Supporting Information

Kinetic investigation of aerobic epoxidation of limonene over cobalt substituted mesoporous SBA-16

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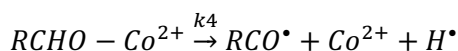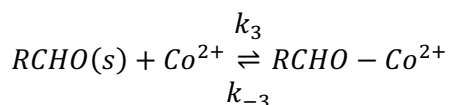
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Kinetic studies of the aerobic epoxidation of limonene

Theoretical Analysis

Based on a proposed reaction mechanism shown in Scheme 3 in the text [1], in this kinetic analysis it was necessary to introduce two different reaction pathways (pathways A and B) because some limonene epoxidation had been observed in absence of catalyst (see Table 5 in [1]). Therefore, the reaction pathway A involves homogeneous epoxidation of limonene by the acyl radical ($RCO^{\bullet}$) which could be generated either homogenously by reaction (3S):

$$RCHO\ (l) + \frac{1}{2}O_2 \rightarrow RCO^{\bullet} + \frac{1}{2}H_2O_2$$
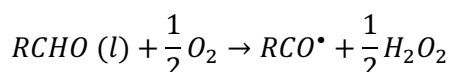
Or by a process involving adsorbed aldehyde RCHO(s) (reaction (S4a) and (S4b)):

$$RCHO(s) + Co^{2+} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} RCHO - Co^{2+}$$

$$RCHO - Co^{2+} \overset{k4}{\rightarrow} RCO^{\bullet} + Co^{2+} + H^{\bullet}$$

In the reaction pathway B, the adsorbed aldehyde formed through surface reaction (S4a) interacts with O_2 and generates an adsorbed peroxy radical with $H^{\bullet}$ being kept in the vicinity of the adsorption site (reaction S24):

$$RCHO - Co^{2+} + O_2 \underset{k_{-b}}{\overset{k_b}{\rightleftharpoons}} Co^{3+}(RCO_3(SiO)_4H)$$
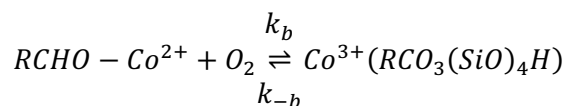
Therefore, it is proposed that two possible types of reaction pathway account for the epoxidation of limonene over the heterogeneous Co/SBA-16 catalyst. One is similar to the homogeneous liquid phase epoxidation of olefins by acylperoxy radicals generated using Co^{2+} ions as catalyst, in the bulk solution (pathway A) [2, 3]. The other pathway is a typical heterogeneous catalytic reaction. In this case, the formation of limonene epoxide occurs on the surface of the catalyst (pathway B). These proposed mechanisms will be discussed in line with a kinetic analysis of the experimental data obtained in the present part of work. Following the reaction mechanism described in Part 1 of this study, the reaction equations can be listed as below:

Mechanism pathway A:

Transport of reactants

$$RCHO(l) \xrightarrow{k1} RCHO(s) \tag{S1}$$

In general, oxygen in the gas phase, $O_2(g)$, is dissolved and absorbed in the bulk solution of the liquid phase, $O_2(l)$ within the range of our oxygen pressure can be defined as:

$$O_2(g) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} O_2(l) \tag{S2}$$

where the notations g, l, and s indicate the species in the gas phase, bulk solution, and on the surface of catalyst, respectively.

Initiation

in the liquid phase

$$RCHO \ (l) + \frac{1}{2}O_2 \rightarrow RCO^\bullet + \frac{1}{2}H_2O_2 \tag{S3}$$

and at the catalyst surface

$$RCHO(s) + Co^{2+} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} RCHO-Co^{2+} \tag{S4a}$$

$$RCHO - Co^{2+} \overset{k4}{\rightarrow} RCO^\bullet + Co^{2+} + H^\bullet \tag{S4b}$$

Eqs. (S3) and (S4) correspond to initiation steps generating the acyl radical ($RCO^\bullet$) through homogenous (non-catalyzed) and heterogenous (catalyzed) routes, respectively. The acyl radical ($RCO^\bullet$) generated by Eq. (S3), however can be neglected especially at initial time of the reaction for the sake of avoiding complexity of kinetic analysis. It is worth noting that in many systems of catalytic oxidation of aldehydes Eq. (S3) was not considered [2-4]. The hydrogen atom generated during the formation of the $RCO^\bullet$ radical (Eq. (S4b)) is assumed to stay in the vicinity of the cobalt site and available for the radical reaction producing acid.
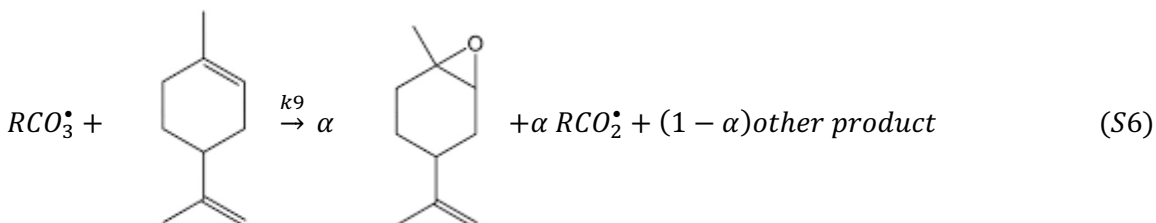
Propagation

