Effects of Potassium and Manganese Promoters on Nitrogen-Doped Carbon Nanotube-Supported Iron Catalysts for CO2 Hydrogenation

Praewpilin Kangvansura\(a\), Ly May Chew\(b\), Chanapa Kongmark\(c\), Phatchada Santawaja\(d\), Holger Ruland\(b\), Wei Xia\(b\), Hans Schulz\(c\), Attera Worayingyong\(c\), Martin Muhler\(b,⁎\)

\(a\) Scientific Equipment Center, Faculty of Science, Kasetsart University, Bangkok 10900, Thailand
\(b\) Laboratory of Industrial Chemistry, Ruhr-University Bochum, Bochum 44780, Germany
\(c\) Department of Materials Science, Faculty of Science, Kasetsart University, Bangkok 10900, Thailand
\(d\) Department of Chemistry, Faculty of Science, Kasetsart University, Bangkok 10900, Thailand
\(e\) Engler-Bunte-Institute, Karlsruhe Institute of Technology, Karlsruhe 76131, Germany

**Abstract**

Nitrogen-doped carbon nanotubes (NCNTs) were used as a support for iron (Fe) nanoparticles applied in carbon dioxide (CO2) hydrogenation at 633 K and 25 bar (1 bar = 105 Pa). The Fe/NCNT catalyst promoted with both potassium (K) and manganese (Mn) showed high performance in CO2 hydrogenation, reaching 34.9% conversion with a gas hourly space velocity (GHSV) of 3.1 L·(g·h)\(^{-1}\). Product selectivities were high for olefin products and low for short-chain alkanes for the K-promoted catalysts. When Fe/NCNT catalyst was promoted with both K and Mn, the catalytic activity was stable for 60 h of reaction time. The structural effect of the Mn promoter was demonstrated by X-ray diffraction (XRD), temperature-programmed reduction (TPR) with molecular hydrogen (H\(_2\)), and \textit{in situ} X-ray absorption near-edge structure (XANES) analysis. The Mn promoter stabilized wüstite (FeO) as an intermediate and lowered the TPR onset temperature. Catalytic ammonia (NH\(_3\)) decomposition was used as an additional probe reaction for characterizing the promoter effects. The Fe/NCNT catalyst promoted with both K and Mn had the highest catalytic activity, and the Mn-promoted Fe/NCNT catalysts had the highest thermal stability under reducing conditions.

© 2017 THE AUTHORS. Published by Elsevier LTD on behalf of the Chinese Academy of Engineering and Higher Education Press Limited Company. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

**Keywords:** CO2 hydrogenation, Iron catalyst, Nitrogen-doped carbon nanotubes, Manganese promoter, Potassium promoter

**1. Introduction**

Emission of the primary greenhouse gas, carbon dioxide (CO2), from human activities has continuously risen in recent years. Hydrogenation of CO2 is considered to be an alternative route for converting it to valuable chemicals and fuel. It is generally accepted that the hydrogenation process occurs in two consecutive reactions: the reverse water gas shift (RWGS) reaction, followed by the Fischer-Tropsch synthesis (FTS), as described in Eqs. (1) and (2) [1,2]:

\[
\text{RWGS: } \text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O} \quad \Delta_H^{\text{H}_2\text{O} \text{at}} = 38 \text{kJ} \cdot \text{mol}^{-1} \quad (1)
\]

\[
\text{FTS: } n\text{CO} + (2n+1)\text{H}_2 \rightarrow \text{C}_n\text{H}_{2n+2} + n\text{H}_2\text{O} \quad \Delta_H^{\text{C}_2\text{H}_5\text{O} \text{at}} = -166 \text{kJ} \cdot \text{mol}^{-1} \quad (2)
\]

The reaction of molecular hydrogen (H\(_2\)) and CO\(_2\) to produce water (H\(_2\)O) and carbon monoxide (CO) is the RWGS reaction, which is industrially catalyzed by magnetite (Fe\(_3\)O\(_4\)). CO, which is produced as the reactant gas for the FTS reaction, is catalytically converted in the presence of H\(_2\) into hydrocarbons through a surface hydrogenation-polymerization reaction. FTS is catalyzed by metals such as cobalt (Co), iron (Fe), or ruthenium (Ru). Fe catalysts have been a favored choice in CO\(_2\) hydrogenation because they are readily available and have a high RWGS activity, producing olefins and branched hydrocarbons. Co catalysts are not suitable for CO\(_2\) hydrogenation, even with added RWGS promoters such as manganese (Mn) and potassium (K), because the partial pressure of the CO produced is too low [3–5].

