SUPPORTING INFORMATION

$Ag_5PV_2Mo_{10}O_{40}$, a Heterogeneous Catalyst for Air-Based Selective Oxidation at Ambient Temperature

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Table S1. Crystal Data and Structure Refinement for $Ag_{10.4}P_2V_4Mo_{20}O_{80}(NO_3)_{0.4}$•$(MeCN)_{17.3}(H_2O)_{1.5}$

Table S2. Selected Bond Lengths (Å) and Angles (deg.) for Ag_5**1**.

Table S3. Anisotropic displacement parameters ($Å^2$x 10^3) for Ag_5**1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2 a^{*2}U^{11} + ... + 2\, h\, k\, a^*\, b^*\, U^{12}\,]$

Table S4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Ag_5**1**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table S5. Ambient-Temperature Air Oxidation of CEES in 2,2,2–Trifluoroethanol Catalyzed by Selected Materials.

Figure S1. Continued oxidation of CEES to CEESO after isolation and resuspension of the heterogeneous catalyst, Ag_5**1**.

Figure S2. Reaction profile for the ambient-temperature air oxidation of CEES (○) to CEESO catalyzed by Ag_5**1** in 2,2,2-trifluoroethanol and its inhibition by added DMSO (■).

Figure S3. Adsorption of CEES onto the solid catalyst Ag_5**1**. Concentrations of CEES ($CH_3CH_2SCH_2CH_2Cl$; ●) and the hydrolysis product ($CH_3CH_2SCH_2CH_2OH$; ■) are plotted versus time. After 8.4 hours, 5.26 x10^{-5} mols of CEES was absorbed onto 3.53 x10^{-5} mols of catalyst. No CEESO was detected.

Figure S4. Comparison of ^{31}P Solid State NMR of Ag_5**1** before and after catalysis as evidence for bound CEESO.

Detailed experimental section including calculation of surface accessible Ag_5**1** in the Ag_5**1** powder.

Table S1. Crystal Data and Structure Refinement for $Ag_{10.4}P_2V_4Mo_{20}O_{80}(NO_3)_{0.4}$•$(MeCN)_{17.3}(H_2O)_{1.5}$ (Ag_5**1**)

Empirical formula	$C_{34.6}$ $Ag_{10.4}$ Mo_{20} $N_{17.7}$ $O_{82.7}$ P_2 V_4
Formula weight	5293.07
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	*a* = 13.038(5) Å
	b = 21.175(8) Å
	c = 22.353(8) Å
	α= 85.966(7)°
	β= 83.556(7)°
	γ= 77.854(7)°
Volume	5988(4) $Å^3$
Z	2
Density (calculated)	2.936 Mg/m^3
Absorption coefficient	4.093 mm^{-1}
F(000)	4888
Theta range for data collection	1.61 to 30.69°.
Reflections collected	71417
Independent reflections	36109 [R(int) = 0.1276]
Completeness to theta = 30.69°	97.2 %
Absorption correction	Empirical
Goodness-of-fit on F^2	1.032
Final R indices [I > 2 sigma (I)]	R_1 = 0.0937, wR_2 = 0.1731

Table S2. Selected Bond Lengths (Å) and Angles (deg.) for Ag_5**1**.

Ag1 – O31	2.437(9)	Ag5 – N12S	2.202(13)
Ag1 – O37	2.590(9)	Ag6 – N3S	2.186(12)
Ag1 – N1S	2.200(13)	Ag6 – N8S	2.332(15)
Ag1 – N10S	2.258(17)	Ag6 – N9S	2.182(13)
Ag2 – N13S	2.196(13)	Ag7 – O19	2.475(9)
Ag2 – N14S	2.154(13)	Ag7 – O29	2.447(9)
Ag2 – N16S	2.625(14)	Ag7 – N5S	2.222(13)
Ag3 – O6	2.503(9)	Ag8 – O64	2.560(9)
Ag3 – O12	2.493(9)	Ag8 – O76	2.459(10)
Ag3 – N6S	2.198(13)	Ag8 – O40	2.404(9)
Ag3 – N11S	2.289(13)	Ag8 – N15S	2.182(14)
Ag4 – O62	2.534(10)	Ag8 – O64	2.560(9)
Ag4 – N2S	2.307(13)	Ag8 – O76	2.459(10)
Ag4 – N7S	2.230(14)	Ag8 – O40	2.404(9)
Ag5 – O80	2.447(9)	Ag8 – N15S	2.182(13)
Ag5 – N4S	2.280(15)		
N1S – Ag1 – N10S	115.2(5)	N9S – Ag6 – N8S	116.0(5)
N1S – Ag1 – O31	130.8(4)	N4S – Ag5 – O80	104.7(4)
N10S – Ag1 – O31	104.8(5)	N9S – Ag6 – N3S	146.3(5)
N1S – Ag1 – O37	125.8(4)	N9S – Ag6 – N8S	116.0(5)
N10S – Ag1 – O37	106.2(5)	N7S – Ag4 – N2S	110.8(5)
O31 – Ag1 – O37	62.7(3)	N7S – Ag4 – O62	142.0(4)
N14S – Ag2 – N13S	158.2(5)	N2S – Ag4 – O62	94.3(4)
N14S – Ag2 – N16S	98.5(5)	N12S – Ag5 – N4S	114.6(5)
N13S – Ag2 – N16S	102.7(5)	N12S – Ag5 – O80	134.2(4)
N6S – Ag3 – N11S	114.4(5)	N4S – Ag5 – O80	104.7(4)
N6S – Ag3 – O12	125.7(4)	N9S – Ag6 – N3S	146.3(5)
N11S – Ag3 – O12	110.6(4)	N9S – Ag6 – N8S	116.0(5)

N6S – Ag3 – O6	131.9(4)	N3S – Ag6 – N8S	97.2(5)
N11S – Ag3 – O6	100.8(4)	N5S – Ag7 – O29	126.6(4)
O12 – Ag3 – O6	62.9(3)	N5S – Ag7 – O19	145.3(4)
N7S – Ag4 – N2S	110.8(5)	O29 – Ag7 – O19	64.9(3)
N7S – Ag4 – O62	142.0(4)	N15S – Ag8 – O40	113.7(4)
N2S – Ag4 – O62	94.3(4)	N15S – Ag8 – O76	137.7(4)
N12S – Ag5 – N4S	114.6(5)	O40 – Ag8 – O76	79.8(3)
N12S – Ag5 – O80	134.2(4)	N15S – Ag8 – O64	147.2(4)
N4S – Ag5 – O80	104.7(4)	O40 – Ag8 – O64	92.3(3)
N9S – Ag6 – N3S	146.3(5)	O76 – Ag8 – O64	63.7(3)