$$RCO^\bullet + O_2(l) \overset{k5}{\rightarrow} RCO_3^\bullet \tag{S5a}$$

$$RCO_3^\bullet + RCHO \overset{k6}{\rightarrow} RCO_3H + RCO^\bullet \tag{S5b}$$

During the propagation step, the dissolved oxygen rapidly reacts with the acyl radical ($RCO^\bullet$) in solution to form the free radical $RCO_3^\bullet$. Kuo et al. [3] reported that in free radical chain oxidation reactions, usually oxygen transfer is not the rate-determining step and the rate of the overall process is controlled by the chemical reaction steps. It was indicated that

the constant k_5 of Eq. (S5a) was usually higher than the rate constant k_6 of Eq. (S5b) [5, 6].

Therefore, the free radical $RCO^{\bullet}$ is effectively scavenged at increased oxygen pressure.

Formation of epoxide

$$RCO_3^{\bullet} + \quad \xrightarrow{k9} \alpha \qquad \qquad + \alpha\, RCO_2^{\bullet} + (1-\alpha)other\ product \qquad\qquad (S6)$$

$$RCO_2^{\bullet} + RCHO \xrightarrow{k10} RCOOH + RCO^{\bullet} \qquad\qquad (S7)$$

The value of α in Eq. (S6) is defined as the ratio of the initial reaction rate of the limonene epoxidation to the initial reaction rate of limonene consumption $(\alpha = \frac{R_e}{R_l})$.

Termination

$$2RCO_3^{\bullet} \xrightarrow{k7} T.P. \qquad\qquad (S8a)$$

$$RCO_3^{\bullet} + S \xrightarrow{k8} T.P. + S \qquad\qquad (S8b)$$

Eq. (S8b) indicates that the termination of the free radical $RCO_3^{\bullet}$ occurs due to combination with surface, S, of catalyst as the third body [7].

$$2RCO^{\bullet} \rightarrow T.P. \qquad\qquad (S8c)$$

$$RCO_3^{\bullet} + RCO^{\bullet} \rightarrow T.P. \qquad\qquad (S8d)$$

Under our reaction conditions and especially at initial stage of the reaction the concentration of RCO_3H is very small. Hence, the possibility of percarboxylic acid as the

potential epoxidizing intermediate was ignored [1]. The termination step is reduced to Eqs. (S8a) and (S8b). Because with excess of oxygen the rate of the reaction (S5a) is higher than that of (S5b), therefore the system may be assumed to contain almost solely $RCO_3^{\bullet}$ radicals and the rate of oxidation becomes independent of the oxygen concentration [2, 8].

Case(I): If the rate determining step (RDS) is reaction in the bulk solution, the rates of the free radicals and intermediate species concentration equations are:

$$\frac{d[RCO^{\bullet}]}{dt} = k_4[RCHO - Co^{2+}] - k_5[RCO^{\bullet}][O_2(l)] + k_6[RCO_3^{\bullet}][RCHO] +$$

$$\qquad k_{10}[RCO_2^{\bullet}][RCHO] \qquad\qquad (S9)$$

$$\frac{d[RCO_2^{\bullet}]}{dt} = \alpha k_9[RCO_3^{\bullet}][L] - k_{10}[RCO_2^{\bullet}][RCHO] \qquad\qquad (S10)$$

$$\frac{d[RCO_3^{\bullet}]}{dt} = k_5[RCO^{\bullet}][O_2(l)] - k_6[RCO_3^{\bullet}][RCHO] - 2k_7[RCO_3^{\bullet}]^2 - k_8[RCO_3^{\bullet}][S]$$

$$\qquad - k_9[RCO_3^{\bullet}][L] \qquad\qquad (S11)$$

$$\frac{d[RCHO - Co^{2+}]}{dt}$$

$$\qquad = k_3[RCHO(s)][Co^{2+}] - k_{-3}[RCHO - Co^{2+}] - k_4[RCHO - Co^{2+}] \qquad (S12)$$

