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NaOH alone can be a homogeneous catalyst for selective aerobic oxidation of alcohols in water

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ABSTRACT

Sodium hydroxide (NaOH) has been an indispensable additive in the selective aerobic oxidation of alcohols/polyols in water for ketone and carboxylic acid syntheses over supported metal catalysts, including Au, though the exact function of NaOH remains far from clear. We disclose here that NaOH alone can independently serve as a homogeneous catalyst for the oxidation reactions. This conclusion is supported by rigorous investigations of the effects of NaOH alone (without the presence of any metal catalyst) on the reactivity of aqueous glycerol, ethylene glycol, 2-propanol, and ethanol and their product distribution. Computational results based on density functional theory are also provided to explain the experimentally measured reactivity order of the various alcohols and to generate insight into the molecular mechanisms for the oxidation reactions. Besides challenging existing knowledge about the function of NaOH in alcohol oxidation reactions, this study opens a new avenue for catalytic alcohol/polyol upgrading.

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1. Introduction

Interest in catalytic conversion of biorenewable feedstock to high-value chemicals has made the selective aerobic oxidation of alcohols/polyols to various carbonyl compounds (aldehydes, ketones, and carboxylic acids) one of the important research directions in current chemistry [1,2]. Probably because the bioderived alcohol/polyol is always produced in aqueous solution, the selective aerobic oxidation reaction is usually conducted using an aqueous solution of the alcohol/polyol and involves supported Au or Au-based bimetallic nanoparticles as selective catalysts [3]. However, the activity and selectivity of Au catalysts in enabling the oxidation reactions, especially for polyol oxidation, depends critically on the co-presence of a base (usually NaOH, or in essence OH^-) [4–9]. For instance, in the oxidation of aqueous glycerol (GL), various supported Au nanoparticle catalysts have frequently been documented to produce fairly high yields for glyceric acid (GLA) formation under highly basic (molar NaOH/GL ≥ 1) conditions, but show no activity in the absence of NaOH [5,6]. Basic OH^- is usually considered to be an initiator or promoter for alcohol/polyol activation by abstracting a proton from the hydroxyl or one of the hydroxyls in the substrate alcohol/polyol molecules [7–9]. In the presence of NaOH, even the nature of the Au–support interface, which plays a crucial role in catalysis of many other reactions by Au, appears to be of little importance for aerobic GL oxidation in water [7,8]. Our recent study on aerobic GL oxidation in water at pH < 7 or in base (NaOH)-free water clearly revealed that regardless of the supporting materials, Au nanoparticle catalysts were able to show specific catalysis for the formation of dihydroxyacetone (DHA); when the variables of the reaction were optimized to reduce the possible secondary reactions, DHA yields up to 80% were demonstrated on an Au/CuO catalyst at 40–50 °C [10]. The presence of NaOH (base) therefore would impact not only the activity but also the selectivity of Au catalysts in the aerobic oxidation of alcohols/polyols. This indicates that any further understanding of the catalytic chemistry would be impossible without unraveling the effects of NaOH alone (without the presence of any Au catalyst) on the reactivity and product selectivity of alcohols/polyols in the aerobic oxidations.

Reported here are unprecedented observations on the function of NaOH as an independent homogeneous catalyst for aerobic oxidation of alcohols in water. These observations are made on the aerobic oxidation reactions of different alcohols, including GL, ethylene glycol (EG), 2-propanol (2-PO), and ethanol (EtOH) in water under 1.0 MPa oxygen at 60–100 °C in the absence of any solid catalyst. The obtained data also provide a rigorous assessment of the relative reactivity of the different alcohols and their product

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selectivity features. Calculations based on density functional theory (DFT) are conducted to gain information on the activation of molecular oxygen and the substrate alcohol, which further entitles us to propose possible catalytic mechanisms. The independent catalytic function of NaOH disclosed in this study would certainly shake the earlier understanding of the effect of NaOH on Au catalysis in the selective oxidation reactions of many bioderivative oxygenated platform molecules. Besides, the present data could point to a new dimension of chemistry for selectively upgrading various alcohols/polyols, especially those derived from bioresources.

