Supplementary Material (ESI) for Chemical Communications

Iron oxide and alumina nanocomposites applied to Fischer-Tropsch synthesis

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Electronic Supplementary Information (ESI)

Experimental Section

Synthesis of Fe_3O_4 nanoparticles $Fe(acac)_3$ (2 mmol), 1-hexadecane (20 mmol), oleic acid (6 mmol), oleylamine (6 mmol), and phenyl ether (20 ml) were mixed and magnetically stirred under flow of N_2. The mixture was heated to 373 K for 1h and then 473 K for another 1 h. After that, the mixture was heated to reflux for 1.5 h. The resulting dark solution was cooled to room temperature. After 40 ml ethanol was added to the solution, the black deposit, separated by centrifugation, was dispersed in hexane and re-centrifuged to remove all other residues. The product was finally precipitated with ethanol, centrifuged to remove the solvent. The sol with the iron oxide nanoparticles dispersed in hexane is obtained and used for preparation of catalyst in next steps.

Synthesis of Fe-Al nanocomposites catalysts The catalysts with different Fe/Al_2O_3 weight ratio (Fe content of the catalyst was determined by chemical analysis) were prepared using iron sol above mentioned and an alumina sol prepared by the controlled hydrolysis of aluminium isopropoxide. In a typical procedure, 60 ml hexane containing 91.2 mg Fe_3O_4 nanoparticles (the quantity of organic protective agent attached to Fe_3O_4 accounted for around 10 % of the total mass, which were determined by TG analysis) and 60 ml ethanol containing 600 mg Al_2O_3 nanoparticles were added dropwise to 60 ml 1-butanol under vigorous stirring. After continuously stirring for 1 h, the mixture was transferred to fume hood where solvent was allowed to evaporate over 12h. The resultant mixture then was heated at 453 K for 6 h in air to remove residual organic solvents. The Fe_3O_4 nanoparticles were oxidized to Fe_2O_3 during the heating. In this manner, three catalysts with different Fe/Al_2O_3 weight ratios, i.e., 10/100, 20/100, 50/100, are obtained and respectively named as 10Fe-100Al, 20Fe-100Al and 50Fe-100Al.

Fischer-Tropsch synthesis The catalytic test was conducted in a fix-bed reactor (stainless steel, 3.6 mm i.d.). 0.2 g catalyst was reduced *in situ* in hydrogen at 623 K and 0.1 MPa. After 3 h reduction, the reactor was cooled to room temperature and then the synthesis gas in molar ratio of $H_2/CO = 2.0$ with 7% Ar as an internal standard was passed through the catalyst. The reactor was gradually

pressurized to 2.0 MPa and the temperature was then increased to the desired reaction temperature at 10 K/min. The space velocity of the reaction was kept at 2000 ml^{-1} g^{-1} h^{-1} for all the catalytic tests. The composition of the reactants and effluents were analyzed by two online gas chromatography equipped with four columns and two flame ionized and two thermal conduct detectors.

Catalyst characterization

Transmission electron microscopy (TEM) measurements were performed using JEOL JAM-2100 transmission electron microscope. The samples were prepared by dipping a Cu grid into a colloidal suspension of Fe_3O_4 nanoparticles dispersed in hexane, Al_2O_3 nanoparticles dispersed in ethanol and the catalysts dispersed in ethanol. X-ray diffraction (XRD) analysis was performed on a Philips X'Pro X-ray diffract meter with Cu Kα irradiation. The X-ray source was operated at 40 KV and 30 mA. The reducibility of catalyst was measured by H_2 temperature-programmed reduction using TP-5080 automatic multi-absorption instrument (Tianjin Xian Quan). The sample of 30-110 mg for Fe-Al nano-composites and ~10 mg for Fe_2O_3 were reduced in 5% H_2/Ar (50 ml/min) as the temperature was increased from 323 K to 1073 K at a heating rate of 5 K/min. The H_2 consumption was measured by TCD.

