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Fischer–Tropsch synthesis on a ruthenium catalyst in two-phase systems: an excellent opportunity for the control of reaction rate and selectivity†

Vitaly V. Ordomsky,* Andrei Y. Khodakov, Benoit Legras and Christine Lancelot

The activity and selectivity of Fischer–Tropsch synthesis over hydrophobic Ru/C catalysts were efficiently controlled in the reaction medium consisting of organic and aqueous phases. A higher reaction rate was observed in two-phase systems compared to Fischer–Tropsch synthesis in the organic phase; however, catalyst localization in the organic phase leads to higher and tuneable selectivity to long-chain hydrocarbons.

Low temperature Fischer–Tropsch (FT) synthesis converts syngas (mixture of carbon monoxide and hydrogen) into valuable aliphatic linear long-chain hydrocarbons. Methane, light paraffins and carbon dioxide are undesirable products. Their production should be reduced for better reaction efficiency. The syngas for FT synthesis can be produced from fossils and renewable resources (natural gas, coal, carbon residues, and biomass), making this reaction suitable for manufacturing alternative sustainable liquid fuels.

Iron-, cobalt- or ruthenium-based catalysts are common catalysts for FT synthesis.[1–3] Although more expensive than cobalt and iron, Ru possesses a number of advantages for FT synthesis compared to Co and Fe. These advantages are higher catalytic activity, higher selectivity to long-chain hydrocarbons, higher stability compared to any other FT metal and the capacity to operate in the presence of large amounts of water.[4–8] Addition of water during FT synthesis over Ru-based catalysts leads to a significant increase in the reaction rate[9,10] with major modifications in hydrocarbon selectivity. Recently Xiao *et al.*[11] showed higher FT activity of Ru nanoparticles in the aqueous phase with the reaction rate more significant than for conventional supported catalysts. Quek[12] and Pendyala[13] studied the effect of reaction temperature on FT synthesis in the aqueous phase over Ru catalysts. It was found that at low reaction temperature (100–150 °C) oxygenates such as aldehydes and alcohols were predominant products, while at higher temperature (150–220 °C) light hydrocarbons were the major products. This phenomenon is probably due to the higher probability of chain termination in the presence of large amounts of water.

In contrast to aqueous phase FT synthesis, higher selectivity to long-chain hydrocarbons is usually observed in organic phase FT synthesis on ruthenium catalysts. At the same time, the overall FT reaction rate on Ru catalysts in the organic phase is somewhat lower than in the aqueous phase.

It would be interesting therefore to combine the advantages of FT synthesis in aqueous and organic phases. It can be expected that a combination of aqueous phase and organic phase FT synthesis would lead to the enhancement of the catalytic performance: higher reaction rate and better selectivity to the desired products. Recently, the authors applied a Ru catalyst supported over a composite constituted by carbon nanotubes and $MgO–Al_2O_3$ in two-phase FT synthesis.[14] Because of its hydrophilic properties, the catalyst was principally located in the aqueous phase. Consequently, only slight modifications of the catalytic performance and, in particular, hydrocarbon selectivity were observed. Quek *et al.*[15] studied the effect of organic capping agents (polar organic solvents and polymers) on the performance of Ru nanoparticles in aqueous phase FT. Strong interaction of the functional groups with Ru resulted in a lower catalytic activity and significant catalyst deactivation.

The present paper shows that the two-phase reaction medium with a hydrophobic ruthenium catalyst provides an excellent opportunity for efficient control of both reaction rate and hydrocarbon selectivity in FT synthesis. Higher reaction rates were observed in the two-phase systems and in aqueous phase FT synthesis, coinciding with high and controllable hydrocarbon selectivity. The catalytic results obtained in the two-phase medium are compared to the catalytic results of FT synthesis obtained either in the aqueous phase or in the organic phase.