Making the pseudo steady state assumption:

$$\frac{d[RCO^{\bullet}]}{dt} = \frac{d[RCO_2^{\bullet}]}{dt} = \frac{d[RCO_3^{\bullet}]}{dt} = 0 \qquad , \qquad \frac{d[RCHO - Co^{2+}]}{dt} = 0$$

and summing Eqs. (S9)-(S11), $(k'_3 = \frac{k_3}{k_{-3}+k_4})$:

$$[RCO_3^{\bullet}] = \frac{1}{4k_7} \left[-k_8[S] - (1-\alpha)k_9[L] \right.$$

$$\qquad \left. + ((k_8[S] + (1-\alpha)k_9[L])^2 + 8k_7k_4k'_3[RCHO(s)][Co^{2+}])^{\frac{1}{2}} \right] \qquad (S13)$$

a) Assuming $k_8[S] + (1-\alpha)k_9[L] \gg 8k_7k_4k'_3[RCHO(s)][Co^{2+}]$, then Eq. (S13) can be reduced to $[RCO_3^{\bullet}] = 0$, which is not reasonable for a chain reaction where the free-radical concentration is zero. It indicates that the reactions are completely retarded or inhibited.

b) Assuming $k_8[S] + (1-\alpha)k_9[L] \ll 8k_7k_4k'_3[RCHO(s)][Co^{2+}]$, then Eq. (S13) can be reduced to:

$$[RCO_3^{\bullet}] = \frac{-k_8}{4k_7}[S] - \frac{(1-\alpha)k_9}{4k_7}[L] + \left(\frac{k_4k'_3}{2k_7}\right)^{\frac{1}{2}} [RCHO(s)]^{\frac{1}{2}} [Co^{2+}]^{\frac{1}{2}} \qquad (S14)$$

Based on mechanism pathway A, the total rate equation of epoxidized limonene (R_e) and isobutyraldehyde oxidation (R_a) can be obtained by Eqs. (S15) and (S16) respectively:

$$R_e = \alpha k_9[RCO_3^{\bullet}][L] \qquad (S15)$$

$$R_a = k_6[RCO_3^{\bullet}][RCHO] \qquad (S16)$$

By substitution of Eq. (S14) into Eqs. (S15) and (S16) the general rate equation of R_e and R_a can be obtained:

$$R_e = -\frac{\alpha(1-\alpha)k_9{}^2}{4k_7}[L]^2 \frac{-\alpha k_9 k_8}{4k_7}[S][L] + \alpha k_9 (\frac{k_4k'_3}{2k_7})^{\frac{1}{2}} [RCHO(s)]^{\frac{1}{2}} [Co^{2+}]^{\frac{1}{2}}[L] \qquad (S17)$$

$$R_a = \frac{-k_8 k_6}{4k_7}[S][RCHO] - \frac{(1-\alpha)k_9 k_6}{4k_7}[L][RCHO] + k_6\left(\frac{k_4k'_3}{2k_7}\right)^{\frac{1}{2}} [RCHO(s)]^{\frac{3}{2}} [Co^{2+}]^{\frac{1}{2}} \quad (S18)$$

Eqs. (S17) and (S18) are simplified as:

$$R_e = -0.16K_2[L]^2 - 0.8K_1[S][L] + 0.8K_3 [RCHO(s)]^{\frac{1}{2}} [Co^{2+}]^{\frac{1}{2}}[L] \qquad (S19)$$

$$R_a = K_4[S][RCHO] - 0.2K_5[L][RCHO] + K_6 [RCHO(s)]^{\frac{3}{2}} [Co^{2+}]^{\frac{1}{2}} \qquad (S20)$$

Where the average value of α for the typical run at initial reaction time was found to be

around α=0.8, and $K_1 = \frac{k_9 k_8}{4k_7}$, $K_2 = \frac{k_9^2}{4k_7}$, $K_3 = k_9(\frac{k_4 k'_3}{2k_7})^{\frac{1}{2}}$, $K_4 = \frac{k_8 k_6}{4k_7}$, $K_5 = \frac{k_9 k_6}{4k_7}$, $K_6 =$

$k_6 \left(\frac{k_4 k'_3}{2k_7}\right)^{\frac{1}{2}}$.

