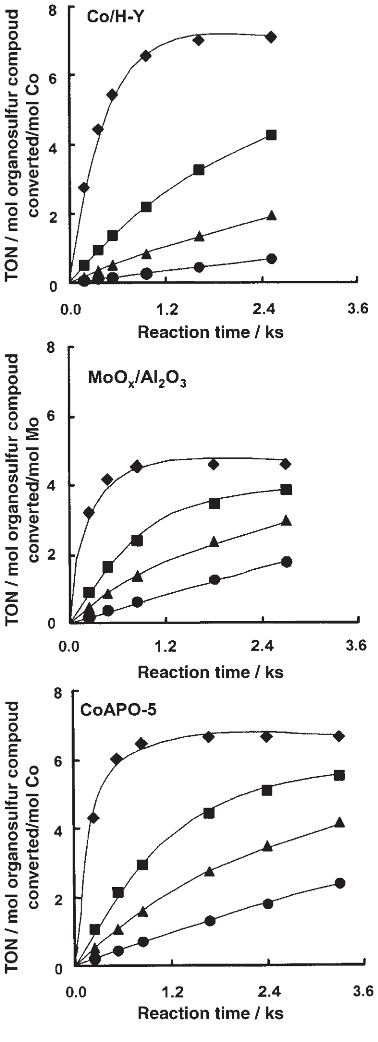


Figure 4. Oxidation turnover of: ◆ methyl phenyl sulfide, ■ diphenyl sulfide, ▲ 4-methyldibenzothiophene, and ● 2,5-dimethylthiophene with *tert*-butyl hydroperoxide as a function of reaction time over Co/H-Y, MoO_x/Al_2O_3, and CoAPO-5 catalysts. Reaction conditions: methyl phenyl sulfide ($0.090\,mol\,L^{-1}$), diphenyl sulfide ($0.080\,mol\,L^{-1}$), 4-methyldibenzothiophene ($0.080\,mol\,L^{-1}$), 2,5-dimethylthiophene ($0.116\,mol\,L^{-1}$), *tert*-butyl hydroperoxide/S ratio of 3 ($mol\,mol^{-1}$), catalyst concentration $20\,g\,L^{-1}$, and 353 K of reaction temperature.

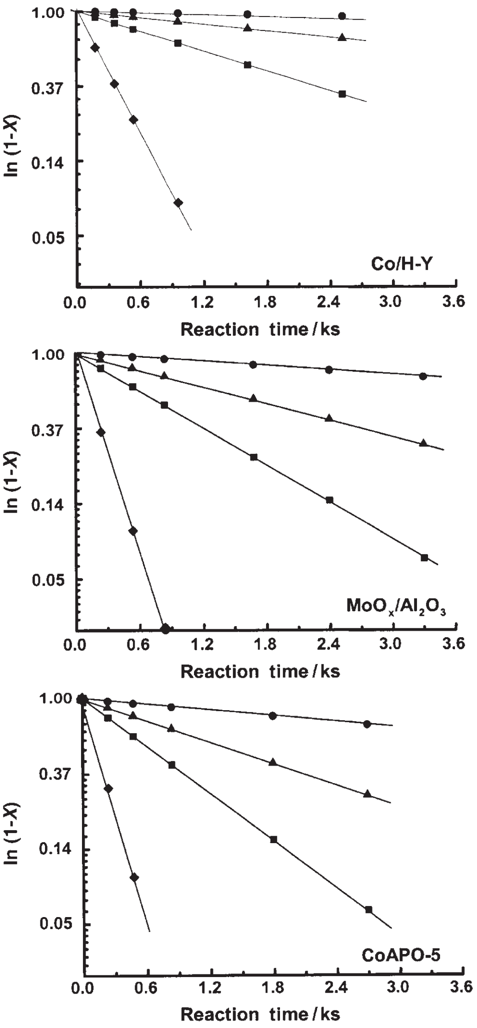


Figure 5. Conversion (X) to oxidized organosulfur compounds. Lines are obtained by linear regression of the data points shown. The slope is proportional to the pseudo-first-order rate constant, k, for ◆ methyl phenyl sulfide, ■ diphenyl sulfide, ▲ 4-methyldibenzothiophene, and ● 2,5-dimethylthiophene oxidation reactions over Co/H-Y, MoO$_x$/Al$_2$O$_3$, and CoAPO-5 catalysts with *tert*-butyl hydroperoxide as the oxidant. Reaction conditions: methyl phenyl sulfide (0.090 mol L^{-1}), diphenyl sulfide (0.080 mol L^{-1}), 4-methyldibenzothiophene (0.080 mol L^{-1}), 2,5-dimethylthiophene (0.116 mol L^{-1}), *tert*-butyl hydroperoxide/S ratio of 3 (mol mol^{-1}), catalyst concentration 20 g L^{-1}, and a reaction temperature of 353 K.

