

Hydrogenation of carbon oxides over promoted Fe-Mn catalysts prepared by the microemulsion methodology

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Abstract

The microemulsion technology was used in order to improve the preparation of iron-based catalysts for the CO and CO₂ hydrogenation reactions. This technique led to a sample with a higher surface area when compared with a similar solid prepared by conventional precipitation. As a consequence, a higher catalytic activity was obtained.

The hydrogenation of carbon oxides was also performed over promoted iron-manganese catalysts. The preparation of these samples by the microemulsion methodology yielded to homogeneous mixed oxides. Manganese-containing catalysts presented a higher activity towards the formation of hydrocarbons, at the same conversion levels, than the iron counterparts.

These catalysts were promoted with copper, sodium and potassium. Carbon dioxide conversion was favoured by alkaline addition, especially by potassium, due to the promotion of the water-gas shift reaction. Furthermore, alkaline promotion enhanced selectivity towards long-chain products either in CO₂ and CO hydrogenation processes. Addition of copper caused a more facile reducibility of the solids, resulting in a significant increment in both carbon monoxide and carbon dioxide conversion without modifying products selectivity.

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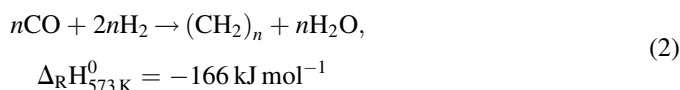
1. Introduction

Fischer–Tropsch Synthesis (FTS), consisting of the CO hydrogenation to hydrocarbons, has been an important topic in the last years and it is currently attracting a renewed interest as a key technology for the production of clean transportation fuels and chemicals [1,2]. The products derived from Fischer–Tropsch Synthesis are endowed with a tremendous environmental value due to the lack of harmful substances such as sulphur, nitrogen and aromatic compounds. The starting feedstock of this reaction, the so-called synthesis gas or syngas, is a mixture of H₂ and CO with different H₂/CO ratios. This mixture can be produced from coal, natural gas or biomass [3]. When coal or biomass are used as source, the resulting syngas contains large amounts of carbon dioxide, thus demanding expensive purification steps (about 5\$/MT CO₂) [4] which increase significantly the process expenses.

Unlike CO hydrogenation, the understanding of carbon dioxide hydrogenation process is still a major challenge. There have been various attempts to transform carbon dioxide into hydrocarbons, mainly using those catalysts that have been proved active in the Fischer–Tropsch Synthesis, such as Ni, Ru and Co. Most attempts yielded methane as the only product, even if water-gas shift active promoters were added [5]. It seems likely that carbon dioxide hydrogenation proceeds *via* a two-step reaction mechanism [6]. In the first step, carbon dioxide is converted into carbon monoxide through the reverse water-gas shift reaction:



The carbon monoxide produced in this way reacts subsequently according to the Fischer–Tropsch Synthesis producing mainly hydrocarbons:



Some authors have also proposed a mechanism which implies direct carbon dioxide hydrogenation [7,8]. Such reaction

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pattern would only apply for processes carried out under relatively severe conditions (temperature over 673 K). Under reaction conditions similar to those employed in the present work, CO₂ conversion into hydrocarbons occurred mainly *via* CO intermediates as proved by using isotopic-marked carbon dioxide in the feed [9].

Iron oxides have been used as Fischer–Tropsch (FT) catalysts for many years [10,11]. Besides, they are active in both water-gas shift and reverse water-gas shift reactions [12]. In principle, iron-based catalysts would be ideal candidates to be used in the Fischer–Tropsch Synthesis of CO₂-containing syngas feeds [1,13]. Moreover, iron catalysts are attractive because of the highly olefinic nature of the obtained products which allows their use as a feedstock for chemical industry [14]. However, pure iron catalysts have some drawbacks like a high selectivity to non-desired products such as methane [15] or rapid deactivation. Therefore, promoters must be added in order to improve their stability and to tune the selectivity.

It has been reported that manganese, as a promoter for iron catalysts, enhances the activity of iron-based FT catalysts [16,17], particularly in producing short-chain olefins [18–21]. The catalytic behaviour of mixed iron-manganese oxides was found to be influenced by the preparation technique and the structural properties of the catalytic precursors [22,23].