Case (II): If the RDS is a mass transfer of isobutyraldehyde from bulk solution to the surface of catalyst both R_e and R_a can be obtained by Eq. (S1), in this case the concentration of isobutyraldehyde on the surface of catalyst will approach zero $[RCHO(s)] = 0$.

$$R_e = R_a = k_1[RCHO] \tag{S21}$$

Case (III): If the RDS is a mass transfer of oxygen from gas phase to the liquid phase then:
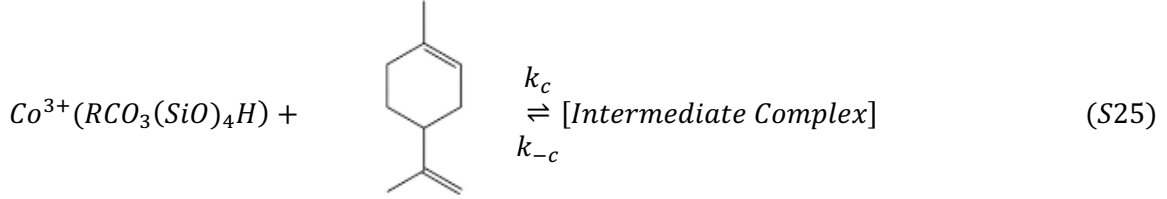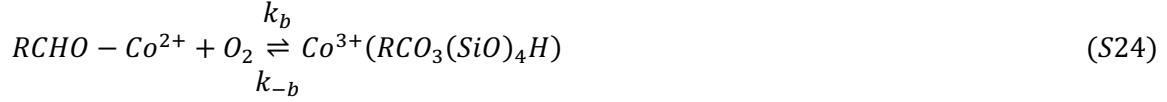
$$R_e = R_a = kPO_2 \tag{S22}$$

Where PO_2 is the pressure of oxygen. It was found that at lower oxygen pressure the reaction rate equation is related to the oxygen pressure because of dependence on the type of termination step as discussed earlier [4, 9].

Mechanism pathway B:

The other possible reaction mechanism for the epoxidation of limonene is the formation of limonene epoxide on the surface of the catalyst. The proposed mechanism is defined as:
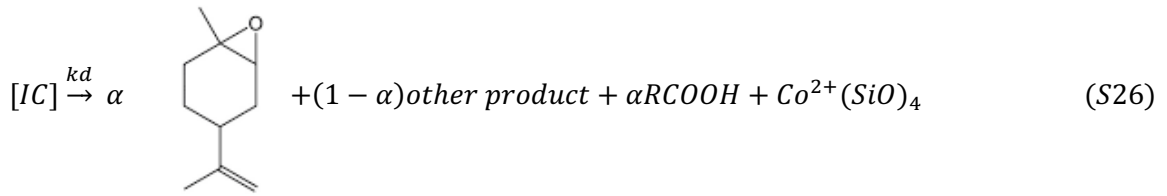
$$RCHO(s) + Co^{2+} \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} RCHO - Co^{2+} \tag{S23}$$

$$RCHO - Co^{2+} + O_2 \underset{k_{-b}}{\overset{k_b}{\rightleftharpoons}} Co^{3+}(RCO_3(SiO)_4H) \qquad (S24)$$

$$Co^{3+}(RCO_3(SiO)_4H) + \quad\underset{k_{-c}}{\overset{k_c}{\rightleftharpoons}} [Intermediate\ Complex] \qquad (S25)$$

$$[IC] \overset{kd}{\rightarrow} \alpha \qquad\qquad + (1-\alpha)other\ product + \alpha RCOOH + Co^{2+}(SiO)_4 \qquad (S26)$$

the change of concentrations of the intermediates are determined as:

$$\frac{d[RCHO - Co^{2+}]}{dt}$$

$$= k_a[RCHO(s)][Co^{2+}] - k_{-a}[RCHO - Co^{2+}] - k_b[RCHO - Co^{2+}][O_2]$$

$$+ k_{-b}\ [Co^{3+}(RCO_3(SiO)_4H)] \qquad (S27)$$

$$\frac{d[Co^{3+}(RCO_3(SiO)_4H)]}{dt}$$

$$= k_b[RCHO - Co^{2+}][O_2] - k_{-b}[Co^{3+}(RCO_3(SiO)_4H)]$$

$$- k_c[Co^{3+}(RCO_3(SiO)_4H)][L] + k_{-c}[IC] \qquad (S28)$$

$$\frac{d[IC]}{dt} = k_c[Co^{3+}(RCO_3(SiO)_4H)][L] - k_{-c}[IC] - k_d[IC] \qquad (S29)$$

Under the pseudo steady state assumption, the concentration of the intermediates can be determined:

$$\frac{d[RCHO - Co^{2+}]}{dt} = 0, \quad \frac{d[Co^{3+}(RCO_3(SiO)_4H)]}{dt} = 0, \quad \frac{d[IC]}{dt} = 0$$

$[RCHO - Co^{2+}]$

$$= \frac{k_a[RCHO(s)][Co^{2+}]}{k_{-a} + k_b[O_2]}$$

$$+ \frac{k_{-b}k_bk_a[O_2][RCHO(s)][Co^{2+}]}{(k_{-a} + k_b[O_2])^2\left(k_{-b} + k_c[L] - \frac{k_bk_{-b}[O_2]}{k_{-a} + k_b[O_2]} - \frac{k_{-c}k_c[L]}{k_{-c} + k_d}\right)} \qquad (S30)$$