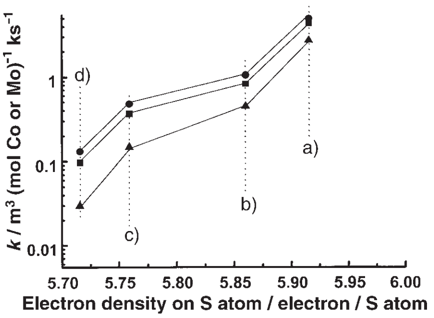


Figure 6. Oxidation rate constant (per metal atom), k, as a function of electron density of the sulfur atom present in each of the sulfur compounds. ▲ = Co/H-Y, ■ = MoO$_x$/Al$_2$O$_3$, and ● = CoAPO-5. a) methyl phenyl sulfide, b) diphenyl sulfide, c) 4-methyldibenzothiophene, and d) 2,5-dimethylthiophene. Reaction conditions: methyl phenyl sulfide (0.090 mol L^{-1}), diphenyl sulfide (0.080 mol L^{-1}), 4-methyldibenzothiophene (0.080 mol L^{-1}), 2,5-dimethylthiophene (0.116 mol L^{-1}), *tert*-butyl hydroperoxide/S ratio of 3 (mol mol^{-1}), catalyst concentration 20 g L^{-1}, and a reaction temperature of 353 K.

Conclusion

The oxidation of different sulfur compounds (sulfides, dibenzothiophenes, and thiophenes) with *tert*-butyl hydroperoxide occurs on CoAPO-5, Co/H-Y, and MoO$_x$/Al$_2$O$_3$ catalysts. CoAPO-5 produced the highest organosulfur oxidation rates (per Co or Mo atom), reflecting the role of tetrahedral Co^{2+} framework cations that undergo facile redox cycles. Co^{2+} cations at exchange sites in H-Y catalysts do not undergo redox cycles or remain grafted as such sites during oxidation reactions. The reactivity of the largest organosulfur compounds (diphenyl sulfide and 4-methyldibenzothiophene) suggests that CoAPO-5 channels do not hinder site accessibility, even for the largest organosulfur molecules. The relative reactivity of these organosulfur compounds increased with increasing electron density at their S atom (phenyl sulfide > diphenyl sulfide > 4-methyldibenzothiophene > 2,5-dimethyl thiophene) on all catalysts. The stable nature and redox lability of framework Co cations in CoAPO-5 (and potentially in other MeAPO materials) make them useful as potential catalysts for the selective oxidation of organosulfur molecules with *tert*-butyl hydroperoxide.

Table 3. Co and Mo content on the fresh and used catalysts (after 600 s of reaction time) in the oxidation of 4-methyldibenzothiophene.[a]

	Fresh catalyst	After reaction	With catalyst		Without catalyst	
Catalyst	Co or Mo [wt %]	Co or Mo [wt %]	k [ks^{-1}]	k [m^3 (mol Co or Mo)$^{-1}$ ks^{-1}]	k [ks^{-1}]	k [m^3 (mol Co or Mo)$^{-1}$ ks^{-1}]
Co-acetate	33.33	–	2.6×10^4	2.3×10^{-3}	–	–
Co/H-Y	3.74	< 0.1	1.3×10^4	5.2×10^{-3}	2.6×10^3	2.1×10^{-3}
MoO$_x$/Al$_2$O$_3$	9.38	7.25	5.8×10^4	14.8×10^{-3}	1.3×10^3	1.5×10^{-3}
CoAPO-5	4.0	3.70	5.3×10^4	19.4×10^{-3}	u.r.[b]	u.r.[b]

[a] Rate constants have been expressed per volume of liquid, gram of catalyst, and per active metal atom to obtain values, which can be compared before and after the catalyst removal from the reaction media. Reaction conditions: 4-methyldibenzothiophene (0.080 mol L^{-1}), *tert*-butyl hydroperoxide/S ratio of 3 (mol mol^{-1}), catalyst concentration 20 g L^{-1}, and a reaction temperature of 333 K. [b] Undetectable reaction rates.

Experimental Section

Reagents: Methyl phenyl sulfide (Aldrich, 98 %), dimethyl phenyl sulfide (Aldrich, 98 %), 4-methyldibenzothiophene (Aldrich, 99 %), and 2,5-dimethylthiophene (Aldrich, 99 %) were used as the organosulfur reactants. Decalin (Aldrich, mixture of *cis* and *trans*, anhydrous 99 %) was used as the solvent and *n*-decane (Aldrich, 99 %) as the internal standard. *tert*-Butyl hydroperoxide (Aldrich, 5.0–6.0 M solution in nonane) was used as the oxidant. Only traces of decalin oxidation products (<0.1 % mol in reactor contents) were detected, even at nearly complete conversion of organosulfur reactants.