Riedel et al. [6] found that the trends of catalytic activity and selectivity in both processes were almost the same when using K-promoted Fe catalysts for CO/H\(_2\) and CO\(_2)/\text{H}_2\) synthesis. The duration...
of different kinetic regimes was longer when using CO$_2$/H$_2$ than when using CO/H$_2$. Their product selectivity results indicated that the CO$_2$ hydrogenation reaction occurs together with CO hydrogenation (FTS reaction) [7,8]. They also reported that iron carbide (Fe$_3$C) formed on the Fe catalyst surface via CO produced from the RWGS reaction [6]. For Fe catalysts, the formation of surface carbides is required before the catalyst can exhibit Fischer-Tropsch (FT) activity [4,9–15]. Potassium is assumed to enhance basicity and to inhibit H$_2$ dissociative adsorption [6,7,16,17]. In this way, it increases olefin selectivity and chain-growth probability, suppresses methane formation, and improves iron carbide formation [15,18,19]. Nevertheless, carbon deposition on the iron carbide phase induces catalyst deactivation. Manganese acts as a structural and electronic promoter, enhancing the dispersion of iron oxide on the surface and suppressing reduction and carburization of the catalyst in the syngas reduction process. As a result, it decreases the deactivation rate of Fe catalysts under FTS reaction conditions [20–22]. Davis [23] proposed that an oxygen-containing structure as a formate species could form from either CO or CO$_2$ for chain initiation. Under reaction conditions, the catalyst consists of a core of Fe$_{3}O_{4}$, which is covered by a layer of iron carbide. During the reaction, the layer of iron carbide must be maintained.

Carbon nanotubes (CNTs) are promising support materials [24–27] due to their large surface area and their ability to disperse catalytically active nanoparticles [28]. They also prevent sintering, thus improving the stability and activity of Fe FTS catalysts [8,17]. Oxygen- and nitrogen-containing functional groups in CNTs are assumed to act as coordination sites for metal active species [24,25]. Nitrogen-doped CNTs (NCNTs) can be obtained by the post-treatment of partially oxidized CNTs (OCNTs) in flowing ammonia (NH$_3$) [24,29]. Kundu et al. [29] found that after an NH$_3$ treatment at 673 K, NCNTs contain mainly pyridinic groups, which are considered to be coordination sites for metal active species. A mixture of 49% wüstite (FeO) and 51% metallic iron was observed by Chew et al. [2] after 5 h at 753 K. Fe/NCNT, Fe/OCNT, and Fe/SlO$_2$ were used for CO$_2$ hydrogenation, with Fe/NCNT having a lower CO selectivity than Fe/OCNT. Fe/SlO$_2$ was found to be much less suitable for CO$_2$ hydrogenation compared with the CNT-supported catalysts. The C$_x$–C$_y$ hydrocarbon selectivities that were obtained with Fe/NCNT were clearly higher than those obtained with Fe/OCNT. Based on the proposed CO$_2$ hydrogenation reaction step, CO produced from the RWGS reaction is hydrogenated to hydrocarbons. Chew et al. [2] concluded that the hydrogenation of CO on Fe/NCNT was faster than the reaction on Fe/OCNT, and that all catalysts after the reaction were in the carbidized state.

The decomposition of NH$_3$ is a reaction that is catalyzed by many transition metal surfaces [30,31]. Recombinative desorption of chemisorbed atomic nitrogen is the rate-determining step in NH$_3$ decomposition [30]. Thus, NH$_3$ decomposition was used to characterize the effects of promoters on the thermal stability of the reduced catalysts.

