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Enhanced Carbon Dioxide Oxidative Dehydrogenation of 1-Butene by Iron-doped Ordered Mesoporous Alumina

Bing Yan, Yue Gao, Bolong Wang, Xingting Fan, Fakhre Alam, Jian Li and Tao Jiang*[a]

Abstract: Iron-doped ordered mesoporous alumina (meso-FeAl) was synthesized through "one-pot" method and applied for 1, 3-butadiene (BD) synthesis through oxidative dehydrogenation of 1-butene using CO_2 as soft oxidant. X-ray diffraction, N_2 adsorption and transmission electron microscopy results made confirm the ordered mesoporous structure of meso-FeAl catalyst with high specific surface area and large pore volume. Results also revealed that iron species were highly dispersed inside the alumina matrix. Compared with Fe_2O_3 impregnated meso-Al_2O_3 catalyst and conventional Fe_2O_3/γ-Al_2O_3 catalyst, meso-FeAl showed excellent catalytic activity, good stability and high selectivity for BD synthesis. Structural properties as well as the existence form of iron species in meso-FeAl matrix positively contribute to the catalyst performance.

Global warming, ocean acidification and other environmental problems which mainly arise due to the excessive emission of CO_2 are detrimental world-widely.[1] Thus, finding routes to reduce CO_2 level in atmosphere and its utilization for valuable material is not only exciting but also intensely desirable.[1b, 1d, 2] Amongst numerous technologies, the application of CO_2 as a soft oxidant has gained much attention.[2g, 3] CO_2 acts as a mild oxidant and possesses many advantages over other oxidants, such as moderate oxidation capacity, minimization of hot-spots and low explosion risks.[2g, 3a, 3d-f, 4]

1-Butene is considered as a kind of "cheap" chemical which is mostly extracted from refinery waste gases and from natural gas condensates.[5] Most of 1-butene burns as liquefied gas in China every year, which drastically diminishes hydrocarbon resources. The oxidative dehydrogenation (ODH) of 1-butene to 1, 3-butadiene (BD) using CO_2 as a mild oxidant (Equation 1) not only transforms 1-butene to BD (a value-added petrochemical product due to wide applications, such as acting as an important monomer for preparing high molecular synthetic materials, a raw material for production of vinylite, plastic and rubber, and a key intermediate for manufacturing a variety of chemicals) but also converts CO_2 to CO.[3d, 6] For the first time, Yan Liu et al. reported the catalytic ODH of 1-butene to BD using CO_2 as soft oxidant and Fe_2O_3/γ-Al_2O_3 as a catalyst.[7] Although Fe_2O_3/γ-Al_2O_3 proved effective catalyst for BD synthesis, there still exist some serious problems of low activity, low BD selectivity and fast deactivation. Therefore, it is extremely desirable to develop catalysts for BD synthesis which have high catalytic activity, stability and good product selectivity.

$$CH_2=CH-CH_2CH_3+CO_2 \rightarrow CH_2=CH-CH=CH_2+CO+H_2O \quad (1$$

Since from its first synthesis, the ordered mesoporous alumina gained much attention due to wide applications.[8] Owing the benefits of large surface area, high thermal stability, large surface Lewis acid sites and tunable pore size, made ordered mesoporous alumina as a competitive candidate in the field of catalysis.[8] Moreover, it provides a confinement environment which assists the incorporation and dispersion of active metal in its matrix and contributes in the fabrication of high efficient, durable and stable catalysts.[9]

Inspired by the above mentioned properties, we aimed to synthesize iron-doped ordered mesoporous alumina (meso-FeAl by "one-pot" method and subjected to catalytic ODH of 1-butene to BD using CO_2 as oxidant. Samples of Fe_2O_3 impregnated on meso-Al_2O_3 (Fe_2O_3/meso-Al_2O_3) and Fe_2O_3/γ-Al_2O_3 were also prepared to compare the catalytic properties as well as the effect of catalyst structural properties and the existential states of iron species on the catalytic activities of all the three types of catalysts. The loading of Fe in all the three samples was controlled at a comparable level (shown in Table 1).

Table 1. Textural parameters and the loading of Fe of Meso-FeAl, Meso-Al_2O Fe_2O_3/Meso-Al_2O_3 and Fe_2O_3/γ-Al_2O_3.

