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Dynamic Structure evolution of Iron Oxide Catalysts during CO_2 Hydrogenation as Revealed by Operando Techniques

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Highlights
- α-Fe trends to transform into χ-Fe_5C_2, but γ-Fe to θ-Fe_3C during the CO_2 hydrogenation.
- θ-Fe_3C shows higher chain growth ability than χ-Fe_5C_2, while χ-Fe_5C_2 produces more low olefins.
- Structure-performance relationship of α-Fe_2O_3 and γ-Fe_2O_3 catalysts for CO_2 hydrogenation during the activation and reaction processes has been built.

1. Introduction

CO_2 conversion and utilization is arousing great interests as it will facilitate a closing carbon cycle and promote the development of sustainable energy. The catalytic hydrogenation of CO_2 to hydrocarbons (CTH) process provides a promising approach in alleviating the energy shortage and the global warming.[1-2] However, the development of high efficient catalysts is still a big challenge for this process. Hence, rational design and controllable synthesis of the CTH catalysts is the key to accelerate the commercialization of this process. *Operando* techniques have opened up new vistas that allow visualization of the active phases/sites evolution during reactions [3], especially at high pressures and high temperatures. The rational design and controllable synthesis should still be the ultimate goal for chemists or chemical engineers. The greatest challenge is how to establish the relationship of structure and performance of industrial catalysts under real reaction conditions.

Recently, with the combination of *Operando* Raman spectroscopy, *Operando* X-ray diffraction (XRD), and some other techniques, such as X-ray Photo-electron Spectroscopy (XPS), Temperature-Programmed techniques and in situ DRIFTS, we studied the iron oxide catalysts for CTH process from birth to death under harsh reaction conditions. Surface-Subsurface-Bulk structures of Fe-based catalysts before and after CO_2 hydrogenation, have been elaborated to explore the structure evolution of the catalysts Such a study is critical for us to explore the reaction mechanism and to design the next generation industrial catalysts.

2. Methods

Catalyst source: High purity of α-Fe_2O_3 and γ-Fe_2O_3 (Aladdin, 99.5%) were used as reference samples. Fe_5C_2 and Fe_3C were synthesized in situ by exposing the α-Fe_2O_3 (Aladdin, 99.5%, 30 nm) to a pure CO flow (99.995%, 25 mL/min), subsequently heating up to 350 ^oC and 450 ^oC , respectively, at 2 ^oC/min and then keeping for 2 h. [4]

Operando techniques: The laser Raman spectra were recorded with a home-build Operando setup using a confocal Raman spectroscopy (LabRAM HR, Horiba J.Y.) equipped with a high-grade Leica microscope (long working distance objective 50x). XRD patterns were recorded using Riguku D/max 2550 diffractometer with accelerated voltage 40 kV and detector current 100 mA. Cu-Kα (λ =51.540589 Å) radiation was used for a continuous scanning with the step-size of 0.01^o over a 2 theta range 10-80 ^{o}. The scan speed was 4 ^{o}/min.

3. Results and discussion

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A comparison study has been performed over two different commercial iron oxides, i.e., α-Fe$_2$O$_3$ and γ-Fe$_2$O$_3$, under CTH process. A selectivity of 2.87 % and 15.60 % for C$_{5+}$, and reaction rate of 8.54 mmol/g$_{Fe}$/h and 21.48 mmol/g$_{Fe}$/h of α-Fe$_2$O$_3$ and γ-Fe$_2$O$_3$ were measured, respectively. It indicates that, compared to α-Fe$_2$O$_3$, the activated γ-Fe$_2$O$_3$ facilitates the production of long-chain hydrocarbons due to its strong chain-growth ability.

With the combination of *Operando* Raman spectroscopy and *Operando* XRD, The panoramic structure evolution of iron oxides (α-Fe$_2$O$_3$ and γ-Fe$_2$O$_3$) during CTH process were elaborated., i.e. α-Fe$_2$O$_3$ (γ-Fe$_2$O$_3$)$\rightarrow\alpha$-Fe$_3$O$_4$ (γ-Fe$_3$O$_4$)$\rightarrow\alpha$-Fe (γ-Fe)$\rightarrow\chi$-Fe$_5$C$_2$ (θ-Fe$_3$C). In the meantime, the activated α-Fe$_2$O$_3$ and γ-Fe$_2$O$_3$ could exclusively transform to χ-Fe$_5$C$_2$ and θ-Fe$_3$C, respectively, and both iron carbides show high activities. Moreover, χ-Fe$_5$C$_2$ showed higher selectivity to lower olefins but weaker chain growth probability than θ-Fe$_3$C. The preliminary relationship of catalyst structure and performance of iron catalysts under harsh working conditions was established (Figure 1.).
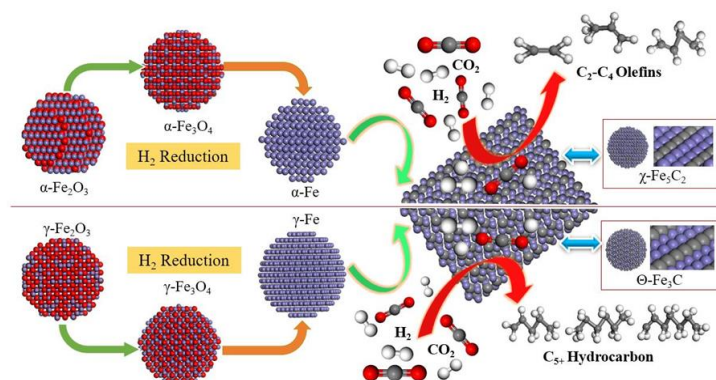

Figure 1. Scheme of structure-performance relationship of α-Fe$_2$O$_3$ and γ-Fe$_2$O$_3$ catalysts for CO$_2$ hydrogenation during the activation and reaction processes.

4. Conclusions

In summary, using operando techniques complemented with control experiments, the structure evolution and structure-performance relationship of α-Fe$_2$O$_3$ and γ-Fe$_2$O$_3$ catalysts during CTH process have been illustrated under real reaction conditions. Specifically, the different catalytic performance of α-Fe$_2$O$_3$ and γ-Fe$_2$O$_3$ could be attributed to the generation of χ-Fe$_5$C$_2$ and θ-Fe$_3$C, respectively. Furthermore, control experiments showed that the higher selectivity of lower olefins on χ-Fe$_5$C$_2$ is due to its weaker basicity and alkenes hydrogenation ability, while the high selectivity of C$_{5+}$ hydrocarbons on θ-Fe$_3$C is caused by its strong basicity which can enhance the chain-growth ability of adsorbed carbonaceous species. We believe this work will be beneficial to the rational design and optimization of catalysts for CO$_2$ hydrogenation reaction.

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