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Confinement of Ultrasmall Cobalt Oxide Clusters within Silicalite-1 Crystals for Efficient Conversion of Fructose into Methyl Lactate

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Abstract: Chemocatalysis of sugars to methyl lactate (MLA) exhibits great advantages over the conventional fermentation approach due to its higher productivity and cost-effective separation process. However, widely used supported metal oxide catalysts suffer from deactivation resulting from sintering during the reaction and removal of coke at high temperatures. Herein, we report ultrasmall cobalt oxide clusters (~1.7 nm) stabilized within silicalite-1 crystals catalyst (CoO@silicalite-1), exhibiting superior catalytic activity and resistance to sintering for the conversion of fructose into methyl lactate. HAADF-STEM, EDS-mapping, and XRD experiments identify the existence of confined CoO clusters. XANES and Raman spectra demonstrated the covalent interaction between CoO and silicalite-1. Thanks to the ultrasmall CoO particle size (~1.7 nm), the CoO@silicalite-1 affords nearly 100-fold higher Co-mass-based activity (mg MLA/mg Co) compared to CoO or Co_3O_4 particles outside the silicalite-1 framework. More importantly, this catalyst exhibits good reuse performance via the removal of coke with facile calcination.

Keywords: Biomass conversion; Silicalite-1; Methyl lactate; Cobalt oxide clusters; Sinterresistance.

1. Introduction

Biomass, as an inexpensive, abundant, and renewable source of organic carbon from the earth, could produce liquid fuels and chemicals.¹⁻³ Among these chemicals, methyl lactate

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(MLA) is one of the most important platform compounds, which has been widely used in the food, chemical, green solvents, and pharmaceutical fields.⁴ To date, very few studies have been reported for the direct production of MLA from carbohydrates using nonfermentive approaches.⁵ However, the fermentation route results in the formation of large amounts of gypsum, hampering large-scale operation due to the extensive separation and purification process.⁶⁻⁷ MLA can be produced by the chemocatalytic esterification of lactic acid (LA, obtained from carbohydrates) with the corresponding alcohol, but this two-step conversion process is not economical.⁸⁻⁹

Recently, much attention has been paid to the catalytic one-step conversion of fructose (a basic monosaccharide derived from biomass) to MLA because of higher productivity and cost-effective separation process compared to fermentation processes.^{5,6} Sn-Beta zeolite has been successfully developed for the highly efficient production of MLA, however, the use of hydrofluoric acid during the synthesis step significantly hinders its large-scale applications.^{7,10-13} Homogeneous Co²⁺ catalysts have also been reported and exhibited superior catalytic activity and less by-products, however, the sintering of heterogeneous CoO_x active site driven by the decrease of surface free energy at high temperature is still a major problem.^{14,15} To minimize sintering, the strong metal-support interaction as well as the deposition of a protective layer has been used to design catalysts with sinter-resistant properties.¹⁶⁻¹⁸

Metal oxides coating has been reported to prevent leaching and sintering of metal particles for the aqueous-phase hydrogenation reaction.^{18,19} Additionally, high-dispersed metals are usually stabilized by strong metal support interactions (SMSI) on carriers using different strategies, such as metal cations coordination, organic ligand complexation, voids or defects anchoring and metal–metal interactions.²⁰⁻²³ Quite recently, Xiao and co-workers reported that a sinter-resistant noble metal (Pt, Pd, Rh, Ag) nanoparticle catalyst can be achieved by immobilization within zeolite crystals.²⁴ More importantly, these noble metal@zeolite catalysts show long reaction lifetimes for the catalytic conversion of C₁ molecules. Additionally, the Co²⁺ site has been reported as the homogeneous catalyst to exhibit good catalytic activity for the conversion of fructose.²⁵⁻²⁷ Therefore, it is urgently needed to develop highly thermally stable and cost-effective CoO active sites within the zeolites crystals for the one-step production of MLA from fructose.

