Electronic Supplementary Material (ESI) for Green Chemistry

Supplementary information

Mastering a biphasic single-reactor process for direct conversion of glycerol into liquid hydrocarbon fuels

Vitaly Ordomsky*, Andrei Khodakov

Preparation of catalysts

The powdered ruthenium on carbon (Ru/C) catalyst with 5 wt. % Ru was prepared by incipient wetness impregnation of hydrophobic carbon by aqueous solution of $RuCl_3$. The catalyst was dried at 100 °C and reduced in H_2 atmosphere at 500 °C. Afterwards the catalyst was passivated in the flow of He at ambient temperature.

The Pt/Al_2O_3 catalyst with 5 wt. % Pt was prepared by incipient wetness impregnation of alumina powder by aqueous solution of $[Pt(NH_3)_4]\ (NO_3)_2$. The catalyst was dried at 100 °C and reduced in H_2 atmosphere at 500 °C. Afterwards the catalyst was passivated in the flow of He at ambient temperature.

Catalytic tests

Experiments were carried out in a 100 ml stirred autoclave working in a batch mode and equipped with valves for sampling the liquid and gas phase. The experiments were conducted during 7 h. The stirring rate was 600 rpm.

The procedure for testing catalysts in the reaction of CO hydrogenation was as follows: water (40 ml) and decane (10 g, in the case of the biphasic experiment – entry 2), catalyst Ru/C (0.5 g) in the aqueous (entry 1) or organic phase (entry 2) was poured into the autoclave. The autoclave was purged and filled with CO (10 bar) and hydrogen (20 bar), the temperature was increased to 220 °C and thereafter the catalytic experiment was started.

The procedure for testing catalysts in the reaction of CO_2 hydrogenation was as follows: water (40 ml) with 0.1 M H_2SO_4 in the case of the experiment with acid addition (entry 4) with Pt/Al_2O_3 (0.5 g) and decane (10 g) with catalyst Ru/C (0.5 g) were poured into the autoclave. The autoclave was purged and filled with CO_2 (10 bar) and hydrogen (20 bar), the temperature was increased to 220 °C and thereafter the catalytic experiment was started.

The procedure for testing catalysts in the APR was as follows: water (40 ml) and 5 g glycerol with 0.1 M H_2SO_4 in the case of the experiment with acid addition (run 2) with Pt/Al_2O_3 (0.5 g) were poured into the autoclave. The autoclave was purged and filled with N_2 (5 bar), the temperature was increased to 220 °C and thereafter the catalytic experiment was started.

The procedure for testing catalysts in the APR combined with FTS was as follows: water (40 ml) and 5 g glycerol with 0.1 M H_2SO_4 in the case of the experiment with acid addition (run 4) with Pt/Al_2O_3 (0.5 g) and decane (10 g) with catalyst Ru/C (0.5 g) were poured into the autoclave. The autoclave was purged and filled with N_2 (5 bar), the temperature was increased to 220 °C and thereafter the catalytic experiment was started.

Periodically gas samples were taken from the autoclave. Gaseous reaction products were analyzed online by gas chromatography. Analysis of H_2, CO, CO_2 and CH_4 was performed using Alltech CTR I column and a thermal conductivity detector. The composition of the liquid phase was analyzed at the end of the experiments. The amount of glycerol in the samples was analyzed by HPLC (Shimadzu) equipped with a refractive index detector. Products in the aqueous phase were analyzed by GC (Varian) with the addition of external standards (acetone). Products were identified by GC-MS (Shimadzu 2010 Plus) and the use of pure compounds. Light products (till C_{10}) in organic phase (decane) were analyzed by GC (Varian) using a capillary CP PoraBond Q column. Simulated distillation (SIMDIST) by gas chromatography was used to analyze the long chain hydrocarbon (C_{12}-C_{60}) with addition of octadecane as external standard. Analysis of the hydrocarbon during FTS in the aqueous phase (entry 1) was conducted after extraction of hydrocarbons by addition of decane after reaction.

