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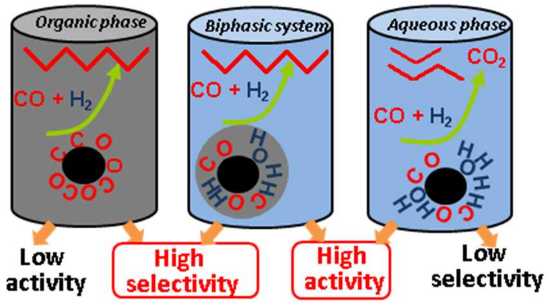
Localization of Ru/C in organic phase in biphasic system leads to high selectivity to long chain hydrocarbons similar to that in organic phase at higher overall Fischer-Tropsch reaction rate



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COMMUNICATION

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

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**The activity and selectivity of Fischer-Tropsch synthesis over hydrophobic Ru/C catalysts is efficiently controlled in the reaction medium consisting of organic and aqueous phases. Higher reaction rate was observed in two-phase systems compared to Fischer-Tropsch synthesis in organic phase, while catalyst localization in 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 fossil and renewable resources (natural gas, coal, carbon residues, and biomass). This makes this reaction suitable for manufacturing alternative sustainable liquid fuels.

Iron, cobalt or ruthenium based catalysts are common catalysts for FT synthesis [1-3]. Though being 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 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 reaction rate [9,10] with major modifications in hydrocarbon selectivity. Recently Xiao [11] et al uncovered higher FT activity of Ru nanoparticles in 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 aqueous phase over Ru catalyst. 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. The phenomenon is probably due to higher probability of chain termination in the presence of large amounts of water.

In contrast to aqueous phase, 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 organic phase is somewhat lower than in 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 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 tended to apply a Ru catalyst supported over a composite constituted by carbon nanotube and MgO−$Al_2O_3$ in the two-phase FT synthesis [14]. Because of the hydrophilic properties, the catalyst was principally located in the aqueous phase. Consequently, only slight modifications of the catalytic performance and in particular of 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 rates and hydrocarbons selectivity in FT synthesis. Higher reaction rate is observed in two phase systems similar to aqueous phase FT synthesis, which coincides with high and controllable hydrocarbon selectivity. The catalytic results obtained in two-phase medium are compared to the catalytic results of FT synthesis obtained either in aqueous or organic phases.

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

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

## FT synthesis in aqueous phase

Table 1. CO hydrogenation over Ru/C in aqueous, 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×h | CO conversion, % | Selectivity, mol. C% | | | | | α |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $C_{12}H_{26}$ | $H_2O$ | Surf. | | | $CO_2$ | $CH_4$ | $C_2$-$C_4$ | $C_5$-$C_7$ | $C_8$+ | |
| FT synthesis in aqueous phase | | | | | | | | | | | |
| 1 | - | 40 | - | 25 | 83 | 17.7 | 8.2 | 21.2 | 41 | 7 | - |
| FT synthesis in 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 the preheated reactor (180℃) with subsequent heating up to 220℃

[b] Stirring rate 200 rpm

Ru/C catalyst exhibited a high initial FT reaction rate in 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 previous report by Xiao [11] et al. In addition, aqueous phase FT synthesis with Ru catalyst produced significant amounts of $CO_2$. $CO_2$ formation can be attributed to water gas shift reaction (WGS): $CO+H_2O=CO_2+H_2$ which may proceed rapidly in aqueous phase. Analysis of the gas phase product distribution suggests that WGS took place mainly at low carbon monoxide conversions (Figure 3S, ESI). At higher conversions, the $CO_2$ selectivity decreased and $CH_4$ selectivity significantly increased (Figure 3S, ESI). 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.

## FT synthesis in organic phase

Table 1 shows a much lower FT catalytic activity on Ru/C catalysts in organic phase (dodecane). The initial carbon monoxide conversion rates were several times lower compared to the aqueous phase FT synthesis (4-10 $mol_{CO}/mol_{Ru}^{-1}$ $h^{-1}$, Table 1). The catalyst exhibited however, a much more significant selectivity to long-chain hydrocarbons ($S_{C8+}$=30-60 %) relative to FT synthesis in aqueous phase.