Herein, we report, for the first time, CoO clusters encapsulated within silicalite-1 crystals catalyst (CoO@silicalite-1) synthesized using a steam-assisted method²⁸ for the conversion of fructose to MLA in methanol. The structure is characterized by transmission electron microscopy (TEM), Fourier transform infrared (FTIR), N₂ adsorption-desorption, and X-ray diffraction (XRD). The reason for the immobilization of ultra-stable CoO cluster within silicalite-1 crystals is suggested by Raman and X-ray adsorption near-edge spectroscopy (XANES) results. The catalytic activity of CoO@silicalite-1 catalysts with

2. Experimental Section

2.1 Materials

Silica nanoparticles (Ludox, 30 wt.% in H₂O), Co₃O₄ (99.5%) were purchased from Mecklin Co., China. Co(NO₃)₂·6H₂O (99%), polyvinyl pyrrolidone (PVP, K29-32), Dxylose (98%), D-glucose (99.5%), Sucrose (AR) and D-fructose (99%) was purchased from the Aladdin Industrial Corporation, China. Tetrapropyl ammonium hydroxide (TPAOH, 25 wt.% in H₂O), sodium carbonate anhydrous (\geq 99.8%), NH₄Cl (99.5%) were purchased from Sinopharm Chemical Reagent Co., China. Glycolaldehyde dimethyl acetal (GADMA, 98%) was purchased from Alfa Aesar. Methoxyacetaldehyde dimethyl acetal (MADDA, 98%), 1,3-dihydroxyacetone (98%) and pyruvaldehyde (40% solution in H₂O) were purchased from J&K Co., China. All reagents were used without further purification.

2.2 Catalyst synthesis

The Co@silicalite-1 catalysts were synthesized according to a steam-assisted method. Briefly, different amounts of $Co(NO_3)_2 \cdot 6H_2O$ were mixed with 0.1g PVP in deionized water and stirred to a clarified solution. Then, colloidal silica and tetrapropyl ammonium hydroxide (TPAOH) were added into the solution with a molar ratio of 8:1. After stirred 15 mins, the

solution was evaporated at 50 °C to remove the water. The obtained dry gel was transferred to a 50 mL Teflon cup, which was placed in a 100 mL Teflon-lined autoclave with water added outside the cup to create the steam for hydrothermal synthesis, as shown in Figure S1. Afterwards, the autoclave was heated to 130 °C for 72 h for a moisture-assisted hydrothermal crystallization. The obtained solid was washed by deionized water and filtrated for three times, after drying under 60 °C for 12 h, the template was removed by calcination in air at 550 °C for 6 h. Before catalytic reaction, the alkali-treatment was applied to tune the pore size of catalysts with aqueous solutions of 0.1M Na₂CO₃ at 60 °C for 2 h, then filtered, washed with deionized water and dried at 100 °C for 12 h; Finally, the solid was ionexchanged with 1 M NH₄Cl at 70 °C for three times, after calcined in air at 550 °C for 6 h, the Co@Silicalite-1 was obtained without further reduction. A series of Co@Silicalite-1 catalysts were identified as Co_x, where x is the content of cobalt calculated from ICP-AES results in Table S1. It might be assumed that the Co loading was limited by the silicon sites, and the excess Co(NO₃)₂ was reinstated by steam vapor during the hydrothermal crystallization and filtrated after washing.

2.3 Experimental procedures

The batch reactor was made of stainless steel with a volume of 14 mL. In a typical experimental run, 0.06 g fructose, 0.03 g catalyst and 6 mL of methanol were added into the

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reactor. Then, the sealed reactor was put into a furnace, which had been previously heated to the setting temperature. The reactor was removed at fixed time intervals of setting times and quickly placed into cool water to quench the reaction. The products were collected and rinsed in a 25 mL volumetric flask by methanol and then filtered through a $0.22 \,\mu m$ filter membrane. The calculated conversion of the reactants and the yield of the products were based on the equivalent amount of carbon, and the experimental result was the average value of two replicate experiments.

3. Results and discussion

3.1 Characterizations

Scheme 1 shows a general route for the synthesis of CoO@Silicalite-1 with different Co loadings. Co(NO₃)₂, polyvinylpyrrolidone, tetrapropylammonium hydroxide (TPAOH), and Ludox first formed a starting dry gel via rotary evaporation. The obtained dry gel was transferred to a 50 mL Teflon cup, placed in a 100 mL Teflon-lined autoclave with water added outside the cup to create the steam for hydrothermal synthesis, as shown in Figure S1. After crystallization and calcination, ultrasmall CoO clusters (~1.7 nm) encapsulated within silicalite-1 crystals were formed, however, excessive Co loading lead to the aggregation of CoO_x particles and collapse of the silicalite-1 structure. A series of CoO@silicalite-1 catalysts were identified as Co_x, where x is Co content determined by inductively coupled

plasma-atomic emission spectroscopy (ICP-AES) in Table S1.

