Interfacial Sites in Ag Supported Layered Double Oxide for Dehydrogenation Coupling of Ethanol to \( n \)-Butanol

Jian Zhang, Kai Shi, Yanru Zhu, Zhe An, Wanning Wang, Xiaodan Ma, Xin Shu, Hongyan Song, Xu Xiang, and Jing He[a]

Upgrading of ethanol to \( n \)-butanol through dehydrogenation coupling has received increasing attention due to the wide application of \( n \)-butanol. But the enhancement of ethanol dehydrogenation and followed coupling to high selectivity to \( n \)-butanol is still highly desired. Our previous work has reported an acid-base-Ag synergistic catalysis, with Ag particles supported on Mg and Al-containing layered double oxides (Ag/MgAl-LDO). Here, Ag-LDO interfaces have been manipulated for dehydrogenation coupling of ethanol to \( n \)-butanol by tailoring the size of Ag particles and the interactions between Ag and LDO. It has been revealed that increasing the population of surface Ag sites at Ag-LDO interfaces promotes not only the dehydrogenation of ethanol to acetaldehyde but also the subsequent aldol condensation of generated acetaldehyde. A selectivity of up to 76 % to \( n \)-butanol with an ethanol conversion of 44 % has been achieved on Ag/LDO with abundant interfacial Ag sites, much superior to the state-of-the-art catalysts.

1. Introduction

Production of \( n \)-butanol has drawn arising attention due to its wide application as a raw bulk chemical in the manufacture of chemical products.[1] Also, \( n \)-butanol is one of promising alternatives to gasoline as it has 86 % energy density compared to gasoline and is easier to store due to its water immiscible nature.[2] Traditionally, \( n \)-butanol has been produced through fossil-based o xo process (hydroformylation of propylene)[3] or by the fermentation of sugars (acetone-butanol-ethanol process).[4,5] The increased availability of ethanol from biomass[6] drives the interest to upgrade ethanol into more valuable chemicals.[7] Ethanol can undergo C–C formation via Guerbet reaction, offering an economical and sustainable route for \( n \)-butanol production. So far, it has been generally accepted that the Guerbet reaction involves an aldol-condensation route,[7] even though some researches support the direct condensation mechanism.[8] The aldol-condensation route implies ethanol dehydrogenation to acetaldehyde, aldol condensation of generated acetaldehyde to crotonaldehyde, and hydrogenation of crotonaldehyde to 1-butanol through a hydrogen transfer.

In 1901, Guerbet first reported the dehydrogenation coupling of ethanol to \( n \)-butanol over barium ethoxide.[9] Inspired by Guerbet’s work, both homogeneous[10–12] and heterogeneous catalysts[13–15] have been widely developed in upgrading of ethanol to \( n \)-butanol. Even though excellent performance (>90 % selectivity to \( n \)-butanol and >20 % conversion of ethanol) has been achieved in homogeneous systems in a batch reactor with the addition of extra base (EtONa)[13a,b] nickel or copper hydroxide complexes[14c], heterogeneous catalyst, including solid acids and/or bases (i.e. oxide or mixed oxides[15a–e] alkali metal-modified zeolites,[15d] and hydroxyapatite[15g–m]) and supported metals[15h–q] for continuously upgrading of ethanol to \( n \)-butanol has been attracting continuous attention due to the potential industrial application. Incorporation of metals in the catalytic system allows the reaction to be carried out at lower temperature with higher ethanol conversion due to the enhanced ethanol dehydrogenation on the metal sites. Cu–CeO2/AC affords a selectivity of 40 % towards \( n \)-butanol with ethanol conversions of 44–46 % at 523 K and 2 MPa N2.[15e] Encapsulation of Pd into UIO-66 gives a selectivity of 49.9 % toward \( n \)-butanol with an ethanol conversion of 50.1 %.[15g] Ethanol dehydrogenation to acetaldehyde is commonly considered as the rate-determining step in the upgrading of ethanol to \( n \)-butanol.[15a–q] In our previous work, the dehydrogenation of ethanol to acetaldehyde has been proposed to be promoted on the metal-support interfacial sites.[11d] Despite this progress, the metal-support interfaces in the dehydrogenation coupling of ethanol to \( n \)-butanol desire more attention. The development of catalyst with tunable interfaces is thus of great importance to enhance the catalytic performance. We previously reported an acid-base-Ag synergistical catalyst with Ag supported on Mg and Al-containing layered double oxides (Ag/MgAl-LDO), derived from Ag loading Mg and Al-containing layered double hydroxides (Ag+/MgAl-LDHs). A selectivity of up to 77 % toward \( n \)-butanol have been achieved with ethanol conversion of 23.2 % at 350 °C, 0.1 MPa and selectivity of 60 % toward \( n \)-butanol with ethanol conversion of 45 % at 250 °C, 2 MPa.[15a–d]
Intrigued by our recent discoveries, Ag-LDO interfaces have been manipulated for dehydrogenation coupling of ethanol to n-butanol in this work. To the best of our knowledge, this is an original report of interfacial catalysis for upgrading of ethanol to n-butanol. A n-butanol yield of 39% and a selectivity of 65% toward n-butanol have been achieved on Ag-MgAl-LDO with abundant interfacial Ag sites, which is much superior to the state of art catalysts.¹⁻¹⁰

