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Facet-Regulated Oxidative Dehydrogenation of Lactio Acid to GC03468A Pyruvic Acid on α-Fe₂O₃

Received 00th January 20xx, Accepted 00th January 20xx Chunyu Yin,^a Xinli Li,*^a Yunsheng Dai,^b Zhi Chen,^a Dingfeng Yang,^a Ruixue Liu,^a Weixin Zou,^c Congming Tang *^a and Lin Dong ^c

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We propose a highly active α -Fe₂O₃ catalyst for oxidative dehydrogenation of lactic acid to value-added pyruvic acid with air. The activity is determined by crystal face due to different adsorption energies of lactic acid molecule on the exposed plane. Furthermore, Fe site is more preferentially adsorbed than crystal O site.

Biomass and its derivatives, as renewable resources are desired to produce chemicals and fuels, instead of fossil resources such as petroleum, coal and natural gas^{1, 2}. Like ethene and acetylene, lactic acid (LA) is acted as a platform molecule for producing various chemicals such as pyruvic acid (PA)^{3, 4}, propionic acid⁵, acetaldehyde⁶, acrylic acid^{7, 8}, 2,3pentanedione⁹ and polylactic acid¹⁰. Pyruvic acid (PA), a vital intermediate, is widely used in chemical, pharmaceutical, food, agriculture, environmental protection and other fields³. Compared with traditionally industrial production of PA from tartaric acid, consuming stoichiometric amount of potassium hydrogen sulfate and high energy, direct catalytic synthesis of PA from LA via oxidative dehydrogenation is viewed as a potential and environmental route^{3, 11}.

On oxidative dehydrogenation of LA to PA, iron phosphates were firstly used, and the M phase composing of Fe²⁺ and Fe³⁺ showed the catalytic performance with LA conversion of 60% and PA selectivity of 62%^{12, 13}. Later, metal and its oxides were investigated by several groups. Notably, Pb-Pt bimetallic supported on carbon materials displayed better activity, achieving 70.7% of LA conversion together with 80.1% of PA selectivity³. Besides, bimetallic oxides such as Nb-Ni-O¹¹, and Mo-Ti-O⁴, have also been investigated for this reaction, obtaining 30.5% of LA conversion and 50.3% of PA selectivity for the former, and 60.6% of LA conversion and 80.2% of PA selectivity for the latter. Recently, the activity on oxidative dehydrogenation of LA to PA has been further enhanced by P modified Fe-Mo bimetallic oxides, achieving 88.7% of LA

Sino-Platinum Metals Co., Ltd.

- Kunming 650106, PR China
- ^{c.} Dr. W.X. Zou, Prof. Dr. L. Dong
- Jiangsu Key Laboratory of Vehicle Emissions Control, Center of Modern Analysis Nanjing University

conversion and 75.3% of PA selectivity¹⁴. These investigations mainly focused on the relation between activity and chemical composition, and the correlation between the crystal plane structure of catalyst and the activity was peculiarly lacking. Thus, it requires continuous effort to reveal the structure-activity relationship for deep understanding the mechanism on oxidative dehydrogenation of LA to PA.

In recent years, the constructed nano-catalysts with specific morphology, particle size and crystal structure have displayed a promising application in whether thermal catalysis¹⁵ or cool catalysis including photocatalysis¹⁶⁻¹⁸ and electrocatalysis¹⁹. Consequently, the basic principles related to structural-selectivity correlations can be directly addressed. α -Fe₂O₃^{16, 17} is naturally abundant and environmentally benign, and displays a bright prospect in chemical industry. Herein, by catalyst characterization and first-principle calculation based on Density Functional Theory, we discuss the selective oxidative dehydrogenation of LA on four regularly shaped α -Fe₂O₃ crystallites (nano-truncated hexagonal bipyramid (THB), nanocubes (QC), nano-plates (HS) and nano-spheres (RC)) with welldefined facets and disclose the structure-activity relationship. The research findings will provide a very powerful method for catalytic synthesis of oxy-organics from biomass and its derivatives.