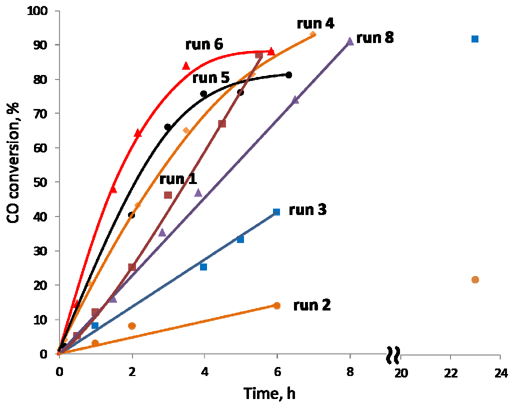

Figure 1. Carbon monoxide conversion as a function of time in different systems (run numbers according to Table 1

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 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 rate after catalysts exposure to syngas at room temperature can be therefore explained by "poisoning" of Ru catalysts 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 results in high reaction rate similar to that obtained when syngas was added to the catalysts at the reaction temperature. Continuous removal of CO from the surface by 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. The similar mechanism of initiation of the FT reaction over Ru catalyst by $CO_2$ formation was previously proposed by Jacobs et al. [18].

Figure 1 also displays carbon monoxide conversion versus reaction time when syngas was added to ruthenium catalysts in dodecane at 180°C (run 3). After 23 h of reaction, carbon monoxide conversion reached 86% with selectivity to $C_{8+}$ about 57% (Figure 1, Table 1). Figure 2 shows hydrocarbon distributions produced during FT synthesis in 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 ($\alpha$) of 0.87 (Table 1).

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

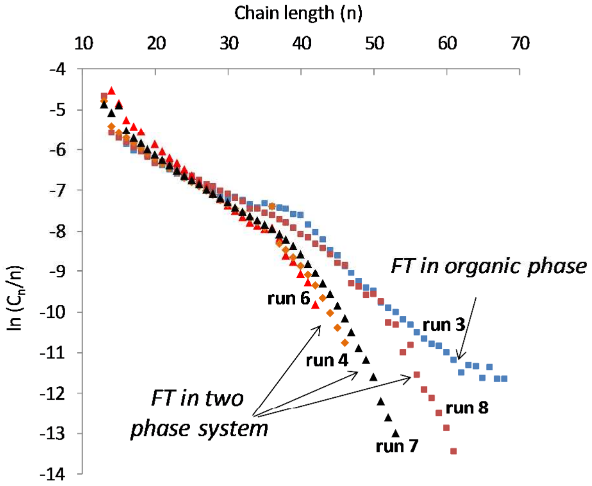

Figure 2. ASF hydrocarbon distributions obtained in organic phase and two phase-systems.

### FT synthesis in two-phase systems

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

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

Similar to organic phase, the distribution of long chain hydrocarbon in two-phase medium also followed Anderson-Schulz-Flory (ASF) curve up to $C_{35}$-$C_{40}$ hydrocarbons (Figure 2, Figure 4S, ESI). High fraction of organic phase in 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 was somewhat lower in two-phase system compared to organic phase FT synthesis (Fig. 2).

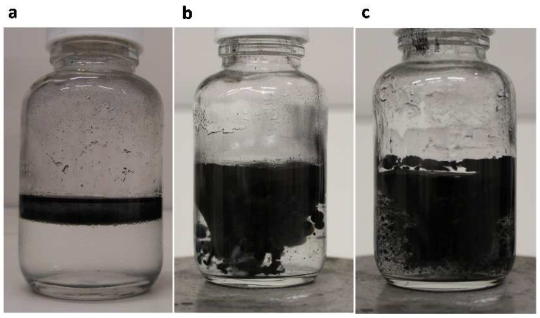

Figure 3. Distribution of dodecane with catalyst relative to aqueous phase before reaction (a), during stirring at 700 rpm without surfactant (b) and after addition of surfactant (0.5 g hexanol-1) (c)

## Conclusion

In summary, conducting FT synthesis with supported ruthenium catalyst in two-phase medium consisting of aqueous and organic phases can overcome major drawbacks of FT synthesis in aqueous and in organic phase. A much higher FT reaction rate is observed in two-phase medium compared to FT synthesis in 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 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.

## Notes and references

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