

## MgO modification of Fe-based Al<sub>2</sub>O<sub>3</sub> catalysts for the conversion of syngas to light olefins

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### Highlights

- Magnesium aluminate spinel was formed after the supports were calcined at 700 °C and above. The specific surface changed little in the order of 30 m<sup>2</sup>/g with the mol ratio of MgO/Al<sub>2</sub>O<sub>3</sub> varied.
- CO conversion was 92%, and the selectivity of C<sub>2</sub>=-C<sub>4</sub>= was 31% at the optimum conditions (1.5 MPa, 340 °C, 1500 mL·g<sup>-1</sup>·h<sup>-1</sup>).

### 1. Introduction

Light olefins are mainly made from petrochemical industry. These short-chain hydrocarbons including ethylene and propylene are traditionally produced by steam cracking of naphtha or as byproducts of oil refining processes. Fischer–Tropsch synthesis obtains long-chain hydrocarbons from syngas (a mixture of H<sub>2</sub> and CO)<sup>[1-4]</sup>. A promising process to produce lower olefins from synthesis gas is so-called FTO process<sup>[5]</sup>. A variety of catalysts have been explored for FTO reaction<sup>[6]</sup>.

Unsupported iron oxide catalysts have been investigated, and in some cases they have exhibited high selectivity towards lower olefins when the iron was modified by the addition of promoters. However, the bulk catalysts are mechanically unstable when the reaction is performed at high temperature, which would switch product selectivity to higher hydrocarbons. Under these conditions, the undesirable boundouard reaction  $2\text{CO}(\text{g}) \rightarrow \text{C}(\text{s}) + \text{CO}_2(\text{g})$ , leads to the deposition of carbon<sup>[7]</sup>.

The poor mechanical stability of the bulk catalysts may lead to plugging of the catalyst bed in fixed-bed operation or to fouling of the separation equipment in a fluidized bed process<sup>[7]</sup>. To overcome the low activity and stability problems, the use of supported iron catalysts have been explored.

The FTO reaction is a structure sensitive reaction. The catalytic performance is strongly related to the particle size of the metal or active phase. The addition of support changed the morphology of the catalyst and affects the particles size and dispersion.

Iron forms mixed oxides when supported on alumina or silica which are difficult to reduce, and the formation of the active iron carbide phase is hindered. The MgO supported catalyst shown a more dispersion of the particles and also has shown lower particles adhesion, consequently shown a better catalytic performance<sup>[8]</sup>. In the case of CNF supported catalysts, iron loading is directly related to particle size, thus higher iron contents result in larger iron-containing particles. The iron nanoparticles supported on CNF have narrow size distributions and they are homogeneously distributed on the support<sup>[9,10]</sup>. In order to optimize the support of FTO catalysts, MgO modified Al<sub>2</sub>O<sub>3</sub> supports have been studied in this research.

### 2. Methods

#### Supports preparation

MgO modified Al<sub>2</sub>O<sub>3</sub> supports have been synthesized by co-precipitation method and co-complexation. Mixture MgO·Al<sub>2</sub>O<sub>3</sub> supports are prepared from Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub>·9H<sub>2</sub>O and precipitation or complexation reagents, and then dried at 100 °C. NH<sub>3</sub>, citric acid (CA) and ethylenediaminetetraacetic acid (EDTA) have been used as precipitation or complexation reagents. The calcination of mixture have been done for 5h at 900 °C in air.

#### Catalysts preparation

With magnesium nitrate[Mg(NO<sub>3</sub>)<sub>2</sub>] and aluminium nitrate[Al(NO<sub>3</sub>)<sub>3</sub>] as precursors, we prepared a series of magnesium aluminate spinel supports and iron-based catalyst loading with K and Mn promoters,

which were characterized by XRD, BET and SEM to investigate the influence of preparation conditions on their structure. The FTO was performed at 1.2 MPa and 300 °C in a fixed bed reactor. The catalyst was reduced at 350 °C by mixed H<sub>2</sub> and N<sub>2</sub> (flow rate of H<sub>2</sub>/N<sub>2</sub> is 1/3) for 12h.

#### Catalytic reaction

Catalytic reaction were performed on a fixed-bed reactor. The catalyst was loaded in the reactor and reduced at 350 °C by mixture of H<sub>2</sub> and N<sub>2</sub> with total flow rate of 160 mL/min, which contains 20% H<sub>2</sub>. The temperature and pressure were increased to 340 °C and 1.5 MPa, respectively. The products were analyzed by online gas chromatography.

### 3. Results and discussion

The morphology of the supports varied with the mol ratio of MgO /Al<sub>2</sub>O<sub>3</sub>, but the specific surface changed little in the order of 30 m<sup>2</sup>/g. FTO reaction was recognized as a structure sensitive reaction which means that the catalytic performance is strongly related to the particle size of the metal or active phase.

Different agents (EDTA and CA) had no effect on characteristic peak pattern and position of magnesium aluminate spinel on XRD patterns. When the calcination temperature increased, the peaks of magnesium aluminate spinel didn't change, but the peaks became sharper and denser. Although there were characteristic peaks of magnesium oxide when the content of magnesium increased, there are obvious characteristic peaks of magnesium aluminate spinel, indicating that magnesium aluminate spinel was formed.

CO conversion increased with the temperature, but the selectivity of C<sub>2</sub><sup>=</sup>-C<sub>4</sub><sup>=</sup> decreased slightly. The increase of reaction space velocity caused CO conversion decreased rapidly and sharply but the selectivity of C<sub>2</sub><sup>=</sup>-C<sub>4</sub><sup>=</sup> changed very little. Both CO conversion and the selectivity of C<sub>2</sub><sup>=</sup>-C<sub>4</sub><sup>=</sup> changed slightly with the increase of reaction pressure. The content of synthesis gas in the feed gas had a great influence on CO conversion, while have a little effect on the the selectivity of C<sub>2</sub><sup>=</sup>-C<sub>4</sub><sup>=</sup>. Under the optimum conditions (1.5 MPa, 340 °C, 1500 mL·g<sup>-1</sup>·h<sup>-1</sup>), CO conversion was 93%, and the selectivity of C<sub>2</sub><sup>=</sup>-C<sub>4</sub><sup>=</sup> was 31%.

### 4. Conclusions

Spinel phase was formed after the supports were calcined at 700 °C and above. The specific surface changed little in the order of 30 m<sup>2</sup>/g with the mol ratio of MgO/Al<sub>2</sub>O<sub>3</sub> varied.

Different ratio of MgO/Al<sub>2</sub>O<sub>3</sub> give different shapes of the mixed oxide layer. Catalytic performance is strongly related to the active phase–support interaction in FTO reacton.

Reaction condition has been optimized as 1.5 MPa, 340 °C, 1500 mL·g<sup>-1</sup>·h<sup>-1</sup>. CO conversion was 92%, and the selectivity of C<sub>2</sub><sup>=</sup>-C<sub>4</sub><sup>=</sup> was 31% at this condition.

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#### Keywords

FTO; Spinel; Syngas; Light Olefins;