In order to understand the true performance of the asprepared catalyst, preliminary experiments were carried out on the internal and external diffusion limits^{20, 21}, and the results were shown in Fig. S1 and Fig. S2. Catalyst particle size of 20-40 meshes along with the LA flow rate of 2 mL h⁻¹ was selected to evaluate the catalytic performance of samples during the catalytic oxidative dehydrogenation of LA to PA, which fully eliminated the influence of mass transfer. Initially, over the α -Fe₂O₃ with different morphologies catalytic activity for oxidative dehydrogenation of LA to PA was investigated and the results were shown in Table 1 and Fig. S3a-b. Conversion of LA drastically changed with the morphology of α -Fe₂O₃. LA was almost completely converted with RC and HS. However, the conversion of LA was less than 50% for THB and QC. Similar to the tendency of LA conversion with the morphology of α -Fe₂O₃, PA selectivity decreased from 81.7% with RC to only 2.1% over THB. The formation of other products such as acetaldehyde, acetic acid, and acrylic acid was also influenced by α-Fe₂O₃ with different morphologies (Table S1). In terms of LA conversion and PA selectivity, RC offered more excellent performances than other catalysts.

To evaluate the reactivity of hematite architectures quantitatively, the apparent reaction rate constant $(k)^{22}$ of LA

 ^{a.} C.Y. Yin, Dr. X.L. Li, Dr. Z. Chen, Dr. D.F. Yang, R.X. Liu, Prof. Dr. C.M. Tang School of Chemistry and Chemical Engineering Chongqing University of Technology Chongqing 400054, PR China E-mail: lixinli@cqut.edu.cn (X.L. Li), tcmtang2001@cqut.edu.cn(C.M. Tang)
 ^b Prof. Dr. Y.S. Dai Catalysis

Nanjing 210093, PR China

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Table 1. Comparison of reactivity in the conversion of Lactic acid to pyruvic acid over α -Fe₂O₃ with different morphology, along with other catalysts from the literatures.

	Catalyst	Catalytic pe							
Entry		LA Conv. [%]	PA Sel. [%]	<i>k</i> [h ⁻¹] ^[a]	<i>k</i> s [h ⁻¹ m ⁻²] ^[b]	stability [h]	SSA [m ² g ⁻¹] ^[c]	Dominant planes ^[d]	Ref.
1	3Pb-1Pt/CB	70.7	80.6	N/A	N/A	N/A	756	N/A	3
2	Fe(PO ₄) ₃	60.2	62.3	N/A	N/A	N/A	N/A	N/A	12, 13
3	Mo/Fe(PO ₄) ₃	70.1	63.2	N/A	N/A	N/A	N/A	N/A	23, 24
4	Nb-Ni-O	30.5	50.3	N/A	N/A	10	48	N/A	11
5	Mo-Ti-O	60.6	80.2	N/A	N/A	N/A	N/A	N/A	4
6	FeMoO/P	88.7	75.3	N/A	N/A	60	23.7	N/A	14
7	тнв	36.7	2.1	1.27	0.23	N/A	12.82	{113}	This work
8	QC	43.1	4.2	1.28	0.49	N/A	7.97	{012}	This work
9	HS	94.0	55.3	7.49	0.95	N/A	21.26	{001}	This work
10	RC	94.6	81.7	13.13	2.02	100	16.91	{001}	This work

[a] The apparent reaction rate constant (*k*) of oxidative dehydrogenation of LA to PA on α -Fe₂O₃ architectures is calculated based on a pseudo-first-order kinetic model. [b] k_s represents the rate constant (*k*) normalized to SSA. $k_s=k$ (catalyst mass SSA)⁻¹. [c] The specific surface area, (SSA). [d] Dominant planes are confirmed using TEM and HRTEM. This work conditions: catalyst, 0.30-0.40g; reaction temperature 230 °C; particle size, 20-40 meshes; carrier gas air, 3 mL min⁻¹; LA feedstock, 10 wt% in water, feed flow rate, 2 mL h⁻¹, TOS on 4-5 h.

to PA was calculated, and the results were also summarized in Table 1 and Figure 1a. For the blank experiment without catalyst, the oxidative dehydrogenation of LA to PA was relatively slow at 230 °C, with an apparent reaction rate constant k=0.45 h⁻¹. Under the identical experimental conditions, the apparent reaction rate in the presence of catalysts was conspicuously elevated, and k was normalized to the specific surface area in order to explore intrinsic catalytic activity, referred to $k_s^{25, 26}$. RC shows the greatest catalytic activity with k_s =2.02 h⁻¹ m⁻², while ks are 0.23, 0.49 and 0.95 h⁻¹ m⁻² for THB, QC and HS, respectively. From the standpoint of industrial application, the stability test is extremely significant for the study of heterogeneous catalysts²⁷. The stability test of RC was carried out under controlling the initial LA conversion at less than 60% by reducing the amount of catalyst in order to realize adequately saturation of active sites of the catalyst by reaction molecules, and ensure authentic stability (Figure 1b). We can clearly observe that LA conversion always remains at 50% and PA selectivity almost maintains constant (~81%)



