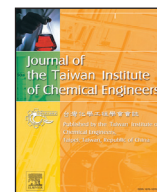




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Iron ore catalysts for methane decomposition to make CO_x free hydrogen and carbon nano material

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ABSTRACT

In this work, for the first time, iron ores with 91.7%–96.2% Fe₂O₃, 1.3%–2.3% Al₂O₃, 1.2%–4.5% SiO₂, 1.3%–3.9% Na₂O, were studied directly as bulk catalysts for methane decomposition. By hydrogen pre-reduction at 850 °C, Fe₂O₃ species on iron ores were gradually reduced into Fe₃O₄, FeO and then finally into Fe⁰ species. After reduction of 1.6g of iron ore catalysts of 50 μm particle size with 100 mL/min pure H₂ for 3.5 h at 850 °C, CMD life testing was conducted at 850 °C and GHSV of 3.75 L/g_{cat} h and the catalyst showed a stable methane conversion for 5 h. When methane decomposition proceeded on Fe⁰ sites, Fe₃C species would be formed to deposit graphite around themselves to finally form carbon nano onions. This carbon nano onions material showed excellent application for wastewater purification. All samples were fully characterized with XRF, XRD, H₂-TPR, TEM and Raman.

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1. Introduction

Catalytic methane decomposition (CMD, CH₄ = C + 2H₂, Eq. (1)) is an interesting way to produce hydrogen without CO_x emission. In our previous research, a series of Fe catalysts with different loadings and supports were synthesized and tested in CMD [1–3]. The alumina supported 65 wt% Fe catalyst showed a stable performance, in term of hydrogen yield of 780 mmol/g_{cat.}, during a 10 h CMD test at 750 °C and gas hourly space velocity (GHSV) of 1.875 L/g_{cat.}·h. Bulk Ni catalysts prepared from reverse micro emulsion method were also tried by us [4,5] for CMD at 750 °C and GHSV of 1.875 L/g_{cat.} h, where a hydrogen yield of 450 mmol/g_{cat.} was achieved in 10 hours. In literature [6–9], Ni based catalysts supported on hard reduced oxides as Al₂O₃, SiO₂, MgO and so on are always reported for CMD. Meshkani [6] reported that the addition of iron to nickel catalyst decreased the degree of reducibility, also improved the catalytic stability by enhancing the rate of carbon diffusion and preventing the formation of encapsulating carbon. They also discussed the CMD performance of nickel catalysts

with various nickel loadings supported on mesoporous nanocrystalline MgO·Al₂O₃ powders with different MgO/Al₂O₃ molar ratios (0.5, 1, 1.5, and 2), and found out that the sample with the highest amount of Ni (55 wt% Ni_{1/2}MgO·Al₂O₃) possessed an acceptable catalytic performance [9]. As summarized in Table 1, Ni and/or Fe are most reported catalysts for CMD. Although Ni based catalysts show much better CMD activity than that of Fe catalysts, the latter would make the process more economical and environmental friendly. According to techno-economic evaluation [16], the CMD process will become competitive with commercial steam reforming process only when at a carbon by product selling price of \$100–300/ton. The co-produced solid carbon during CMD is usually a mixture of spent catalysts and carbon. A purification treatment will be required to separate carbon from catalysts, which will further increase the cost of hydrogen produced from CMD process. Some researchers reported to regenerate the catalysts by burning the carbon with air or steam [17], which is obviously against the significance of CMD to produce hydrogen without CO_x emission. At the moment, storing the produced carbon/catalysts mixture and waiting for a possible remarkable market of this material, is a reasonable way. Under such circumstance, a very cheap and safe catalyst is indeed required for CMD commercialization.

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Table 1

Literature review of Ni/Fe catalysts for CMD.

Sample	Reaction temperature [°C]	Hydrogen yield [mol/g _{cat.}]	Ref.
Fe/Al ₂ O ₃	675	4.4	[10]
Fe/SiO ₂	800	2.3	[11]
Fe/Al ₂ O ₃	700	0.6	[12]
Ni	500	66	[13]
Ni/SiO ₂	500	32	[14]
Ni-Fe-Al	650	92	[15]

Iron ores are rocks and minerals containing high quantities of iron oxides in term of hematite (Fe₂O₃), with limited content of SiO₂, Al₂O₃ and/or Na₂O impurities. Compare to Ni (10,000 \$/ton), iron ore is extremely cheap as 80 \$/ton. Iron ores are industrially reduced by cokes in blast furnace to produce metal iron. There are some studies to use iron ores for catalytic reactions as glycerol decomposition [18], iron carbide preparation [19], Fischer–Tropsch Synthesis [20]. One of the focus of this study is to investigate the application of iron ores for CMD to produce hydrogen.