X-ray diffraction (XRD) patterns in Figure 1 and S2 were collected with the λ of 0.45226 Å, which was much lower than traditionally used 1.54 Å. As a result, 20 value in our XRD results shifted to the lower angle. XRD results revealed the characteristic peaks (ranging from 2 to 8 degrees) ascribed to MFI zeolite structure in Co_x (x=0~5.87), which indicated the formation of silicalite-1. For Co_{6.50} catalyst, MFI structure was collapsed completely and Co_3O_4 crystalline structure was discovered in Figure 1, suggesting excessive Co loading destroy the structure of silicalite-1 and promote the formation of Co₃O₄. A representative transmission electron microscope (TEM) image of $Co_{1,21}$ in Figure 2d revealed the ordered porous structure of silicalite-1. The electronic energy-loss spectroscopy (EELS) measurements in Figure 2a confirmed the existence of ultrasmall CoO with the silicalite-1 framework. The CoO clusters in Co_{1 21} were further identified as the brighter spots in Figure 2b-c using a high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM). Several CoO clusters were highlighted by red circles and arrows. Moreover, the average CoO particle size in $Co_{1,21}$ was found to be 1.7 nm in Figure 2c.

The silicalite-1 framework with MFI zeolite structure was also verified by Raman spectra (band at 372 cm⁻¹) and Fourier transform infrared (FTIR) spectroscopy (bands at 550 cm⁻¹ and 1242 cm⁻¹) results in Figure 3a, and Figure 4 respectively. The energy-dispersive X-ray spectroscopy mapping (EDS-mapping) analysis of Co_{1,21} in Figure 2e suggested an even

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distribution of Co and O, as well as the existence of isolated CoO clusters. The CoO clusters should be stabilized in the intersectional void spaces due to narrow MFI channels.²⁹ XRD results in Figure 1 further demonstrated that no CoO and Co₃O₄ particles can be found in Co_{1,21} catalyst. In comparison, the MFI structure was collapsed completely, and a Co₃O₄ particles were formed in the Co_{6,50} catalyst, revealed by TEM (Figure 2f) and XRD (Figure 1) results. This suggested that excessive Co loadings destroy the structure of silicalite-1, and Co²⁺ was further oxidized to Co₃O₄ during the calcination process. The Raman peaks at 458 cm⁻¹ and 497 cm⁻¹ corresponded to Co₃O₄ was also discovered in Co_{6,50}, but no bands ascribed to silicalite-1 was seen in Figure 3a. EDS-mapping result of Co_{6,50} in Figure 2g also proved the existence of large Co₃O₄ particles.

The N₂ adsorption-desorption isotherms and pore size distributions of silicalite-1, $Co_{1,21}$, $Co_{1,68}$ and $Co_{6,50}$ were shown in Figure 5a. A type I and IV isotherm with a plateau starting at a very low relative pressure and remarkable hysteresis loop was discovered in silicalite-1, indicating the hierarchical porous structure. With the increase of Co loading, the adsorption amount at low relative pressure gradually decreased, indicating the reduction of micropores. The pore size distribution by Barrett-Joyner-Halenda (BJH) model was shown in Figure 5b. The co-existence of micropores and mesopores in silicalite-1, $Co_{1,21}$, $Co_{1,68}$ samples was discovered, however, $Co_{6,50}$ exhibited only mesopores, furthering confirming the collapse of silicalite-1 framework. The textural properties were summarized in Table S2. The specific

surface area decreased significantly after modification with Co (silicalite-1, 935 m²/g; Co_{1.21}, 462 m²/g; Co_{1.68}, 349 m²/g; Co_{6.50}, 284 m²/g;). Additionally, the micropore surface area also decreased from 678 m²/g (silicalite-1) to 45 m²/g (Co_{6.50}) when the Co content increased. Amorphous mesoporous SiO₂ became the main structure in Co_{6.50}, in accordance with the XRD and TEM results.

X-ray absorption spectroscopy (XAS) was carried out to investigate the correlation between structural characteristics. Co K-edge XANES spectra for $Co_{1,21}$ and $Co_{6,50}$ are shown in Figure 3b, alongside the spectra of the reference materials CoO and Co_3O_4 .³⁰ Different spectral features were observed with varying Co loadings. First, the average Co valence was slightly increased (i.e., oxidized) when the Co loading is increased ($Co_{1,21} \rightarrow Co_{6,50}$) and becomes more similar to the valence of Co_3O_4 (average valence of ~2.7). Interestingly, a spectral difference between $Co_{1,21}$ and $Co_{6,50}$ was observed from the shoulder peak (B), related to the ligand-to-metal charge transfer process.³¹ The dominant B peak intensity indicated the increased degree of covalent character of Co(3d)-O(2p) in the CoO@Silicalite-1 materials. Therefore, the strong intensity of peak B for the $Co_{1,21}$ might be the strong interaction between CoO and silicalite-1.