Table S3. Anisotropic displacement parameters ($Å^2$x 10^3) for Ag_5**1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Mo(1)	16(1)	5(1)	17(2)	-3(1)	-5(1)	-2(1)
Mo(2)	14(1)	6(1)	21(1)	2(1)	-7(1)	2(1)
Mo(3)	14(1)	14(1)	17(1)	-5(1)	2(1)	-1(1)
Mo(4)	14(1)	7(1)	20(1)	-3(1)	0(1)	-2(1)
Mo(5)	8(1)	5(1)	21(1)	-3(1)	0(1)	1(1)
Mo(6)	15(1)	8(1)	13(1)	1(1)	-3(1)	-1(1)
Mo(7)	10(1)	10(1)	20(1)	0(1)	5(1)	-3(1)
Mo(8)	14(1)	6(1)	26(1)	-2(1)	-2(1)	3(1)
Mo(9)	22(1)	5(1)	20(2)	2(1)	-7(1)	-4(1)
Mo(10)	13(1)	10(1)	21(1)	-4(1)	0(1)	-5(1)
Mo(11)	14(1)	9(1)	17(1)	-3(1)	-4(1)	-2(1)
Mo(12)	24(1)	8(1)	16(1)	0(1)	-7(1)	-2(1)
Mo(13)	16(1)	15(1)	18(1)	-3(1)	-5(1)	2(1)
Mo(14)	13(1)	9(1)	15(1)	-1(1)	-3(1)	2(1)
Mo(15)	13(1)	9(1)	21(1)	3(1)	-2(1)	-5(1)
Mo(16)	19(1)	7(1)	19(1)	-4(1)	-4(1)	-2(1)
Mo(17)	19(1)	7(1)	22(1)	3(1)	-6(1)	0(1)
Mo(18)	14(1)	10(1)	16(2)	2(1)	-4(1)	0(1)
Mo(19)	11(1)	9(1)	20(1)	-2(1)	-2(1)	-3(1)
Mo(20)	18(1)	5(1)	21(1)	0(1)	-2(1)	-3(1)
Mo(21)	14(1)	10(1)	19(1)	1(1)	-7(1)	-1(1)
Mo(22)	12(1)	8(1)	22(1)	-1(1)	1(1)	-2(1)
Mo(23)	12(1)	11(1)	18(1)	-2(1)	0(1)	-1(1)
Mo(24)	13(1)	6(1)	15(1)	0(1)	-4(1)	0(1)
Ag(1)	24(1)	22(1)	48(1)	-4(1)	-14(1)	3(1)
Ag(2)	20(1)	18(1)	38(1)	1(1)	0(1)	5(1)
Ag(3)	19(1)	15(1)	43(1)	-7(1)	-7(1)	0(1)
Ag(4)	18(1)	21(1)	54(1)	1(1)	-6(1)	-2(1)

Ag(5)	23(1)	19(1)	44(1)	2(1)	-13(1)	1(1)
Ag(6)	24(1)	15(1)	39(1)	-2(1)	-6(1)	1(1)
Ag(7)	44(1)	10(1)	41(1)	-2(1)	-16(1)	-5(1)
Ag(8)	49(1)	16(1)	36(1)	-7(1)	2(1)	-6(1)
Ag(1D)	72(2)	26(1)	62(2)	-1(1)	-6(2)	-17(1)
Ag(2D)	68(2)	27(1)	51(2)	-6(1)	-9(1)	-8(1)
Ag(3D)	58(2)	36(2)	83(2)	-9(2)	-21(2)	-10(1)
Ag(4D)	75(2)	34(2)	75(2)	-16(2)	-16(2)	9(2)

Table S4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Ag_5**1**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Mo(1)	9920(3)	247(2)	1783(1)	12(1)
Mo(2)	9849(2)	1740(2)	1106(2)	14(1)
Mo(3)	12148(2)	643(2)	1097(1)	16(1)
Mo(4)	8745(3)	975(2)	3211(2)	14(1)
Mo(5)	8652(2)	2479(2)	2551(2)	12(1)
Mo(6)	11094(2)	2894(1)	1750(1)	12(1)
Mo(7)	13409(2)	1805(1)	1731(1)	14(1)
Mo(8)	13456(2)	175(2)	2460(2)	16(1)
Mo(9)	11281(2)	-232(1)	3197(1)	15(1)
Mo(10)	9871(1)	2040(1)	3834(1)	14(1)
Mo(11)	12323(2)	2485(1)	3038(1)	13(1)
Mo(12)	12411(3)	856(2)	3782(2)	16(1)
Mo(13)	5307(2)	6837(1)	3930(1)	17(1)
Mo(14)	4002(2)	7353(1)	2690(1)	13(1)
Mo(15)	4164(2)	5807(1)	3274(1)	14(1)
Mo(16)	7665(2)	7353(1)	3158(1)	15(1)
Mo(17)	6341(2)	7861(1)	1937(1)	16(1)
Mo(18)	5127(3)	6752(2)	1190(1)	14(1)
Mo(19)	5277(2)	5205(1)	1758(1)	13(1)
Mo(20)	6698(3)	4645(1)	3119(2)	15(1)
Mo(21)	7858(2)	5691(2)	3774(2)	14(1)
Mo(22)	8682(3)	6820(2)	1751(2)	14(1)
Mo(23)	7439(2)	5676(2)	1064(2)	14(1)
Mo(24)	8891(2)	5138(1)	2413(1)	11(1)
V(1)	9950(30)	239(19)	1877(16)	10
V(2)	10000(30)	1751(19)	1079(19)	10
V(3)	12290(30)	651(18)	1019(16)	10
V(4)	8860(30)	928(19)	3236(19)	10