Moreover, since the spent iron ores are covered with graphite carbon, they may be suitable for water purification application. Nowadays, humic substances have been considered as one of the main challenges for membrane technology based water purification processes, because they can clog the membrane pores [21]. To improve the removal of humic substances, activated carbon adsorption has been applied in combination with membrane technology [22]. Besides humic substances, micro pollutants are also an emerging concern in drinking water purification. Micro pollutants present in low concentrations (µg range) in water body, but the long-term exposure has been demonstrated to lead to feminizations in fish and frogs. Therefore, it is critical to remove these micro pollutants from the drinking water as well. The commercial activated carbon has been proved that it cannot remove all micro pollutants in water [22], so it is important to find another material that can remove more micro pollutants from water. Therefore, another focus of this study is to evaluate the pollutants removal from synthetic wastewater by spent iron ores with carbon, and compare it with commercial powdered activated carbon (PAC).

2. Experimental

2.1. Catalysts preparation

Iron ores were provided from four different suppliers as A₁ (Luossavaara-Kiirunavaara AB company), A₂ (Metalloinvest company), A₃ (Vale SA company) and A₄ (Anglo American company). The received iron ore concentrated pellets with 1 cm diameter were crushed to c.a. 50 µm by using in a horizontal oscillatory mill (Retsch Planetary Ball Mill PM 200) operating at 400 rpm.

2.2. Characterization

Elemental analyses were conducted with the X-ray fluorescence (XRF) on XGT-7000 (Horiba).

Nitrogen adsorption–desorption isotherms were obtained by a Micromeritics ASAP-2420 surface area and porosity analyzer instrument. Before the measurement, the samples were degassed in vacuum at 300 °C for 3 h. Specific surface areas and adsorption–desorption isotherms calculated according to Brunauer–Emmett–Teller (BET), and Barret–Joyner–Halenda (BJH) method, respectively from the adsorption data.

Both normal and in-situ X-ray Powder Diffraction (XRD) patterns were collected using a Bruker D8 Advanced A25 diffractometer in Bragg–Brentano geometry fitted with a copper tube operating at 40 kV and 40 mA and a linear position sensitive detector (opening 2.9°). The diffractometer was configured with a 0.36°

Table 2

Wastewater composition.

Pollutants	Concentration
pH (-)	7.8
Humic acids, from soil (mg/L)	120
Micro pollutant: Atenolol (µg/L)	10
Micro pollutant: Atrazine (µg/L)	10
Micro pollutant: Primidone (µg/L)	10
Micro pollutant: Caffeine (µg/L)	10

Note: Humic acids and micro pollutants were purchased from Fisher Scientific and Sigma Aldrich (Atenolol: 29122-68-7, Atrazine: 45330, Primidone: 125-33-7, Caffeine: C0750), respectively.

diverging slit, 2.9° anti scattering slit, 2.5° Soller slits, and a Ni filter. The data sets were acquired in continuous scanning mode (0.008°/s) over the 2θ range 10°–80°, using a step interval of 0.04° and a counting time of 5 s per step.

Hydrogen Temperature Programmed Reduction (H₂-TPR) was performed on an Altamira instrument. The catalyst powder (50 mg) was placed in a U-shaped quartz reactor and pre-treated in flowing Ar (50 mL/min) for 0.5 h at 300 °C, followed by cooling to room temperature. The temperature was then raised from room temperature to 1000 °C at a rate of 10 °C/min under a 5% H₂/Ar flow (50 mL/min). A thermal conductivity detector was employed to monitor the H₂ consumption.

Transmission electron microscopy (TEM) samples were prepared by the conventional method of dispersing a small amount of sample in ethanol and stirring in an ultrasonic bath for 10 min, allowing the homogenized liquid to settle for 5 min and, taking a drop from the top of the vessel to a conventional TEM holder. The nature of the carbon deposit, size and properties were observed using high-resolution transmission electron microscopy (HRTEM) micrographs obtained from a Titan 60–300 TEM (FEI Co, Netherlands) equipped with an electron emission gun operating at 300 kV.

Raman spectra of carbons deposited on the catalysts by the MCD reaction was measured with a laser Raman spectrometer (DXR Smart Raman Spectrometer). The spectra were taken with 514.5-nm line of an argon laser at room temperature. The incident laser power was adjusted to 2 mW at the sample. The spectra were recorded with a resolution of 4 cm⁻¹.

2.3. Catalytic reaction

In Fig. 1, the CMD performance on the prepared catalysts in this work was conducted in the Microactivity Effi fluidized bed reactor from Process Integral Development Eng & Tech S.L. equipped with a stainless tube reactor (internal diameter of 27 mm). The inner wall of the reactor was coated with alpha alumina to avoid CMD occurrence with reactor itself. The reaction temperature was controlled by a thermocouple placed in the centre of the catalyst layer. Pure methane was used as the feed for CMD. The loaded catalysts were pre-reduced with pure hydrogen at a selected condition. The outlet gases were screened by online gas chromatography (GC; Varian 450) and micro GC (Soprane MicroGC 3000).

2.4. Water purification with produced carbon

Comparison experiments were conducted to evaluate the effectiveness of produced carbon on pollutants removal from wastewater. The spent catalysts mixed with carbon from CMD process was compared with commercial PACs applied for water purification (C272-212, Fisher chemical). One gram of each carbon was spiked in two 150-mL bottles with 100 mL synthetic wastewater (composition as shown in Table 2) and magnetically stirred at 100 rpm

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