Sample	BET area (m^2/g)	Volume (cm^3/g)	Diameter (nm)	Loading of Fe[a] (wt%)
Meso-FeAl	382	0.92	6.6	5.23
Meso-Al_2O_3	312	0.81	6.6	0.00
Fe_2O_3/Meso-Al_2O_3	224	0.34	5.6	4.18
Fe_2O_3/γ-Al_2O_3	185	0.56	7.4	4.59

[a] Loading of Fe was determined by ICP.

Figure 1 a shows small-angle XRD patterns of all the three types of catalysts and pure meso-Al_2O_3. The characteristic peaks at ~ 1° and weak diffraction peaks at ~ 1.7° are the reflection indexes of (100) and (110) respectively, demonstrating 2D p6mm hexagonal mesostructure for Meso-Al_2O_3, meso-FeAl and Fe_2O_3/meso-Al_2O_3.[8b] In contrast, Fe_2O_3/γ-Al_2O_3 sample shows no diffraction peak at low angles, suggesting no ordered mesoporous structure exists for conventional catalyst.

Figure 1 b shows wide-angle XRD patterns of all the three types of catalysts as well as pure meso-Al_2O_3. All samples exhibit characteristic peaks for γ-Al_2O_3 (JCPDS Card No. 10-0425). For Fe_2O_3/meso-Al_2O_3 and meso-FeAl, no associated peaks of iron are found, which indicates the high dispersion of

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Fe species. $Fe_2O_3/\gamma\text{-}Al_2O_3$ exhibits the apparent diffraction peaks at 24.138°, 33.152°, 35.611°, 40.854°, 49.479°, 54.089°, 57.428°, 57.589°, 62.449° and 63.989°, which are associated with the $\alpha\text{-}Fe_2O_3$ nanoparticles (JCPDS Card No. 33-0664) and are different from ordered mesoporous samples. These results indicate that the formed $\alpha\text{-}Fe_2O_3$ particles on the surface of $\gamma\text{-}Al_2O_3$ have poor dispersion.

N_2-sorption isotherms and pore size distributions of all the three types of catalysts and pure meso-Al_2O_3 are shown in Figure 1 c and d respectively. It reveals that all the samples possess type-IV isotherms with hysteresis loops which are the characteristics of mesoporous structure. Particularly, H1-type hysteresis loops of meso-FeAl and meso-Al_2O_3 indicate the presence of uniform "cylindrically shaped" channels, with narrow pore size distributions.[9e] On the other hand, $Fe_2O_3/\gamma\text{-}Al_2O_3$ shows H2-type of hysteresis loops which are the typical features of "ink bottle" shape of mesopores structure with extremely wide pore size distribution.[9e] After loading of Fe_2O_3, the meso-Al_2O_3 sample shows a double hole distribution.

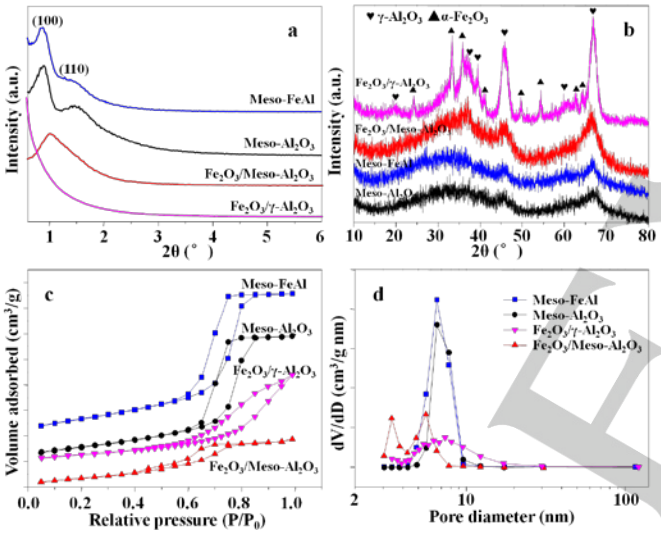

Figure 1. (a) Small- and (b) wide-angle XRD patterns, (c) N_2 sorption isotherms and (d) pore size distributions of Meso-Al_2O_3, Meso-FeAl, Fe_2O_3/Meso-Al_2O_3 and $Fe_2O_3/\gamma\text{-}Al_2O_3$.

