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## Effects of Potassium and Manganese Promoters on Nitrogen-Doped Carbon Nanotube-Supported Iron Catalysts for CO<sub>2</sub> Hydrogenation

Praewpilin Kangvansura<sup>a</sup>, Ly May Chew<sup>b</sup>, Chanapa Kongmark<sup>c</sup>, Phatchada Santawaja<sup>d</sup>, Holger Ruland<sup>b</sup>, Wei Xia<sup>b</sup>, Hans Schulz<sup>e</sup>, Attera Worayingyong<sup>c</sup>, Martin Muhler<sup>b,\*</sup>

<sup>a</sup> Scientific Equipment Center, Faculty of Science, Kasetsart University, Bangkok 10900, Thailand

<sup>b</sup> Laboratory of Industrial Chemistry, Ruhr-University Bochum, Bochum 44780, Germany

<sup>c</sup> Department of Materials Science, Faculty of Science, Kasetsart University, Bangkok 10900, Thailand

<sup>d</sup> Department of Chemistry, Faculty of Science, Kasetsart University, Bangkok 10900, Thailand

<sup>e</sup> Engler-Bunte-Institute, Karlsruhe Institute of Technology, Karlsruhe 76131, Germany

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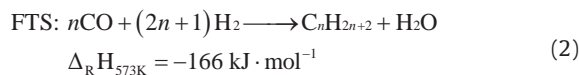
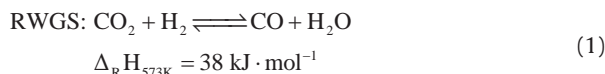
### ABSTRACT

Nitrogen-doped carbon nanotubes (NCNTs) were used as a support for iron (Fe) nanoparticles applied in carbon dioxide (CO<sub>2</sub>) hydrogenation at 633 K and 25 bar (1 bar = 10<sup>5</sup> Pa). The Fe/NCNT catalyst promoted with both potassium (K) and manganese (Mn) showed high performance in CO<sub>2</sub> hydrogenation, reaching 34.9% conversion with a gas hourly space velocity (GHSV) of 3.1 L·(g·h)<sup>-1</sup>. 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<sub>2</sub>), and *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<sub>3</sub>) 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.

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### 1. Introduction

Emission of the primary greenhouse gas, carbon dioxide (CO<sub>2</sub>), from human activities has continuously risen in recent years. Hydrogenation of CO<sub>2</sub> 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]:



The reaction of molecular hydrogen (H<sub>2</sub>) and CO<sub>2</sub> to produce water (H<sub>2</sub>O) and carbon monoxide (CO) is the RWGS reaction, which is industrially catalyzed by magnetite (Fe<sub>3</sub>O<sub>4</sub>). CO, which is produced as the reactant gas for the FTS reaction, is catalytically converted in the presence of H<sub>2</sub> 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<sub>2</sub> hydrogenation because they are readily available and have a high RWGS activity, producing olefins and branched hydrocarbons. Co catalysts are not suitable for CO<sub>2</sub> 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<sub>2</sub> and CO<sub>2</sub>/H<sub>2</sub> synthesis. The duration

\* Corresponding author.

E-mail address: [muhler@techem.rub.de](mailto:muhler@techem.rub.de)

of different kinetic regimes was longer when using CO<sub>2</sub>/H<sub>2</sub> than when using CO/H<sub>2</sub>. Their product selectivity results indicated that the CO<sub>2</sub> hydrogenation reaction occurs together with CO hydrogenation (FTS reaction) [7,8]. They also reported that iron carbide (Fe<sub>3</sub>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<sub>2</sub> 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<sub>2</sub> for chain initiation. Under reaction conditions, the catalyst consists of a core of Fe<sub>3</sub>O<sub>4</sub>, 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<sub>3</sub>) [24,29]. Kundu et al. [29] found that after an NH<sub>3</sub> treatment at 673 K, NCNTs contain mainly pyridinic groups, which are considered to be coordination sites for active metal 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/SiO<sub>2</sub> were used for CO<sub>2</sub> hydrogenation, with Fe/NCNT having a lower CO selectivity than Fe/OCNT. Fe/SiO<sub>2</sub> was found to be much less suitable for CO<sub>2</sub> hydrogenation compared with the CNT-supported catalysts. The C<sub>1</sub>–C<sub>5</sub> hydrocarbon selectivities that were obtained with Fe/NCNT were clearly higher than those obtained with Fe/OCNT. Based on the proposed CO<sub>2</sub> 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 carbided state.

The decomposition of NH<sub>3</sub> 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<sub>3</sub> decomposition [30]. Thus, NH<sub>3</sub> 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<sub>2</sub> (H<sub>2</sub>-TPR) and *in situ* X-ray absorption near-edge structure (XANES) analysis were used to investigate the reducibility of the Fe catalysts. NH<sub>3</sub> decomposition and CO<sub>2</sub> 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<sub>6</sub>H<sub>8</sub>O<sub>7</sub>·xFe<sup>3+</sup>·yNH<sub>3</sub>) as an Fe precursor [29,33,34] followed by impregnation with aqueous solutions of manganese (II) nitrate hydrate (Mn(NO<sub>3</sub>)<sub>2</sub>·xH<sub>2</sub>O) and potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) 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 2 $\theta$  range of 20°–80°. The identification of crystalline phases was accomplished using the inorganic crystal structure database (ICSD). H<sub>2</sub>-TPR was performed by heating 40 mg of catalyst with a heating rate of 10 K·min<sup>-1</sup> in a mixture gas of 4.73% H<sub>2</sub> in argon (Ar) with a flow rate of 84.1 cm<sup>3</sup>·min<sup>-1</sup>. 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<sup>3</sup>·min<sup>-1</sup> of H<sub>2</sub> and 80.1 cm<sup>3</sup>·min<sup>-1</sup> of Ar, heating from 323 K to 923 K (10 K·min<sup>-1</sup>), 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<sub>3</sub>O<sub>4</sub>, and hematite (Fe<sub>2</sub>O<sub>3</sub>) were used as references.

### 2.3. Catalytic tests

NH<sub>3</sub> decomposition was conducted as a test reaction in order to probe the promoter effects and the thermal stability of the reduced catalysts. The NH<sub>3</sub> 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<sup>3</sup>·min<sup>-1</sup> of helium (He) for 30 min at room temperature; next, it was reduced using 25 cm<sup>3</sup>·min<sup>-1</sup> of H<sub>2</sub> at 673 K with a heating rate of 5 K·min<sup>-1</sup> for 1 h. The reactor was cooled to 323 K under 25 cm<sup>3</sup>·min<sup>-1</sup> of He to flush out H<sub>2</sub>. Subsequently, the reactant gases (5 cm<sup>3</sup>·min<sup>-1</sup> of 10% NH<sub>3</sub> in He and 45 cm<sup>3</sup>·min<sup>-1</sup> 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<sup>-1</sup> 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<sup>-1</sup> rate in the same atmosphere. The effluent was connected to a non-dispersive infrared (IR) detector (Rosemount Analytical, NGA 2000) to monitor the NH<sub>3</sub> concentration.

For CO<sub>2</sub> hydrogenation, a mixture of 40 mg of catalyst and 160 mg

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