2. Results and Discussion

Figure 1 shows the XRD patterns of Mg₄Al-LDHs, Ag⁺/Mg₄Al-LDHs, and Ag/MgAl-LDO prepared in this work. For as-prepared or Ag⁺ loaded Mg₄Al-LDHs, the reflections characteristic of hydrotalcite-like structure are clearly observed (Figure 1A, a and b). No phase change occurs in the impregnation of as-prepared Mg₄Al-LDHs with AgNO₃ aqueous solution. By thermal treatment of Ag⁺/Mg₄Al-LDHs under either N₂ (Figure 1B, a) or H₂ (Figure 1B, b–d) atmosphere, both of Mg–Al mixed oxide (MgAl-LDO) (JCPDS: 45-0946) and metallic Ag (JCPDS: 04-0783) are clearly observed for the resulting Ag/Mg₄Al-LDO-N-3h and Ag/Mg₄Al-LDO-H-x. The reflections characteristic of Ag particles become obvious gradually with the thermal treatment time increasing from 1 h to 5 h under H₂ atmosphere (Figure 1B, b–d). In the TEM images (Figure 1C), Ag particles are observed in a maximum distribution at 7.4 nm for Ag/MgAl-LDO-N-3h (Figure 1C, a). But larger Ag particles are observed for Ag/MgAl-LDO-H-x, the sample prepared by thermal treatment of Ag⁺/Mg₄Al-LDHs under H₂ (Figure 1C, b–d). Increasing thermal treatment time in H₂ obviously results in Ag agglomeration, with the maximum distribution shifting from 17.9 to 34.1 nm. The Ag dispersion was determined by HOT as being 17.2%, 8.3%, 5.6%, and 4.3% (Table 1). Each Ag/MgAl-LDO shows a BET surface area around 90 m²/g (Table 1, entry 1–4).

The surface basicity has been determined by CO₂-TPD technique (Figure 2A). On each Ag loaded Mg₄Al-LDO, a broad CO₂ desorption is observed in the TPD profiles between 50 and 400 °C, which can be deconvoluted into three contributions identified¹¹⁻¹³ as the adsorption of CO₂ on weak basic sites at

![Figure 1](image-url)

Figure 1. (A) XRD patterns of (a) Mg₄Al-LDHs and (b) Ag⁺/Mg₄Al-LDHs; (B) XRD patterns and (C) TEM images, size distribution, and HRTEM images of metallic Ag nanoparticle of (a) Ag/Mg₄Al-LDO-N-3h, (b) Ag/Mg₄Al-LDO-H-1h, (c) Ag/Mg₄Al-LDO-H-3h, and (d) Ag/Mg₄Al-LDO-H-5h.
Table 1. Specific surface area and acid-base properties of Ag supported LDO.

