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Recent advances in selective C–C bond coupling for ethanol upgrading over balanced Lewis acid-base catalysts

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ABSTRACT Ethanol is a considerable platform molecule in biomass conversion, which could be acquired in quantity through acetone-butanol-ethanol (ABE) fermentation. People have been working on the upgrading of ethanol to value added chemicals for decades. In the meantime, 1-butanol and a series of value added products have been selectively generated through C–C bond coupling. In this mini-review, we focus on the recent advances in selective C–C bond formation over balanced Lewis acid-base catalysts such as modified metal oxide, mixed metal oxide, hydroxyapatite and zeolite confined transition metal oxide catalysts. Among them, Pd-MgAlO_x and Sr-based hydroxyapatite exhibit >70% 1-butanol selectivity, while Zn_xZr_{1-x}O₂ and Ta-SiBEA zeolite achieve >80% of isobutene and butadiene selectivity respectively. The mechanism and reaction pathway of C–C bond formation in each reaction system are described in detail. The correlation between C–C bond coupling and the acidity/basicity of the Lewis acid-base pairs from the surface of the catalysts are also discussed.

Keywords: balanced Lewis acid-base pair, aldol condensation, ethanol upgrading, C–C bond formation, metal oxide

INTRODUCTION

The demands for energy and rising tension on conventional fossil resources cause increasing exploration of renewable alternatives for fuels and chemicals. Biomass is regarded as one of the most promising resources to produce biofuels, which could be grown globally on an available basis providing nearly 100 EJ of energy per year [1,2].

The newly founded acetone-butanol-ethanol (ABE) fermentation method could easily convert biomass feed

stock (mainly cellulose and hemi-cellulose) into ethanol, acetone and butanol at high efficiency. These platform chemicals could be readily upgraded *via* C–C bond coupling to value-added long chain products. Taking ethanol as an example, 90% of bioethanol around the world is derived from biomass [3], and its partial substitution for conventional gasoline or diesel decreases crude oil consumption and harmful gas emission in many countries, especially in the USA, China, and Brazil. However, ethanol possesses a series of drawbacks as gasoline additives involving low energy density (19.6 MJ L⁻¹) and excessive water solubility (100% in water) leading to the corrosion of engine and pipelines [4,5]. At present, ethanol blending with gasoline is normally applied in the conventional infrastructures and fuels with ~10% volumetric concentration. Yet, further increasing the proportion of ethanol would result in engine combustion. 1-Butanol converted from ethanol can effectively settle the above problem due to its higher energy density (29.2 MJ L⁻¹), lower volatility (boiling point at 117.4°C compared to 78.4°C for ethanol) and limited water solubility (7% in water) [6–8]. During the transformation of ethanol to 1-butanol, it involves at least four reaction pathways, such as dehydration, dehydrogenation, hydrogenation, hydrogen transfer (Meerwein-Ponndorf-Verley, MPV), and aldol condensation. However, for such cascade reaction, opting and designing the appropriate multifunctional catalysts to accomplish highly selective products has become a very important subject.

In the upgrading process of ethanol to value-added chemicals such as 1-butanol (potential gasoline additives), gasoline (C₈–C₁₂ hydrocarbons mixtures) and even diesel (C₉–C₂₅ hydrocarbons mixtures), the formation of C–C

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bond is the key reaction step [9–12]. However, the efficiency and selectivity to the desired products are always the major challenges due to the complexity of C–C bond coupling between oxygenates. Extensive studies suggest that the formation of C–C bond requires to control the strength of Lewis acid and base sites. Most of the studies on C–C bond coupling following aldol condensation reaction were over metal oxide catalysts with modest Lewis acid sites or Brønsted base sites [13], such as TiO_2 [14], ZrO_2 [15] and MgO (Lewis base) [16]. However, the uncontrollable Lewis acid (or base) density/strength would lead to the formation of side-product rather than selective C–C bond coupling, which arouses a lot of studies about mixed metal oxide catalysts with balanced Lewis acid-base pairs [10,13,17,18]. Mg–Al mixed metal oxides have been extensively studied as one of the typical acid-base catalysts in recent years, such as Mg– ZrO_x , Zn– ZrO_x , and Ce– ZrO_x [13,19–24]. Hydroxyapatite (HAP) with both acidic and basic sites is also widely used in the same catalytic reaction process, mainly focusing on ethanol coupling to 1-butanol. Another system for ethanol upgrading is zeolite confined transition metal oxide catalysts, such as Zr–BEA, Ti–BEA and Sn–BEA. These catalysts have strong Lewis acid sites, resulting in high dehydration activity forming butadiene and iso-butene instead of the oxygenates (such as butanol, 2-butenol,

2-buten-1-ol, etc.) [13,25–29].

Hence, balancing Lewis acid-base pairs is vital for the effectively selective C–C bond coupling in upgrading of the platform molecules to value-added chemicals. In this mini-review, we summarize the pathway of C–C bond formation in detail and the progress on heterogeneous catalysts for the ethanol upgrading in recent years aiming at the relationship between C–C bond formation and the Lewis acid-base properties on the surface of the metal oxide catalysts.