V(5)	8830(20)	2482(17)	2510(16)	10
V(6)	11140(20)	2883(12)	1920(10)	10
V(7)	13580(20)	1810(15)	1641(14)	10
V(8)	13600(30)	178(19)	2400(18)	10
V(9)	11190(30)	-222(17)	3090(14)	10
V(10)	10125(18)	2047(14)	3812(13)	10
V(11)	12380(20)	2452(16)	3165(13)	10
V(12)	12410(30)	830(20)	3714(19)	10
V(13)	5120(20)	6869(14)	3843(13)	10
V(14)	3910(20)	7362(15)	2559(12)	10
V(15)	4070(20)	5866(16)	3168(14)	10
V(16)	7570(30)	7403(16)	3052(14)	10
V(17)	6230(20)	7919(13)	1802(11)	10
V(18)	5110(30)	6766(18)	1079(15)	10
V(19)	5110(20)	5219(15)	1865(13)	10
V(20)	6800(30)	4706(17)	3141(18)	10
V(21)	7690(30)	5721(18)	3757(17)	10
V(22)	8600(30)	6772(19)	1760(19)	10
V(23)	7600(30)	5705(18)	1055(18)	10
V(24)	8860(20)	5130(15)	2272(12)	10
O(1)	10864(7)	1111(4)	1870(4)	14(2)
O(2)	11754(7)	788(4)	2810(4)	12(2)
O(3)	11715(7)	1892(4)	2316(4)	13(2)
O(4)	10051(7)	1603(5)	2850(4)	16(2)
O(5)	9239(8)	-285(5)	1618(5)	25(3)
O(6)	9270(7)	1012(5)	1279(4)	17(2)
O(7)	9188(7)	2118(5)	540(4)	15(2)
O(8)	11042(7)	1260(4)	698(4)	13(2)
O(9)	12859(7)	298(5)	492(4)	17(2)
O(10)	11063(7)	124(5)	1205(4)	15(2)

O(11)	10640(8)	-139(5)	2425(4)	18(2)
O(12)	8860(7)	720(5)	2420(4)	16(2)
O(13)	8970(7)	2126(4)	1818(4)	12(2)
O(14)	10688(7)	2386(5)	1244(4)	15(2)
O(15)	12815(7)	1301(4)	1205(4)	10(2)
O(16)	12785(7)	167(4)	1725(4)	13(2)
O(17)	7705(8)	708(5)	3541(5)	20(2)
O(18)	8019(7)	1851(5)	2904(4)	15(2)
O(19)	9868(7)	2929(4)	2259(4)	14(2)
O(20)	10940(7)	3612(5)	1375(4)	15(2)
O(21)	12597(7)	2563(5)	1444(4)	16(2)
O(22)	14589(7)	1812(5)	1344(4)	16(2)
O(23)	13746(7)	954(4)	2175(4)	14(2)
O(24)	14594(8)	-343(5)	2303(4)	18(2)
O(25)	12593(8)	-451(5)	2779(4)	18(2)
O(26)	11010(8)	-942(5)	3477(5)	19(2)
O(27)	9859(7)	354(4)	3413(4)	14(2)
O(28)	8940(8)	1492(5)	3880(5)	19(2)
O(29)	9004(7)	2652(5)	3351(4)	14(2)
O(30)	11800(7)	3086(4)	2460(4)	12(2)
O(31)	13539(7)	2181(5)	2453(4)	16(2)
O(32)	13559(7)	333(4)	3269(4)	13(2)
O(33)	11763(7)	85(5)	3824(4)	17(2)
O(34)	9594(7)	2373(4)	4494(4)	12(2)
O(35)	11064(7)	2470(5)	3470(4)	17(2)
O(36)	12880(8)	2923(5)	3446(5)	19(2)
O(37)	12810(7)	1600(4)	3436(4)	12(2)
O(38)	12923(8)	751(5)	4434(5)	21(2)
O(39)	11019(7)	1352(5)	3975(4)	15(2)
O(40)	7666(7)	3112(5)	2438(4)	15(2)

O(41)	5439(7)	6464(4)	2911(4)	11(2)
O(42)	7027(7)	6817(4)	2377(4)	11(2)
O(43)	7155(7)	5675(4)	2806(4)	12(2)
O(44)	6167(7)	6061(4)	1901(4)	12(2)
O(45)	5073(8)	7093(5)	4626(5)	24(3)
O(46)	4326(7)	7420(5)	3514(4)	17(2)
O(47)	2923(8)	7944(5)	2653(5)	21(2)
O(48)	3368(7)	6631(5)	3026(4)	16(2)
O(49)	3201(8)	5438(5)	3590(5)	24(3)
O(50)	4451(8)	6224(5)	3949(5)	20(2)
O(51)	6400(8)	7292(5)	3586(4)	18(2)
O(52)	5112(7)	7808(5)	2435(4)	16(2)
O(53)	4178(8)	7042(5)	1922(4)	19(2)
O(54)	4333(8)	5562(5)	2444(5)	22(2)
O(55)	5419(7)	5160(5)	3358(4)	16(2)
O(56)	6518(8)	6128(5)	3999(4)	18(2)
O(57)	8222(8)	7781(5)	3578(4)	18(2)
O(58)	7015(8)	8005(5)	2614(4)	19(2)
O(59)	6055(7)	8609(5)	1609(4)	16(2)
O(60)	5862(8)	7383(5)	1395(4)	18(2)
O(61)	4374(7)	7148(4)	663(4)	14(2)
O(62)	4586(8)	5980(5)	1305(5)	22(2)
O(63)	4635(8)	4651(5)	1545(4)	18(2)
O(64)	6155(7)	4726(5)	2327(4)	16(2)
O(65)	6547(8)	3917(5)	3349(4)	18(2)
O(66)	7325(8)	4879(5)	3753(5)	21(2)
O(67)	8422(7)	5565(5)	4418(4)	18(2)
O(68)	8195(7)	6467(5)	3461(4)	16(2)
O(69)	9785(7)	6884(5)	1354(4)	16(2)
O(70)	8080(7)	6356(5)	1214(4)	14(2)