| Entry | Samples          | \(S_{\text{BET}}\) m\(^2\) g\(^{-1}\) | Acidic density/\(\mu\text{mol g}^{-1}\) | Acidic density/\(\mu\text{mol m}^{2}\) | Acid/ Basic sites | Acid/– Al (%) |
|-------|------------------|--------------------------------------|--------------------------------------|--------------------------------------|------------------|----------------|
| 1     | Ag/Mg-Al-LDO-N-3h | 90.2                                 | 4.88                                 | 0.25                                 | 2.77             | 0.57           |
| 2     | Ag/Mg-Al-LDO-H-1h | 88.3                                 | 4.98                                 | 0.26                                 | 2.94             | 0.59           |
| 3     | Ag/Mg-Al-LDO-H-3h | 87.7                                 | 4.90                                 | 0.26                                 | 2.96             | 0.60           |
| 4     | Ag/Mg-Al-LDO-H-5h | 89.8                                 | 5.01                                 | 0.27                                 | 3.01             | 0.60           |
| 5     | Ag/Mg-Al-LDO*-N-3h| 92.4                                 | 4.98                                 | 0.26                                 | 2.81             | 0.57           |
| 6     | Ag/Mg-Al-LDO-H-3h | 89.0                                 | 4.94                                 | 0.31                                 | 3.48             | 0.71           |

(a) The concentration of weak, medium-strong, and strong basic sites are calculated according to the results of CO\(_2\)-TPD and the deconvoluted TPD profile in the temperature region of 50–400 °C. (b) The acidic sites are calculated according to the results of pyridine-FITR. (c) The Ag–O–Al sites are calculated according to the results of XPS.

Figure 2. (A) CO\(_2\)-TPD profiles and (B) FT-IR spectra of pyridine adsorption for (a) Ag/Mg-Al-LDO-N-3h, (b) Ag/Mg-Al-LDO-H-1h, (c) Ag/Mg-Al-LDO-H-3h, and (d) Ag/Mg-Al-LDO-H-5h.

<170 °C, medium-strong basic sites at 170–260 °C, and strong basic sites at >260 °C. Quantitatively, the total amount and density of base sites are summarized in Table 1. Similar amount and density of basic sites are detected on the Ag/Mg-Al-LDO prepared by thermal treatment of Ag\(^{+}\) loaded MgAl-LDHs under either \(N_2\) or \(H_2\) (Table 1, entry 1–4). The surface acidity has been determined by FT-IR spectra of pyridine adsorption (Figure 2B). On the Ag/Mg-Al-LDO prepared by thermal treatment of Ag\(^{+}\) loaded MgAl-LDHs under either \(N_2\) or \(H_2\) atmosphere, only Lewis acid sites\(^{14}\) are observed. The total amount of acid sites shows no marked change with thermal treatment atmosphere or thermal treatment time (Table 1, entry 1–4). All samples show similar ratio of acid to base sites (Table 1, entry 1–4).

Then the Ag/Mg-Al-LDO, with varied Ag particle size while similar acidic-basic properties, have been applied in the dehydrogenation coupling of ethanol under ambient pressure at 350 °C (Table 2 and Figure 3). An ethanol conversion of 32.6% is obtained on Ag/Mg-Al-LDO-N-3h with a selectivity of 61.3% to n-butanal (Table 2, entry 1). Acetaldehyde and acetate