This study focuses on the effect of K and Mn on the activity, product selectivity, and thermal stability of NCNT-supported Fe catalysts. Iron nanoparticles supported on NCNTs were synthesized via impregnation. Phase analysis was performed by X-ray diffraction (XRD). Temperature-programmed reduction with H$_2$ (H$_2$-TPR) and in situ X-ray absorption near-edge structure (XANES) analysis were used to investigate the reducibility of the Fe catalysts. NH$_3$ decomposition and CO$_2$ hydrogenation over K/Mn-promoted iron nanoparticles supported on NCNTs were applied to assess the catalytic performance of the Fe catalysts and to probe the promoter effects. A recent study focused on the influence of the promoters on the product distribution [32].

2. Experimental section

2.1. Catalyst preparation

The Fe catalysts were synthesized by the impregnation of NCNTs using ammonium ferric citrate (C$_6$H$_{8}$O$_7$·Fe$^{3+}$·3NH$_3$) as an Fe precursor [29,33,34] followed by impregnation with aqueous solutions of manganese (II) nitrate hydrate [Mn(NO$_3$)$_2$·xH$_2$O] and potassium carbonate (K$_2$CO$_3$) to obtain the K- and Mn-promoted Fe catalyst (K/Mn/Fe/NCNT), as described in detail in Ref. [32].

2.2. Characterization

The actual catalyst compositions were determined quantitatively using atomic absorption spectrometry (AAS). XRD was performed to determine the crystalline phases present in the catalysts using a diffractometer (PANalytical; X’Pert PRO MPD) with Cu K$_\alpha$ radiation ($\lambda$ = 1.54 Å) and an electron current of 40 mA with an accelerating voltage of 45 kV. The spectra were scanned with a step size of 0.026° in the 2θ range of 20°–80°. The identification of crystalline phases was accomplished using the inorganic crystal structure database (ICSD). H$_2$-TPR was performed by heating 40 mg of catalyst with a heating rate of 10 K·min$^{-1}$ in a mixture gas of 4.73% H$_2$ in argon (Ar) with a flow rate of 84.1 cm$^3$·min$^{-1}$. The sample was heated from 323 K to 1073 K and held at that temperature for 1 h.

The reduction behavior of the catalysts was monitored using in situ XANES analysis under a hydrogen atmosphere at the time-resolved X-ray absorption spectroscopy (XAS) beamline (BL2.2) of the Synchrotron Light Research Institute (SLRI) in Thailand. A bent crystal Si(111) in the energy-dispersive monochromator was used to focus a polychromatic X-ray beam onto the sample [35]. The X-rays pass through the sample and then diverge toward a position-sensitive detector (an NMOS-linear image sensor), with a data collection time of 250 ms. Samples of 4.5 mg were prepared as 4 mm diameter pellets. In situ Fe K-edge XANES analysis was carried out during the catalyst reduction using 4 cm$^3$·min$^{-1}$ of H$_2$ and 80.1 cm$^3$·min$^{-1}$ of Ar, heating from 323 K to 923 K (10 K·min$^{-1}$), and subsequently holding this temperature for 2 h. Iron foil was used to calibrate the Fe K-edge absorption peak at 7112 eV. Linear combination analysis was performed using the Athena software [36]. Iron foil, FeO, Fe$_3$O$_4$, and hematite (Fe$_2$O$_3$) were used as references.

2.3. Catalytic tests

NH$_3$ decomposition was conducted as a test reaction in order to probe the promoter effects and the thermal stability of the reduced catalysts. The NH$_3$ decomposition experiments were carried out in a quartz U-tube reactor. A mixture of 10 mg of catalyst and 100 mg of silicon carbide (SiC) was packed between quartz wool plugs. Before the catalytic test, the catalyst was purged using 25 cm$^3$·min$^{-1}$ of helium (He) for 30 min at room temperature; next, it was reduced using 25 cm$^3$·min$^{-1}$ of H$_2$ at 673 K with a heating rate of 5 K·min$^{-1}$ for 1 h. The reactor was cooled to 323 K and 25 cm$^3$·min$^{-1}$ of He to flush out H$_2$. Subsequently, the reactant gases (5 cm$^3$·min$^{-1}$ of 10% NH$_3$ in He and 45 cm$^3$·min$^{-1}$ of He) were fed to the reactor for approximately 20 min to obtain constant flow conditions. The reactor was then heated to 923 K with a 5 K·min$^{-1}$ heating rate, and this temperature was subsequently held for 1 h. Afterward, the reactor was cooled from 923 K to room temperature with a 5 K·min$^{-1}$ rate in the same atmosphere. The effluent was connected to a non-dispersive infrared (IR) detector (Rosemount Analytical, NGA 2000) to monitor the NH$_3$ concentration.