2. Experimental and computational methods

2.1. Catalytic reaction and product analysis

The alcohol oxidation reactions were conducted in a 50 ml high-pressure Hastelloy autoclave equipped with a Parr 4843 controller [10,11]. Unless otherwise specified, the autoclave was charged with 20 ml of water, 6 mmol of alcohol (GL, EG, 2-PO, or EtOH), and a proper amount of NaOH before it was sealed. After being purged six times with O_2 (~0.8 MPa), the reactor was pressurized to 1.0 MPa at room temperature. Zero reaction time was taken as soon as the autoclave was heated to the reaction temperature (60–100 °C) and the mechanical stirring (900 rpm) was switched on at that very moment. The reaction was terminated by switching off the stirrer and immediately cooling the reactor in an ice-water bath. Under our chosen reaction conditions it was confirmed that there was no mass-transfer limitation effect by varying the stirring speed in sets of reaction measurements at 100 °C using 18 mmol NaOH (molar NaOH/alcohol = 3).

The liquids after the reactions of GL, EG, and EtOH were filtered and analyzed on an Agilent 1260 high-performance liquid chromatograph (HPLC) equipped with an ultraviolet detector (UVD) and a refractive index detector (RID). The column used for separation was a Bio-Rad HPX-87H column (300 × 7.8 mm) operating at 50 °C with 5 mM H_2SO_4 solution as the eluent (0.5 ml/min) [10,11]. Analysis of the liquid from the 2-PO oxidation was conducted on an Agilent 7890A gas chromatograph (GC) equipped with a BP-20 capillary column and a flame ionization detector (FID). To detect possible gas products, the gases in the reactor were also collected with a gas bag after termination of the reactions and then analyzed on an Agilent 6890N GC with a TDX-01 packed column and a FID. Product identification was done by comparison with known pure compounds.

2.2. Computational methods

All the calculations were based on DFT and were initially performed using SIESTA, where optimized double-ζ plus polarization numerical atomic orbital basis sets were utilized, along with the Troullier–Martins norm-conserving pseudopotentials [12–14]. The exchange correlation functional utilized was at the generalized gradient approximation level proposed by Perdew, Burke, and Ernzerhof (GGA-PBE) [15]. The cutoff for the real space grid was set as 250 Ry. The L-BFGS method was employed for geometry relaxation until the maximal force on each relaxed atom was less than 0.01 eV/Å. The finite difference method was utilized to compute the eigenvalues of the Hessian and correct the zero point energy (ZPE) of the system. All transition states (TSs) of the reaction were searched using constrained Broyden based methods designed for treating complex reaction systems [16–18]. Both explicit (with the first shell water molecules) and the implicit solvation models have been utilized to model the reactions, where implicit solvation was implemented using the recently developed CM-MPB method [19–21]. To obtain the structures of alcohol molecules in NaOH-containing water, where many possible H-bonding configurations were available, we utilized global optimization methods and the stochastic surface walking method [22] to sample the phase space and identify the most stable configurations.

For the key elementary step (i.e., step 2), a hybrid B3LYP functional as implemented in the Gaussian09 program was utilized to refine the reaction kinetics. The 6-311+G(d,p) [23] basis sets were used to describe C, O, and H elements. It was found that the PBE and the hybrid B3LYP functional showed similar trends for the calculated barriers, but the barriers obtained from the PBE functional were significantly lower than those from B3LYP. This is reasonable, as the pure DFT functional tends to underestimate the reaction barrier [24–27]. All geometry optimizations and vibrational frequency analyses were performed with the solvation effect included, using the IEFPCM solvation model [28].

3. Results and discussion

3.1. Aerobic oxidation of GL in NaOH-containing water

Table 1 shows the data on GL oxidation in NaOH-containing water. The blank test using NaOH-free GL solution for the reaction detected no GL consumption, indicating no reaction of GL in the absence of NaOH. The oxidation of GL in the NaOH-containing solutions produced GLA, tartronic acid (TTA), and lactic acid (LA) as the C3 products and glycolic acid (GCA), acetic acid (AC), oxalic acid (OA), and formic acid (FA) as the products of C—C bond cleavage. To rigorously measure the GL consumption rate at different NaOH numbers, the GL conversion levels were limited to no higher than ca. 10% by adjusting the reaction duration. The measured GL consumption rate is then correlated with the number of NaOH in the reaction solution in Fig. 1A. Clearly, the GL consumption rate

Table 1
Results of selective aerobic oxidation of GL in NaOH-containing water.[a]