Table 2. Catalytic results for dehydrogenation coupling of ethanol on LDO supported Ag particles.\(^{24}\)

| Entry | Catalyst          | Con. / % | STC\(^{25}\%) | Sel. in liquid product/mol % | Ethyl ether | Acetaldehyde | Ethyl acetate | n-Butanol | i-Hexanol | Others | C\(_{\text{gas prod}}\)/ mol % |
|-------|-------------------|----------|---------------|-------------------------------|-------------|--------------|---------------|-----------|-----------|--------|-----------------------------|
| 1     | Ag/Mg-Al-LDO-N3h  | 32.6     | 50.8 (50.6)   | 9.6                           | 14.0        | 4.1          | 6.1            | 61.3      | 2.1       | 3.4    | 4.0 (13.8 (14.2)            |
| 2     | Ag/Mg-Al-LDO-H-1h | 27.9     | 90.1          | 10.7                          | 14.2        | 10.7         | 2.6            | 54.5      | 1.6       | 2.1    | 3.6 (14.5)                  |
| 3     | Ag/Mg-Al-LDO-H-3h | 25.7     | 123.0         | 11.2                          | 12.9        | 12.1         | 2.1            | 53.6      | 1.7       | 2.9    | 3.5 (15.8 (16.3)            |
| 4     | Ag/Mg-Al-LDO-H-5h | 17.9     | 111.6         | 11.5                          | 15.0        | 16.8         | 2.8            | 47.5      | 1.4       | 1.7    | 3.3 (18.8)                  |
| 5     | Ag/Mg-Al-LDO*-N-3h| 21.2     | 34.4          | 10.9                          | 14.9        | 16.7         | 0.7            | 52.7      | 0.8       | 1.0    | 2.3 (14.3)                  |
| 6     | Ag/Mg-Al-LDO-H-3h | 43.5     | 19.0 (19.2)   | 11.3                          | 1.5         | 1.3          | 0.3            | 75.6      | 2.0       | 6.8    | 1.2 (6.4 (5.8)              |
| 7     | Ag/Mg-Al-LDO-H-3h | 64.3     | 28.1          | 11.3                          | 2.5         | 2.9          | 0.3            | 63.4      | 2.5 (2.8) | 13.9  | 3.2 (5.7 (6.2)              |
| 8     | Ag/Mg-Al-LDO-H-3h | 63.2     | 27.6 (27.4)   | 9.2                           | 2.2         | 1.7          | 0.5            | 65.7      | 3.2       | 14.8  | 2.7 (6.7 (7.2)              |

| [a] Conversion and selectivity were obtained at initial point; reaction conditions: 500 mg of catalyst, 350 °C, 60 mL min\(^{-1}\) of \(N_2\) (0.1 MPa), LHSV = 6 mL (g cat)\(^{-1}\) h\(^{-1}\). | [b] STC for ethanol conversion was calculated by the mole of ethanol converted on per mole of surface Ag per minute. | [c] Conversion and selectivity were obtained at initial point; reaction conditions: 250 °C, 2 MPa. | [d] Conversion and selectivity were obtained at the steady-state; reaction conditions: 250 °C, 2 MPa. Other products include butyl acetate, ethyl butyrate, 2-ethyl-butanal, hexanal, ethyl 2-ethyl butyrate, butyl butyrate, ethyl caproate, etc. The data in parentheses are the reproduced experimental data. |
have also been produced in a selectivity of 14.0% and 4.1% (Table 2, entry 1). But an ethanol conversion of 27.9% with a selectivity of 54.5% to n-butanol and a selectivity of 10.7% to acetate is obtained on Ag/Mg-Al-LDO-H-1h (Table 2, entry 2). Further increasing the Ag particle size disfavors not only the conversion of ethanol but also the formation of n-butanol while promotes the selectivity to ethyl acetate (Table 2, entry 3–4). But the site time conversion (STC), determined by ethanol conversion on per surficial Ag atom, first increases with increasing Ag particle size from 7.4 nm to 22.9 nm and then drops slightly with increasing Ag particle size further to 34.1 nm (Table 2, entry 1–4). No obvious changes are observed in the selectivity to ethyl ether with the increase in Ag particle size (Table 2, entry 1–4). 14%–19% of methane and CO2 are detected in the gaseous products (Table 2, entry 1–4). In our previous work, the acid-base properties showed clearly influence on the selectivity to n-butanol. But the great difference in ethanol conversion and selectivity to n-butanol is supposed to result from the difference in Ag particle size because the acid-base properties of the catalysts prepared in this work are similar. The catalytic results clearly demonstrates that smaller Ag particles favor the formation of n-butanol. The conversion of ethanol and the selectivity to n-butanol on each catalyst exhibit no visible change in 12.5 h reaction at 350 °C (Figure 3).

