Liquid-phase Fischer–Tropsch synthesis over Fe nanoparticles dispersed in polyethylene glycol (PEG)†

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The Fe nanoparticles dispersed in polyethylene glycol (PEG) can catalyze Fischer–Tropsch (F-T) synthesis at mild conditions (150 °C, 2.0 MPa H_2, 1.0 MPa CO) with an activity as high as 1.5 mol_{CO} mol_{Fe}^{-1} h^{-1}. The F-T products, hydrocarbons, are insoluble in the green solvent PEG, and could be easily separated from the reaction mixture.

Fischer–Tropsch (F-T) synthesis, an effective process producing hydrocarbons from syngas, is recently receiving great attention as a way of upgrading abundant natural gas and coal as well as renewable biomass resources into valuable energy and chemical products.[1–3] Conventional supported or unsupported Ru, Fe and Co catalysts, which usually work at a temperature higher than 200 °C, have been widely investigated.[4] For example, iron-based catalysts working at 270 °C in a slurry-bed reactor produced an activity of 2 mol_{CO} mol_{Fe}^{-1} h^{-1}.[5] Since the F-T reaction is highly exothermic with a reaction enthalpy of about 170 kJ mol^{-1}, the higher temperature (>200 °C) currently used is not demanded by the reaction itself but by the prerequisite to get the solid catalyst, supported or unsupported, activated. Therefore, it is desirable to set up a reaction system which could be running at a relatively lower temperature.

Three-dimensionally rotationable metal particles[6] dispersed in green solvents, ionic liquids or water, exhibit excellent low-temperature catalytic performances in the hydrogenation,[7–9] dehydrogenation[10] and oxygenation[11–12] reactions of various organic substrates. In our previous work, it has been shown that Ru nanoparticles stabilized by polyvinylpyridine (PVP) could catalyze the F-T reaction in the aqueous phase, resulting in a much higher low-temperature activity over the traditional heterogeneous process.[13] As Ru is relatively expensive, it was suggested to show that we can "also do it with the much cheaper conventional F-T catalyst: iron" (*Chemistry World*, Dec. 12, 2007). Although iron is much cheaper and very green in nature, iron nanoparticles, which could be potentially good catalysts for the F-T process,[14–16] are not stable in water. Meanwhile, even if it was transformed into carbide, oxidation of iron carbide by water to form Fe_3O_4 may occur at low water partial pressures.[1] Under these considerations, green solvents with proper reduction ability to stabilize metallic state of iron nanoparticles are desired. In this study, we show that polyethylene glycol (PEG)[17] is an ideal alternative for water. Using PEG as solvent, the Fe/PEG system keeps all the advantages of Ru/H_2O system, demonstrating a good low temperature activity in the PEG-phase F-T process. The iron nanoparticle catalysts gave out an activity of 1.5 mol_{CO} mol_{Fe}^{-1} h^{-1} at mild conditions (150 °C, 2.0 MPa H_2, 1.0 MPa CO).

The Fe nanoparticles were synthesized by the reduction of iron(II) chloride with sodium borohydride in EG solvent.[18] The morphologies of the Fe nanoparticles were examined by transmission electron microscopy (TEM). As shown in Fig. 1a, the average size of the Fe particles was *ca.* 8 nm. The Fe samples, after drying at room temperature and/or treated at 600 °C for 1 h under nitrogen, were analyzed by X-ray diffraction (XRD). No reflection associated with Fe crystals was detected by XRD from the fresh-prepared Fe nanoparticles, which indicates these particles were amorphous in nature. If the Fe sample was further treated under nitrogen at 600 °C for 1 h, diffractions attributed to metallic α-Fe appeared, suggesting that the fresh-prepared Fe nanoparticles were metallic as well, otherwise, diffractions of ferric oxide or iron oxide would have resulted (Fig. 1b). The Fe nanoparticles as obtained were directly transferred into PEG or other solvents (without stabilizer) under the protection of nitrogen. F-T synthesis under mild conditions (150 °C, 2.0 MPa H_2, 1.0 MPa CO) was subsequently conducted in a stainless steel autoclave running in batch mode. A high-precision pressure meter was used to monitor the reaction and thus to calculate the catalytic activity. The results are shown in Table 1. It was found that the types of solvents had a remarkable influence on the activity of Fe nanoparticles. In dodecane, iron nanoparticles showed no activity at 150 °C. In ionic liquid ([Bmim][BF_4]), the pressure stopped dropping after two to three hours. When the clave was opened, we found that the ionic liquid became yellow and transparent with no precipitates observed, indicating that the Fe nanoparticles dissolved in [Bmim][BF_4] under the reaction conditions. Instead, Fe nanoparticles were found to be stable in alcohols and have acceptable activities, *i.e.* 0.18 h^{-1}