Very interestingly, the new Raman peaks at 290 cm⁻¹, 469cm⁻¹ and 688 cm⁻¹ were discovered in $Co_{1,21}$ and $Co_{1,66}$, which should be attributed to the twisting vibrations and stretching vibrations of the Co–O or Co–Si bonds. Combined with XANES, Raman spectra,

ACS Catalysis

and temperature-programmed reduction (TPR, Figure S3) results, this covalent interaction between CoO and silicalite-1 was the main factor for the immobilization of CoO clusters within silicalite-1 crystals. Linear combination fitting of the XANES spectrum for $Co_{6.50}$ (Figure S4) reveals that the structure of $Co_{6.50}$ might be a hybrid of $Co_{1.21}$ and Co_3O_4 .

Figures 3c and 3d show the k²-weighted EXAFS spectra ($\gamma(k)$) and the respective Fourier transforms of the $Co_{1,21}$ and $Co_{6,50}$, as well as the reference Co_3O_4 . In the case of $Co_{1,21}$, the amplitude of the oscillations at a higher k region (about 7–12k) is significantly reduced compared with the amplitudes of the others. This result indicated the CoO might be well dispersed into the silicalite-1 crystals in the form of ultrasmall clusters, as observed from the TEM images. With the increase in Co loading, the oscillation of the $Co_{6.50}$ sample at higher k regions becomes more pronounced and resembles that of the Co_3O_4 reference. From the Fourier transforms (Figure 3d), the contribution of the longer radial distance (high R) was prominent with the increase in Co loading, and a high degree of similarity of local structure to Co_3O_4 was observed for $Co_{6.50}$, consistently with the Raman and XANES results. The covalent interaction between CoO and silicalite-1 should be the reason for the stability and not further oxidation of CoO clusters. Increasing the Co loading on silicalite-1 resulted in the collapse of the silicalite-1 framework, then leads to the formation of Co₃O₄ by oxidation of CoO.

As for why cobalt stabilized at 2^+ state in Co_{1.21}, we suspected that cobalt nitrate (+2)

was used as the precursor of Co. Thereafter, CoO was obtained during calcination process, and CoO was not further oxidized to Co_3O_4 due to the strong interaction between Co and Si confirmed by XANES and Raman spectra results. In comparison, the structure of silicalite-1 was destroyed in a high Co loading (6.50), and CoO was further oxidized to Co_3O_4 without the covalent interaction between Co and Si. Additionally, the CoO particle size (~1.7 nm), larger than the dimensions of silicalite-1 cage, was due to that CoO particles was in-situ prepared during the synthesis of silicalite-1. As a result, CoO particles was encapsulated within silicalite-1 crystals, not dispersed in the silicalite-1 cage, which was in good agreement with the previous study.²⁴

3.2 Catalytic activity of different catalysts

To investigate the catalytic activity of CoO@silicalite-1 catalysts for the conversion of fructose to MLA, the experiment without catalysts was first carried out, and the yield of MLA was very low. The yield of MLA over pure silicalite-1 was also low due to the absence of Brønsted acidity (Table 1, entry 1, 18.4%).³² The reason was that Lewis and Brønsted acidity was found to the common factor for the production of MLA from sugars.³³ In comparison, the commercial CoO and Co₃O₄ was found to give a higher MLA yield of 37.0 and 34.6%, respectively (entries 2 and 3). Although oxidized Co catalysts exhibited a comparable activity (MBA, mg

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MLA/mg Co) were less than 1. Additionally, $Co_{6.5}$, mainly Co_3O_4 dispersed on mesoporous SiO₂, exhibited a MBA of 7.9 (entry 10). Significantly, a MBA of 620.9 over $Co_{0.13}$ (entry 5) was obtained, substantially higher than un-supported CoO, Co_3O_4 and $Co_{6.5}$ catalysts.