O(71)	8140(8)	5424(5)	402(5)	19(2)
O(72)	8194(7)	5180(5)	1655(4)	14(2)
O(73)	10040(7)	4665(5)	2210(4)	17(2)
O(74)	9078(7)	5950(4)	2148(4)	13(2)
O(75)	9011(8)	5265(5)	3206(4)	18(2)
O(76)	8082(7)	4464(5)	2682(4)	16(2)
O(77)	6411(8)	5137(5)	1163(4)	18(2)
O(78)	6285(7)	6324(5)	729(4)	17(2)
O(79)	7739(7)	7602(5)	1538(4)	15(2)
O(80)	8821(7)	7144(5)	2506(4)	16(2)
P(1)	11097(3)	1348(2)	2459(2)	14(1)
P(2)	6450(3)	6257(2)	2493(2)	15(1)
Ag(1)	14790(1)	1482(1)	3063(1)	32(1)
Ag(2)	4157(1)	7826(1)	9562(1)	27(1)
Ag(3)	7433(1)	1257(1)	1791(1)	26(1)
Ag(4)	2755(1)	6271(1)	1854(1)	31(1)
Ag(5)	10165(1)	6392(1)	3029(1)	29(1)
Ag(6)	8660(1)	2437(1)	9312(1)	27(1)
Ag(7)	9667(1)	3647(1)	3113(1)	31(1)
Ag(8)	7739(1)	4026(1)	1748(1)	34(1)
N(1S)	15893(11)	568(7)	2861(6)	29(3)
C(1S)	16449(13)	104(8)	2749(8)	28(4)
C(2S)	17186(12)	-521(8)	2631(7)	23(4)
N(2S)	2076(10)	5552(6)	1358(6)	23(3)
C(3S)	1416(12)	5392(8)	1169(7)	21(4)
C(4S)	629(12)	5173(8)	868(7)	25(4)
N(3S)	10246(9)	1824(6)	9289(5)	17(3)
C(5S)	11015(12)	1465(7)	9242(7)	20(3)
C(6S)	12066(11)	948(7)	9214(7)	17(3)
N(4S)	10669(12)	7008(7)	3701(7)	36(4)

C(7S)	11197(13)	7273(8)	3892(8)	27(4)
C(8S)	11894(13)	7587(8)	4165(8)	27(4)
N(5S)	10506(10)	4114(6)	3712(6)	22(3)
C(10S)	10988(13)	5069(8)	4247(8)	28(4)
C(9S)	10730(13)	4498(8)	3936(8)	26(4)
N(6S)	6324(10)	2173(6)	1979(6)	25(3)
C(11S)	5794(12)	2636(7)	2126(7)	19(3)
C(12S)	5121(11)	3239(7)	2343(7)	18(3)
N(7S)	1497(11)	7116(7)	2125(6)	30(3)
C(13S)	950(12)	7604(8)	2249(7)	22(4)
C(14S)	283(14)	8250(9)	2371(8)	34(4)
N(8S)	7872(12)	1748(7)	8830(7)	36(4)
C(15S)	7175(11)	1534(7)	8739(7)	16(3)
C(16S)	6310(12)	1277(8)	8634(7)	24(4)
N(9S)	7603(10)	3300(6)	9662(6)	24(3)
C(17S)	7009(12)	3726(7)	9823(7)	19(3)
C(18S)	6187(13)	4297(8)	10010(8)	29(4)
N(10S)	15414(13)	2161(8)	3592(7)	46(4)
C(19S)	16010(14)	2308(9)	3843(8)	33(4)
C(20S)	16806(14)	2532(9)	4190(8)	33(4)
N(11S)	6711(10)	499(6)	1394(6)	24(3)
C(21S)	6100(11)	344(7)	1131(6)	15(3)
C(22S)	5323(13)	120(8)	835(7)	26(4)
N(12S)	11346(10)	5520(6)	2773(6)	25(3)
C(23S)	11917(13)	5049(8)	2689(8)	30(4)
C(24S)	12609(13)	4425(8)	2548(8)	30(4)
N(13S)	5192(10)	6903(6)	9325(6)	25(3)
C(25S)	5948(13)	6519(8)	9259(7)	24(4)
C(26S)	6882(12)	5997(7)	9193(7)	19(3)
N(14S)	2712(10)	8530(6)	9712(6)	24(3)

C(27S)	2033(12)	8914(7)	9817(7)	18(3)
C(28S)	1097(12)	9404(7)	9969(7)	19(3)
N(15S)	8597(11)	3771(7)	872(6)	31(3)
C(29S)	9308(11)	3602(7)	528(7)	15(3)
C(30S)	10216(12)	3385(8)	70(7)	25(4)
N(16S)	5399(11)	8410(7)	10067(6)	30(3)
C(31S)	6219(13)	8088(8)	10052(7)	24(4)
C(32S)	7295(12)	7661(7)	10063(7)	18(3)
N(17S)	3166	8717(13)	4517	28(4)
C(33S)	3853	8772	4085	18(3)
C(34S)	4602	8818	3614	18(3)
N(18S)	4585	1471	4726	28(4)
C(35S)	4001	1794	4833	18(3)
C(36S)	2938	2285	4941	18(3)
N(19S)	8	8985	4737	28(4)
C(37S)	-843	9038	4468	18(3)
C(38S)	-1720	9195	4153	18(3)
Ag(1D)	9972(2)	3391(1)	4894(1)	53(1)
Ag(2D)	6868(2)	4330(1)	4826(1)	49(1)
Ag(3D)	5787(2)	539(1)	4499(2)	57(1)
Ag(4D)	1554(3)	9111(1)	5038(2)	63(1)
N(1AN)	3980(30)	4197(18)	4477(17)	35(4)
O(1AN)	5250(20)	4127(14)	4560(13)	35(4)
O(2AN)	3667	4701	4751	35(4)
O(3AN)	4150(20)	3775(15)	4115(14)	35(4)
O(1W)	8416	3873	4898	35(4)
O(2W)	5686	-380	4130	35(4)
O(3W)	2773	9304	5084	35(4)

Table S5. Ambient-Temperature Air Oxidation of CEES in 2,2,2–Trifluoroethanol Catalyzed by Selected Materials.[a]

catalyst	mol of POM, 10^{-5}	mol of Ag salt, 10^{-5}	TON[b]
None	NA	NA	0[c]
Ag_5**1**	2.30	NA	2300
$Na_5PV_2Mo_{10}O_{40}$	2.80	NA	0[c]
AgCl	NA	3.35	0[c]
$Na_5PV_2Mo_{10}O_{40}$ + AgCl	2.90	14.5	0[c]
$Ag_5PV_2W_{10}O_{40}$	2.45	NA	0[c]
$Ag_9P_2V_3W_{15}O_{62}$	2.50	NA	0[c]
$AgNO_3$[d]	NA	2.82	9.29[e]
Na_3VO_4[f]	NA	NA	0[c]
$Na_2MoO_4{\bullet}2H_2O$[f]	NA	NA	0[c]
Na_3VO_4 + $Na_2MoO_4{\bullet}2H_2O$[f]	NA	NA	0[c]