C–C BOND FORMATION PATHWAY

Research on ethanol upgrading to value-added chemicals in recent years focuses on tuning the activities in different reaction pathways, including aldol condensation, esterification, and dimerization, as shown in Scheme 1 [30]. Step (1)–converting ethanol to 1-butanol *via* dimerization was firstly proposed by Yang *et al.* [31] and then supported by Ndou and coworkers [16]. They proposed that the C–H bond at the β -position of ethanol was deprotonated at the Lewis base sites and coupled with another ethanol molecule through dehydration over the Lewis acid sites to produce one molecule of 1-butanol. This mechanism was based on the fact that the carbonyl species added to the system did not increase the reaction rate of C–C bond coupling. However, the control experiment

Scheme 1 Reaction pathways of ethanol upgrading to value-added chemicals. Reprinted with permission from ref [30]. Copyright 2018, Elsevier.

did not consider other factors which could influence the formation of C–C bond, for example the coverage of hydrogen on the surface of catalyst as well as the coverage of the aldehydes (which might be derived from *in-situ* reaction of alcohol dehydrogenation). If the aldehydes adsorbed on the surface of the metal oxide catalyst were abundant, the formation rate of C–C bond would not change much by only increasing the partial pressure of the aldehydes. Therefore, it brought up another reaction mechanism of C–C bond formation named Guerbet reaction [14] with ketones or aldehydes as the key reaction intermediates.

The Guerbet reaction includes the following sequential steps (step (2–6)): (i) dehydrogenation of ethanol to acetaldehyde, (ii) aldol condensation between two molecules of aldehydes to create one molecule of aldol, (iii) dehydration of aldol molecule to form 2-butenal, (iv) hydrogenation of 2-butenal or butanal *via* MPV reaction (or butanal hydrogenation) and finally (v) hydrogenation of 2-butenol/butanal to 1-butanol. The Guerbet reaction is regarded as the most widely accepted pathways for C–C bond coupling upon ethanol upgrading. Acetaldehyde is the key intermediate during C–C bond formation (step (2)) [9,33,34]. The dehydrogenation and hydrogenation reactions between ethanol and acetaldehyde are reversible over transition metal or metal oxide decorated catalysts, such as Ni/MgO [35], Cu/Al₂O₃, Cu/ZrO₂, etc. [36]. During C–C bond coupling through aldol condensation (step (3)), a proton could be extracted from the β position of an aldehyde to form an surface active species called the enolate ($\cdot\text{CH}_2\text{CHO}^*\text{A}$ in Scheme 2), which would attack the carbonyl group of the adjacent adsorbed acetaldehyde to generate a C–C bond and obtain one molecule of adsorbed aldol. These two steps were proposed to be the kinetically relevant step separately following the Guerbet reaction by several groups working on the mechanisms of the C–C bond formation from ethanol [14]. The reaction can be accomplished both in gas and liquid phase, which would result in different product distributions (some-

times different reaction mechanisms) due to the difference in the transferring/returning of proton between gas and liquid phase during molecular activation and/or elementary steps of products generation that is related to the concentrations of the proton on the surface of the catalyst.

Step (4) shows that 2-butenal is formed by the dehydration of aldol, which is a highly active step for scarce aldol molecule detected in previous reports. Then, the hydrogenation of 2-butenal to saturated 1-butanol involves two separated hydrogenation pathways including hydrogenation at the C=C double bonds and C=O double bonds as described in step (5) and (6). Butanal is barely identified in the reaction system due to the weak reaction activity of MPV against the C=C double bond in 2-butenal compared to the hydrogenation (also through MPV reaction route) of C=O functional group. It is commonly accepted that one such pathway primarily forms unsaturated alcohols (2-butenol) by surface-mediated hydrogen-transfer (MPV reaction) followed by hydrogenation at the C=C bond to form saturated alcohols [10,11]. The reaction mechanism of C–C bond coupling to 1-butanol through co-feeding ethanol and acetaldehyde was also proposed by Mella *et al.* [37].

Besides, some side reactions could be observed (step (7–12) in Scheme 1). 1-Butanol produced from chain-growth production of ethanol molecule reacts with another molecule of ethanol *via* intermolecular dehydration to form butyl ethyl ether (step (7)). And intramolecular dehydration of 1-butanol could lead to the formation of 1-butylene, which could be further hydrogenated to produce butane (step (8 and 9)). In addition, ethanol can convert to carbon monoxide, carbon dioxide or C₁–C₃ products through oxidation or hydration (step (10)) [38–40], while carbon monoxide/dioxide can also be formed from acetaldehyde decarbonylation [41,42] or from organic acids (*in-situ* generated) decarboxylation [43]. Additionally, intermolecular dehydration can undergo at relatively low temperatures (<623 K) to form ethyl ether (step (11)) over zeolite-based catalysts between two molecules of ethanol. At relatively high temperature (>673 K), ethylene could be selectively generated from intramolecular dehydration of ethanol [44]. This type of dehydration reaction is typically catalyzed by transition metals or rare earth metals, such as Cu, Fe, Mn and Ce [45,46]. The primary esterification between one molecule of ethanol and one molecule of acetaldehyde over Lewis acid sites yields ethyl acetate (step (12)) [48], while Tishchenko reaction is another pathway of esters formation from two molecules of aldehydes, which generally

Scheme 2 Elementary steps of adsorbed acetaldehyde deprotonation and nucleophilic attack between two molecules of acetaldehyde over Lewis acid-base pair catalyst.

happens over aluminum alkoxides or sodium alkoxides catalysts [48,49].