For CO$_2$ hydrogenation, a mixture of 40 mg of catalyst and 160 mg
of SiC was loaded into the reactor and placed between quartz wool plugs. SiC was used as a diluent to minimize the effect of heat generated by the mildly exothermic reaction. Before the catalytic test, the catalyst was reduced at 653 K and 25 bar (1 bar = 10^5 Pa) under 50 cm^3·min⁻¹ of H₂ for 5 h. The reactor was then cooled to 633 K under 30 cm^3·min⁻¹ of Ar to flush out H₂. The reactant gases (22.5 cm^3·min⁻¹ of H₂, 7.5 cm^3·min⁻¹ of CO₂, and 3.3 cm^3·min⁻¹ of Ar) were passed through the catalyst bed with a gas hourly space velocity (GHSV) of 50 L(g.h)^⁻¹ at 633 K and 25 bar. The products were directly measured by an online gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) and two flame ionization detectors (FIDs) using argon as the internal standard. The experimental setup is described in detail elsewhere [37].

### 3. Results and discussion

Table 1 [32] summarizes the metals’ weight percentages in the calcined samples, as analyzed via AAS. The XRD patterns of the unpromoted Fe/NCNT and the promoted Fe/NCNT samples after calcination revealed the presence of Fe₃O₄ as a major iron phase in all catalysts, in addition to hexagonal graphite [32].

Fig. 1 shows the TPR profiles of the calcined Fe/NCNT, K/Fe/NCNT, Mn/Fe/NCNT, and K/Mn/Fe/NCNT catalysts. For the unpromoted iron catalysts, in addition to hexagonal graphite [32]. At the beginning of the reduction, most of the calcined precursors consisted of a mixture of hematite and magnetite phases, except for Fe/NCNT, which was mainly composed of hematite. The reduction of hematite to magnetite started at around 473 K, 473 K, 613 K, and 523 K for Fe/NCNT, K/Fe/NCNT, Mn/Fe/NCNT, and K/Mn/Fe/NCNT, respectively. This phase transformation occurred progressively until the hematite fully transformed into magnetite at about 593 K and 623 K for the K-promoted catalysts K/Fe/NCNT and K/Mn/Fe/NCNT, respectively. In contrast, a coexistence of magnetite and wüstite was found at the depletion of hematite at about 513 K and 773 K for Fe/NCNT and

<p>| Table 1 Composition of metals in the catalysts [32]. |</p>
<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe/NCNT</td>
<td>Fe 34.2 K — —</td>
</tr>
<tr>
<td>K/Fe/NCNT</td>
<td>Fe 31.2 K 1.3 —</td>
</tr>
<tr>
<td>Mn/Fe/NCNT</td>
<td>Fe 32.8 K — 7.1</td>
</tr>
<tr>
<td>K/Mn/Fe/NCNT</td>
<td>Fe 22.5 K 1.0 5.4</td>
</tr>
</tbody>
</table>

Fig. 1. H₂-TPR profiles of the calcined (a) Fe/NCNT, (b) K/Fe/NCNT, (c) Mn/Fe/NCNT, and (d) K/Mn/Fe/NCNT precursors before reaction.
Fig. 2. XANES spectra of (a) Fe/NCNT, (b) K/Fe/NCNT, (c) Mn/Fe/NCNT, and (d) K/Mn/Fe/NCNT during heating from 323 K to 923 K (10 K·min$^{-1}$) using a flow rate of 4 cm$^3$·min$^{-1}$ of H$_2$ and 80.1 cm$^3$·min$^{-1}$ of Ar.