$[Co^{3+}(RCO_3(SiO)_4H)]$

$$= \frac{k_ak_b[O_2]}{(k_{-a} + k_b[O_2])\left(k_{-b} + k_c[L] - \frac{k_bk_{-b}[O_2]}{k_{-a} + k_b[O_2]} - \frac{k_ck_{-c}[L]}{k_d + k_{-c}}\right)}[RCHO(s)][Co^{2+}] \qquad (S31)$$

$[IC]$

$$= \frac{k_ak_bk_c[O_2]}{(k_{-a} + k_b[O_2])\left(k_{-b} + k_c[L] - \frac{k_bk_{-b}[O_2]}{k_{-a} + k_b[O_2]} - \frac{k_ck_{-c}[L]}{k_d + k_{-c}}\right)(k_d + k_{-c})}[RCHO(s)][Co^{2+}][L]$$

$$(S32)$$

Case(I): If the rate determining step (RDS) is Eq. (S23):

$$R_e = -R_a = k_a[RCHO(s)][Co^{2+}] \qquad (S33)$$

Case(II): If the rate determining step (RDS) is Eq. (S24):

$$R_e = -R_a = k_b[RCHO - Co^{2+}][O_2] \qquad (S34)$$

$$R_e = -R_a$$

$$= (\frac{k_a k_b [O_2]}{k_{-a} + k_b [O_2]}$$

$$+ \frac{k_{-b} k_b{}^2 k_a [O_2]^2}{(k_{-a} + k_b [O_2])^2 \left(k_{-b} + k_c [L] - \dfrac{k_b k_{-b} [O_2]}{k_{-a} + k_b [O_2]} - \dfrac{k_c k_{-c} [L]}{k_d + k_{-c}}\right)}) [RCHO(s)][Co^{2+}] \qquad (S35)$$

This assumption cannot explain the observed finite order for limonene, as if Eq. (S24) (formation of $Co^{3+}(RCO_3(SiO)_4H)$) is the rate determining step, one would expect zero order in limonene.

Case(III): If the rate determining step (RDS) is the surface reaction between adsorbed oxygen and adsorbed limonene (Eq. (S25)):

$$R_e = -R_a = k_c [Co^{3+}(RCO_3(SiO)_4H)][L] \qquad (S36)$$

$$R_e = -R_a$$

$$= \frac{k_a k_b k_c [O_2]}{(k_{-a} + k_b [O_2]) \left(k_{-b} + k_c [L] - \dfrac{k_b k_{-b} [O_2]}{k_{-a} + k_b [O_2]} - \dfrac{k_c k_{-c} [L]}{k_d + k_{-c}}\right)} [RCHO(s)][Co^{2+}][L] \qquad (S37)$$

if partial pressure of oxygen is constant by rewriting of Eq. (S37) the rate of reaction can be simplified as:

$$R_e = -R_a = K_c [RCHO(s)][Co^{2+}][L] \qquad (S38)$$

at low limonene initial concentration, the items which contains limonene can be ignored and K can be obtained as:

$$K_c = \frac{k_a k_b k_c [O_2]}{(k_{-a} + k_b [O_2]) \left(k_{-b} - \dfrac{k_b k_{-b} [O_2]}{k_{-a} + k_b [O_2]}\right)}$$

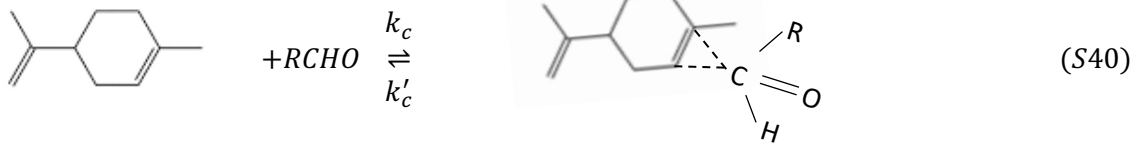But if the initial concentration of limonene is high enough, the rate equations can be written as:

$$R_e = -R_a = K[RCHO(s)][Co^{2+}] \tag{S39}$$
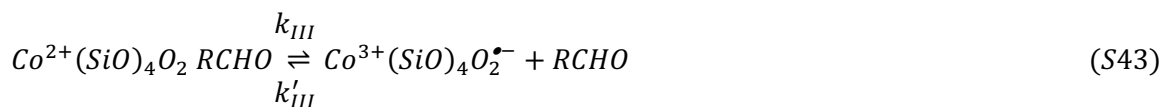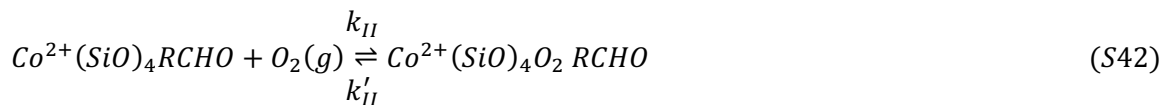
Where,