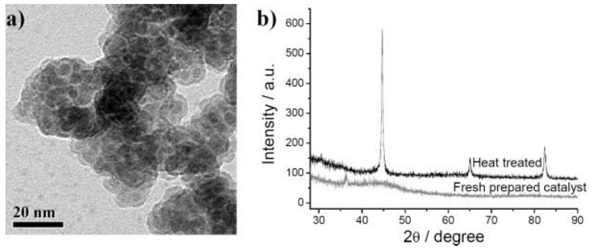

Fig. 1 (a) TEM micrograph and (b) XRD results of Fe nanoparticles.

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Table 1 Catalytic properties of Fe nanoparticles for F-T synthesis in various solvents[a]

Entry	Solvent	CO conversion (%)	$T/°C$	Activity/mol$_{CO}$ mol$_{Fe}^{-1}$ h^{-1}
1	PEG 200	33	150	1.5
2	PEG 200	32	140	0.54
3	PEG 200	30	130	0.29
4	PEG 400	31	150	1.4
5	Ethanol	26	150	0.18
6	Ethanol[b]	32	150	1.0
7	Cyclohexanol	28	150	0.31
8	[Bmim][BF$_4$]	2.8	150	0.30
9	Dodecane	nd	150	nd
10	PEG 200[c]	33	150	1.4
11	PEG 200[d]	32	150	1.3

nd: not detected. [a] Typical reaction conditions: 3.0 MPa H$_2$, 1.5 MPa CO, 2.0×10^{-3} mol Fe, 40 ml solvent. [b] 10.0 ml PEG 200 was added into 30.0 ml ethanol. [c] Second run. [d] Third run.

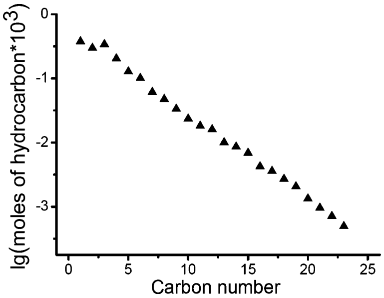

Fig. 2 The Anderson–Schulz–Flory distribution of products. Reaction conditions: 150 °C, 2.0 MPa H$_2$, 1.0 MPa CO, 2.0×10^{-3} mol Fe, 40 ml PEG200.

(Table 1, entry 5). In cyclohexanol the activity is 0.31 h^{-1} (Table 1, entry 7). The relatively low activities in alcohols may be due to their poor abilities to protect Fe nanoparticles. Addition of PEG 200 (MV = 200) to the ethanol system resulted a significant enhancement in activity (Table 1, entry 6) and the activity is 1.0 h^{-1}. When pure PEG 200 was used as the solvent, Fe nanoparticles exhibited very good stability and even higher activities, *i.e.* an activity of 1.5 h^{-1} (Table 1, entry 1). PEG 400 (MV = 400) was also tried, presenting a very similar activity (1.4 h^{-1}, Table 1, entry 4) with that of PEG 200.

The results showed that the PEG is a good reaction medium for F-T reaction catalyzed by the iron nanoparticles under low temperatures. It may be attributed to the fact that Fe nanoparticles can be well dispersed and protected in PEG, which has been reported by Bondera *et al.* when they investigated the synthesis of iron nanoparticles using a borohydride reduction of metal salts in the presence of PEG.[19] In fact, the reaction temperature has a main impact on the activity of the catalyst. As shown in Table 1 (entries 1–3), the activity of the Fe/PEG system decreased with the decrease of reaction temperature, reaching 0.29 h^{-1} (entry 3) at 130 °C. This result shows that the reaction temperature is critical for the successful running of F-T process, while for current system, a reaction temperature at 150 °C is preferred.