Fig. 3. Phase evolution of the Fe catalysts under in situ XANES reduction conditions: 4 cm$^3$·min$^{-1}$ of H$_2$ and 80.1 cm$^3$·min$^{-1}$ of Ar, heating from 323 K to 923 K with a heating rate of 10 K·min$^{-1}$ and holding for 2 h as a function of temperature. (a) Fe/NCNT; (b) K/Fe/NCNT; (c) Mn/Fe/NCNT; (d) K/Mn/Fe/NCNT.
Higher activity of NH₃ decomposition over K/Fe/NCNT. In addition, NH₃ did not decompose on heating up to 923 K during the blank experiment, excluding thermal decomposition at temperatures below 923 K in all the experiments. The onset temperatures for NH₃ decomposition were almost the same for all the catalysts, at about 530 K. The degree of NH₃ conversion over Fe/NCNT increased during heating and reached about 98% at 923 K, indicating that Fe nanoparticles supported on NCNTs were active for NH₃ decomposition. The conversion of NH₃ decreased from 98% to 87% during holding at 923 K for 1 h, indicating deactivation of the catalyst. NH₃ adsorbs on an empty site of the metallic iron surface, followed by sequential NH₃ decomposition [40]:

\[
\begin{align*}
\text{NH}_3^- + e^- &\rightarrow \text{NH}_2^- + H+ \\
\text{NH}_2^- + e^- &\rightarrow \text{NH}^- + H+ \\
\text{NH}^- + e^- &\rightarrow \text{N}^- + H+ \\
2\text{N}^- + e^- &\rightarrow \text{N}_2 + 2e^-
\end{align*}
\]

where * represents an empty site on the metallic iron surface.

For K/Fe/NCNT, the onset of NH₃ decomposition was 583 K, which is slightly lower than the onset that was observed for Fe/NCNT. It has been reported that the recombibative desorption step of adsorbed atomic nitrogen (Eq. (7)) is the rate-determining step of NH₃ decomposition [30]. The K promoter destabilizes N—* species, leading to higher activity of NH₃ decomposition over K/Fe/NCNT. In addition, Jedynak et al. [41] found that the K-promoted Fe catalyst exhibited a higher dispersion of Fe nanoparticles. However, the conversion of NH₃ decreased at about 840 K, presumably due to the sintering of the Fe nanoparticles. Deactivation was significant for K/Fe/NCNT, which decomposed NH₃ at around 70% during holding at 923 K for 1 h.

In contrast to Fe/NCNT and K/Fe/NCNT, NH₃ conversion over Mn/Fe/NCNT reached the highest degree and was almost constant at 99% during holding at 923 K, indicating that Mn stabilized the metallic Fe nanoparticles. K/Mn/Fe/NCNT showed the best performance in NH₃ decomposition, reaching the highest degree at 760 K and remaining constant during the holding period. It can thus be suggested that K performed as an electronic promoter and destabilized the N—* species, leading to higher activity in NH₃ decomposition, whereas Mn performed as a structural promoter, preventing severe sintering.

When the catalysts were cooled down, the degree of NH₃ conversion in the cooling cycle was lower than in the heating cycle, because the catalytic activity of the catalysts deteriorated at 923 K. Correspondingly, hysteresis was observed for all four catalysts. K/Mn/Fe/NCNT still showed the best performance, reaching the highest degree of NH₃ conversion. The catalytic activities of the deactivated catalysts are as follows: K/Mn/Fe/NCNT still reached 99% conversion at 860 K, whereas Mn/Fe/NCNT converted NH₃ by 90% and K/Fe/NCNT by 45%, compared with 65% for the unpromoted Fe/NCNT. Obviously, the Mn promoter enhanced the dispersion of the Fe nanoparticles and prevented their sintering [42].