NaOH (mmol)	Rxn time (h)	Conv. (%)	Product sel. (C%)[b]							Rate (μmol/h)[c]
			GLA	TTA	LA	GCA	AC	OA	FA	
0	12	0	–	–	–	–	–	–	–	–
3.0	15	3.6	49.5	0.7	8.5	22.4	1.2	0.5	17.2	14
6.0	11	6.1	44.3	0.6	4.3	29.3	0.6	0.5	20.4	33
9.0	10	10.0	37.8	0.8	7.2	32.5	1.2	0.5	20.1	60
12.0	6	10.3	36.4	0.5	2.1	35.4	0.4	0.4	24.7	103
15.0	4	8.6	34.7	0.2	1.7	36.6	0.2	0.2	26.4	129
18.0	3	8.8	33.4	0.6	1.8	36.1	0.3	0.4	27.4	176
24.0	2	6.4	32.5	0.4	1.9	36.4	0.7	0.1	28.0	192

[a] Reaction conditions: 6 mmol GL in 20 ml H_2O, 60°C, 1.0 MPa O_2, 900 rpm.
[b] GLA = glyceric acid, TTA = tartronic acid, LA = lactic acid, GCA = glycolic acid, AC = acetic acid, OA = oxalic acid, FA = formic acid.
[c] GL consumption rate.

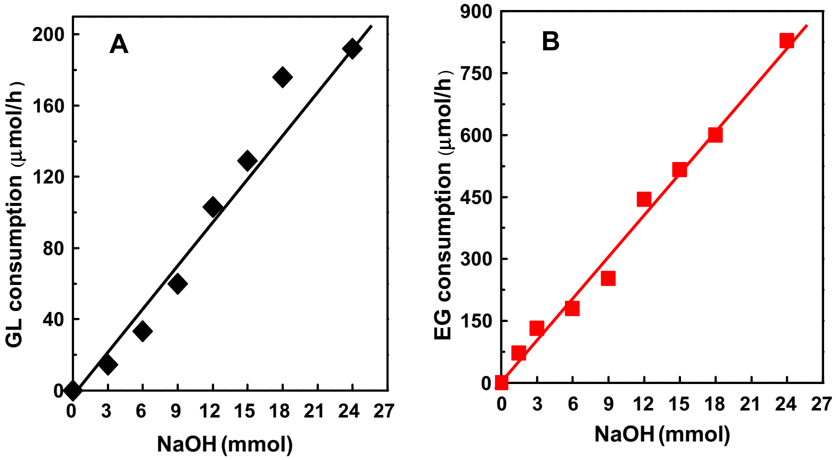


Fig. 1. Dependence of the oxidation rate of (A) GL and (B) EG on the number of NaOH. Reaction conditions: (A) 6 mmol GL in 20 ml H_2O, 60 °C, 1.0 MPa O_2, 900 rpm; (B) 6 mmol EG in 20 ml H_2O, 100 °C, 1.0 MPa O_2, 900 rpm.

increased linearly with the NaOH number, from zero to 192 μmol GL per hour, when the NaOH number increased from zero to 24 mmol (i.e., NaOH/GL = 4), which strongly indicates that NaOH served as an independent homogeneous catalyst for the oxidation of GL in water.

The product selectivity also varied according to the number of NaOH in Table 1. For instance, increasing the NaOH number from 3.0 to 24 mmol lowered the selectivity for GLA from 49.5% to 32.5% but improved the selectivity for GCA and FA to 36.4% and 28.0%, respectively, from 22.4% and 17.2%, though the selectivity for TTA, AC, and OA hardly changed. Qualitatively, the product identities in Table 1 agree with those observed when supported Au was also present as a solid catalyst in the reaction solution [9–11,29,30]. However, the present product selectivity data are quantitatively different from those obtained when the reaction was conducted in the presence of both NaOH and an Au catalyst. For example, the selectivity for GLA (32–50%, Table 1) from the oxidation of one of the terminal carbons was significantly lower, while the selectivity for GCA (22–37%, Table 1) from C—C bond cleavage was significantly higher, than those obtained when a supported Au catalyst was co-present with NaOH (GLA: 40–70%; GCA: 5–25%; FA: 10–28%) [9,10,29,30]. Increasing the NaOH number or the molar NaOH/GL ratio lowered the selectivity for GLA formation in Table 1, which contrasts with the many documentations that the GLA selectivity over supported Au catalysts can be enhanced by increasing the number of co-present NaOH in the reaction solution [5,9,29–31]. The GL consumption rate in the oxidation reaction over Au catalysts also increased with increasing NaOH number [5,29,30]. In particular, we showed earlier that the GL consumption rate over various oxide-supported Au catalysts in the co-presence of NaOH (NaOH/GL = 2) was 10–100 times faster than that measured with no NaOH [10].