Fig. 1. Excellent activity and stability of a-Fe₂O₃-RC. a), A kinetic study of LA to PA showing activity order of RC > HS > QC > THB > Blank. The errors of each conversion (after t hour) were evaluated to be within $\pm 2\%$. b), Stability test of a-Fe₂O₃-RC for LA to PA, reaction conditions: reaction temperature 230 °C; catalyst, 0.1 g; particle size, 20-40 meshes; carrier gas air, 3 mL min⁻¹; LA feedstock, 10 wt% in water, feed flow rate, 2 mL h⁻¹.

during 100 h on stream. It is generally difficult to obtain high conversion and high selectivity simultaneously. Thus the stability at high conversion of LA was also investigated (Figure S3c). Encouragingly, at high LA conversion of 95%, the selectivity of PA still maintained around 80% during 100 h on stream. For the reported FeMoO/P¹⁴, the LA conversion was reduced by around 10% within 60 h, and no longer reaction time was studied. In comparison, the stability of the α -Fe₂O₃-RC catalyst displayed more excellent stability.

Why is obviously different for the activity of α -Fe₂O₃ with different morphologies? We expected that α -Fe₂O₃ with different morphologies expose different crystal facets, and the Fe/O atomic ratio in their corresponding crystal facet is also different, resulting in different oxidation property and reactivity. In order to further verify the assumption, the structure, morphology and oxidation state of the as-prepared α -Fe₂O₃ architectures were characterized. Different samples remain unanimous characteristic diffraction peaks (Fig. 2a), suggesting a pure phase in α -Fe₂O₃ form (JCPDS NO. 33-0664). Furthermore, the SEM images (Fig. 2b-e) show that four samples present obviously different morphologies, namely, nano-truncated hexagonal bipyramid (THB), nano-cubes (QC), nano-plates (HS) and nano-spheres (RC).



Fig. 2. XRD patterns of the α -Fe₂O₃(a), SEM images of (b) α -Fe₂O₃-THB, (c) α -Fe₂O₃-QC, (d) α -Fe₂O₃-HS and (e) α -Fe₂O₃-RC.

A TEM image for THB is shown in Fig. S4a and the illustration of a structural model in Fig. S4b²⁸. All of the THB display a well-defined pseudo-hexagon shape. Based on a SEM (Fig. 2b) and TEM analysis, the crystallites are composed of two truncated facets and twelve side planes. A classic HRTEM

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image (Fig. S4b) and fast Fourier transform (FFT; inset in Figure. S4b) show that four side facets were determined to be (-1-2-4), (124), (-1-24) and (12-4), belonging to the {214}; while the other eight side facets were confirmed to be (2-13), (-123), (-21-3), (-12-3), (1-2-3), (2-1-3), (-213), and (1-23) belonging to the {113}; and the two truncated facets belong to {104}. A SEM (Fig. 2c) and TEM image (Fig. S4c) indicate that nano-cubes (QC) seem to be quasi cubic in shape and the diagram of a structural model in Fig. S4d. A HRTEM image (Fig. S4d) and fast Fourier transform (FFT; inset in Figure. S4d) show that QC consists of three pairs of parallel planes, and the lattice fringe are 0.25 nm and 0.22 nm. Dihedral angle between adjacent planes are 84°, 90° and 96°. The above data show that the QC exposed {012}, {104} and {110}²⁹. A SEM (Fig. 2d) and TEM image (Fig. S4e) reveal that nano-plates (HS) seem to be a hexagonal shape and the illustration of a structural model in Fig. S4f. In view of SEM and TEM analysis with HS, the thickness and width are confirmed to be (460 \pm 20.3) and (14.2 \pm 2.1) nm, respectively. A representative HRTEM image (Fig. S4f) and fast Fourier transform (FFT; inset in Fig. S4f) show that HS is consistent with (110), (-120) and (-210) planes, respectively. And the regular two hexagonal facets are confirmed to {001}. Observed (Fig. S5) vertically arranged plates are frequently wedge-shaped and the side surfaces are determined to {110}³⁰. Shown in Fig. 3a are the TEM image, HRTEM (FFT; inset in Fig. 3b) and selected area electron diffraction (SAED) inset in Fig. 3a. The RC displays a well-defined roundness. Based on SEM image (Fig.2e), the crystallites comprise of spheroidal particle. Furthermore, the TEM image (Fig. 3a) shows the RC crystallites are composed of a large number of overlapped round particles. The microcrystals grow along the c-direction ([001] axis)³⁰, which can be reflected from the SAED pattern (inset in Fig. 3a). The spherical surface is confirmed to be {001} family planes. A HRTEM image (Fig. 3b) and FFT (inset in Fig. 3b) suggest that three sets of lattice fringes (0.25 nm) match well to (-120),



Fig. 3. a) TEM image of the α -Fe₂O₃-RC, Insets: SEAD pattern; b) HRTEM image of the α -Fe₂O₃-RC, Insets: FFT pattern.