This "volcano" type variation in catalytic activity was due to the ultrasmall CoO active site and introduction of Brønsted acidity in CoO@silicalite-1 (seen from FTIR-pyridine adsorption results in Table S3). The highest MLA yield of 51.2% was discovered over Co_{1.21} with a MBA value of 100.0 (Table 1, entry 6). To confirm the optimum reaction condition, the MLA yields and conversion of fructose over Co_{1,21} at different temperatures and time were investigated, as shown in Figure 6. The MLA yields kept increasing with reaction time increased from 0 to 24 h at 160 °C, however, the conversion of fructose was around 80%. A complete conversion could be achieved at 180 °C after 18 h with the highest yield of 52%. Although, the higher reaction rate was observed at 200 °C, the occurrence of side reactions such as dehydration and aggregation leaded to the decrease in MLA yield.^{35,36} The conversion of fructose with different fructose/catalyst ratios over Co1.21 at 180 °C was also performed, and a lower fructose/catalyst ratio contributed a higher MLA yield at the same reaction conditions (Table S4). The possible reaction pathway and intermediates (1,3dihydrooxyactone: DHA; pyruvaldehyde; methyl pyruvate) were shown in Figure S5. With the increase of Co loading from 0.13 to 6.50, the yield of MLA increased firstly then decreased. The increase in MLA yield from $Co_{0.13}$ to $Co_{1.21}$ was attributed to the introduction

of more active sites (CoO clusters). The decrease of MLA yield with further increase of Co loading was ascribed to the formation of larger particles and collapse of silicalite-1 framework, revealed by TEM and XRD results. In addition to MLA, the by-products glycolaldehyde dimethyl acetal (GADMA) and methoxyacetaldehyde dimethyl acetal (MADDA) in Figure S5 were also detected in our reaction system, but the total yield was less than 5%. The other by-products were almost not found in the final products, which leaded to a relatively low carbon balance. The low carbon balance was ascribed to the polymerization and dehydration reaction to humins owing to the presence of the strong acidity.^{5,37}

In order to figure out the correlation of catalyst activity with structures, we have compared the catalytic performance of silicalite-1, CoO, Co₃O₄ and Co_{1.21} for the conversion of different intermediates (DHA and pyruvaldehyde in Figure S5). As shown in Table S5, the yield of MLA over blank silicalite-1 from the conversion of both DHA and pyruvaldehyde was very low, which was similar to the result without catalysts used (~12.5%). In comparison, CoO, Co₃O₄ and Co_{1.21} showed almost the same MLA yield from the conversion of DHA after 6 h compared with the results from the conversion of fructose after 18 h. Moreover, these three catalysts gave the higher MLA yield from the conversion of pyruvaldehyde, since side reactions (isomerisation) were effectively suppressed. The above results exhibited that blank silicalite-1 had almost no catalytic activity towards to the

ACS Catalysis

conversion of fructose and intermediates due to the low acidity. Oxidation state of cobalt was useful for the retro-aldol reaction, dehydration and esterification, and the catalytic activity of CoO was slightly better than Co_3O_4 . The rate-determining step (retro-aldol reaction) could be catalyzed by CoO, and the silicalite-1 provided a place for the ultrasmall CoO clusters due to the formation of Si-Co bonds. Additionally, the conversion of other monosaccharides and disaccharide sucrose over $Co_{1.21}$ were also discussed, shown in Table S7. The MLA yield from the conversion of fructose and sucrose exhibited a similar result, much higher than that obtained from the conversion of glucose and xylose.

3.3 Catalyst stability

The stability of the catalyst is of great importance for commercial processes. The spent catalysts were recovered by filtration and washed thoroughly with methanol and dried with or without calcination in air. The yield of MLA over spent $Co_{1,21}$ catalyst without calcination decreased significantly after four reaction cycles (52% to 23%, Figure S6, Table 1, entry 11). The thermogravimetric (TGA) analysis in Figure S7 revealed that the carbon deposition should be responsible for the reduced reactivity. On the contrary, the spent $Co_{1,21}$ calcination at 550 °C for 6 h maintained original activity (about 50% MLA yield) even after being used four times (Figure S6, Table 1, entry 12). Therefore, the catalytic activity of spent $Co_{1,21}$ catalyst can be easily recovered by the facile calcination, and no CoO clusters aggregation

can be found in Figure S2 due to the strong covalent interaction between CoO clusters and silicalite-1.