Table 1 summarizes the textural parameters of the four samples. Meso-FeAl possesses relatively high specific surface area (382 m^2/g), large pore volume (0.92 m^3/g) with average pore diameter of 6.6 nm. Compared with pure meso-Al_2O_3, the specific surface area, pore volume and average pore diameter of Fe_2O_3/meso-Al_2O_3 have greatly reduced, which suggests the entering of active components into the pore channels of meso-Al_2O_3. The conventional $Fe_2O_3/\gamma\text{-}Al_2O_3$ sample has smaller surface area and pore volume than Meso-FeAl. Over all, the Meso-FeAl sample has uniform mesopores structure, high specific surface area and large pore volume, which promises its potential as a catalyst.

TEM image further made confirm the ordered mesostructure of Meso-FeAl, presenting 1-D cylindrical channels along (110) direction and hexagonally arranged pores along (001) direction (Figure 2 a). Furthermore, EDS elemental maps also display the highly dispersion of iron species in the Meso-FeAl matrix (Figure 2 b). TEM image of Fe_2O_3/meso-Al_2O_3 shows channels along (110) and (001) direction which indicates that the ordered mesostructure remained stable upon loading the active component (Figure 2 c). TEM image of $Fe_2O_3/\gamma\text{-}Al_2O_3$ apparently shows Fe_2O_3 particles on the surface of $\gamma\text{-}Al_2O_3$ (Figure 2 d). In short the ordered mesoporous materials, especially Meso-FeAl shows better dispersion property for active component.

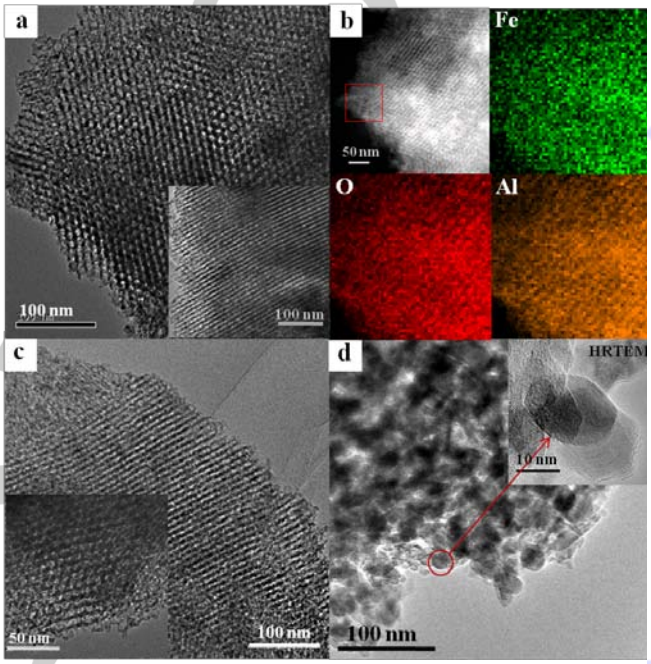

Figure 2. (a) TEM images and (b) EDS elemental maps of Meso-FeAl, TEM images of (c) Fe_2O_3/Meso-Al_2O_3 and (d) $Fe_2O_3/\gamma\text{-}Al_2O_3$.

Catalytic properties were measured by subjecting all the three catalysts to catalytic ODH of 1-butene to BD using CO_2 as soft oxidant (Figure 3). At the beginning (in the first 10 minutes of the reaction), we got 429.7 $g_{BD}/kg_{cat}/h$ BD rate, 13.4 % BD selectivity, 73.7 % 1-butene conversion and 1.5 % CO_2 conversion for $Fe_2O_3/\gamma\text{-}Al_2O_3$ catalyst. The selectivity of BD for this reaction was relatively low, and other byproducts detected were few pyrolysis products (methane, ethane, ethene and propene) and many isomerization products (trans-2-butene and cis-2-butene) (details were shown in the supporting information). In our case, the catalytic properties of $Fe_2O_3/\gamma\text{-}Al_2O_3$ were in the same level as reported earlier for conventional $Fe_2O_3/\gamma\text{-}Al_2O_3$ catalyst.[7b] As BD is the target product of the reaction, therefore we consider the BD rate as a main parameter for evaluating the catalytic properties of the catalysts. In the first 40 minutes of the reaction, the BD rate of conventional $Fe_2O_3/\gamma\text{-}Al_2O_3$ decreases very rapidly, illustrating the poor stability of the catalyst (Figure 3 a, for the catalyst stability, we take the BD rate in the first 40 minutes of the reaction for comparison).

