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## Short Communication

# H<sub>2</sub> production from high temperature shift of the simulated waste derived synthesis gas over magnetite catalysts prepared by citric acid assisted direct synthesis method

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## ABSTRACT

Magnetite (Fe<sub>3</sub>O<sub>4</sub>) has been prepared directly to avoid the reduction process prior to the H<sub>2</sub> production from the high temperature water gas shift reaction of the simulated waste derived synthesis gas. Citric acid has been employed as a complexing agent for the direct synthesis of magnetite. Notably, without the reduction process, the catalyst prepared at the citric acid molar ratio of 1.0 showed 80% CO conversion at 350 °C at a gas hourly space velocity of 40,057 h<sup>-1</sup>.

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## 1. Introduction

H<sub>2</sub> is a fuel for fuel cells. H<sub>2</sub> can be produced from reforming of hydrocarbons [1]. However, the CO level present in the reformed gas (ca.10%) is high enough to poison the Pt electrode in fuel cells [2]. This triggered an immense interest toward water gas shift reaction (WGS). Thermodynamically, WGS is favorable at lower temperatures. However, the reaction is kinetically limited. Hence, in general, WGS is carried out at two different temperature ranges; high temperature

shift (HTS, 350–500 °C) using Fe–Cr oxide catalyst and low temperature shift (LTS, 190–250 °C) using Cu–Zn–Al oxide catalyst [3–6].

Recently, waste to energy has attracted substantial attention due to the depletion of fossil fuels and environmental issues [7,8]. The waste derived synthesis gas consists of wide range of gases including H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub> etc. However, the composition of the waste derived synthesis gas is different from the synthesis gas produced from steam reforming of hydrocarbons. Due to the high concentration of CO in the

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waste derived synthesis gas, it is necessary to develop a novel HTS catalyst to withstand severe conditions. Namely, the presence of higher concentration of CO makes the system more severe. In addition, at a very high gas hourly space velocity (GHSV), higher concentration of CO should be converted selectively into CO<sub>2</sub> through the shift reaction. In our previous results, Fe/Al/Cu oxide catalyst (Cu loading = 15 wt%) exhibited the highest CO conversion and 100% CO<sub>2</sub> selectivity for HTS using the waste derived synthesis gas [9]. However, this catalyst should be reduced to prepare magnetite. Therefore, it is very useful to prepare magnetite directly to avoid the reduction process prior to HTS. This approach is economical and prevents the methanation reaction.

The typical composition of HTS catalyst is Fe<sub>2</sub>O<sub>3</sub> (88–92%) and Cr<sub>2</sub>O<sub>3</sub> (8–12%) [10]. Fe<sub>3</sub>O<sub>4</sub> is active phase, which can be formed by the partial reduction of Fe<sub>2</sub>O<sub>3</sub>. Chromium is a textural promoter [11]. Extreme care should be taken during the reduction process to avoid metallic iron formation through over reduction, which may catalyze some undesirable reactions. Therefore, it is important to maintain a proper ratio of CO + H<sub>2</sub>/CO<sub>2</sub> + H<sub>2</sub>O ( $R < 1.2$ ) [12]. Generally, large amount of steam is employed to avoid the risk of over reduction. This results in higher operational cost. Furthermore, there are more chances for over reduction if there is an imbalance in the ratio R. Hence, preparation of iron oxide based catalyst in its active form, magnetite, with high stability, would be an effective alternate to the aforementioned problem. There are very few reports available in active phase preparation of iron oxide in HTS [13–15].

Sol–gel method is a facile and convenient method for catalyst preparation [16–18]. Especially, catalyst preparation using citric acid (CA) offers an additional advantage due to the three-ligand nature of CA, which forms the three dimensional mixed ion citrate complex [19–21]. This complex releases large amount of heat during the thermal treatment due to the exothermic nature of the metal acid complex. It ensures the formation of oxides at much lower temperatures. In a typical reaction, the citrate ion acts as a reductant and nitrate ions present in the metals as an oxidant during the combustion [22]. Hence, magnetite can be synthesized directly upon thermal decomposition of iron citrate complex due to the reducing nature of CA [23].