To reveal the role of Ag particle size on dehydrogenation of ethanol, FT-IR spectra of ethanol adsorption/desorption were recorded (Figure 4). In addition to the band assigned[12] to δO-H of un-dissociated ethanol at 1250 cm−1, 2987–2868 cm−1 to C–H stretching modes, and 1393–1382 cm−1 to δ modes of –CH3, the bands at 1099–1054 cm−1 assigned to C–O stretching in adsorbed ethoxide and 1617–1604 cm−1 to ν1-adsorbed acetaldehyde have been observed for ethanol adsorption at 50°C in each case, indicating that the activation of ethanol on Ag/Mg-Al-LDO occurs through the adsorption of O–H bond, affording ethoxide, followed by dehydrogenation to acetaldehyde. Increasing desorption temperature, the absorption at 50°C clearly decreases in intensity. The band for C–O stretching of adsorbed ethoxide at 1099–1077 cm−1 blue shifts to around 1119–1124 cm−1 since 100°C in each case, and eventually vanishes since 250°C for Ag/Mg-Al-LDO-N-3h while 300°C for Ag/Mg-Al-LDO-H-1h, Ag/Mg-Al-LDO-H-3h, and Ag/Mg-Al-LDO-H-5h. The weak band for ν1-adsorbed acetaldehyde slightly increases in intensity with increasing desorption temperature in each case and becomes dominant since 150°C for Ag/Mg-Al-LDO-N-3h and 300°C for Ag/Mg-Al-LDO-H-1h, indicating that smaller Ag particles promote the dehydrogenation of ethanol to acetaldehyde, accounting for the higher conversion with decreasing Ag particle size (Table 2, entry 1–4). The bands at 1592–1559 cm−1 and 1416–1443 cm−1 assigned to acetate,[15] which is formed via coupling of ethanol and acetaldehyde[14] or Tishchenko-type disproportionation of two molecules of acetaldehyde,[17] are hardly observed at 50°C on Ag/Mg-Al-LDO-N-3h (Figure 4A) and Ag/Mg-Al-LDO-H-1h (Figure 4B) while clearly observed on Ag/Mg-Al-LDO-H-3h (Figure 4C) and Ag/Mg-Al-LDO-H-5h (Figure 4D), demonstrating the strong ability for acetate formation on larger Ag particles. The band assigned to acetate at 1559 cm−1 is hardly observed even at increased desorption temperature for Ag/Mg-Al-LDO-N-3h (Figure 4A), while emerges since 250°C for Ag/Mg-Al-LDO-H-1h (Figure 4B). For Ag/Mg-Al-LDO-H-3h (Figure 4C) and Ag/Mg-Al-LDO-H-5h (Figure 4D), the bands for acetate are observed at 1559 and 1381 cm−1 since 50°C and become dominant since 250°C. With increasing Ag particle size, the bands to acetate not only are observed at lower temperature, but also become more visible and even dominant in the spectra (Figure 4A–D), indicating that larger Ag particles favors the formation of acetate, accounting for the increase in the selectivity to ethyl acetate. The band at 1456–1451 cm−1 assigned to δ modes of –CH2[12] is hardly observed on Ag/Mg-Al-LDO-N-3h (Figure 4A) and Ag/Mg-Al-LDO-H-1h (Figure 4B), while clearly observed on Ag/Mg-Al-LDO-H-3h (Figure 4C) and Ag/Mg-Al-LDO-H-5h (Figure 4D) upon adsorption at 50°C and following desorption, consistent with the acetate formation on larger Ag particles.
In our previous work, the introduction of Ag particles promoted the aldol condensation of acetaldehyde\(^\text{[12,15]}\). The FT-IR spectra of acetaldehyde adsorption at 10 °C on Ag particles in 7.4 nm.