Although, the initial catalytic activity of Fe_2O_3/Meso-Al_2O_3 (408.3 $g_{BD}/kg_{cat}/h$) was almost comparable to that of $Fe_2O_3/\gamma\text{-}$

Al_2O_3, it possessed the poorest stability among the three catalysts. This poor catalytic stability attributed to the coke deposition as well as the existence of unstable active components on the surface of Meso-Al_2O_3 (Figure S4 and S6 in the supporting information).[7b, 9c, 9d]

Compared with Fe_2O_3/γ-Al_2O_3 and Fe_2O_3/Meso-Al_2O_3, Meso-FeAl shows the highest initial activity (752.2 $g_{BD}/kg_{cat}/h$) for BD synthesis, which is about 1.75 times to the activity of Fe_2O_3/γ-Al_2O_3. It also shows high BD selectivity, high CO_2 conversion and excellent stability for BD rate (in the first 40 minutes of the reaction). The excellent catalytic properties of Meso-FeAl might be due to the highly dispersed iron species which are doped inside the alumina matrix. And it was also reported that homogeneous distribution of active sites as well as the strong metal-support interactions were the reason of high catalytic activity and excellent stability for this kind of materials.[9c, 9d] Moreover, high specific surface area and large pore volume of Meso-FeAl also contribute much in BD synthesis.

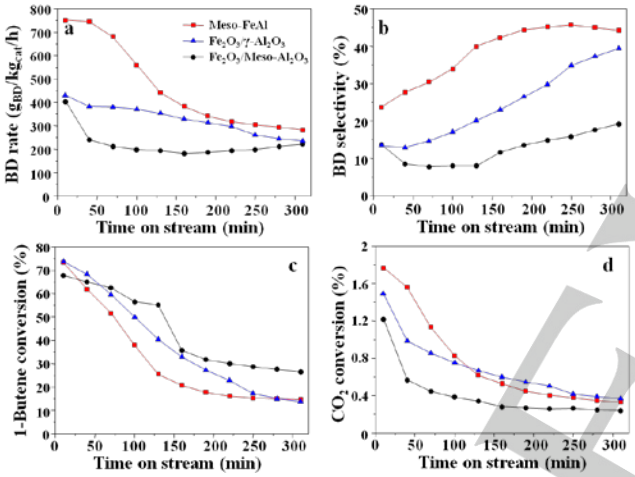

Figure 3. Catalytic properties for Meso-FeAl, Fe_2O_3/γ-Al_2O_3 and Fe_2O_3/Meso-Al_2O_3: (a) BD rate, (b) BD selectivity, (c) 1-butene conversion and (d) CO_2 conversion. Reaction conditions: T = 873 K, P = 0.1 MPa, weight hourly space velocity (WHSV) = 4.5g/g-cat·h, 1-butene/CO_2 = 1:9 (vol.%). (More details were shown in the supporting information.)

In conclusion, we synthesized Meso-FeAl catalyst with ordered mesoporous structure. It shows high specific surface area, large pore volume and high dispersion of iron species in alumina matrix. Furthermore, Meso-FeAl displays effectiveness and stability during catalytic ODH of 1-butene to BD using CO_2 as oxidant. Compared with conventional Fe_2O_3/γ-Al_2O_3, the BD rate of Meso-FeAl improved by 75% (from 429.7 $g_{BD}/kg_{cat}/h$ to 752.2 $g_{BD}/kg_{cat}/h$). We investigated that not only the structural properties but also the existence of iron species in catalyst matrix play important role in BD synthesis. Fruther, We explored that Meso-FeAl is a novel Fe-based catalyst material which has great potential to convert 1-butene to BD using CO_2 as soft oxidant.

Acknowledgements

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Keywords: Iron-doped ordered mesoporous alumina • 1, 3-Butadiene • Oxidative dehydrogenation • CO_2 • 1-Butene

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Entry for the Table of Contents

Layout 1:

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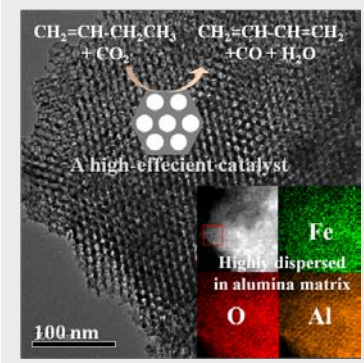
Highly dispersed iron-doped ordered mesoporous alumina was synthesized and demonstrated as an excellent catalyst for carbon dioxide oxidative dehydrogenation of 1-butene. The structural properties as well as the existence form of iron species in catalyst were found to have played a key role in the reaction.



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