$$K = \frac{k_a k_b k_c [O_2]}{(k_{-a} + k_b [O_2]) \left(k_c - \dfrac{k_c k_{-c}}{k_d + k_{-c}} \right)}$$
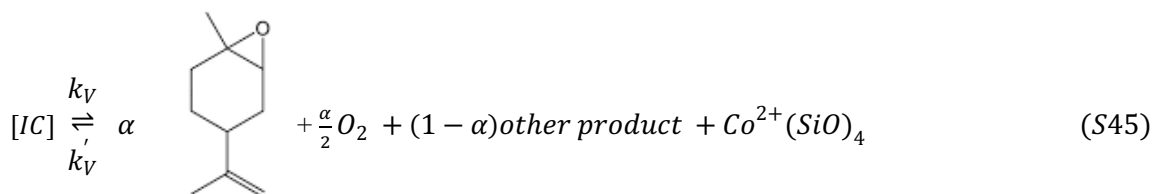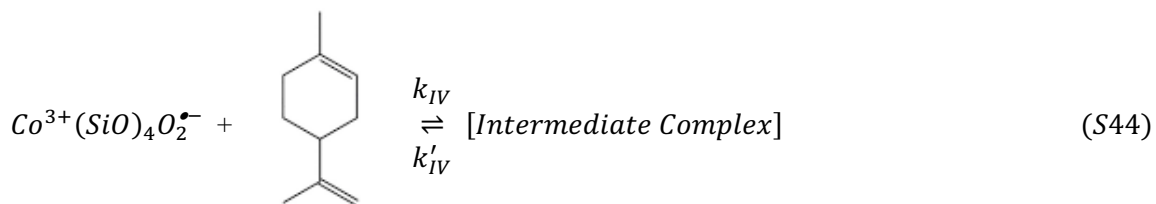
Mechanism pathway C:

The reaction pathway C involves homogeneous interaction of isobutyraldehyde to the double bonds of limonene which could be expressed by reaction (S40):

$$\tag{S40}$$

Or by a process involving adsorbed aldehyde (reaction (S41 to S45)):

$$Co^{2+}(SiO)_4 + RCHO \underset{k_I'}{\overset{k_I}{\rightleftharpoons}} Co^{2+}(SiO)_4 RCHO \tag{S41}$$

$$Co^{2+}(SiO)_4 RCHO + O_2(g) \underset{k_{II}'}{\overset{k_{II}}{\rightleftharpoons}} Co^{2+}(SiO)_4 O_2\, RCHO \tag{S42}$$

$$Co^{2+}(SiO)_4 O_2\, RCHO \underset{k_{III}'}{\overset{k_{III}}{\rightleftharpoons}} Co^{3+}(SiO)_4 O_2^{\bullet-} + RCHO \tag{S43}$$

$$Co^{3+}(SiO)_4 O_2^{\bullet -} + \ [\text{limonene}] \quad \underset{k'_{IV}}{\overset{k_{IV}}{\rightleftharpoons}} \quad [Intermediate\ Complex] \tag{S44}$$

$$[IC] \underset{k'_V}{\overset{k_V}{\rightleftharpoons}} \alpha\ [\text{epoxide}] + \frac{\alpha}{2}O_2 + (1-\alpha)other\ product + Co^{2+}(SiO)_4 \tag{S45}$$

Owing to the reaction expressed by Eq. (S40), isobutyraldehyde and liomonene concentrations are related as:

$$[L][RCHO] = \frac{k'_c}{k_c}[C] \tag{S46}$$

$$[C] = [RCHO]_0 - [RCHO]$$

Where [C] is the concentration of complex generated in Eq. (S40) and $[RCHO]_0$ is the total aldehyde introduced in the reactor.

$$[L][RCHO] = \frac{k'_c}{k_c}([RCHO]_0 - [RCHO]) \tag{S47}$$

$$[RCHO] = \frac{[RCHO]_0}{1 + \dfrac{k_c}{k'_c}[L]} \tag{S48}$$

From Eq. (S41) to (S45), the change of concentrations of the intermediates are determined as:

$$\frac{d[Co^{2+}(SiO)_4RCHO]}{dt}$$

$$= k_I[Co^{2+}][RCHO] - k_I'[Co^{2+}(SiO)_4RCHO] - k_{II}[Co^{2+}(SiO)_4RCHO][O_2]$$