The product distribution of the Fe nanoparticles/PEG 200 system is shown in Table S1.† The selectivity of CO$_2$ for this system is less than 3 mol%, showing the effectiveness of the relatively low reaction temperature to suppress the water–gas shift reaction. The hydrocarbons are the main products with a selectivity of 76.6 wt%, whereas the selectivity towards oxygenates (mainly alcohol) is 23.4 wt%. Among the hydrocarbons, the selectivity of C$_{5+}$ is 56.1 wt%, with a relatively low methane selectivity of 5.6 wt%. It is worth noting that the content of alkenes in hydrocarbons is higher than 50 wt%. It is clear from Fig. 2 that the selectivities for hydrocarbons follow the Anderson–Schulz–Flory (ASF) distribution, with the ASF growth factor (α) of hydrocarbon products of 0.72, similar to that obtained with traditional heterogeneous iron catalysts.[20] In previous work, we have demonstrated the one-step synthesis of dioxolanes from syngas and EG over Ru and Fe catalyst.[18] In the current Fe/PEG system, however, no formation of acetals from PEG was detected, indicating that PEG cannot participate the reaction of CO and H$_2$.

In order to confirm whether the Fe nanoparticles are stable in PEG 200, the catalysts after reaction were collected for TEM and XRD analyses (Fig. S1†). The TEM image of the Fe nanoparticles after a reaction of 5 h showed that the size distribution of Fe nanoparticles did not change, and no particle conglomeration was found. The XRD result revealed that the Fe nanoparticles remained amorphous. However, diffractions associated with iron carbide as well as metallic iron were observed from the sample calcined at 600 °C under nitrogen flow, suggesting that iron carbide was possibly formed in the reaction condition.[21] As the catalysts are iron particles, they are magnetically separable. It makes the separation of the catalyst after the reaction very easy. As shown in Fig. S2,† after the reaction, the catalyst could be easily collected by an external magnetic field, and the remaining reaction mixture is transparent. Therefore, the recycle of the reaction is easily conducted. We have recycled the Fe catalyst/PEG 200 reaction system three times successfully at 150 °C, although a slight drop of activity was discovered. The recovered catalysts could be reused in PEG phase without further treatment. It is clear from Table 1 (entry 11) that the activity is 1.3 h^{-1} for the third cycle, which demonstrated the effectiveness of the concept of reusable magnetically separable iron nanoparticle catalysts for F-T process.

Cobalt catalysts are highly active catalysts for F-T synthesis as well,[22] and recently cobalt nanoparticles dispersed in ionic liquid[23] and squalane[24] as F-T catalysts that worked over 200 °C were developed. The performance of Co nanoparticles in a liquid phase F-T process at low temperatures was also studied. The amorphous Co nanoparticles with a size of about 5 nm were synthesized by reducing Co(CH$_3$COO)$_2$ with NaBH$_4$ in H$_2$O and were characterized by TEM and XRD (Fig. S3†). Since Co nanoparticles are stable in water, the Co nanoparticles dispersed in water (with PVP as stabilizer when in water) or PEG 200 were tried in F-T process at mild conditions (130–170 °C, 2.0 MPa H$_2$, 1.0 MPa CO). The results were shown in Table S2.† Clearly, all the liquid phase systems with Co nanoparticles as catalysts showed inferior activities compared to the Fe systems in F-T process. For example, even at 170 °C, the activity of Co catalyst in water phase is still 0.12 h^{-1}, far less than that observed on iron catalyst. This result unambiguously confirmed the efficiency of Fe nanoparticles catalyst in liquid phase F-T process over the Co nanoparticles system.

In summary, we reported that both Fe nanoparticles and Co nanoparticles could be used in liquid phase F-T process at low reaction temperatures. The Fe nanoparticles dispersed in PEG showed a relatively high activity of 1.5 (mol_{CO} mol_{Fe}^{-1} h^{-1}) for F-T synthesis in mild condition (150 °C, 2.0 MPa H_2, 1.0 MPa CO). Moreover, the iron nanoparticle catalysts were magnetically separable, which renders the recycling of the reaction easy to be conducted. This work opens a new window for the applications of Fe nanoparticles as catalysts and PEG as a green solvent.

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