Unité de catalyse et de chimie du solide (UMR 8181 CNRS), Université Lille 1, Sciences et Technologies de Lille, Bat. C3, Cité Scientifique, 59655 Villeneuve d'Ascq, France. E-mail: Vitaly.Ordomsky@univ-lille1.fr; Fax: +33 0320336236; Tel: +33 0320436953

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The Ru/C catalyst with a Ru loading of 5 wt.% was prepared by aqueous impregnation of the carbon support. Further experimental details are given in the ESI.† Analysis by TEM showed that the size of Ru nanoparticles varied in the range of 1 to 10 nm (Fig. 1S, ESI†). The average ruthenium dispersion estimated from SSITKA experiments was about 28% (Fig. 2S, ESI†). The FT synthesis over the Ru/C catalyst in the aqueous phase, organic (dodecane) phase and two-phase systems was performed in a batch autoclave reactor.

The carbon monoxide hydrogenation data are shown in Fig. 1 and Table 1.

FT synthesis in the aqueous phase

The Ru/C catalyst exhibited a high initial FT reaction rate in the aqueous phase (25 $mol_{CO}\ mol_{Ru}^{-1}\ h^{-1}$, Table 1). The aqueous phase FT synthesis resulted in the production of mostly light hydrocarbons. The selectivity to C_{8+} products was 7%, while C_6–C_7 hydrocarbons were the major products of FT synthesis (Table 1). The reaction products also contained trace amounts of higher alcohols (C_1–C_6). The obtained catalytic results were consistent with the previous report by Xiao *et al.*[11] In addition, aqueous phase FT synthesis with the Ru catalyst produced significant amounts of CO_2. CO_2 formation can be attributed to the water-gas shift (WGS) reaction, $CO + H_2O = CO_2 + H_2$, which may proceed rapidly in the aqueous phase. Analysis of the gas phase product distribution suggests that WGS took place mainly at low carbon monoxide conversions (Fig. 3S, ESI†). At higher conversions, the CO_2 selectivity decreased and CH_4 selectivity significantly increased (Fig. 3S, ESI†). The high amount of hydrogen formed during WGS seems to favour methanation. Finally, at the CO conversion of 100%, the selectivity to CH_4 and CO_2 was 8 and 17%, respectively.

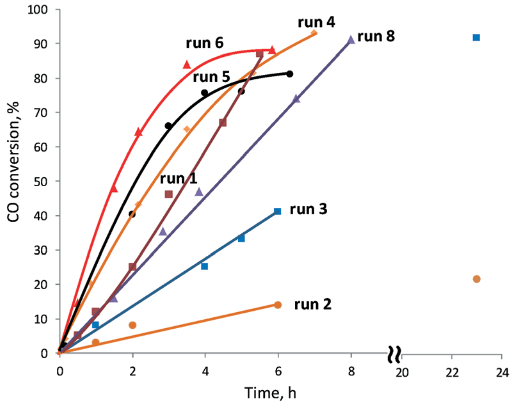

Fig. 1 Carbon monoxide conversion as a function of time in different systems (run numbers according to Table 1).

FT synthesis in the organic phase

Table 1 shows a much lower FT catalytic activity on the Ru/C catalyst in the organic phase (dodecane). The initial carbon monoxide conversion rates were several times lower compared to those in the aqueous phase FT synthesis (4–10 $mol_{CO}\ mol_{Ru}^{-1}\ h^{-1}$, Table 1). However, the catalyst exhibited a much more significant selectivity to long-chain hydrocarbons ($S_{C_{8+}}$ = 30–60%) relative to FT synthesis in the aqueous phase.

Interestingly, the catalyst exposed to syngas at room temperature before starting the reaction (run 2, Table 1) showed a much lower catalytic activity compared to the catalyst which was exposed to syngas in dodecane at 180 °C (run 3). Previous reports[16,17] indicate a very low activation energy for carbon monoxide dissociation on ruthenium nanoparticles compared to that for carbon monoxide desorption or hydrogenation. This suggests that carbon monoxide adsorption and dissociation could be fast and irreversible even at low temperatures. It can be suggested that strong carbon monoxide adsorption followed by its rapid dissociation could block[13] the active sites for hydrogen adsorption. This could lead to low activity in FT synthesis. Lower FT reaction rates after the catalyst's exposure to syngas at room temperature can therefore be explained by "poisoning" of the Ru catalyst by CO under these conditions. The reaction under these conditions also yielded significant amounts of CO_2 (selectivity of 36%). Note that in the aqueous phase, addition of syngas at room temperature before starting the reaction resulted in a high reaction rate similar to that obtained when syngas was