All catalysts were applied in CO₂ hydrogenation at 633 K and 25 bar for 60 h. After the reaction, the catalysts were characterized by XRD, resulting in the patterns shown in Fig. 5. For the Fe/NCNT catalyst (Fig. 5(a)), the diffraction peaks at 40.9°, 43.5°, and 44.2° originate from Hägg carbide (χ-Fe₅C₂), whereas the diffraction peaks at 30.4° and 35.8° are due to magnetite. During CO₂ hydrogenation, the reduced iron phase was transformed into iron carbide, which is catalytically active for the FTS reaction, whereas water produced by the FTS reaction partly oxidized the iron to magnetite. On the other hand, the K/Fe/NCNT catalyst (Fig. 5(b)) exhibited χ-Fe₅C₂ as the major iron phase even after the long reaction time of 60 h. The diffraction peaks of Mn/Fe/NCNT (Fig. 5(c)) showed diffraction peaks at 40.9°, 43.5°, and 44.2°, which correspond to χ-Fe₅C₂, and peaks at 24.3°, 31.4°, and 51.8°, which correspond to manganese carbonate (MnCO₃). The MnCO₃ peaks were clearly observed for the Mn/Fe/NCNT catalyst (Fig. 5(d)). Gryzbe et al. [43] studied Mn/Fe oxide catalysts and found that the catalyst surface was enriched in Mn, which may inhibit the oxidation of iron to magnetite [43]. Mn is also able to retard the agglomeration of iron oxide nanoparticles, which are formed during the reaction [42]. After 60 h reaction time, K/Mn/Fe/NCNT still exposed the XRD pattern of the active χ-Fe₅C₂ phase without detectable magnetite reflections.
Fig. 6(a) shows the CO₂ conversion over Fe/NCNT, K/Fe/NCNT, Mn/Fe/NCNT, and K/Mn/Fe/NCNT as a function of time on stream at 633 K. The reaction over Fe/NCNT had a degree of CO₂ conversion of about 38% at the beginning, and the activity continuously decreased with time on stream. The deactivation of the catalyst points to sintering of the Fe nanoparticles at high temperature over the long reaction time. The Mn-promoted Fe catalyst (Mn/Fe/NCNT) showed a lower conversion at the beginning of around 30%, but it was more constant than the unpromoted Fe catalyst. Grzybek et al. [43] found that the surface of the catalyst was enriched with Mn and was larger after reduction. It is assumed that an outer surface enriched in Mn shields the active Fe from the reaction [42], but carbon atoms were still able to diffuse through the Mn-rich surface to form iron carbide that was available for the hydrogenation reaction [43]. Thus, the Mn promoter is a structural promoter that stabilizes the active iron phase, as indicated by the H₂-TPR and NH₃ decomposition experiments, resulting in stable catalytic activity for CO₂ hydrogenation during the 60 h on stream. Both K-promoted catalysts exhibited high CO₂ conversion of over 30%. The doubly promoted iron catalyst K/Mn/Fe/NCNT showed a slightly lower conversion of about 30%, but more constant CO₂ hydrogenation performance. It is clear that K promotes CO₂ hydrogenation and Mn enhances the structural stability of the active iron carbide nanoparticles.

Fig. 6(b) and Table 2 show the product selectivities over Fe/NCNT, K/Fe/NCNT, Mn/Fe/NCNT, and K/Mn/Fe/NCNT. All the catalysts produced mainly CO, a result that was in agreement with the findings of Lee et al. [44]. Wang et al. [1] also reported that K acts as a promoter for CO₂ adsorption, creating new active sites for decomposition to CO. It has also been reported that the FTS reaction rate is much slower than that of the RWGS reaction [43], which results in the suppression of methane formation and high selectivity for long-chain hydrocarbons. The product selectivity over Mn-promoted Fe/NCNT was somewhat similar to that of the unpromoted Fe/NCNT. In addition, the formation of oxygenated hydrocarbons over Mn/Fe/NCNT was not observed.

To investigate the catalytic performance of K/Mn/Fe/NCNT in high CO₂ conversion of over 30%. The doubly promoted iron catalyst K/Mn/Fe/NCNT showed a slightly lower conversion of about 30%, but more constant CO₂ hydrogenation performance. It is clear that K promotes CO₂ hydrogenation and Mn enhances the structural stability of the active iron carbide nanoparticles.