[a]Reaction conditions: 0.275 M CEES (~20 mol CEES:1 mol catalyst) in 2,2,2-trifluoroethanol at room-temperature for 7.1 days. Reactions were quantified by GC (5% phenyl methyl siloxane column) using 1,3-dichlorobenzene as an internal standard. [b]Turnovers = [(mols of CEESO)/(mole of surface accessible Ag_5**1**)]. [c]Below the detectable limit. [d]Homogeneous reaction where the catalyst was soluble. [e]Turnovers = [(mol of CEESO)/(mol of catalyst)]. [f]Reaction conditions: 0.172 M CEES (~20 mol CEES:1 mol catalyst) in 2,2,2-trifluoroethanol at room temperature for 10.7 days.

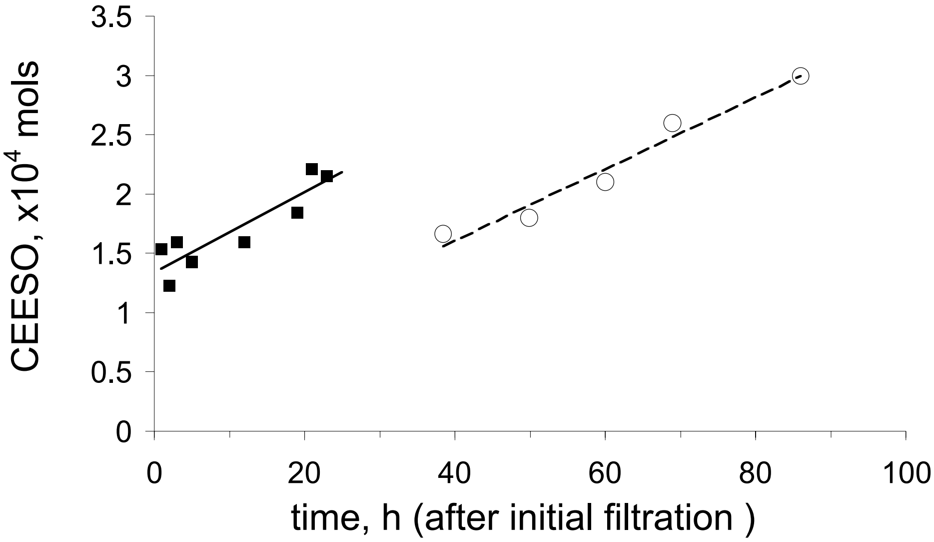


Figure S1. Continued oxidation of CEES to CEESO after isolation and resuspension of the heterogeneous catalyst. The solid line is a plot of CEESO formation after Ag_5**1** was removed from the initial reaction mixture, isolated and resuspended in a reaction vial with a fresh CEES solution. The dashed line is a plot of CEESO formation after Ag_5**1** was isolated a second time and resuspended in a another reaction vial with a fresh CEES solution. The catalytic activities of the clear filtrates from both trials were monitored. None showed any catalytic activity whatsoever. Reaction conditions: CEES was 0.275 M (~20 mol CEES : 1 mol catalyst) in 2,2,2-trifluoroethanol at 40 ^{o}C (higher temperature used to increase rate of reaction). Reactions were quantified by GC (5% phenyl methyl siloxane column) using 1,3-dichlorobenzene as an internal standard.

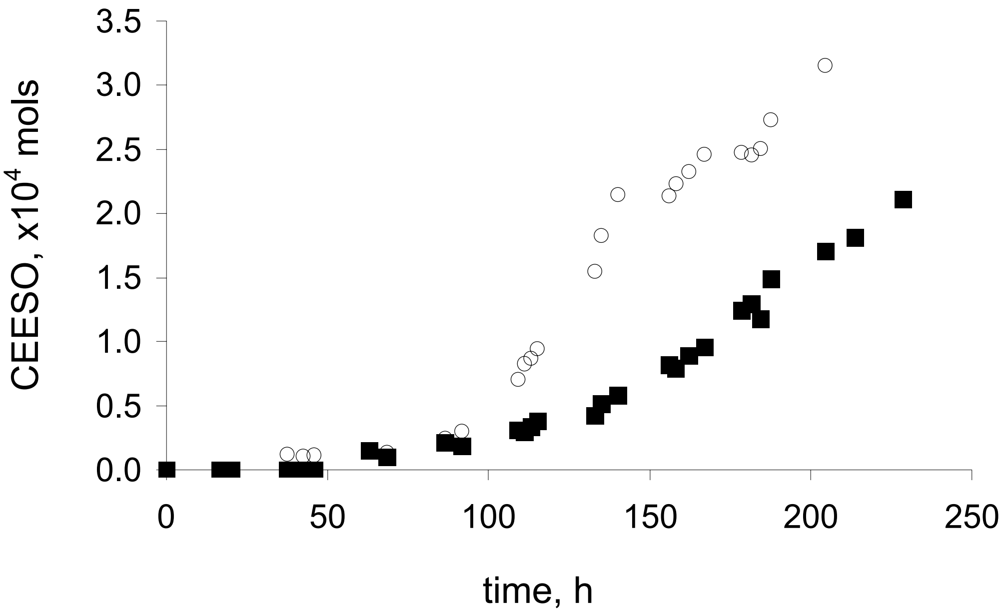


Figure S2. Reaction profile for the ambient-temperature air oxidation of CEES (○) to CEESO catalyzed by $Ag_5\mathbf{1}$ in 2,2,2-trifluoroethanol and its inhibition by added DMSO (■).