CATALYSTS

Metal oxides

Bulk metal oxides have been considered as potential catalysts for heterogeneous aldol condensation due to the moderate Lewis acid and Brønsted base pairs [50]. Initially base-catalyzed aldol reaction over barium hydroxide was described in textbooks, and consequently more types of basic catalysts such as sodium hydroxide and magnesium oxide were reported in patents [51–54]. Condensation of various primary alcohols to produce higher alcohols was reported. And then Ndou [16] studied the reaction of ethanol to 1-butanol over a series of basic oxides (1 bar, 723 K). MgO shows the highest 1-butanol yield (18.4%) (33% selectivity) at 56% ethanol conversion among the catalysts studied, as shown in Table 1. However, pure MgO exhibits strong basic sites and weak acid sites, which motivates ethanol dehydrogenation to produce a mass of acetaldehyde and thus causes deactivation [55].

More studies with various basic metals under high reaction temperature (>573 K) were attempted to improve the 1-butanol selectivity on MgO [55–58]. Yet increasing reaction temperature is not a good way for energy conservation and more gaseous light products would form along with C–C bond coupling at high temperature (>573 K). Besides, they found that it barely improved the catalytic performance and 1-butanol selectivity after alkali metal modification. The condensation rates were inversely decreased as the basicity of oxygen anions in MgO increased. Hence, most researchers currently focus on balancing the strength and distribution of acidic and basic sites on the surface of catalyst to develop proper strength of acid-base pairs [56,59], and find that acid-base bifunctionality of catalysts plays a crucial role in aldol condensation reaction, evidenced by reaction systems of Mg–AlO_x [18–22,56], Mg–ZrO_x [23], and Ce–ZrO_x [24].

Mg–AlO_x mixed oxides, as one typical acid-base bifunctional catalyst attract extensive attention in ethanol upgrading due to their unique properties, such as high tolerance to the moisture environment, high surface area and strong basic sites on the surface [21,22,56]. Di Cosimo *et al.* [56] reported that Mg_{1–x}Al_xO catalysts could be prepared from hydrotalcites decomposition and they elucidated the effects of Al content from the surface of the mixed metal oxide catalyst, which was closely related to the reaction rate of C–C bond formation and selectivity to 1-butanol. Compared to the prime homogeneous O^{2–} basic centers in pure MgO, low, medium and strong basicity co-exist on the surface of Mg–AlO_x oxides, which are derived from OH[–] groups, Mg–O pairs and O^{2–} anions respectively. With increasing Al content at low Al content (Mg/Al>5), the concentration of surface sites with low and medium basicity increases. This diverse basicity is highly correlated to the reaction performance of C–C bond coupling in aldol condensation reaction. For instance, in Di Cosimo's work, pure MgO shows low formation rate of 1-butanol at 0.2 μmol m^{–2} h^{–1}, which is about one magnitude slower than the formation rate of 1-butanol over Mg_{1–x}Al_xO at 1.8 μmol m^{–2} h^{–1}, as shown in Table 2. Pure Al₂O₃ is especially active for ethylene formation (dehydration) with the absence of 1-butanol at 28.6 μmol m^{–2} h^{–1}. The surface density of Lewis acid-strong base (O^{2–} anions) pair sites is considerably increased by further adding Al³⁺ cations (5>Mg/Al>1), in which Al³⁺ cations within the MgO lattice create a defect in order to compensate the positive charge generated, and the adjacent oxygen anions become coordinatively unsaturated. Ethanol conversion rates rise with around one order of magnitude, while those of ethanol dehydrogenation to acetaldehyde and the successive coupling of acetaldehyde to 1-butanol are improved at the same time.

In order to optimize the reaction performance of C–C bond coupling over Mg–AlO_x catalyst, various metal/metal oxides were attempted to be loaded onto the surface of Mg–AlO_x to fine tune the physical properties of the catalyst. For example, Marcu *et al.* [22] reported that Cu

Table 1 Activities of basic oxides in the aldol condensation of ethanol to 1-butanol (Acetal: acetaldehyde; Butanal: butyraldehyde) (Reprinted with permission from Ref. [16]. Copyright 2003, Elsevier)

Cat. *	Conv. * (%)	Yield (Sel. *) (%)				
		Acetal	Butanal	2-Butenal	1-Butanol	2-Buten-1-ol
MgO	56.14	0.7 (1.2)	0.8 (0.01)	0.5 (0.9)	18.4 (32.8)	0.3 (0.6)
CaO	15.16	2.8 (18.7)	2.2 (14.2)	0.3 (2.1)	1.2 (7.7)	0.06 (0.4)
BaO	21.19	6.6 (40.0)	11.4 (53.7)	-	-	-

*Cat.: catalysts; Conv.: ethanol conversion; Sel.: selectivity.

Table 2 Catalytic results on MgO, Al₂O₃ and Mg_{1-x}Al_xO catalysts (Mg_{1-x}Al_xO samples with different Mg/Al molar ratios; T=573 K, P=100 kPa, W/F 0=46 g h mol⁻¹, N₂/ethanol=10 (molar)) (DE: diethyl ether) (Reprinted with permission from Ref. [56]. Copyright 1998, Elsevier)

Al/(Al+Mg) (molar) MgO→Al ₂ O ₃	Reaction rate (μmol h ⁻¹ m ²)	TOR* (μmol h ⁻¹ m ²)			
		Acetal	1-Butanol	DE	Ethylene
0.00	0.9	0.3	0.2	0.03	0.04
0.11	8.4	4.6	1.0	0.3	0.06
0.18	4.2	2.6	0.5	0.1	0.07
0.24	4.6	1.1	1.0	0.2	0.08
0.47	9.2	0.3	1.8	2.0	0.6
0.65	9.8	0.3	0.5	3.9	0.6
1.00	48.2	0.1	-	4.8	28.6

*TOR: turnover rate.