$$+ k_{II}' \ [Co^{2+}(SiO)_4O_2RCHO] \tag{S49}$$

$$\frac{d[Co^{2+}(SiO)_4O_2RCHO]}{dt}$$

$$= k_{II}[Co^{2+}(SiO)_4RCHO][O_2] - k_{II}'[Co^{2+}(SiO)_4O_2RCHO]$$

$$- k_{III}[Co^{2+}(SiO)_4O_2RCHO] \ + k_{III}' \ [Co^{3+}(SiO)_4O_2^{\bullet-}] \ [RCHO] \tag{S50}$$

$$\frac{d[Co^{3+}(SiO)_4O_2^{\bullet-}]}{dt}$$

$$= \ k_{III}[Co^{2+}(SiO)_4O_2RCHO] - k_{III}'[Co^{3+}(SiO)_4O_2^{\bullet-}][RCHO]$$

$$- \ k_{IV}[Co^{3+}(SiO)_4O_2^{\bullet-}][L] + k_{IV}' \ [IC] \tag{S51}$$

$$\frac{d[IC]}{dt} = \ k_{IV}[Co^{3+}(SiO)_4O_2^{\bullet-}][L] - k_{IV}' \ [IC] - k_V \ [IC] \tag{S52}$$

Under the pseudo steady state assumption, the concentration of the intermediates can be determined:

$$\frac{d[Co^{2+}(SiO)_4RCHO]}{dt} = 0, \quad \frac{d[Co^{2+}(SiO)_4O_2RCHO]}{dt} = 0 \ , \quad \frac{d[Co^{3+}(SiO)_4O_2^{\bullet-}]}{dt} = 0,$$

$$\frac{d[IC]}{dt} = 0$$

$$[Co^{3+}(SiO)_4O_2^{\bullet-}]$$

$$= \frac{k_{III}k_{II}k_I[O_2][Co^{2+}][RCHO]}{\left(k_I'k_{II}' + k_{III}(k_I' + k_{II}[O_2])\right)\left(-\dfrac{k_{III}'k_{III}[RCHO]}{k_{II}' + k_{III} - \dfrac{k_{II}k_{II}'[O_2]}{k_I' + k_{II}[O_2]}} + k_{III}[RCHO] + k_{IV}[L] - \dfrac{k_{IV}k_{IV}'[L]}{k_{IV}' + k_V}\right)}$$

$$\tag{S53}$$

$[Co^{2+}(SiO)_4O_2RCHO]$

$$= \frac{1}{\left(k'_I k'_{II} + k_{III}(k'_I + k_{II}[O_2])\right)} \left[\frac{k_{II}k_I[O_2][Co^{2+}][RCHO]}{(k'_I + k_{II}[O_2])}\right.$$

$$+ \frac{k'_{III}k_{III}k_{II}k_I[O_2][Co^{2+}][RCHO]^2}{\left(k'_I k'_{II} + k_{III}(k'_I + k_{II}[O_2])\right)\left(-\dfrac{k'_{III}k_{III}[RCHO]}{k'_{II} + k_{III} - \dfrac{k_{II}k'_{II}[O_2]}{k'_I + k_{II}[O_2]}} + k_{III}[RCHO] + k_{IV}[L] - \dfrac{k_{IV}k'_{IV}[L]}{k'_{IV} + k_V}\right)}\left.\right]$$

$$(S54)$$

$[Co^{2+}(SiO)_4RCHO]$

$$= \frac{k_I[Co^{2+}][RCHO]}{(k'_I + k_{II}[O_2])} + \frac{k'_{II}}{(k'_I + k_{II}[O_2])\left(k'_I k'_{II} + k_{III}(k'_I + k_{II}[O_2])\right)} \left[\frac{k_{II}k_I[O_2][Co^{2+}][RCHO]}{(k'_I + k_{II}[O_2])}\right.$$

$$+ \frac{k'_{III}k_{III}k_{II}k_I[O_2][Co^{2+}][RCHO]^2}{\left(k'_I k'_{II} + k_{III}(k'_I + k_{II}[O_2])\right)\left(-\dfrac{k'_{III}k_{III}[RCHO]}{k'_{II} + k_{III} - \dfrac{k_{II}k'_{II}[O_2]}{k'_I + k_{II}[O_2]}} + k_{III}[RCHO] + k_{IV}[L] - \dfrac{k_{IV}k'_{IV}[L]}{k'_{IV} + k_V}\right)}\left.\right]$$

$$(S55)$$

$[IC]$

$$= \frac{k_{IV}k_{III}k_{II}k_I[O_2][Co^{2+}][RCHO][L]}{(k'_{IV} + k_V)\left(k'_I k'_{II} + k_{III}(k'_I + k_{II}[O_2])\right)\left(-\dfrac{k'_{III}k_{III}[RCHO]}{k'_{II} + k_{III} - \dfrac{k_{II}k'_{II}[O_2]}{k'_I + k_{II}[O_2]}} + k_{III}[RCHO] + k_{IV}[L] - \dfrac{k_{IV}k'_{IV}[L]}{k'_{IV} + k_V}\right)}$$