Table 1 CO hydrogenation over Ru/C in the aqueous phase, organic phase and two-phase systems (*T* = 220 °C, 0.3 g Ru/C, *p*(CO) = 12.5 bar, *P*(H_2) = 25 bar, stirring rate = 700 rpm)

Run number	Reaction medium composition, g	Initial reaction rate, $mol_{CO}\ mol_{Ru}^{-1}\ h^{-1}$	CO conversion, %	Selectivity, mol. C%							
	$C_{12}H_{26}$			H_2O	Surf.	CO_2	CH_4	C_2–C_4	α	C_5–C_7	C_{8+}
FT synthesis in the aqueous phase											
1	—	40	—	25	83	17.7	8.2	21.2	41	7	—
FT synthesis in the organic phase											
2	30	—	—	3.9	23	36	8.1	5.7	4.0	33.7	—
3	30[a]	—	—	10	86	1.8	11.2	5.8	7.0	57.0	0.87
FT synthesis in two-phase systems											
4	10	40	—	31	93	7.8	3.9	6.1	23.8	49	0.88
5[b]	10	40	—	34	81	14.9	15.1	16.0	19.6	29.8	—
6	10	40	0.5	54	87	11.1	3.6	6.4	24.4	51.7	0.84
7	10	40	0.2	41	91	9.2	3.7	5.6	22.5	50.8	0.89
8	30	10	—	21	91	5.5	9.8	6.0	8.2	58	0.90

[a] H_2 and CO were added in a preheated reactor (180 °C) with subsequent heating up to 220 °C. [b] Stirring rate: 200 rpm.

added to the catalyst at the reaction temperature. Continuous removal of CO from the surface by the WGS reaction and competition for surface sites between CO and water seem to protect the catalyst surface area from blocking by strongly adsorbed carbon species which may form from CO dissociation on ruthenium at low temperatures. A similar mechanism of initiation of the FT reaction over Ru catalysts by CO_2 formation was previously proposed by Jacobs *et al.*[18]

Fig. 1 also displays carbon monoxide conversion *versus* reaction time when syngas was added to the ruthenium catalyst in dodecane at 180 °C (run 3). After 23 h of reaction, carbon monoxide conversion reached 86% with about 57% selectivity to C_{8+} (Fig. 1, Table 1). Fig. 2 shows the distribution of the hydrocarbons produced during FT synthesis in the organic phase. FT synthesis in dodecane leads to a wide range of hydrocarbons (up to C_{60}–C_{65}). The distribution curve follows Anderson–Schulz–Flory (ASF) statistics with an apparent chain growth probability (α) of 0.87 (Table 1).

Thus, examination of the catalytic results obtained by FT synthesis in aqueous and organic phases with the Ru/C catalyst suggests that the aqueous phase leads to higher reaction rates, although with lower selectivity to higher hydrocarbons. In the organic phase the FT reaction rate was lower but significantly higher hydrocarbon selectivity to long-chain hydrocarbons was observed.

FT synthesis in two-phase systems

Table 1 displays FT results obtained in an autoclave reactor which simultaneously contained the aqueous and organic phases and the Ru/C catalyst. The important issue is catalyst repartition between the two phases. Fig. 3 shows that hydrophobic Ru/C in the two-phase system was totally localized in the organic phase before and after the reaction. The top layer contained mostly dodecane, while the lower layer was mostly constituted by the aqueous phase with larger droplets of dodecane (Fig. 3b). The observed distinct phase separation and the presence of larger droplets are indicative of insufficient mixing between organic and aqueous phases. In order to intensify the mixing and to form emulsions, 1-hexanol was added as a surfactant. Fig. 3c shows that in the presence of 1-hexanol, the organic phase is uniformly distributed in the aqueous phase with formation of small droplets. In comparison with other surfactants, 1-hexanol was stable under the reaction conditions.