doped Mg-AlO_x oxide catalysts (Cu_xMg₆Al₂O₉) showed enhanced performance for 1-butanol formation compared with bare Mg-AlO_x catalyst (Mg₆Al₂O₉). Over Cu_xMg₆Al₂O₉ catalysts, 1-butanol is the prominent product with 1.7% yield (40.3% selectivity) at 4.1% ethanol conversion, while 1,1-diethoxyethane is the main product with 87.5% selectivity and 0.3% yield at 0.3% ethanol conversion over Mg₆Al₂O₉ under the same reaction condition, as shown in Table 3. Thus, the selectivity to 1-butanol is promoted. Similarly, Pang *et al.* [21] reported 62.6 μmol m⁻² h⁻¹ areal C-C bond formation rate (derived from ethanol) over Ni₄MgAlO with 19.5 wt.% Ni content at 523 K. The products include 10.4% 1-butanol (55.2% selectivity), 4.4% C₆ (23.4% selectivity) and 1.4% C₈ (7.7% selectivity) oxygenates at 18.8% ethanol conversion. Ni₄MgAlO shows a higher 1-butanol selectivity than either Ni_xAl_yO or Ni_xMg_yO catalysts, because the doped metal (Ni) effectively balances the acid and base sites on the surface of Ni₄MgAlO. A series of comparison of ethanol conversion to 1-butanol process over M-Mg-Al mixed oxides (M=Pd, Ag, Mn, Fe, Cu, Sm, Yb) were investigated by Marcu *et al.* [59]. It is suggested that 1-butanol is tightly in connection with the quantity of basic sites with medium and high strength. Pd₅MgAlO catalysts (Pd_xMgAlO, *x* is the metal content as atomic percent with respect to the cations) show a higher selectivity (72.7%)

for 1-butanol at 3.8% conversion than Mg-AlO_x and other M-Mg-AlO_x catalysts.

In addition, many amphoteric metal oxides, such as TiO₂ and ZrO₂, with moderate Lewis acid sites have caught broad attention in platform bio-molecule upgrading with aldol condensation as the key step [14,15,47,55,60–64]. Among them, the anatase TiO₂ has been considerably reported that it possesses high activity and selectivity for aldol condensation reaction [60–62]. Acetaldehyde was reported to adsorb readily on the TiO₂ surface, lattice oxygen served as base sites and a proton could be extracted from β position of an aldehyde molecule to produce surface enolate (·CH₂CHO*), which would attack the carbonyl group (C=O) of another aldehyde molecule to obtain an adsorbed aldol [61]. As a result of the unstable nature of the oxygen within the crystal lattice of TiO₂, oxygen vacancies could be easily generated by exposing TiO₂ in a reducible atmosphere under elevated temperature. Idriss's group [62] investigated the relationship between the condensation reactions and surface states of TiO₂ and found that over TiO₂ (001) catalysts, oxidized (stoichiometric) TiO₂ surface was more active for the formation of 2-butenal/2-buten-1-ol from self-condensation of acetaldehyde followed by dehydration, while reduced surface tended to facilitate the coupling of two acetaldehyde molecules to

Table 3 Ethanol conversion, product yield and selectivity in a blank test and over Mg₆Al₂O₉ and Cu_xMg₆Al₂O₉ catalysts calcined at 823 K (5 h, 473 K) (Acetal C₆: 1,1-diethoxyethane; Acetal C₈: 1,1-diethoxybutane; EA: ethyl acetate) (Reprinted with permission from Ref. [22]. Copyright 2009, Elsevier)

Cat.	Conv. (%)	Yield (Sel.) (%)						
		Acetal C ₆	Acetal C ₈	Acetal	Butanal	Butanol	EA	DE
Blank test	<0.3	0.3 (86.1)	-	0.02 (7.3)	-	-	-	0.02 (6.5)
Mg ₆ Al ₂ O ₉	0.3	0.3 (87.5)	-	0.02 (6.1)	-	-	-	0.02 (6.3)
Cu _x Mg ₆ Al ₂ O ₉	4.1	1.5 (35.9)	0.21 (5.1)	0.4 (9.9)	0.07 (1.7)	1.7 (40.3)	0.3 (6.9)	-

form butene, which might originate from 2-butenal dehydration, at the presence of oxygen vacancies.

TiO₂ is active for aldol condensation reactions between aldehydes and/or ketones, but it typically exhibits rapid deactivation. Barteau *et al.* [60] reported the time-on-stream dependence of aldol condensation from acetaldehyde over anatase TiO₂. Condensation of acetaldehyde is fast and probably preferentially occurs on anatase TiO₂, with turnover frequencies exceeding 0.03 s⁻¹. At low reaction temperature (423 K), 2-butenal selectivity ranges from 86% to 100%, while the selectivity to 2-butenal is independent as a function of time at 523 K, remaining constant at 93% (Table 4). The yield of 2-butenal reaches 4.88%. Whereas, it inevitably leads to the rapid deactivation of catalysts due to the accumulation of strongly adsorbed species on the surface.

Wang *et al.* [47] have studied the mediate condensation and esterification pathways of C₂-C₅ alkanals/alkanones over anatase/rutile TiO₂, as well as the Cu modified TiO₂. They found that the addition of Cu into TiO₂ led to a higher C-C bond formation rate compared with the unmodified TiO₂ with much slower deactivation rates, owing to the enhancement of the hydrogenation rate against the unsaturated intermediate, which could hinder the consecutive reaction following aldol condensation process generating polymerized hydrocarbons. They also found that the corresponding Ti-O-Ti sites on rutile phase had stronger acidic and basic characters and longer Ti-O bond distance at 0.323 nm than anatase phase (0.203 nm), causing that the available Ti-O site pairs on the surfaces were spatially-separated. The anatase phase structure with Ti-O-Ti bond at 0.203 nm showed a moderate Lewis acid-base strength and acid-base site distances, more suitable for the C-C bond formation.