The GL consumption rate employing NaOH alone as the catalyst is compared in Table S1 (Supplementary Material) with those typical in the literature for systems employing supported Au catalysts in NaOH-containing water (molar NaOH/GL = 2). The GL consumption rate employing NaOH alone (without Au catalyst) is 5–70 times lower than the rates in the co-presence of Au and NaOH catalysts. However, the GL consumption rate employing only Au catalyst (e.g., Au/ZrO_2 in Table S2) in NaOH-free solution (i.e., without co-presence of NaOH) was even several times slower than the rate employing NaOH alone, which highlights importance of the co-presence of Au and NaOH for the oxidation reaction (Table S2). As we reported earlier [10], the co-presence of NaOH also significantly changed the product selectivity (Table S2). These results clearly demonstrate that the presence of NaOH impacts not only the activity but also the selectivity of Au catalysts in the aerobic oxidation of alcohols/polyols. As the ultimate purpose of this work is to uncover the role of NaOH alone as an independent homogeneous catalyst for alcohol/polyol oxidation reactions, further investigations and discussion of the effect of Au—NaOH interaction/cooperation on oxidation reactions are in progress.

3.2. Aerobic oxidation of EG in NaOH-containing water

The fact that NaOH can work as an independent homogeneous catalyst for triol (GL) oxidation in water motivated us to investigate the catalysis of NaOH for diol (EG) oxidation. Table 2 shows the results of EG oxidation in the presence of different NaOH numbers. No EG consumption was detected in the NaOH-free solution, but EG conversion to GCA, FA, and OA was observed in the NaOH-containing solutions. As seen in Fig. 1B, the EG consumption rate also directly correlates with the number of NaOH in the reaction solution. The rate increased from zero to 72 μmol/h and then to 828 μmol/h when the NaOH number was increased from zero to 1.5 mmol and then to 24.0 mmol, making it clear that NaOH also functioned as a homogeneous catalyst for the oxidation of EG in water.

The product selectivity of the EG oxidation was also dependent on the NaOH number; the highest selectivity for GCA (90.5%) but the lowest selectivity for FA (8.4%) was observed in the solution with the lowest NaOH number (1.5 mmol). The selectivity for GCA was lowered to 69.4%, but that of FA improved to 24.5%, when the NaOH number was increased to 24.0 mmol. Small quantities of CO_2 were also detected when the NaOH number was increased to 18.0 mmol or higher, which is easily understandable, as CO_2 would reasonably be regarded as the product of deep oxidation of GCA. Apparently the GCA selectivity was lowered with increasing EG conversion level, hinting that GCA would become the primary product of the EG oxidation reaction [4]. These results strongly suggest that GCA is also the primary product of EG oxidation in the NaOH-containing solution, which entitles us to propose the reaction channels as Scheme S1 (Supplementary Material) for EG oxidation in the present NaOH-containing solutions. The scheme is similar to those proposed earlier for the catalytic oxidation of EG in water over supported Au catalysts in the co-presence of NaOH [4,32].

3.3. Aerobic oxidation of 2-PO and EtOH in NaOH-containing water

The oxidation reactions of secondary and primary monohydric alcohols in the NaOH-containing solution were also investigated respectively by taking 2-PO and EtOH as representatives. As it

Table 2
Results of selective aerobic oxidation of EG in NaOH-containing water.[a]

NaOH (mmol)	Conv. (%)	Product sel. (C%)[b]				Rate (μmol/h)[c]
		GCA	OA	FA	CO_2	
0	0	–	–	–	–	–
1.5	0.6	90.5	1.1	8.4	0.0	72
3.0	1.1	88.8	1.4	9.8	0.0	132
6.0	1.5	84.7	1.2	14.1	0.0	180
9.0	2.1	79.9	1.6	18.6	0.0	252
12.0	3.7	76.5	2.3	21.2	0.0	444
15.0	4.3	75.8	2.1	22.1	0.0	516
18.0	5.0	73.8	1.2	22.9	2.1	600
24.0	6.9	69.4	0.7	24.5	5.4	828