\((\text{Ag/Mg}_4\text{Al-LDO-N-3h})\) and 34.1 nm (Ag/Mg\(_4\)Al-LDO-H-5h) were thus recorded (Figure 5). In addition to the bands at 1717 cm\(^{-1}\) assigned\(^\text{[12,16]}\) to \(\nu (\text{C} = \text{O})\), 1463 and 1371 cm\(^{-1}\) assigned to \(\delta \text{(CH)}\) and \(\delta \text{(CH)}_2\), and 1583 cm\(^{-1}\) assigned to \(\nu_\text{as}\) (OCO) of acetate, the bands at 1337 cm\(^{-1}\) assigned\(^\text{[12,16]}\) to the \(\delta \text{(CH)}\) of crotonaldehyde and 1272 cm\(^{-1}\) to the \(\delta (\text{C} = \text{OH})\) in adsorbed 3-hydroxybutanal are also observed in each case. The intensity of \(\delta \text{(CH)}\) at 1371 cm\(^{-1}\) is clearly less dominant than the intensity of \(\delta (\text{C} = \text{OH})\) in adsorbed 3-hydroxybutanal at 1272 cm\(^{-1}\) is more dominant on 7.4 nm Ag (Figure 5, a) than on 34.1 nm Ag (Figure 5, b). That indicates small Ag particles favor the activation of \(\text{C} = \text{H}\) in acetaldehyde to promote the aldol condensation, well accounting for the higher selectivity to \(n\)-butanol on smaller Ag particles.

To make clear the nature of the size effects of Ag particle on the dehydrogenation coupling of ethanol, the electronic state of Ag/Mg\(_4\)Al-LDO with varied Ag particle size was investigated by XPS technique (Figure 6). In the Ag 3d\(_{5/2}\) XPS spectra (Figure 6A), a binding energy at 368.58–368.35 eV assigned\(^\text{[19]}\) to \(\text{Ag}^0\) species is clearly observed in each case. Another binding energy is clearly observed at 371.11 eV for Ag/Mg\(_4\)Al-LDO-N-3h (Figure 6A, a). With an increase in Ag particle size, the binding energy at 371.11 eV shifts to lower value and becomes less obvious (Figure 6A, b–d). So the binding energy higher than \(\text{Ag}^0\), observed in this work, probably originate from the Ag sites interacting with Mg\(_4\)Al-LDO surface. In the Al 2p XPS spectra (Figure 6B), in addition to the binding energy at 74.35–73.95 eV assigned\(^\text{[20]}\) to Mg–O–Al, another binding energy at 75.43–74.91 eV is observed in each case. The peak at 75.43–74.91 eV becomes less obvious with increasing size of Ag particle. In a previous report on Ag doped alumina, an increase in the binding energy of Al 2p has been observed due to the formation of Ag–O–Al chemical bonds.\(^\text{[21]}\) The binding energy at 75.43–74.91 eV is thus proposed to originate from the Al sites interacting with Ag particles. In the Mg 1s XPS spectra (Figure 6C), no obvious change in the binding energy assigned\(^\text{[22]}\) to Mg–O–Mg or Mg–O–Al is observed (Figure 6C) with increasing Ag particle size, further confirming our proposal that the negatively charged Ag sites originates from Ag particles interacting with Al–O sites rather than Mg–O sites. The binding energy of positively charged Ag, such as Ag\(_2\text{O}\), is lower than that of Ag\(_2\text{O}\)\[^{\text{[19a,c]}}\]. The binding energy for Ag-O-Mg is also lower than that for Ag\(_2\text{O}\). In a previous report on alumina supported Ag\(^{\text{[19b]}}\), the binding energy of Ag at interfacial Ag–O–Al sites has been verified to be higher than that for Ag\(_2\text{O}\), which supports our conclusion. In the O 1s spectra (Figure 6D), three deconvoluted peaks, assigned to absorbed O\(_1\text{,2d}\) M–O (M = Mg or Al)\(^{\text{[19d]}}\) and Ag–O\(_{\text{M}}\)\(^{\text{[19d]}}\) are observed. With the increase of Ag particle size, the deconvoluted area of Ag–O sites declines (Figure 6D), consistent with the decrease in the population of Ag–O–Al sites located at Ag-LDO interface. The fraction of Ag–O–Al interfacial sites, estimated by the deconvoluted area, decreases from 29.5 to 8.7% with Ag particle size increasing from 7.4 to 34.1 nm (Table 1, entry 1–4).