Furthermore, we recently reported the study about the kinetically relevant nucleophilic attack of enolates to the aldehyde in the aldol condensation by feeding ethanol and acetaldehyde mixtures over anatase TiO₂ [14]. Product distribution results show 25% C₄ selectivity (2-bu-

tenal, 2-buten-1-ol and 1-butanol), 11% C₆-C₈, 25% C₈ aromatics, 58% esters (ethyl acetate and δ -hexalactone) and <5% unknown products at 10% acetaldehyde conversion over TiO₂ (TiO₂ annealed at ~673 K). On account of the results including *in-situ* infrared spectroscopy, rate measurements as functions of reactant partial pressure, kinetic isotope effects and rate inhibition experiments, we propose that along with the high coverage of CH₃CH₂-OH*, the nucleophilic attack process of an enolate ($\cdot$ CH₂CHO*) toward the adjacent CH₃CHO* species is the kinetically relevant step.

ZrO₂, as another proper amphoteric metal oxide with Lewis acid-base pairs, should be suitable for catalyzing aldol condensation reaction [64]. However, due to the high strength of Lewis acid sites on the surface, pure ZrO₂ is rather active for ethanol dehydration to ethylene than C-C bond formation. That is why people use alkali oxide to neutralize the strong Lewis acid sites in the reaction system. For example, Kozłowski *et al.* [15] reported that the yield of ethanol coupling to 1-butanol was improved from 0.2% to 0.9% by loading 1 wt.% sodium oxide to ZrO₂, while ethylene yield was suppressed from 4.0% to 1.3%. Detailed product yields in ethanol coupling reactions at 673 K over ZrO₂ and Na modified ZrO₂ catalyst are shown in Table 5.

Moreover, Sun *et al.* [13] reported the Zn_xZr_yO_z mixed oxides for direct and high-yield transformation of bio-ethanol to isobutene (83%) (ETIB), with acetone and mesityl oxide as the vital intermediates. The conversion of ethanol to isobutene relies mainly on ethanol dehydrogenation to acetaldehyde, consequently to acetone by aldol condensation, followed by condensation and dehydration of protonated acetone to produce mesityloxide-like species and eventually transformation to isobutene *via* decomposition and ketonization. The product selectivities among various mixed oxides under the same conditions and at similar conversion (~100%) are compared, as shown in Fig. 1. Results show that the main product over pure ZrO₂ catalysts is ethylene (95% se-

Table 4 Ethanol conversion, product yield and selectivity from acetaldehyde transformation on anatase TiO₂ at 423 and 523 K, 19.9 kPa (EC: ethyl crotonate; C₆ DA: 2,4-hexadienal) (Reprinted with permission from Ref. [60]. Copyright 2011, American Chemical Society)

Temp.*/(K)	Time* (min)	Conv. (%)	Yield (Sel.) (%)				
			Ethanol	2-Butenal	EC	C ₆ DA	Benzene
423 K	1	3.14	0.01 (0.4)	2.7 (86.1)	0.3 (9.1)	0.1 (2.7)	0.01 (0.5)
423 K	120	0.30	-	0.3 (100)	-	-	-
523 K	1	5.20	0.06 (1.2)	4.9 (93.9)	0.02 (0.3)	0.1 (2.5)	0.02 (0.4)
523 K	120	1.70	0.02 (1.3)	1.6 (94.2)	0.02 (1.5)	0.03 (1.7)	0.01 (0.8)

*Temp.: temperature; Time: Time on stream.

Table 5 Ethanol consumption rate, conversion, product yield and selectivity during ethanol coupling reactions at 673 K and at similar conversions (Reprinted with permission from Ref. [15]. Copyright 2013, Elsevier)

Na content (wt%)	Reaction rate ($\text{nmol}^{-1} \text{s}^{-1} \text{m}^{-2}$)	Conv. (%)	Yield (Sel.) (%)			
			Ethylene	Acetal	2-Butenal	1-Butanol
0	200	9.4	4.1 (44)	5.1 (54)	0	0.2 (2.2)
0.1	160	9.6	3.1 (32)	6.1 (63)	0.2 (2.5)	0.3 (2.7)
1.0	40	7.7	1.3 (17)	5.5 (71)	0	0.9 (12)

Figure 1 (a) Performance of various acid-base catalyst combinations for the ETIB reaction: 0.1 g of catalyst, 1.8 mol% ethanol, steam to carbon ratio (S/C)=5, residence time (W/F) = 0.11 s g mL⁻¹, 723 K. (b) Performance of the Zn_{0.5}Zr_{0.5}O₂ mixed oxide catalyst for the ETIB reaction as a function of gas flow rate and ethanol concentration: 0.1 g of catalyst, S/C=5, 723 K. Isobutene* represents isobutene yield. Reprinted with permission from Ref. [13]. Copyright 2011, American Chemical Society.

lectivity) at 723 K, suggesting that pure ZrO₂ possesses the excessive acidic strength and is extremely active for ethanol dehydration to ethylene.