$$(S56)$$

Assuming the rate determining step (RDS) is the oxidative insertion of oxygen in the adsorbed aldehyde (step 2 in Scheme 4, Equation (S42)), the rate of epoxidation is represented as:

$$R_e = \alpha\, k_{II}[Co^{2+}(SiO)_4RCHO][O_2] \qquad (S57)$$

Now since only Eq. S41 is possibly reversible, we can assume $k'_{II} = k'_{III} = k'_{IV} = k'_V = 0$.
Therefore, Eq. (S52, S55) can be obtained as:

$$[Co^{2+}(SiO)_4RCHO] = \frac{k_I[Co^{2+}][RCHO]}{(k'_I + k_{II}[O_2])} \tag{S58}$$

$$R_e = \frac{\alpha k_{II}k_I[O_2][Co^{2+}][RCHO]}{(k'_I + k_{II}[O_2])}$$

Or more simply,

$$R_e = \frac{\alpha_1[O_2]}{(\alpha_2 + \alpha_3[O_2])}[Co^{2+}][RCHO] \tag{S59}$$

Substitution of [RCHO] from Eq. (S48),

$$R_e = \frac{\alpha_1[O_2]}{(\alpha_2 + \alpha_3[O_2])}[Co^{2+}]\frac{[RCHO]_0}{1 + \frac{k_c}{k'_c}[L]} \tag{S60}$$
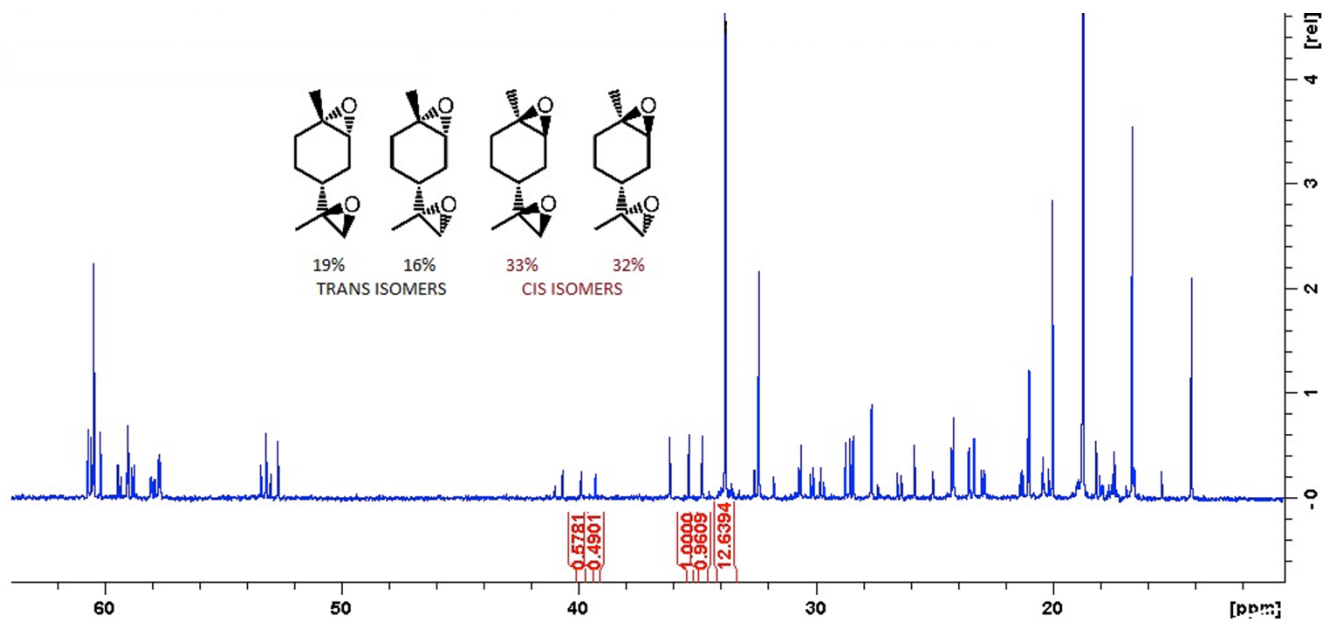
Fig. S1. C13 NMR spectrum of the sample prepared by aerobic epoxidation of limonene over Co-SBA-16(1.1%). Reaction conditions: temperature 301 K; limonene, 3.6 mmol; IBA, 12 mmol; oxygen pressure, 44 psi; catalyst mass, 0.17 g; reaction time, 240 min; solvent ethylacetate.

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