(-210), (110) planes, respectively. Therefore, the base plane of the α -Fe₂O₃ nano-sphere is {001}¹⁶. The physical parameters of the prepared samples, including specific surface area and main planes are also summarized in Table 1.

THB exposes the $\{113\}$, $\{214\}$ and $\{104\}$ family planes, and each takes up 4/7, 2/7, 1/7 of the whole surface, respectively, judged from the area fraction of each crystal surface²⁸. QC

exposes the {104}, {012}, and {110} family planes, and each occupies 1/3 of the whole surface²⁸. HS exposes the {001} and {110} family planes, and each takes up 7/9 and 2/9 of the whole surface, respectively²⁸. RC exposes the {001} facets, exclusively. Thus, the dominant exposed planes on the four α -Fe₂O₃ catalysts, THB, QC, HS and RC, are {113}, {012}, {001} and {001}, respectively. While the order of catalytic activity of four α -Fe₂O₃ catalysts is THB < QC < HS < RC. It is clearly concluded that the facet {001} is active for oxidative dehydrogenation of LA to PA.

It is necessary for us to further disclose the relation between activity and facets in order to understand why the facet {001} is active for production of PA from LA. The adsorption energies of LA molecule on various surfaces of α -Fe₂O₃ were evaluated by DFT calculations, and the results were shown in Table S2 and Fig. S6a. Clearly, the surface adsorption energy of LA on facet {001} is -0.39 eV, far lower than other facets {113} and {012}, which intensifies the adsorption. Lactic acid is adsorbed over α -Fe₂O₃, and the lower the energy required, the easier it is to adsorb on the surface of the catalyst. Further calculation about adsorption energy of LA molecule on different sites of α -Fe₂O₃ {001} was performed, and the results were depicted in Table S3-4 and Fig. S6b-e. The optimized adsorption structures of LA at different adsorption sites on the α -Fe₂O₃ (001) facets show two stable adsorption configurations A (Fe-O) and B (O-H), and the adsorption energy of configuration A is lower than B, suggesting that type A is preferentially adsorbed. It is noted that the ratios of Fe/O on facets are 0.31, 0.46, and 0.60, corresponding to the {113}, {012} and {001}, respectively, and the results are shown in Table 2. This further suggests that the facet {001} is more beneficial for adsorption of LA molecule than other facets. The electronic structures of the four fresh as-prepared samples were explored by diffuse-reflectance UV-Vis spectra and derived Tauc plots. Fig. S7a shows that all α -Fe₂O₃ sample possess a comparable absorption edges around 550-600 nm.

Table 2. The atomic density of surface O and Fe atoms on the {113}, {012}, {001} planes.

	Atomic density [nm ⁻²]					
	{113}	{012}	{001}			
Surface O	8.4	10.8	7.7			
Surface Fe	2.6	4.7	4.6			
Fe/O ratio	0.31	0.46	0.60			

The band gaps (E_g) are confirmed to be 2.13, 2.10, 2.14, 2.15 eV for THB, QC, HS and RC, respectively. Larger band gap indicates smaller particle size of sample, producing larger specific area and favoring the transport of hot electron. According to the empirical formula $E_{CB} = X-E_c -1/2E_g$ (1) and $E_{VB} = E_{CB} + E_g$ (2), where E_{CB} is the conduction band (CB) energy, E_{VB} the valence band energy (VB), X absolute electronegativity of α -Fe₂O₃, and E_c a constant relative to the NHE. E_{VB} values have been obtained as 2.455, 2.440, 2.460 and 2.465 eV for THB, QC, HS, RC, respectively, by using Ec = 4.50 eV (seen in Table S5). Larger E_{VB} suggests stronger oxidizability. Binding energy of RC is the highest among four catalysts from the XPS

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of Fe 2p shown in Fig. S7b, which has the strongest oxidation accordingly. At the same time, the type A is preferentially adsorptive location. As a result, the adsorbed LA molecule can be effortlessly oxidized by the located Fe (III). In the four catalysts, RC revealed the lowest reduction peak, centered at 385° C from the result of H₂-TPR shown in Fig.S7c, demonstrating that hydrogen easily reduces surface Fe-O of catalyst. Similarly, proton transferred from –OH group of LA easily combined with surface Fe-O of catalyst, leading to form product of pyruvic acid by removal of H₂O, promoting the oxidative dehydrogenation of LA during the catalytic reaction.