Alkaline elements are used as promoters because they can modify the adsorption pattern of the reactants (H₂ and CO) on the active sites. The overall effect of potassium on the behaviour of iron-based FTS catalysts, *i.e.*, CO chemisorption enhancement, has been justified as a consequence of the iron tendency to withdraw electronic density from potassium, resulting in a strengthening of the Fe–CO bond [24]. The enhancement in carbon monoxide chemisorption leads to the increment of the selectivity towards olefins and high molecular products along with the depleting of methane formation [25]. Nearly all commercial iron-based catalysts contain potassium amongst several other promoters. When potassium loading is high, CO dissociation proceeds faster than carbon hydrogenation, leading to an excessive carbon deposition that eventually deactivates the catalyst surface. Jiang et al. [26] investigated the effect of potassium on Fe–Mn catalysts by *in situ* Diffuse Reflectance Infrared Fourier Transformed Spectroscopy (DRIFTS). Their results indicated a moderate interaction between potassium and surface iron species that promotes iron oxide reduction to form fine metallic iron clusters. Although potassium is the most common alkaline promoter used, there have been some attempts to study the effect of other alkaline and alkaline-earth elements [5,27,28]. However, the difference amongst alkaline promoters has not been satisfactorily explained yet. Although the effect on the FT performance by potassium promotion of iron-based catalysts has been extensively investigated, not many papers have been published dealing with the effect of potassium on the manganese-promoted precipitated iron catalysts [24]. It has been reported that the addition of alkali metals to Fe–Mn catalysts improves the selectivity to alkenes. Therefore, it is assumed that the interaction between surface iron and the surface manganese species is somehow altered by the presence of potassium [28].

Copper is usually added to iron-based Fischer–Tropsch catalysts because of its ability to enhance hematite reducibility [29]. When copper oxide is reduced to metallic Cu, the crystallites formed provide H₂ dissociation sites, which in turn lead to reactive hydrogen species that are capable to reduce Fe oxides at lower temperatures.

The method of catalyst preparation plays an important role in the physical properties and catalytic performance of the catalysts. In this work, the microemulsion technology has been chosen as preparation method in order to obtain a series of Fe–Mn oxides displaying a homogeneous distribution of both elements throughout the solid. A microemulsion is an optically transparent and thermodynamically stable dispersion of a water phase into an organic phase stabilized by a surfactant [30]. If the minority phase is the aqueous one, then reversed micelles are obtained. In the last years, it has been generalized the use of microemulsions as nanoreactors in order to synthesize nanoparticles of controlled size [31,32].

Amongst advantages such as rendering nanosized particles, usually displaying high surface area and low microporosity, microemulsion is an ideal technique for the preparation of materials containing two (or more) metallic or oxide phases. The different species (oxide precursors) are homogeneously mixed within the micelles, therefore rendering solids displaying high internal homogeneity and an optimal interaction between its constituents [32]. Some authors have prepared supported iron-based Fischer–Tropsch catalysts by microemulsion, reporting high activity and marked selectivity to oxygenates [33]. However, there are still few works dealing with the preparation of non-supported catalysts even though the synthesis of mixed ferrites by microemulsion has been reported [34,35].

In the present work, the catalytic performance of Fe–Mn samples in the CO₂ hydrogenation reaction was studied. The expected path for this reaction is the following: (i) water-gas shift reaction to produce CO and (ii) CO hydrogenation. Therefore, the performance of the samples in the CO hydrogenation reaction was previously evaluated. We have found that the extension of the CO₂ hydrogenation accounts for both water-gas shift and CO hydrogenation processes.

The influence of some promoters, such as Na, K and Cu, on the catalytic performance of Fe–Mn mixed oxides in the hydrogenation of carbon monoxide and carbon dioxide has been also studied.

2. Experimental

2.1. Catalysts preparation

The Fe–Mn catalyst precursors were prepared by coprecipitation in a water-in-oil microemulsion. A water solution of metal precursors, Fe(NO₃)₃·9H₂O (Fluka puriss, p.a. ACS: 98–100%) and/or Mn(NO₃)₂·4H₂O (Fluka, purum, p.a. >97%) was added to a mixture of an oil phase (isooctane, Aldrich, >99%) and the commercial available non-ionic surfactant Tergitol 15-S-5, which consists in a secondary alcohol ethoxylate {C_{12–14}H_{25–29}O(CH₂–CH₂O)_x} with hydrophilic-to-lipophilic

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