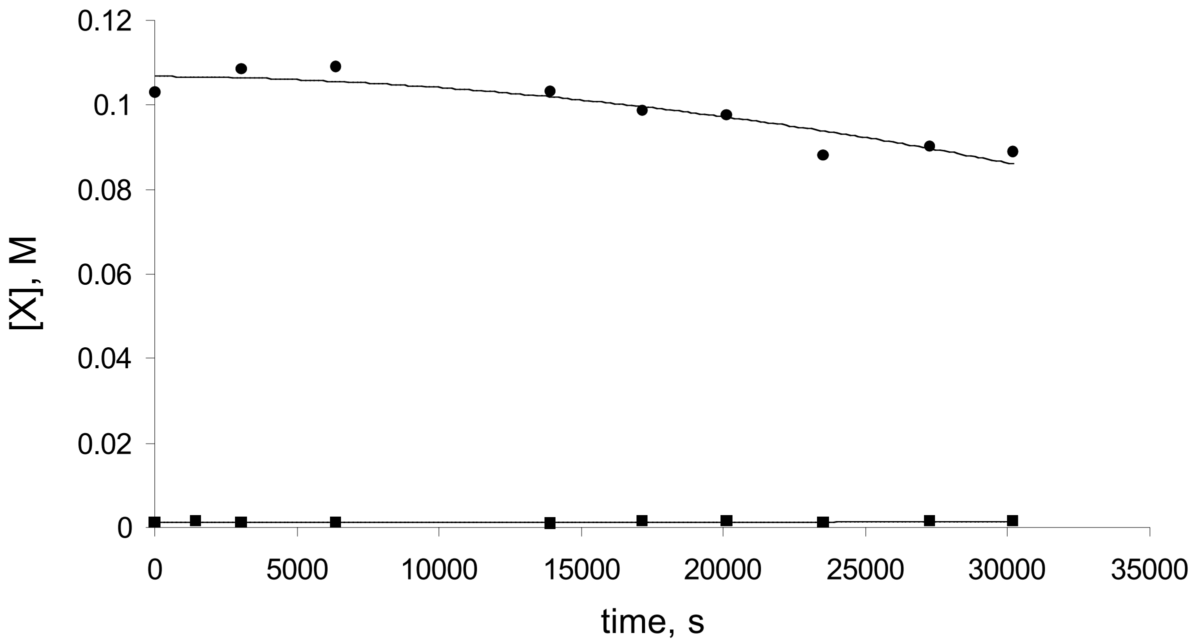


Figure S3. Absorption of CEES onto the solid catalyst Ag_5**1**. Concentrations of CEES (●) and the hydrolysis product ($CH_3CH_2SCH_2CH_2OH$ (■) are plotted versus time. After 8.4 hours, 5.26 x10^{-5} mols of CEES was absorbed onto 3.53 x10^{-5} mols of catalyst. No CEESO was detected.

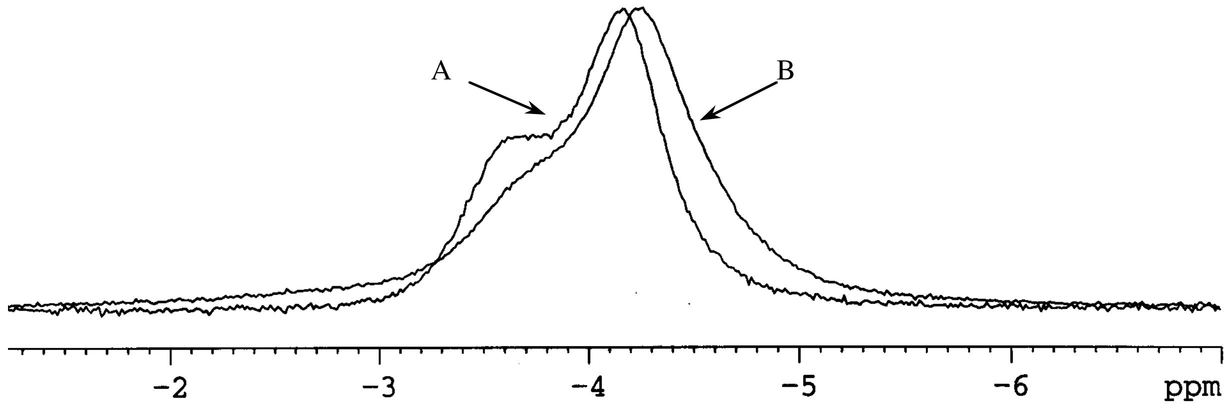


Figure S4. Determination of CEESO Bound to the Catalyst by ^{31}P Solid State NMR of Ag_5**1** Before and After catalysis. A) catalyst before reaction, B) catalyst after reaction. The spectra were collected on a Bruker DSX400 NMR spectrometer operating at xxxx T, using an MAS probe. The following parameters were implemented: single pulse excitation, 4.5 µs pulse length (p1), x µs dead time after pulse, 10 s repetition delay (d1), 32 averages, 4096 complex data points in FID, spectral width of 8100 Hz, and a sender frequency of 161.86 MHz. A x-mm (outer diameter) rotor was used and samples were referenced to the external standard ammonium dihydrogen phosphate (ADP) at 0 ppm. The observed shoulder for the spectra is due to the presence of two crystallographically inequivalent POMs within the unit cell of the crystal (Z = 2).

Experimental Section

Synthesis and Characterization of $Ag_5PV_2Mo_{10}O_{40}$. $Na_5PV_2Mo_{10}O_{40}{\bullet}xH_2O$ was synthesized and purified according to the literature procedure (Pettersson, L.; Andersson, I.; Selling, A.; Grate, G. H. *Inorg. Chem.* 1994, *33*, 982-993). $Na_5PV_2Mo_{10}O_{40}$ (39.5 g, 21.4 mmol) was dissolved in 100 mL of distilled water at room temperature. Any undissolved POM was removed by filtration over a medium fritted funnel to yield a bright red-orange solution (0.214 M POM). An aliquot of this solution (40 mL, 8.55 mmol POM) was removed to which $AgNO_3$ (7.26g, 42.7 mmol) was added. Addition of $AgNO_3$ resulted in immediate precipitation of a red-orange amorphous powder. The precipitate was removed by suction filtration over a medium fritted funnel. The product was washed three times with room temperature water, three times with ether and then allowed to dry on the funnel (yield 5.07 g, 26.1% based on $Na_5PV_2Mo_{10}O_{40}$). TGA and DSC data showed Ag_5**1** was stable up to 832 ºC. Water molecules of solvation (11 per POM, ~8.4 % weight loss) were driven off between 36 to 450 ºC. Anal. Calcd. (found) for $Ag_5PV_2Mo_{10}O_{40}$ $(NaNO_3)_{0.35}$. Anal. Calcd. (found) for $Ag_5PV_2Mo_{10}O_{40}$ Ag, 23.74 (23.99); Mo, 42.82 (44.30); P, 1.36 (1.29); V, 4.50 (4.80) FTIR (KBr, 1100-400 cm^{-1}): 1073 (sh), 1062 (m), 1048 (m), 946 (s), 863 (m), 777 (vs) cm^{-1}. SSA = 0.93 m^2 g^{-1}. X-ray quality crystals were obtained by diffusion of diethyl ether into an acetonitrile solution of Ag_5**1** at 25 ºC.