[a] Reaction conditions: 6 mmol EG in 20 ml H_2O, 100°C, 1.0 MPa O_2, 900 rpm, 30 min.
[b] GCA = glycolic acid, OA = oxalic acid, FA = formic acid.
[c] EG consumption rate.

would be expected, 2-PO showed no reaction in the NaOH-free solution but was converted to acetone when NaOH was present in the solution, revealing that NaOH is indispensable for activating the 2-PO molecules to the oxidation reaction. We confirmed that no other product except acetone was produced during the reaction, regardless of the number of NaOH. As shown in Fig. 2A, the 2-PO consumption rate increased linearly with increasing NaOH number up to 6 mmol (NaOH/2-PO = 1) and then leveled off at higher NaOH numbers (NaOH/2-PO > 1). This leveling off would be explained by considering the following two aspects: (1) the 2-PO molecule has only one hydroxyl group bonded to the central carbon atom, and its activation would require only one active OH^- (i.e., the catalyst); (2) unlike the oxidation of those alcohols having hydroxyl group(s) bonded to the terminal carbon atom(s), which produce carboxylic acid (or carboxylate) as the main product, the only product of 2-PO oxidation was acetone, which cannot react with the catalyst OH^-. As it will be shown later, these explanations are supported by the results from DFT calculations.

The primary alcohol, EtOH, also showed no reaction in the NaOH-free solution, but was oxidized to produce only acetic acid (AC) in the NaOH-containing solution. The number of NaOH also showed a significant effect on the consumption rate of EtOH, as demonstrated in Fig. 2B, which is similar to the effects of NaOH on the consumption of GL, EG, and 2-PO. With the number of NaOH increasing from 1.2 to 24.0 mmol, the oxidation rate of EtOH increased linearly from 3.0 to 24.0 μmol/h. These data reveal that NaOH can be a homogeneous catalyst for alcohol oxidation in water.

Neither acetaldehyde (AcH) nor ethyl acetate (AcOEt) was detected in the reaction, regardless of the number of NaOH. The direct formation of AC in the present reaction system is distinct from earlier observations on the aerobic oxidation of EtOH over supported Au catalysts in base-free water, where AcH was clearly demonstrated to be the intermediate leading to AC production [33,34]. The invisibility of AcH in this present study would be due to the instability of AcH in the basic solution; it can quickly react with the catalyst OH^- to form a geminal diol intermediate leading to AC (or acetate) [9]. Also, no formation of AcOEt in this present study seems reasonable, as NaOH in the solution cannot catalyze the esterification reaction between EtOH and AC but can catalyze the hydrolysis of AcOEt.

3.4. Catalytic activity of NaOH for the aerobic oxidation of GL, EG, 2-PO, and EtOH by turnover frequency (TOF)

To obtain the relative reactivity of the investigated alcohols in NaOH-containing water, rigorous comparison of the intrinsic catalytic activity of the homogeneous NaOH catalyst for the aerobic oxidation of the different alcohols was measured as the TOF rate of each alcohol at 90 °C with the same NaOH number (6 mmol NaOH or NaOH/alcohol = 1) by limiting the alcohol conversion levels to no higher than 6%; the data are listed in Table 3. Apparently, the TOF data show the following reactivity order for the different alcohols: GL ≫ EG ≫ 2-PO > EtOH.

Thus, the relative reactivity of the alcohols is correlated with the number and location of the hydroxyl groups in a specific