Scheme 1. Reaction mechanism for the oxidative dehydrogenation of LA to PA over the RC catalyst.

On the basis of the above observations and DFT calculations on adsorption of lactic acid molecule on the facet (001), we propose the mechanism on the oxidative dehydrogenation of LA to PA (Scheme 1). The adsorption energies of iron and oxygen located at different positions on the (001) plane for the hydroxyl and carboxyl functional groups of the lactic acid molecule were calculated (The detailed adsorption model and results were shown in (Figure S6a-e and Table S2-4). It is found that the top iron species (Fe³⁺) attacks the hydroxyl group of the lactic acid molecule with the lower adsorption energy, indicating that lactic acid molecules are adsorbed and activated at the top iron site (1A), so that O-H bond is broken, and H^+ is transferred to the adjacent oxygen at the iron site to form new Fe-OH. In this process, the enhancement of iron oxidation state contributes significantly to activate hydroxyl group. Among four shaped α -Fe₂O₃ catalysts, the iron species in RC has a higher electron binding energy, which means stronger oxidizability. At the same time, the UV-Vis spectra and valence band analysis show that RC has a higher valence band, indicating stronger oxidation, which is consistent with the XPS results. In addition, the RC mainly exposed with crystal plane (001) has a higher Fe/O atomic ratio, which also conduces to the Fe site to adsorb and activate the hydroxyl group in the lactic acid molecule. Then the formed Fe-OH attacks C-H to break the C-H bond and form PA. At the same time, the dissociated H⁺ combines with Fe-OH to

form water. And the Fe³⁺ is reduced to Fe²⁺, supported by H₂-TPR results, since RC has a lower reduction peak, which is conducive to C-H activation and dissociation. Iron oxides with other morphologies such as THB and QC have a higher

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reduction peak temperature, which is not conducive to the process. If the reaction temperature is increased, it is beneficial to enhance the oxygen departure on the iron oxide surface and promote the process. In order to verify the assumption, we enhanced the reaction temperatures to observe the activity on THB and QC. As a result, catalytic performance of THB and QC was improved (Table S6), which demonstrated that this step has an extent influence in the oxidative dehydrogenation of lactic acid. The Fe²⁺ is oxidized to Fe^{3+} by O_2 in air. Meanwhile the lost lattice oxygen is replenished. The catalyst returns to the initial state and completes the catalytic cycle. In the blank experiment, PA was almost not detected under the condition of lactic acid and air without catalyst, indicating that molecular oxygen could not directly oxidize LA to PA. In addition, under the only lactic acid and catalyst, the PA was observed and the amount of PA decreased rapidly over time without air, indicating that the process of oxidative dehydrogenation of PA consumed lattice oxygen in the catalyst. The departure of lattice oxygen directly affects the oxidation dehydrogenation of LA, and it is related to the exposed crystal surface of iron oxide. Therefore, the crystal surface of iron oxide can effectively regulate the activity on oxidative dehydrogenation of lactic acid.

Comparing to previous work focusing on amorphous and non-stoichiometric catalysts in the oxidative dehydrogenation of LA to PA^{3, 4, 31}, this work reveals that the structure of the thermo-catalysts on the nanoscale with exclusive constructions and their corresponding facets are crucial for the design of high-performance nano-catalysts. The arrangement and coordination state of the surface atoms have important influence on the surface properties, including stability, hydrophilicity, adsorption capacity, etc., and these properties determine the catalytic activity.

Conclusions

In summary, the oxidative dehydrogenation of LA to PA with O_2 at 230 °C over hematite is powerfully structural-dependent and the reactivity trend can be reasonably interpreted as enclosed facets in the sequence of {001} > {012} > {113}. The hematite α -Fe₂O₃ (RC with dominant enclosed {001}) exhibited remarkable activity and stability for oxidative dehydrogenation of LA to PA. This study demonstrates a prospective way for thermally catalytic conversion of lactic acid. In addition, this study has broadened applications of hematite α -Fe₂O₃ in biomass and its derivatives.

Conflicts of interest

The authors declare no conflicts of interest.

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