Ambient-Temperature Air Oxidation of CEES in 2,2,2–Trifluoroethanol Catalyzed by Selected Materials. A stock solution of CEES (0.275 M) was prepared in 2,2,2-trifluoroethanol with 1,3-dichlorobenzene added as an internal standard. The different catalysts were placed in 18-mL glass vials fitted with polytetrafluoroethylene (PTFE) septa and screw tops. Aliquots (2 mL) of CEES solution were added to each vial and each reaction was allowed to proceed for 11.9 days at room temperature with stirring (400 rpm). All reactions were monitored by GC.

Determination of the Effect on Catalysis from solvated H_2O within Ag_5**1**. A sample of Ag_5**1** was dried under vacuum at 150 °C for 2 hours. TGA confirmed the loss of approximately half the solvated water molecules as compared with the thermogram of the original Ag_5**1**. The dried catalyst was suspended in 2 mL of a CEES solution (0.178 M CEES in 2,2,2-triflouroethanol with 1,3-dichlorobenzene added as an internal standard), stirred for 10.7 days, and CEESO and CEES were quantified by GC. The solvated water molecules did not effect the catalytic activity of Ag_5**1**.

Confirmation of Reaction Stoichiometry. Ag_5**1** (0.3008 g, 1.33x10^{-4} mol) was placed in a 25-mL Schlenk flask with 5.0 mL of a 0.2576 M solution of CEES in 2,2,2-trifluoroethanol. The flask was connected to a modified manometer and the system was purged with oxygen. The flask was then submerged in a 40 ºC water bath and allowed to thermally equilibrate. The volume of consumed oxygen versus time was recorded. The system was allowed to react for 36 hrs.

Determination of Mass Balance for Oxidation of CEES to CEESO Catalyzed by Ag_5**1**. Reaction conditions: 2 mL aliquot of a 0.172 M CEES solution in 2,2,2-trifluoroethanol with 1,3-dichlorobenzene added as an internal standard for quantification by GC. Ag_5**1** was suspended in the CEES solution and allowed to catalyze the oxidation at room temperature with air in an 18 mL vial fitted with a polytetrafluoroethylene (PTFE) septum and stirred at 400 rpm for 10.7 days. The ratio of CEES:CEESO after the reaction was 1:1, indicating CEESO to be the only product.

Determination of Radical vs. Non-Radical Mechanism of CEES Oxidation catalyzed by Ag_5**1** via BHT as a Radical Trap. A solution of 0.172 M CEES was prepared in 2,2,2-trifluoroethanol with 1,3-dichlorobenzene added as an internal standard. Ag_5**1** (1.74 x 10^{-5} mol) was suspended in 2 mL aliquots of the CEES solution and placed in 18-mL glass vials fitted with polytetrafluoroethylene (PTFE) septa and screw tops. BHT (2.45 x 10^{-5} mol) was added after 114 hours and CEESO production was observed (5.3 TON). The reaction was allowed to continue and CEESO continued to evolve at a similar rate to the reactions where no BHT was added.

Confirmation that the Solid is the Active Catalyst by Filtration. Ag_5**1** (0.292 g, 1.29 x10^{-4} mol) was added to a glass vial fitted with a PTFE septum to which 4.5 mL of a 0.257 M solution of CEES in 2,2,2-trifluoroethanol was added. The reaction mixture was purged with O_2, placed in a thermostated water bath at 40 ºC, and the suspension was stirred at 200 rpm. The reaction was monitored for 43 h during which aliquots were removed and analyzed by GC. After 43 h, the vial was removed from the water bath and the contents centrifuged and then filtered through a pipette that had been tightly packed with cellulose. The clear, very faint yellow supernatant was placed in a new vial fitted with a PTFE septum. The contents and vial were then purged with O_2, placed back into the 40 ºC water bath, and stirred at 200 rpm. The recovered yellow-orange powder (POM) was mixed with 5.0 mL of fresh 0.257 M CEES solution in a second vial. The vial was fitted with a PTFE septum, and the vial and contents purged with O_2. The vial was then placed back into the 40 ºC water bath, and the contents stirred at 200 rpm. All reactions were monitored by GC. The resuspended POM was allowed to react for 40 h, after which time the reaction vessel was removed from the water bath and the contents centrifuged and then filtered through a pipette that had been tightly packed with cellulose. The clear, very faint green supernatant was placed in a new vial, fitted with a PTFE septum and purged with O_2. The reaction mixture was then put back into the 40 ºC water bath, and stirred at 200 rpm. The recovered yellow-green powder (POM) was placed into a vial which contained 5.0 mL of fresh 0.257 M CEES solution. The vial was fitted with a new PTFE septum and the contents and vial purged with O_2. The vial was then placed back into the 40 ºC water bath and the reaction stirred at 200 rpm. GC was used to monitor all reactions.