By adding ZnO to ZrO₂ crystal structure, the hydroxyls from ZrO₂ surface and Lewis acid-base sites are suppressed without generating new acid-base sites based on their CO₂-TPD (Temperature-programmed desorption) results. Combined with diffuse reflectance infrared Fourier transform spectra (DRIFTS) studies, it is further confirmed that the introduction of ZnO neutralizes both the strong Brønsted acid sites and Lewis acid sites with no new acidic sites generated. Accordingly, ethanol dehydrogenation on the surface basic sites and acetaldehyde condensation *via* acetone to isobutene on acidic sites are dominated on the Zn_xZr_yO_z mixed oxide catalysts, while the undesirable reactions such as ethanol dehydration/carbon deposition are primarily inhibited. With other mixed oxide catalysts containing CeO₂/ZrO₂ and ZnO/ZSM-5, ethylene is produced with no enormous amount of isobutene formed [13]. The above results indicate that choosing proper bifunctional mixed metal oxides with optimized composition plays a vital role in acid-base-pair-catalyzed aldol condensations. At a higher reaction temperature (753 K), acetone selectivity decreases from 15% to 5% along with the reduction of isobutene se-

lectivity, while H₂ and CO₂ selectivities increase significantly, revealing that ethanol steam reforming dominates at higher temperatures (such as 753 K) [13].

Hydroxyapatite

Apart from mixed metal oxides, hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂, Ca-P) is another bifunctional catalyst with acid-base feature on the surface being applied in the upgrading of ethanol to 1-butanol, which shows up to 85% 1-butanol selectivity [65]. The highest reaction performance comes from modified hydroxyapatite, in which the Ca²⁺ ions and PO₄³⁻ ions are substituted by other cations or anions [66,67]. For instance, Onda *et al.* [67] investigated systematically the catalytic transformation of ethanol to 1-butanol over several ion-exchanged hydroxyapatites at 573 K. The Ca-P hydroxyapatite catalyst shows up to 74.5% selectivity to 1-butanol, while Sr₁₀(PO₄)₆(OH)₂ (Sr-P) catalyst possesses 81.2% selectivity to 1-butanol at 5%–8% ethanol conversion. With acetaldehyde as reactant, the product distribution in the aldol condensation reaction over the above-mentioned catalysts shows that the main product is 2-butenal at 30%–40% acetaldehyde conversion. Furthermore, control experiment implies that Sr-P hydroxyapatite is more active in hydrogen-transfer (MPV reaction), and the amount of

aldehydes/ketones on the surface of the catalyst is reduced, which facilitates 1-butanol formation and suppresses coking [67].

Subsequently, Onda *et al.* [65] also discussed the influence of Sr/P ratios on the selectivity of ethanol upgrading, as shown in Table 6. It shows that 1-butanol selectivity could reach the maximum at around 86.4% with the highest Sr/P molar ratio at 1.70 and highest Lewis acid-base pair density, demonstrating the strong correlation between 1-butanol formation and the density of the Lewis acid-base pairs on the surface of the catalyst. The reaction mechanism for ethanol coupling over Ca- and Sr- hydroxyapatites were systematically investigated by Flaherty's group [11], and they proposed an adapted step-growth polymerization model which accurately predicted the distribution of carbon numbers among the products over hydroxyapatites. Furthermore, they proposed that the deprotonation of acetaldehyde to enolate elementary step is the rate determining step for C–C bond formation with ethoxide as the most abundant surface intermediates [68]. The proposed tandem reaction pathways for the generation of methylbenzaldehydes would be helpful to understand the process of catalytic deactivation by uncontrolled multi-step C–C bond coupling.

Davis' group [57] reported the comparison of ethanol transformation reaction performance among MgO, hydroxyapatite and TiO₂ catalysts to investigate the reaction mechanism of C–C bond formation following aldol condensation, as shown in Table 7. With ethanol as reactants, it shows the product yields at 2.9% for 1-butanol, 1.4% for acetaldehyde and 0.04% for ethylene at 613 K over hydroxyapatite catalyst used. Compared with MgO and TiO₂, hydroxyapatite exhibits a higher surface density of acid-base site pairs with a weaker binding affinity to ethanol, which accounts for the highest turnover rate and 1-butanol selectivity (67%). The superior selectivity toward 1-butanol over hydroxyapatite is ascribed to a large

number of appropriate strength of acid-base pairs on the surface. Over TiO₂ catalyst, it shows product selectivities of 51% to acetaldehyde and 42% to diethyl ether at only 1.9% ethanol conversion. TiO₂ does not deactivate readily at the presence of ethanol unlike the case for hydroxyapatite or MgO. Besides, TiO₂ is the most active catalyst for aldol condensation of acetaldehyde, followed by hydroxyapatite and MgO, according to the initial reaction rates. Above all, hydroxyapatite with bifunctional properties possesses excellent ethanol coupling behavior due to its balancing nature of acid-base pairs in comparison with acid or base metal oxides, indicating that people need to balance the strength of the Lewis acid-base pair to achieve a better reaction performance on ethanol upgrading.

M-zeolite

Zeolite-based materials have been an attractive catalyst for aldol condensation owing to their unique pore structure and tunable acid-base pair strength through ion exchange. Two factors are significant to modify the aldol rate and reaction selectivity. (i) The substituted elements: as an example, incorporation of trivalent cations into Si–O–Al framework to form metallosilicate sites may fine tune the acid strength of zeolites. (ii) The Si/Me³⁺ ratio: adjusting Si/Me³⁺ ratio could effectively control the acid-base distribution and the number of active sites.