Catalytic materials: A Co/H-Y catalyst with a Co/Al atomic ratio of 0.14 was prepared by contacting H-Y zeolite (Si/Al = 5.2, CBV-500; Zeolyst) with a 0.5 M $Co(NO_3)_2$ aqueous solution [$Co(NO_3)_2{\cdot}6H_2O$, Aldrich 99 %] at 353 K for 16 h (the Co/Al mol ratio in the mixture was 1.7). The slurry was filtered, washed with deionized water, dried in ambient air at 393 K overnight, and then treated in flowing, dry air (Airgas, zero grade) at 773 K for 3 h.[64]

CoAPO-5 was prepared by mixing $Al(OH)_3$ (Aldrich, 99 % hydrated), H_3PO_4 (Aldrich, 85 %), and distilled water while stirring until a uniform gel was formed. $Co(CH_3COO)_2$ (Aldrich, 99.9 %) and tetraethylammonium hydroxide (TEAOH, Aldrich, 35 %) were then added in sequence and the resulting gel ($0.08\,Co:0.92\,Al:1.5:35\,H_2O:0.8\,TEAOH$) was crystallized under its autogenous pressure in a Teflon-lined autoclave at 463 K for 24 h. Crystallinity and phase purity were confirmed by powder X-ray diffraction (ARL X'TRA diffractometer; $Cu_{K\alpha}$ radiation, 30 mA; 40 kV; min 2θ 0.9°; and 0.3 mm slits for scattering, divergence, and receiving) with a graphite monochromator and a Peltier detector.

Al_2O_3-supported MoO_3 was prepared by incipient wetness impregnation of γ-Al_2O_3 (Degussa, AG, 101 m^2g^{-1}) with a solution of $(NH_4)_6Mo_7O_{24}$ (Aldrich, 99 %) at pH 5. The impregnated sample was dried overnight in ambient air at 393 K and then treated in flowing dry air (Airgas, zero grade) at 773 K for 3 h.

Textural properties and chemical compositions of these catalysts are shown in Table 1. Surface areas were measured by using N_2 at its normal boiling point (Autosorb-1; Quantachrome) and BET analysis methods. Co and Mo contents were measured by inductively coupled plasma emission spectrometry (Galbraith Analytical).

Temperature-programmed reduction in H_2: Reduction (TPR) rates were measured on samples (0.2 g) held within a quartz cell. Before these measurements, any organic template was removed in 1.67 cm^3s^{-1} He (Praxair, UHP) within the cell as the temperature was increased to 773 K at 0.05 Ks^{-1} and then decreased to ambient temperature. Helium was replaced by 1.67 cm^3s^{-1} air (Praxair, UHP) and the sample heated to 773 K at 0.167 Ks^{-1} and held at 773 K for 3 h to remove any remaining carbonaceous residues, and then cooled to ambient temperature. The dry air stream was replaced with He (1.33 cm^3s^{-1}) for 0.5 h to remove residual O_2 and then a flow of 0.67 cm^3s^{-1} 1 % H_2/Ar (Praxair) was started. The effluent was analyzed by using a differentially-pumped mass spectrometer (MKS Instruments, Orion Compact Residual Gas Analyzer) as the sample temperature was linearly increased from 0.167 Ks^{-1} to 823 K. H_2 (2 amu), H_2O (18 amu), and Ar (36 and 40 amu) concentrations were measured at 10 s intervals. Response factors were measured from the complete reduction of standard CuO samples. The temperature was measured by using K-type thermocouples and set with a Watlow controller (Series 982) and a resistively heated furnace.

Diffuse reflectance UV-visible spectroscopy: UV-visible spectra were measured in diffuse reflectance mode on powder samples held within a cell with optical quartz walls and attached to a vacuum system capable of a dynamic vacuum of $<6.7\times10^{-5}$ kPa. Spectra were measured with a Perkin–Elmer Lambda 900 spectrophotometer equipped with an integrating sphere in "Ultra-White Teflon", the same material that composes the integrating sphere was used as a reference for recording the background spectrum. All samples were treated at 823 K for 15–20 h in 133 kPa O_2 with sequential replenishing with fresh O_2 to remove any organic templates. These samples were then treated in 133 kPa H_2 at 623 K for 15–20 h.

Catalytic rate measurements: Reactivity studies were conducted in a six-reactor batch system equipped with a temperature controller, individual magnetic stirrers, and condensation systems (PRS50–120R, J-Kem Scientific). These reactors were heated to the desired reaction temperature (333–353 K) and the catalyst (0.1 g) was introduced while stirring a mixture of organosulfur reactants [methyl phenyl sulfide (0.090 $mol\,L^{-1}$), diphenyl sulfide (0.080 $mol\,L^{-1}$), 4-methyldibenzothiophene (0.080 $mol\,L^{-1}$), 2,5-dimethylthiophene (0.116 $mol\,L^{-1}$)], decalin (5 mL), and decane (0.1 mL). *tert*-Butyl hydroperoxide was then added (*tert*-butyl hydroperoxide/sulfur molar ratio = 3) and several small aliquots (<0.05 mL) of the reactor liquids were collected for chromatographic analysis over a period of one hour. Reactant and product concentrations were measured by gas chromatography [Hewlett–Packard 5890; HP-5 (5 %-phenyl)-methylpolysiloxane capillary column, 30 m, 0.25 mm i.d. 0.25 μm film thickness] with flame ionization detection. *n*-Decane, which does not react at these conditions, was used as the internal standard. A pseudo-first order reaction constant k (in excess *tert*-butyl hydroperoxide) was measured from the time evolution of reactant conversion (X) of each reactant and a least squares fit to its expected behavior with reaction time (t) $\{\ln(1-X)=-kt\}$.

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