Table 2
Product selectivities, olefin selectivities in the C₂–C₅ range, chain-growth probabilities (α), and CO₂ conversion (Xₐₐ) over the iron catalysts after 60 h time on stream.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Product selectivity (%)</th>
<th>C₂=C₅/C₂–C₅</th>
<th>α</th>
<th>Xₐₐ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe/NCNT</td>
<td>38.4 39.8 12.1 6.3 1.9 0.2</td>
<td>0.29</td>
<td>25.4</td>
<td></td>
</tr>
<tr>
<td>K/Fe/NCNT</td>
<td>74.6 5.6 5.2 5.3 3.1 3.7 2.0</td>
<td>0.44</td>
<td>31.8</td>
<td></td>
</tr>
<tr>
<td>Mn/Fe/NCNT</td>
<td>48.5 35.6 9.3 4.3 1.3 1.0 0.1</td>
<td>0.34</td>
<td>27.6</td>
<td></td>
</tr>
<tr>
<td>K/Mn/Fe/NCNT</td>
<td>72.1 5.9 5.2 5.9 3.7 4.9 2.4</td>
<td>0.45</td>
<td>30.1</td>
<td></td>
</tr>
</tbody>
</table>

Reaction conditions: 633 K, 25 bar, GHSV of 50 L·(g·h)⁻¹.
more detail, the residence time in the reaction zone was increased by increasing the catalyst weight. Fig. 7 and Table 3 show higher CO conversion and hydrocarbon selectivities, with lower CO selectivity and high olefin and alcohol selectivities.

High olefin selectivities and alcohols produced from CO2 hydrogenation were obtained with K-promoted catalysts. In the FTS mechanism for the formation of hydrocarbons, adsorbed CO on the active Fe species is reduced to CH2, and then forms CH3–CHx, where x = 1–5. If the surface of the catalyst is polar, as in the presence of K+, it can abstract hydride ions from adsorbed ethyl species, producing CH3–CHx as a product. Thus, both K-promoted catalysts produced high olefin contents, although K/Fe/NCNT was easily sintered, causing unstable activity during the long reaction time. The K-promoted catalyst seemed to adsorb H2O, thus favoring the partial oxidation of CH2–CHx species to alcohols, and the doubly promoted K/Mn/Fe/NCNT with Mn as an additional structural promoter showed a more constant performance. Further studies are in progress, aiming at optimization of the amounts of K and Mn promoters. These studies will include sulfur as an additional promoter because it is known to be highly effective when combined with sodium.

4. Conclusions

The influence of the promoters K and Mn on Fe nanoparticles (K/Mn/Fe/NCNT) supported on NCNTs was studied during CO2 hydrogenation at 25 bar. In all the calcined catalysts, Fe3O4 was mainly present; it then transformed into χ-Fe2C during CO2 hydrogenation. After the reaction with the doubly promoted catalyst K/Mn/Fe/NCNT, the active χ-Fe2C phase was the dominant iron phase, with some additional MnCO3. The K promoter lowered the reducibility of the catalysts, as shown by the H2-TPR and in situ XANES analysis. The Mn promoter stabilized FeO as an intermediate and lowered the H2-TPR onset temperature. NH3 decomposition was used as a probe for the dynamics of structure and function. Stud Surf Sci Catal 2007; 163:177–99.


5. Acknowledgements

This work is supported by the Synchrotron Light Research Institute (Public Organization), Thailand (GS-54-D01) and the Commission on Higher Education, Ministry of Education, Thailand, and was performed under the project “Sustainable Chemical Synthesis (SusChemSys),” which is co-financed by the European Regional Development Fund (ERDF) and the state of North Rhine-Westphalia, Germany, under the Operational Programme “Regional Competitiveness and Employment” 2007–2013.

Compliance with ethics guidelines

Praewpilin Kangvansura, Ly May Chew, Chanapa Kongmak, Phatchada Santawaj, Holger Ruland, Wei Xia, Hans Schulz, Attera Worayingyong, and Martin Muhler declare that they have no conflict of interest or financial conflicts to disclose.

References