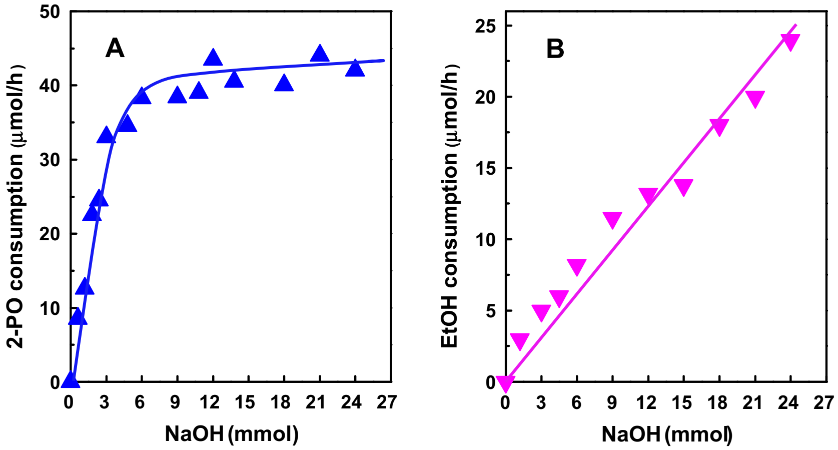


Fig. 2. Dependence of the oxidation rate of (A) 2-PO and (B) EtOH on the number of NaOH. Reaction conditions: (A) 6 mmol 2-PO in 20 ml H_2O, 100 °C, 1.0 MPa O_2, 900 rpm; (B) 6 mmol EtOH in 20 ml H_2O, 90 °C, 1.0 MPa O_2, 900 rpm.

Table 3
Reactivity of the different alcohols in NaOH-containing water.[a]

Substrate alcohol	Reaction time (h)	Conv. (%)	TOF × 10^{-3} (h^{-1})[b]
EtOH	11	1.5	1.4 (1)
2-PO	11	2.9	2.6 (2)
EG	2	5.5	27.5 (20)
GL	0.5	3.9	78.0 (57)

[a] Rxn conditions: 6 mmol alcohol in 20 ml H_2O, NaOH/alcohol = 1 (mol/mol), 90°C, 1.0 MPa O_2, 900 rpm.

[b] TOF = alcohol consumption rate (mol/h)/(molar number of NaOH in the solution); number in parentheses shows the TOF value relative to that of EtOH.

molecule. In detail, the TOF of GL, with three hydroxyl groups, was almost three times that of EG, containing two hydroxyl groups, and one order of magnitude higher (30–60 folds) than that of 2-PO and EtOH, with only one hydroxyl group. Another observation that should be noted is that the TOF of 2-PO (the secondary alcohol) was twice that of EtOH (the primary alcohol). It is therefore conclusive that the reactivity of polyols would be much higher than that of monohydric alcohols, and the secondary alcohols would be more reactive than the primary alcohols, when NaOH was employed as a homogeneous catalyst for oxidation reactions in water.

One might doubt that the base catalyst NaOH used in the above experiments was of not enough high purity (96.0%); it could involve contaminants of significant catalytic consequence. This possibility is clearly excluded by repeating the catalytic oxidation reactions with Alfa Aesar high-purity NaOH (99.99%); as one can judge from the results shown in Tables S3 and S4 (Supplementary Material), the high-purity NaOH catalyst offered almost the same activity and product selectivity in the reactions of GL, EG, 2-PO, and EtOH. The above conclusions are therefore further confirmed with high-purity NaOH for the catalyst.

3.5. Possible mechanisms from DFT calculations

Though there is no prior information on the aerobic alcohol oxidation catalysis of soluble bases in water, we have found a couple of earlier studies that were concerned with base catalysis for aerobic oxidation of other monohydric alcohols in aprotic organic solvents in recent literature. One used NaH as a base catalyst to promote the oxidation in tetrahydrofuran (THF) of various secondary aryl alcohols to synthesize the corresponding ketones [35]. The other employed NaOH and ^{t}BuONa to catalyze, also in THF, the aerobic oxidation of benzylic, heterocyclic, allylic, and aliphatic monohydric alcohols for production of carboxylic acids [36]. The oxidation reactions in these two studies were speculated to occur with radical mechanisms, in which the radical intermediates were assumed to be generated by homolytic cleavage of the α-C—H bond in the base-activated alcohol, as a consequence of O_2 attack at the H of the α-C—H bond, as shown by Scheme S2 [35,36].

As EG and 2-PO have some solubility in THF, we also studied possible oxidation of EG and 2-PO in NaOH-containing THF (solvent). Under conditions similar to those used in Ref. [36] (60 °C, NaOH/alcohol = 2 (mol/mol)), we detected no reaction of EG and 2-PO. When benzyl alcohol was used as the reactant (instead of EG and 2-PO) in the NaOH-containing THF, we detected only selective formation of benzaldehyde (but no benzoic acid) (Table S5). These contrasting observations might hint that our observed alcohol oxidation in NaOH-containing water could not involve radical intermediates.