Figure 5. FT-IR spectra of acetaldehyde adsorption at 10 °C on (a) Ag/Mg\(_4\)Al-LDO-N-3h and (b) Ag/Mg\(_4\)Al-LDO-H-5h.

Figure 6. XPS spectra of (A) Ag 3d\(_{5/2}\), (B) Al 2p, (C) Mg 1s, and (D) O 1s for (a) Ag/Mg4Al-LDO-N-3h, (b) Ag/Mg4Al-LDO-H-1h, (c) Ag/Mg4Al-LDO-H-3h, and (d) Ag/Mg4Al-LDO-H-5h.
Figure 7. (A) XRD patterns of (a) Mg/Al-LDO, (b) $\text{Ag}^{+}/\text{Mg/Al-LDO}$, and (c) $\text{Ag}/\text{Mg/Al-LDO}$-N-3h. (B) TEM image and (C) XPS spectrum of Ag 3d for $\text{Ag}/\text{Mg/Al-LDO}$-N-3h. Insertion in (B) is the size distribution of Ag particles.

Figure 8. (A) XRD patterns of (a) Mg/Al-$\text{Ag}^4(\text{Si}2\text{O}{5})^+$-LDHs and (b) Ag-Mg/Al-LDO-H-3h. (B–C) STEM image in the view of cross section, (D–E) HAADF-STEM images and (F) XPS spectrum of Ag 3d for Ag-Mg/Al-LDO-H-3h. Insertion in (D) is the shape simulation for Ag particles.
have been observed with increasing concentration of Ag–O–Al interfacial sites (Figure 9). Due to the slightly higher acidic sites, higher selectivity to n-butanol (75.6%) and lower selectivity to acetaldehyde (1.5%) than expected have been achieved on Ag-Mg/Al-LDO-N-3h (Figure 9). These results well verify that the interfacial Ag–O–Al sites play a key role in promoting the dehydrogenation coupling of ethanol to n-butanol. But the correlation between STC and Ag–O–Al interfacial sites is still ambiguous, even though the results on Ag/MgAl-LDO-N-4h and Ag/MgAl-LDO-N-3h showed that the Ag–O–Al interfacial sites promoted the ethanol conversion. This result indicates that besides the Ag–O–Al interfacial sites, some other factors on the Ag particle that might affect the ethanol conversion should be taken into consideration.

The catalytic stability in 50 h has been performed with Ag-MgAl-LDO-H-3h. Satisfactory stability has been observed in 18 h. A slow decrease in the conversion of ethanol was observed since 18 h and a rapid decrease since 38 h. But the selectivity to n-butanol was well retained in 38 h (Figure 10). Carbon deposition or aggregation of Ag particles might be the reason for the deactivation, which needs further investigation.