Spectroscopic Assessment of Ag_5**1** Solubility. Ag_5**1** (0.146 g, 6.43x10^{-5} mol) was suspended in the reaction mixture, containing TFE (2.0 mL), CEES (0.1 mL) and 1,3-dichlorobenzene (25 µL) as a reference. The mixture was stirred at 400 rpm for a 15 min and then centrifuged, followed by filtering through a pipette packed with cellulose. The clear supernatant was collected and the partially reacted Ag_5**1** was resuspended in a fresh reaction mixture. After stirring for 30 min, the reaction mixture was again centrifuged, followed by filtering through a cellulose packed pipette. This process was repeated 11 times at room temperature, at 40 ºC, and at different stirring times (varying from 15 min to 18 h). At the conclusion, the collected supernatants (~20 mL) were combined, concentrated by roto-evaporation to a volume of 3 mL and filtered through a fine fritted funnel. The resulting solution was clear and very faintly yellow. An aliquot was removed and placed in an IR solution cell fitted with AgBr windows and a 0.015 mm Teflon spacer. Examination of the IR spectrum indicated no POM (absence of the M-O-M (797 cm^{-1}) and P-O (1046 cm^{-1}) bands). The solution (1 mL aliquot) was placed in a 5-mm NMR tube with a small amount of CD_3CN to achieve solvent lock. The sample was placed in the NMR and 3300 scans were acquired. No vanadium was detected. To insure that any vanadium present was oxidized to diamagnetic d^0 V(V) (reduced vanadium is paramagnetic and therefore would cause line-broadening and thus, no NMR signal) the sample was removed and bromine was added to the NMR tube. The sample was shaken vigorously and placed back into the NMR. Again, 3300 scans were acquired, and no vanadium was detected. Finally, the 3 mL of concentrated solution was again roto-evaporated until only a dark, oily substance remained. This was placed in an IR solution cell, fitted with AgBr windows and analyzed by IR. The spectrum did not display any bands associated with the Ag_5**1** catalyst.

Inhibition of the Reaction by DMSO. Ag_5**1** (0.104 g, 4.58 x10^{-5} mol) was suspended in 10 mL of a 0.185 M solution of CEES in 2,2,2-trifluoroethanol which had been placed in a glass vial with a PTFE septum. DMSO (0.14 mL, 2.0 mmol, used as a model for CEESO) was added to the system, and it was allowed to react under ambient conditions. A similar reaction (identical experimental conditions but without addition of DMSO) was run in parallel (see Figure S2). After 48 and 72 h, additional aliquots of DMSO (0.14 mL, 2.0 mmol) were added to the reaction mixture. Both reactions were monitored using quantitative GC.

Substrate Adsorption onto the Catalyst. A stock solution of CEES (0.1047 M) was prepared in 2,2,2-trifluoroethanol with 1,3-dichlorobenzene added as an internal standard. The CEES solution was placed in a 18-mL glass vial fitted with polytetrafluoroethylene (PTFE) septum and screw top. The solution was stirred at 400 rpm at room temperature for 2.6 hours, during which aliquots were removed and analyzed by GC. Ag_5**1** (0.130 g, 5.26 x10^{-5} mol) was then added to the stirring solution and the concentrations of CEES and $CH_3CH_2SCH_2CH_2OH$ (hydrolysis product of CEES) were monitored by GC. After 8.4 hours, 5.26 x10^{-5} mols of CEES was absorbed onto 3.53 x10^{-5} mols of catalyst. After reaction, the green (reduced form) catalyst was removed from the reaction mixture by suction filtration, suspended in TFE and washed for an hour, isolated and then dried *in vacuo*. This process was repeated three times, with the final *in vacuo* drying done overnight. Solid FTIR (5% KBr) analysis of the catalyst revealed new bands present at 3300 cm^{-1} (C – H stretching) and 1100 cm^{-1} (likely sulfoxide stretch) as well as the intact POM skeleton.

X-ray crystallography of Ag_5**1** after reaction failed to yield a viable structure of CEESO bound to the catalyst. However, the X-ray data indicated CEESO molecules proximal to the Ag(I) centers. Elemental analysis confirmed the presence of S on the recovered catalyst.

Calculation of Surface Accessible Ag_5**1**.

1. What is the size of the Ag_5**1** catalyst particles?

Assume spherical catalyst particles

Each Ag_5**1** unit has a surface area of 1.2 nm^2

based on analysis of the packing diagram for crystalline Ag_5**1**.

Spherical catalyst particles have 0.93 $m^2\ g^{-1}$ surface area from BET analysis

Density of Ag_5**1** from X-ray crystallography = $3 \bullet 10^6\ g\ m^{-3}$

$$\text{Volume (v)} = \frac{4}{3}\pi r^3$$

$$\text{Surface (s)} = 4\pi r^2$$

$$\text{Density (d)} = \frac{\text{mass (m)}}{\text{volume (v)}}$$

$$\text{Specific Surface Area (SSA)} = \frac{s}{m} = \frac{4\pi r^2}{\frac{4}{3}\pi r^3 d} = \frac{3}{rd}$$

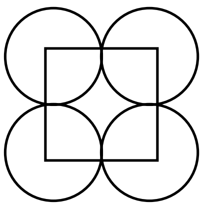
$$r = \frac{3}{\text{SSA} \times \text{d}} = \frac{3}{0.93\ m^2 g^{-1} \times 3 \bullet 10^6\ gm^{-3}} = \frac{1}{10^6}\,m = \ \sim 1\ \mu m$$

thus, diameter of a Ag_5**1** catalyst sphere = 2000 nm

2. How many Ag_5**1** molecules are on the surface of the 1000 nm radius sphere?

$$n_s = \frac{s}{1.2\ \text{nm}^2} = \frac{4\pi r^2}{1.2\ \text{nm}^2} = \frac{4\pi(1000\ \text{nm})^2}{1.2\ \text{nm}^2} = 1.0 \bullet 10^7 \text{ molecules on the surface}$$

3. How many Ag_5**1** molecules are in a 1000 nm radius sphere?



x = distance between catalytic spheres = √1.2 nm² = 1.2 nm

$$n_\theta = \frac{volume}{\text{x}^3} = \frac{\frac{4}{3}\pi r^3}{(1.2\ \text{nm})^3} = \frac{\frac{4}{3}\pi(1000\ \text{nm})^3}{(1.2\ \text{nm})^3} = 2.4 \bullet 10^9 \text{ Ag}_5\mathbf{1} \text{ molecules in the 1 } \mu\text{m sphere}$$

4. What percentage of Ag_5**1** molecules is on the surface?

$$\frac{\text{n}_s}{\text{n}_\theta} \times 100 = 0.41\% = \text{Ag}_5\mathbf{1} \text{ molecules are on the surface}$$

Thus, if there are 9.6 observed turnovers per mole of POM molecule and only 0.42% of these POMs are surface accessible then (9.6/0.0041) = ~2300 turnovers per surface exposed Ag_5**1** molecule. The surface area of Ag_5**1** after catalysis was measured (in duplicate) to be 0.93 m^2 g^{-1}.