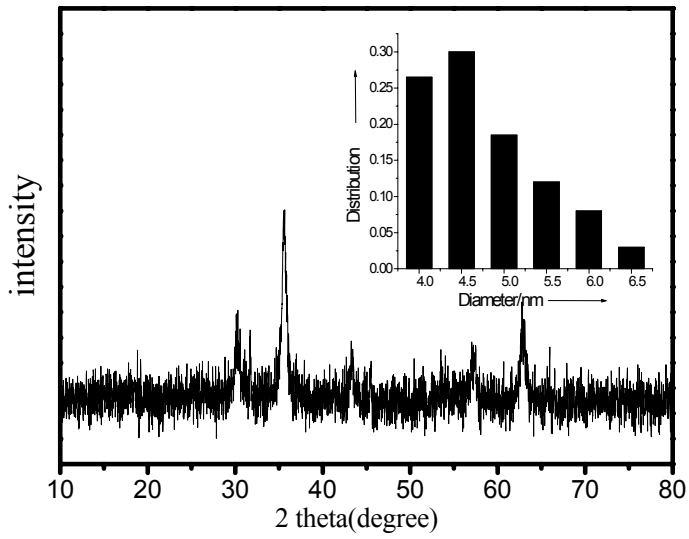

Fig. S1. XRD profiles of Fe_3O_4 nanoparticles. The inset shows the size distribution of Fe_3O_4 nanoparticles.

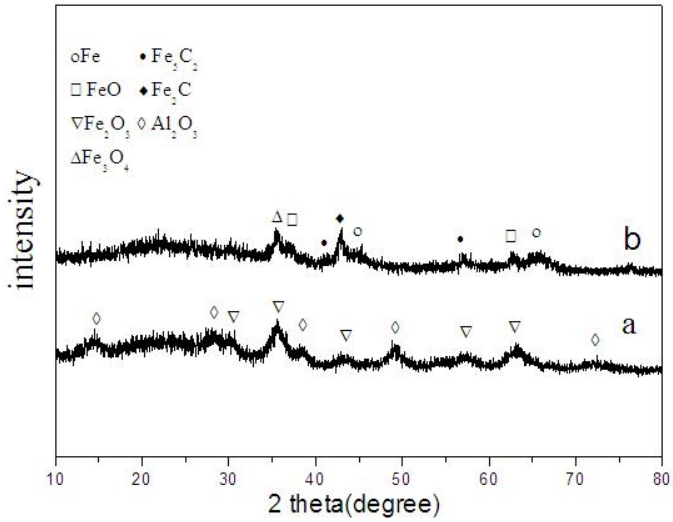

Fig S2. XRD profiles of 50Fe-100Al. (a) before reaction; (b) after reaction, reaction conditions: 533K, 2Mpa, H_2/CO =2.0. It appears that iron carbides are formed during the reaction and the oxide phases are also observed.

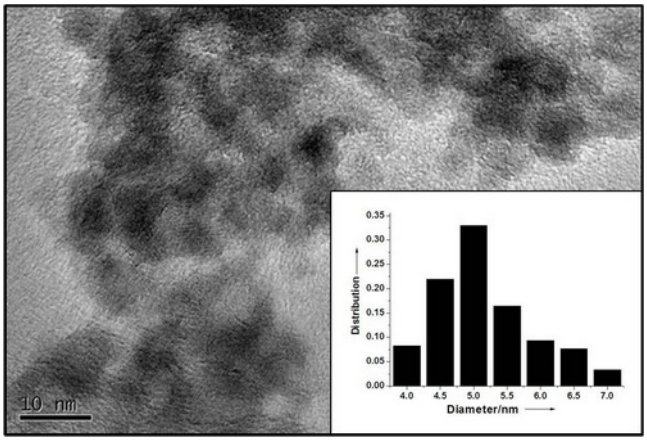

Fig S3. Additional TEM image of 50Fe-100Al nanocomposites after reaction (533K, 2MPa, H_2/CO= 2.0). The inset picture shows the size distribution of the nanoparticles after reaction, which is calculated by more than 150 nanoparticles from multi images of TEM. Statistically, the particles size has minor changed after the reaction.