Yang *et al.* [31] reported the transformation of ethanol to 1-butanol through a bimolecular condensation process over alkali cation zeolites. The exchanged zeolites are significantly different from Rb-containing samples in catalytic behavior. Particularly, LiX possesses a high reaction rate of converting ethanol, but most of ethanol is converted into gaseous light products rather than condensation products, as shown in Table 8. Rb–LiX exhibits moderate reaction rate but the highest 1-butanol selectivity (40.9%) at 693 K, while aldol reaction rates and selectivities to C₄ alcohol and acetaldehyde on them de-

Table 6 Acidic, basic site density, catalytic conversion of ethanol, product selectivity and yield over Sr-HAP catalysts with various Sr/P molar ratios (catalyst 2.0 g; temperature 573 K; W/F ethanol 130 h g mol^{−1}; ethanol 16.1 mol% (Ar balanced)) (C₆, C₈-OH: C₆, C₈ alcohols) (Reprinted with permission from Ref. [65]. Copyright 2012, Elsevier)

Sr/P	D_{ac}^* ($\mu\text{mol m}^{-2}$)	D_{bas}^* ($\mu\text{mol m}^{-2}$)	Conv. (%)	Yield (Sel.) (%)			
				Acetal	1-Butanol	2-Butenal	C ₆ , C ₈ -OH
1.58	<0.01	0.37	1.1	0.02 (1.5)	0.8 (69)	0.2 (22.3)	0.03 (2.6)
1.64	0.13	0.58	5.9	0.04 (0.7)	4.6 (78.1)	0.4 (6.5)	0.6 (10.7)
1.67	0.11	0.79	7.9	0.04 (0.5)	6.5 (81.7)	0.2 (3.0)	0.9 (12)
1.70	0.22	1.0	11.3	0.1 (0.7)	9.8 (86.4)	0.3 (3.0)	0.9 (7.8)

* D_{ac} : acidic site density; D_{bas} : basic site density.

Table 7 Ethanol conversion, turnover rate, product selectivity and yield (~8 kPa) over HAP, MgO and TiO₂ (Results for hydroxyapatite and MgO were previously reported by Davis *et al.*; HAP: hydroxyapatite) (Reprinted with permission from Ref. [56]. Copyright 2016, American Chemical Society)

Cat. *	Temp. (K)	Conv. (%)	TOR (10 ⁻⁸ mol m ⁻² s ⁻¹)	Yield (Sel.) (%)				
				Ethylene	Ethane	Acetal	1-Butanol	DE
MgO	653	4.5	1.4	0.5 (12)	0	3.0 (67)	1.0 (21)	0
HAP	613	4.3	4.4	0.04 (1)	0	1.4 (32)	2.9 (67)	0
TiO ₂	613	1.9	1.3	0	0.1 (7)	1.0 (51)	0	0.8 (42)

*Cat.: catalysts.

Table 8 Ethanol consumption rate, turnover rate and selectivity of product over each catalyst (EB: 2-ethyl-1-butanol; C₄: 1-butanol+butanal) (Reprinted with permission from Ref. [31]. Copyright 1993, Elsevier)

Cat.	TOR (10 ⁴ mol min ⁻¹ g ⁻¹)						Reaction rate (*10 ⁴ mol min ⁻¹ g ⁻¹)	Sel. (%)	
	1-Butanol	Acetal	Butanal	EB	C ₄	Other		1-Butanol	C ₄
LiX	0	2.1	0	0	0	15.4	17.5	0	0
NaX	0	1.7	0	0	0	7.9	9.6	0	0
KX	-	1.4	0	-	-	3.5	4.9	-	-
Rb-LiX	2.6	1.4	0.2	0.3	2.7	1.7	6.2	40.9	43.3
Rb-NaX	2.4	1.7	0.2	0.4	2.7	1.6	6.6	36.6	40.2
Rb-KX	1.0	2.0	0.1	0.1	1.1	1.6	5.0	20.4	22.8

crease with decreasing basicities of the substituted cations. And they also suggest that the reaction mechanism over basic zeolites is one molecule of ethanol with C-H bond in the activated β -position condensed with another molecule of ethanol by dehydration, different from the well accepted Guerbet reaction with acetaldehyde as the key reaction intermediate following aldol condensation process.

Dumitriu *et al.* [69] reported the aldol condensation of aldehydes over MFI zeolites (Si/Me) (Me: B, Fe, Ga, etc.) with various Lewis acid intensities. The acid strength of the above zeolites are determined in the following order: Al>Ga>Fe>B, while the trend of selectivity to aldol products is opposite: B>Fe>Ga>Al, indicating that the acidity dominates the behavior of catalysts in the aldol condensation of acetaldehyde. Besides, with Si/Me³⁺ ratio varying, the acidity of MFI zeolites is strongly affected. Recently, Lewis *et al.* [70] studied a series of metal-substituted Al-Beta zeolites, including Hf-, Sn-, and Zr-, which catalyzed the cross-aldol condensation of aromatic aldehydes with acetone. Among them, Zr-Beta zeolites show the highest aldol condensation rate at 363 K. Selectivities to benzaldehyde and 4-ethylbenzaldehyde reach 98% at 94% aldehyde conversion and >99% at 42% aldehyde conversion, respectively.

Furthermore, ethanol upgrading to butadiene over zeolite catalysts were developed back to early 20th century.