In this context, we report here copper and aluminum incorporated direct synthesis of magnetite through the simple sol–gel method using CA as a chelating agent. The effectiveness of the active catalysts was studied by carrying out HTS with and without the reduction process at a very high GHSV of 40,057 h<sup>-1</sup>.

## 2. Experimental method

The iron oxide based catalysts promoted with aluminum and copper were prepared through the sol–gel method using CA. The molar ratio of Fe/Al = 8.0 and Fe/Cu = 8.0 were maintained. In a typical synthesis, proper amounts of metal nitrates of iron, aluminum and copper were dissolved in minimum amount of distilled water. The chelating agent, CA was dissolved separately and added to the mixture of nitrate solutions under stirring condition. After mixing, the solution was kept at 80 °C for 1 h. Once the gel formation was observed,

it was dried at 110 °C for 2 h to get a fluffy mass as a result of combustion reaction. And the catalysts were calcined at 400 °C for 3 h. The catalyst code and its properties are given in Table 1. For example, CA3.0 represents the molar ratio of CA over the metal nitrates during the preparation of the catalyst.

### 2.1. Characterization

The BET surface area was measured by nitrogen adsorption at –196 °C using an ASAP 2010 (Micromeritics). The XRD patterns were recorded using a Rigaku D/MAX–IIIC diffractometer (Ni filtered Cu–K radiation, 40 kV, 50 mA). The crystallite size was estimated using the Debye–Scherrer equation. Temperature programmed reduction (TPR) experiments were carried out using an Autochem 2910 (Micromeritics). TPR was performed using 10% H<sub>2</sub> in Ar with a heating rate of 10 °C/min, from 20 to 1000 °C. The sensitivity of the detector was calibrated by reducing the known weight of NiO.

### 2.2. Catalytic reaction

Activity tests were carried out from 350 to 550 °C at 1 atm in a quartz reactor with an inner diameter of 4 mm. The catalyst charge was 90 mg. T-union was employed at the exit of quartz reactor to install a thermocouple. A thermocouple was inserted into the catalyst bed to measure the reaction temperature. Unless otherwise mentioned, prior to each catalytic measurement, the catalyst was reduced in 2% H<sub>2</sub>/N<sub>2</sub> from room temperature to 400 °C at a heating rate of 4.6 °C/min and then the temperature was maintained for 1 h. Afterward, the temperature was decreased to 350 °C. The simulated synthesis gas consisted of 17.1 vol% CO, 9.6 vol% CO<sub>2</sub>, 1.0 vol% CH<sub>4</sub>, 13.0 vol% H<sub>2</sub>, 55.4 vol% H<sub>2</sub>O, and 3.9 vol% N<sub>2</sub>, which represents a typical syngas from a waste gasifier. The feed H<sub>2</sub>O/(CH<sub>4</sub> + CO + CO<sub>2</sub>) ratio was intentionally fixed at 2.0 to avoid coke formation [24–27]. A GHSV of 40,057 h<sup>-1</sup> was used to screen the catalysts. Water was fed using a syringe pump and was vaporized at 180 °C upstream of the reactor. The effluent was passed through a chiller (JS Research) and moisture trap with absorbent (Drierite) to condense residual water and then analyzed by an on-line micro gas chromatograph (Agilent 3000) equipped with a TCD detector. The micro-GC with Molecular sieve and Plot U columns was used in this study.

## 3. Results and discussion

### 3.1. Characterization

XRD patterns shown in Fig. 1(a) depict magnetite phase in all catalysts. CA0.5, which is highly fuel deficient, shows a small

**Table 1 – Characteristics of Fe/Al/Cu catalysts.**

Catalyst	S <sub>BET</sub> (m <sup>2</sup> /g)	Crystallite size (nm)
CA3.0	65.5	16.5
CA2.0	79.8	18.2
CA1.0	104.9	9.3
CA0.5	43.9	12.7

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