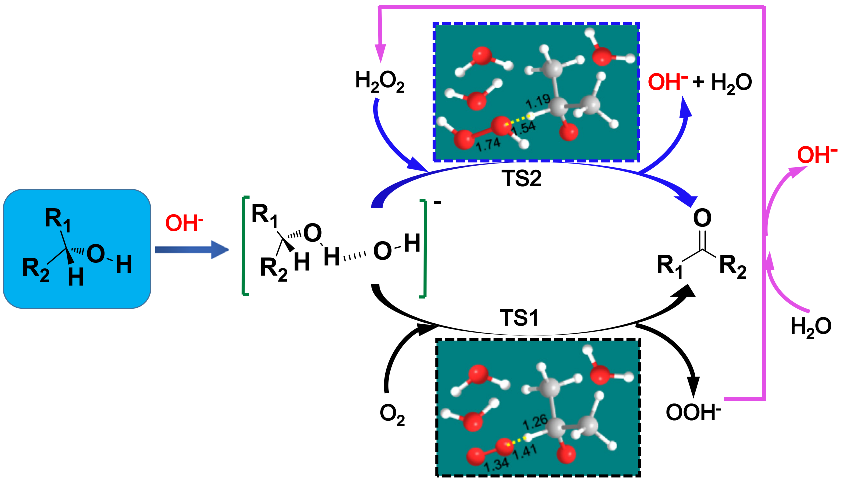
Possible molecular mechanisms for the alcohol oxidation reactions with NaOH as the homogeneous catalyst were investigated using DFT calculations. Scheme 1 shows, for instance, the oxidation of a monohydric alcohol and the transition states (TSs) of 2-PO oxidation. In a catalytic cycle, the base catalyst (OH^-) could initiate the reaction by attacking the H of the hydroxyl group to produce an anionic complex $[R_1R_2CHOH–OH]^-$, in which the O—H bond of the hydroxyl group becomes lengthened and weakened. An oxygen molecule would then react with the H of the R_1R_2CH skeleton via the transition state TS1, in which the C—H bond of R_1R_2CH is weakened. At this TS1 of 2-PO oxidation, the C—H bond is increased to 1.26 Å, while the OO—H bond is 1.41 Å. Via the TS1, the oxygen molecule becomes activated, with the formation of OOH^-, and the H atom in the hydroxyl group transfers to the catalyst OH^-, yielding a H_2O molecule and a ketone product. The as-formed OOH^- would also react with H_2O to generate a H_2O_2 and a OH^- (the catalyst), entering another catalytic cycle. A second channel leading to alcohol oxidation would be opened by the reaction between H_2O_2 and $[R_1R_2CHOH–OH]^-$ to form another ketone product via TS2 as the transition state. The key elementary steps for the two reaction channels are summarized sequentially below:

$$\textbf{Channel I}: \ R_1R_2CHOH + OH^- \rightarrow [R_1R_2CHOH{-}OH]^- \tag{1}$$

$$[R_1R_2CHOH{-}OH]^- + O_2 \rightarrow R_1R_2CO + OOH^- + H_2O \tag{2}$$

$$\textbf{Channel II}: \ OOH^- + H_2O \rightarrow H_2O_2 + OH^- \tag{3}$$

$$[R_1R_2CHOH{-}OH]^- + H_2O_2 \rightarrow R_1R_2CO + OH^- + 2H_2O \tag{4}$$



Scheme 1. Possible mechanisms for aerobic oxidation of alcohols in NaOH-containing water.

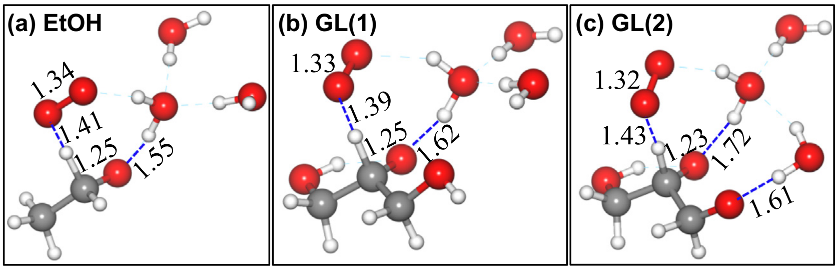


Fig. 3. Calculated transition states for EtOH and GL oxidation reactions in NaOH-containing water. (a) EtOH and (b) GL(1): only one RO—H bond is attacked by OH^-, which forms a RO^-—HOH complex; (c) GL(2): two RO—H bonds are attacked by OH^- at the same time, which forms a HOH—$^-$ORRO$^-$—HOH complex. The key structural parameters (Å) are labeled. Carbon: gray; Oxygen: red; Hydrogen: white.