3. Conclusions

In summary, the Ag-LDO interfacial sites have been tuned by tailoring the size of Ag particles or changing the preparation method of Ag supported MgAl-LDO. Increasing the interfacial sites clearly enhances the ethanol conversion and aldol method of Ag supported MgAl-LDO-N-3h showed that the Ag–O–Al interfacial sites (Figure 9). Due to the slightly higher acidic sites, higher selectivity to n-butanol (75.6%) and lower selectivity to acetaldehyde (1.5%) than expected have been achieved on Ag-MgAl-LDO-N-3h (Figure 9). These results well verify that the interfacial Ag–O–Al sites play a key role in promoting the dehydrogenation coupling of ethanol to n-butanol. But the correlation between STC and Ag–O–Al interfacial sites is still ambiguous, even though the results on Ag/MgAl-LDO-N-4h and Ag/MgAl-LDO-N-3h showed that the Ag–O–Al interfacial sites promoted the ethanol conversion. This result indicates that besides the Ag–O–Al interfacial sites, some other factors on the Ag particle that might affect the ethanol conversion should be taken into consideration.

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3. Conclusions

In summary, the Ag-LDO interfacial sites have been tuned by tailoring the size of Ag particles or changing the preparation method of Ag supported MgAl-LDO. Increasing the interfacial sites clearly enhances the ethanol conversion and aldol method of Ag supported MgAl-LDO-N-3h showed that the Ag–O–Al interfacial sites promoted the ethanol conversion. This result indicates that besides the Ag–O–Al interfacial sites, some other factors on the Ag particle that might affect the ethanol conversion should be taken into consideration.

The catalytic stability in 50 h has been performed with Ag-MgAl-LDO-H-3h. Satisfactory stability has been observed in 18 h. A slow decrease in the conversion of ethanol was observed since 18 h and a rapid decrease since 38 h. But the selectivity to n-butanol was well retained in 38 h (Figure 10). Carbon deposition or aggregation of Ag particles might be the reason for the deactivation, which needs further investigation.
The Auger peak of Mg overlaps with the peak of Ag 3d (1486.6 eV) at a pass energy of 40 eV. Chromated Al-K X-ray source and HRTEM images were taken on a Tecnai G ARM 200F operating at 200 kV. The high-angle annular dark field (HAADF)-scanning transmission electron microscopic (STEM) images were taken on a JEM-2110 FEG electron microscope. The Ag dispersion was determined by hydrogen-oxygen titration (HOT) on a Micrometric Chemisorb 2920 chemisorption system with a thermal conductivity detector (TCD). 100 mg of Ag loaded sample was pre-treated at 350 °C for 1 h under 20 mL min⁻¹ of He and then cooled to 180 °C in the flow of He. Afterwards, O₂ pulses were introduced into the system until saturation and then the absorbed oxygen was titrated by introducing pulses of H₂ at 180 °C. The Ag dispersion was calculated as follows:

\[ D_{Ag} = 2 \times \text{amount of consumed } H_2 / N_{total} \text{ (by ICP)} \times 100 \% \]  

(1)

The X-ray photoelectron spectra (XPS) were recorded on an AXIS SUPRA X-ray photoelectron spectrometer equipped with monochromated Al-K X-ray source (1486.6 eV) at a pass energy of 40 eV. C 1s peak at 284.6 eV was used as a calibration peak. Since the Auger peak of Mg overlaps with the peak of Ag 3d, the peak for Ag 3d was obtained by subtracting the Auger peak of Mg from the original data in this work. The population of Ag−O−Al sites was calculated as follows:

\[ \text{Ag−O−Al } \% = \frac{A_{Ag-O-Al}}{A_{Ag-o-Al} + A_{Ag}} \times 100 \% \]  

(2)

where \( A_{Ag-o-Al} \) was the deconvoluted area for Ag−O−Al or Ag.
Conflict of Interest

The authors declare no conflict of interest.

Keywords: Ag particle size · Ag supported LDO · dehydrogenation coupling · ethanol · interfacial sites