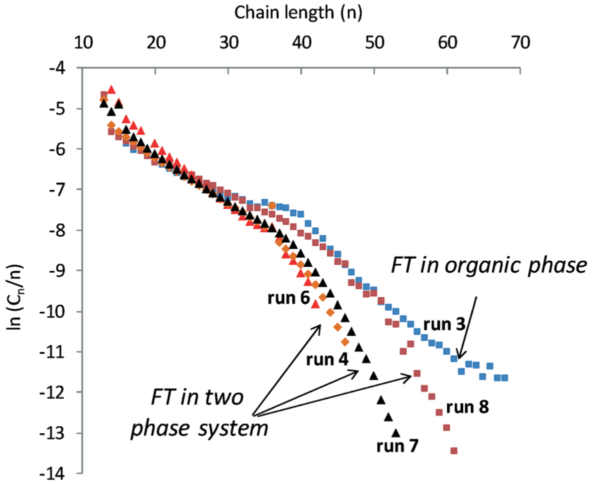

Fig. 2 ASF hydrocarbon distributions obtained in the organic phase and in two-phase systems.

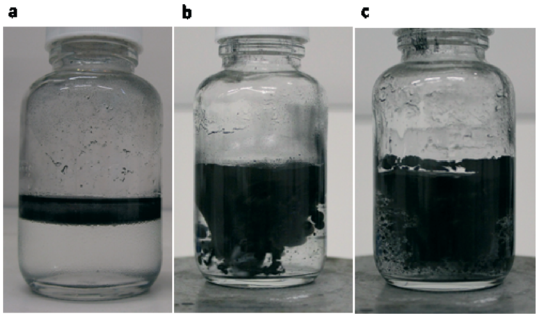

Fig. 3 Distribution of dodecane with the catalyst relative to the aqueous phase before reaction (a), during stirring at 700 rpm without a surfactant (b) and after addition of a surfactant (0.5 g of 1-hexanol) (c).

The catalytic results obtained for two-phase systems are shown in Table 1 and Fig. 1. Carbon monoxide conversion and hydrocarbon selectivity were strongly affected by the presence of both organic and aqueous phases. The FT reaction rate in the two-phase system (run 4) with the addition of 10 g of dodecane was higher in comparison with that of FT synthesis conducted either in the aqueous phase or in the organic phase. Addition of 0.2 and 0.5 ml of 1-hexanol as a surfactant (runs 6 and 7) resulted in an increase in the activity from 31 $mol_{CO}\ mol_{Ru}^{-1}\ h^{-1}$ to 41 and 54 $mol_{CO}\ mol_{Ru}^{-1}\ h^{-1}$. The distribution of reaction products was also affected by the composition of the reaction medium. Interestingly, the amounts of produced methane and CO_2 were almost two times lower in the two-phase systems compared to those obtained from FT synthesis in the aqueous phase. At the same time the selectivity to long-chain hydrocarbons is significantly higher in comparison with that obtained from the aqueous phase experiments. Note that the selectivity to methane and long-chain hydrocarbons was close to the selectivities in the two-phase systems without addition of a surfactant. This suggests that the catalyst is still in the organic phase, whereas a close contact between the catalyst and the aqueous phase leads to a higher reaction rate. A lower autoclave stirring rate (run 5) resulted in a significant increase in the selectivity to methane and CO_2 due to localization of the catalyst mainly in the interface in closer interaction with the aqueous phase. At the same time a higher amount of dodecane (run 8) resulted in a lower reaction rate with a higher selectivity to methane due to the more prolonged catalyst contact with the organic phase.

Similar to that in the organic phase, the distribution of long-chain hydrocarbons in the two-phase medium also followed the Anderson–Schulz–Flory (ASF) curve up to C_{35}–C_{40}

hydrocarbons (Fig. 2 and 4S, ESI†). The high fraction of the organic phase in the two-phase system (run 8) leads to higher chain growth probability. At the same time, the selectivity and chain growth probability for heavy C_{35+} hydrocarbons were somewhat lower in the two-phase system compared to those obtained from organic phase FT synthesis (Fig. 2).

Conclusion

In summary, conducting FT synthesis with a supported ruthenium catalyst in a two-phase medium consisting of aqueous and organic phases can overcome major drawbacks of FT synthesis in the aqueous phase and in the organic phase. A much higher FT reaction rate is observed in the two-phase medium compared to FT synthesis in the organic phase which is probably due to the intensive cleavage of the surface by water molecules. At the same time, the hydrophobic catalyst localised in the organic phase in the two-phase system exhibits high selectivity to long-chain hydrocarbons. The hydrocarbon selectivity in two-phase systems is controlled by the composition of the reaction medium and operating conditions.

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