4. Conclusions

In summary, ultrasmall CoO clusters (~1.7 nm) stabilized within silicalite-1 crystals catalyst have been successfully synthesized and used for the conversion of sugar to MLA in near-critical methanol. The ultrasmall CoO clusters was revealed using HAADF-STEM, EDS-mapping, and XRD experiments. Additionally, a strong covalent interaction between CoO and silicalite-1 was validated and considered as the main reason for the confinement of CoO clusters. The CoO@silicalite-1 catalyst exhibits a nearly 100-fold higher Co-mass-based activity for the production of MLA compared to CoO or Co_3O_4 particles outside the silicalite-1 framework. The metal particle aggregation and collapse of silicalite-1 framework with the increase of Co loading leads to the relatively poor catalytic activity. Under the optimum reaction conditions, the 52.0% MLA yield was achieved at 180 °C over $Co_{1.21}$. More importantly, this catalyst exhibits superior reuse performance with the removal of coke by facile calcination.

Supporting Information

Additional results of catalyst characterization, analysis method, possible reaction pathway, characterization results (XRD, ICP, TGA, N₂ adsorption-desorption, TPR, pyridine-FTIR

and Co K-edge XANES spectrum) and a series of catalytic performance of Co_{1.21}.

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Scheme 1. Synthesis route of CoO@silicalite-1 with different Co loadings

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Co_{6.50}

Co_{1.66}

Co_{1.21}

silicalite-1

M

0





Figure 2. HADDF-STEM images (a-c) of $Co_{1,21}$ and corresponding EELS profiles (a) acquired from the frames I, II and statistical analyses of the mean particle size (c); A representative TEM image of $Co_{1,21}$ (d) and $Co_{6,50}$ (f); STEM-EDS elemental mapping of $Co_{1,21}$ (e) and $Co_{6,50}$ (g) images, CoO clusters are

marked by red circled in (c) and red arrows in (b), Co (red), Si (yellow), O (green).

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Co1.21

 CoO

Co_{6.50}

Co_{1.66}

Co_{1.21}

Silicalite-1

Co₃O₄

Co-Co

Co-Co

R /Å

Co1.2

Co-O

d

F.T. magnitude / a.u.



XANES spectra of Co_{1.21} and Co_{6.50} in comparison with the reference spectra for CoO and Co₃O₄. (c) k^2 -weighted $\chi(k)$ spectra and (d) Fourier transform (FT) magnitude of the k^2 -weighted EXAFS spectra of Co_{1.21} and Co_{6.50} with the reference Co₃O₄ spectra. The FT was not phase corrected, so the actual bond length may be $\sim 0.2-0.4$ Å longer.



Figure 4. FTIR spectroscopy of CoO@Silicalite-1 materials with different Co loading.





Figure 5. N_2 adsorption-desorption isotherms (a) of silicalite-1, $Co_{1.21}$, $Co_{1.68}$ and $Co_{6.50}$ samples and corresponding pore size distribution (b).



Figure 6. Time-course plot of MLA yield (a) and fructose conversion (b) over $Co_{1,21}$ at different

temperature. Reaction Condition: catalyst = 0.03 g, fructose=0.06 g, methanol=6 mL.

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	fructose		methyl la	ictate		
Entry	Catalyst	T (°C)	time (h)	Yield/%(MBA ^[b])		
1	silicalite-1	180	18	18.4		
2	CoO	180	18	37.0(0.9)		
3	Co_3O_4	180	18	34.6(0.7)		
4	Co_3O_4 - $H_2^{[c]}$	180	18	14.0(0.3)		
5	Co _{0.13}	180	18	34.4(620.9)		
6	Co _{1.21}	180	18	51.2(100.0)		
7	Co _{1.66}	180	18	45.1(68.6)		
8	Co _{3.51}	180	18	35.8(35.7)		
9	Co _{5.87}	180	18	23.1(9.4)		
10	Co _{6.50}	180	18	21.6(7.9)		
11	$Co_{1.21}-H_2^{[c]}$	180	18	45.2(23.1)		
12	reuse Co _{1.21} ^[d]	180	18	23.4(45.5)		
13	reuse Co _{1.21} -air ^[e]	180	18	47.3(91.9)		

Table 1. Catalytic conversion of fructose to MLA^[a]

[a] Reaction condition: fructose=0.06 g, catalyst=0.03 g, methanol=6 mL, reaction time=18 h, temperature=180 °C; [b] MBA units: mg MLA per mg Co; [c] The catalyst was treated in H₂ atmosphere at 500 °C before use; [d] The Co_{1.21} was reused four times without calcination; [e] The Co_{1,21} was reused four times after calcination at 550 °C in air.

Table of Contents