In 1903, Ipatiev [3,71] found that a small amount of butadiene can be produced by passing ethanol over aluminum powders. Several decades later, the studies about ethanol to butadiene transformation were reported using clay as catalyst, SiO₂/MgO and other metals or metal oxide mixture catalysts through Lebedev reaction process, including consecutive dehydrogenation, aldol condensation, reduction and dehydration [72,73]. Ordonsky *et al.* [74] investigated ethanol upgrading over various metal oxides dispersed on SiO₂ by co-feeding with acetaldehyde. They found that Au-Zr-SiO₂ catalysts exhibited the highest butadiene selectivity (82%) at 598 K, and simultaneously 81% butadiene selectivity were determined over Ce-Ag-Zr-SiO₂. Clearly, modified Zr was regarded as excellent active species in the synthesis of butadiene through Lebedev process. Beyond SiO₂, ZrBEA zeolite was proved to be another proper catalyst for the upgrading of ethanol to butadiene [75-79]. For example, Ivanova *et al.* [76] reported highly selective synthesis of 1,3-butadiene from ethanol over ZrBEA and Ag/ZrBEA catalysts. The excellent catalytic performance was observed over Ag/ZrBEA with ethanol consumption rate at 0.58 g g⁻¹ h⁻¹ and 1,3-butadiene selectivity at ~60%. Jeong *et al.* [77] discussed the catalytic performances over several Ta/SBA-15 zeolites, in which 1,3-butadiene selectivity can reach the maximum of 79.8% at 46.9% C₂ conversion. Kyriienko *et al.* [79] lately designed a modified catalytic

system over Ta-SiBEA catalysts with 90.3% 1,3-butadiene selectivity at 30.7% C₂ conversion using ethanol/acet-aldehyde mixtures as reactants. Furthermore, Hermans *et al.* [75] discussed the reaction intermediates during 1,3-butadiene formation over Ta-BEA zeolites using DRIFTS-MS. They proposed that fine tuning of the ethanol/acet-aldehyde ratio was crucial to keep the high ethoxy coverage and desorption of intermediate 2-butenol, which was highly related to high 1,3-butadiene productivity.

The long-term stability and deactivation of the zeolite catalysts is another key problem hindering their further application. Ethanol to butadiene conversion (ETB) over Zn-Y/Beta zeolite was used to study the deactivation mechanism by Yan *et al.* [80]. They found that with the deposition of large unsaturated aldehydes/ketones, a gradual coverage of catalytically active Zn and Y species of Zn-Y/Beta zeolite catalyst occurred, resulting in a gradual deactivation of the ETB catalysts. From the above discussion, it can be elucidated that the configuration of acid-base sites by ion exchange in zeolite-based catalysts can effectively optimize the aldol condensation of alcohols, and their shape-selective feature could be promising for improving selectivity of target products likewise. Similar to zeolites, as another porous material with uniform channel structure, metal organic frameworks have also been exploited as catalysts of C–C bond formation in recent years [81–85]. However, the thermostability is still an inevitable issue and needs to be further addressed.

CONCLUSIONS

In summary, the formation of C–C bond in ethanol upgrading to value-added chemicals is the key step for developing the long chain chemicals, which needs to be carried out over the balanced Lewis acid-base catalysts. MgO, TiO₂, ZrO₂, Mg–AlO_x derived from hydrotalcites, transition or noble metal modified MgAlO_x mixed oxides and hydroxyapatites are mainly applied to selectively convert ethanol to 1-butanol *via* sequential reactions of dehydrogenation of ethanol, aldol condensation between acetaldehydes, dehydration of aldol, hydrogen transfer and hydrogenation of 2-butenol. Promising reaction systems for ethanol upgrading *via* at least one-step of C–C bond coupling are selectively high-lighted, in which Pd/Mg–AlO_x mixed metal oxide shows a distinct selectivity of 72.7% for 1-butanol formation, while it can reach 86.4% over Sr-P hydroxyapatite catalysts. In addition, 90% 1,3-butadiene selectivity at 31% C₂ conversion is realized over Ta-SiBEA catalysts, while Zn_xZr_yO_z mixed oxides present a high-yield of isobutene (83%) from ethanol by adjusting Zn/Zr ratio, with acetone and mesityl oxide as the key

intermediates. The above results are entirely aiming at balancing the acid and base sites on the surface of the catalysts to facilitate ethanol upgrading to value-added products *via* equilibrizing rates of different reaction pathways. It turns out that the balance of acid-base sites can selectively facilitate C–C bond formation and inhibit side-product production simultaneously, thus achieving ethanol conversion towards value-added chemicals in high selectivity.

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Conflict of interest The authors declare no conflict of interest.

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平衡Lewis酸碱催化剂催化乙醇转化形成C–C键的最新进展

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摘要 乙醇是生物质转化过程中重要的平台分子, 可以通过ABE (丙酮-丁醇-乙醇) 发酵过程大量获得. 近几十年来, 人们一直致力于将乙醇升级为高附加值化学品. 通过C–C键生成过程, 选择性地生成了1-丁醇和一系列高附加值产品. 本文总结了近年来在平衡Lewis酸碱催化剂上选择性生成C–C键的研究进展, 包括金属氧化物催化剂、混合金属氧化物催化剂、羟基磷灰石和沸石分子筛限域过渡金属氧化物催化剂. 其中Pd-MgAlO_x和Sr基羟基磷灰石催化剂对应1-丁醇的选择性>70%, Zn_xZr_yO_z和Ta-SiBEA沸石对异丁烯和丁二烯的选择性>80%. 本文详细介绍了各反应体系中C–C键形成的机理和反应路径, 并讨论了C–C键生成与催化剂表面Lewis酸、碱强度的关系.