Table 4
Free energy barriers in eV of the rate-determining steps for EtOH, 2-PO, EG, and GL oxidation in NaOH-containing water, according to PBE and B3LYP functionals.[a]

Method	EtOH	2-PO	EG		GL	
			(1)	(2)	(1)	(2)
PBE	0.51	0.47	0.53	0.40	0.59	0.27
B3LYP	1.26	1.17	1.29	0.84	1.28	0.79

[a] (1) One terminal hydroxyl group of alcohols is activated by OH^-. (2) Two hydroxyl groups of alcohols are activated by OH^-.

Among these elementary steps, the R_1R_2C—H bond breaking owing to the O_2 attack (i.e., (2)) is the rate-determining step that possesses the highest barrier.

By focusing on the rate-limiting step, the free energy barriers of the different alcohols oxidation were calculated by PBE and B3LYP functionals, respectively. For 2-PO and EtOH, the alcohol molecule was initially activated by one active site (OH^-) in the NaOH-containing solution. For EG and GL, two situations were considered: (i) only one terminal hydroxyl group of the alcohols was activated by the base catalyst (OH^-), as indicated by EG(1) and GL(1); and (ii) two hydroxyl groups of the alcohols were activated by the base catalyst (OH^-), as indicated by EG(2) and GL(2). As examples, we show in Fig. 3 the transition state structures for the rate-limiting steps in the PBE functional of the EtOH and GL oxidation reactions. The geometries of the EtOH and GL(1) transition states are very similar, as reflected by the same bond length of the involved C—H (1.25 Å, Fig. 3a and b). However, the geometry of the GL(2) transition state shows a shorter C—H bond (1.23 Å) and a greater H—O_2 distance (1.43 Å) (Fig. 3c) due to the co-activation of two hydroxyl groups by two OH^- bases, indicating an earlier transition state and thus a lower activation barrier. The calculated free energy barriers of the rate-limiting steps for 2-PO, EtOH, EG(1), GL(1), EG(2), and GL(2) by PBE are 0.47, 0.51, 0.53, 0.59, 0.40, and 0.27 eV, while those by B3LYP are 1.17, 1.26, 1.29, 1.28, 0.84, and 0.79 eV, respectively, as listed in Table 4. Obviously, the trend of the calculated barrier from PBE is consistent with that from the hybrid B3LYP functional, though the absolute values differ. Combining the calculated energy barrier with the catalytic data, we find that the higher reactivity of the secondary alcohol (2-PO) than of the primary alcohol (EtOH) can be attributed to the lower energy barrier. The co-activation of two hydroxyl groups lowers the energy barrier further, which could explain the much higher reactivity of polyols (GL and EG); the higher energy of EG (2) relative to GL(2) also explains the higher reactivity of GL.

While the mechanisms shown in Scheme 1 for NaOH-catalyzed alcohol oxidation in water are different from that in aprotic solvent involving radicals, shown in Scheme S2, they all demonstrate that a base can be a homogeneous catalyst for the aerobic selective oxidation of various alcohols in organic solvents as well as in water. Further, the present discovery of the catalysis of NaOH in water for the selective oxidation of EG and GL could open a new avenue for selective chemical syntheses through oxidation of bioderivative polyols that have low solubility in aprotic organic solvents.

4. Conclusions

This work reveals for the first time that NaOH can independently serve as a homogeneous catalyst for the aerobic oxidation of alcohols in water. The reactivity order of the alcohols (GL, EG, 2-PO, and EtOH) in NaOH-containing water is established based on rigorously determined catalytic turnover rates. A discussion on the activation modes and possible reaction mechanisms of the different alcohols is provided, based on DFT calculations. Co-activation by the base catalyst (OH^-) of two hydroxyl groups in the polyols (GL and EG) is shown to be the key to the much higher reactivity of the polyols. These new molecular insights would open new avenues to further understanding the role of basic additives in alcohol oxidation either in the presence or in the absence of a metal catalyst, as well as for valorization by selective oxidation of oil-hating bio-derivative polyols.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2017.05.006.

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