Conversions of CO or CO_2 (mol %) and product selectivity (mol %) in hydrogenation experiments were defined as follows:

Conversion (mol %) = (moles of CO or CO_2 reacted)/(moles of initial CO or CO_2) ·100

Selectivity (mol %) = (moles of C atoms of product produced)/(moles of CO or CO_2 reacted)·100.

Conversions of glycerol (mol %) and product selectivity (mol %) in APR and combined APR-FTS was defined as follows:

Conversion (mol %) = (moles of reacted glycerol)/(moles of initial glycerol) ·100

Selectivity to C containing products (mol %) = (moles of C atoms of product produced)/(3×moles of reacted glycerol)·100.

Selectivity to H_2 (mol %) = (moles of H_2 produced)/(7×moles of reacted glycerol)·100.

APR and APR-FTS

Table S1 shows effect of addition of different concentration of sulphuric acid on APR and combined APR-FTS. Addition of acid till the concentration 0.05 M leads to decrease of the selectivity to CO_2 from 36 to 23 %. Although, the selectivity to CO increases only to 0.5 %. At the same time, the selectivity to ethane and propane increases to 27 and 18 %, respectively.

Further increase of the amount of acid to 0.1 M solution does not lead to significant changes in the distribution of products. The selectivity to CO_2 and oxygenates slightly decreases and selectivity to alkanes increases. The main difference is in the amount of CO in the products of the reaction. The selectivity increases to 2.3 %.

Addition of 0.05 M sulphuric acid to the aqueous phase during combined APR-FTS leads to significant decrease of the methane formation (7.8 %) with increase of the contribution of C2-C3 alkanes (31 %) and oxygenates (22 %) like in the case of the APR in the presence of acid. The selectivity to CO in the gas phase of the reactor is 1.2 %. The selectivity to long chain hydrocarbons increases with addition of acid to 5 %. It means that addition of acid indeed shifts the equilibrium in the direction of CO formation, which might be further consumed for the FT synthesis.

Further increase of the concentration of acid till 0.1 M results in the significant increase of the selectivity of carbon transformation into long chain alkanes (15 %). The contribution of C5-C7 hydrocarbons also significantly increases (15 %). Taken together, the selectivity to hydrocarbons with C5+ is around 30 % of all carbon atoms of converted glycerol. The increase of the selectivity to hydrocarbons is accompanied by decrease of the selectivity to oxygenates (12.7 %) and light hydrocarbons (methane, ethane) (22 %).

Table 1S. APR of glycerol over Pt/Al_2O_3 without acid and with different concentration of H_2SO_4 (T=220 °C, 40 ml of water with 5 g glycerol, 0.5 g Pt/Al_2O_3, p(N2)=5 bar, 5h) and combined process of APR of glycerol over Pt/Al_2O_3 and FTS over Ru/C (T=220 °C, 40 ml of water with 5 g glycerol, 0.5 g Pt/Al_2O_3, 10 g dodecane, 0.5 g Ru/C, $p(N_2)$=5 bar, 5h).

Entry	Aqueous phase	Glycerol conversion, %	S_{H2}, %	Selectivity, mol. C%									Alfa
				CO_2	CO	CH_4	C_2	C_3	C_4	C_5,C_6, C_7	C_{8+}	Oxygenates	
APR													
1	Pt/Al_2O_3	55	68	36.7	0.1	2.1	3.1	1.9	0.2	2.7	-	27.8	-
2	Pt/Al_2O_3+0.05M H_2SO_4	47	41	23.5	0.5	1.5	27.3	18.5	0.5	8.4	-	14.5	-
3	Pt/Al_2O_3+0.1M H_2SO_4	51	33	20.9	2.3	1.2	27.6	16.2	3.8	9.1	-	7.8	-
APR + FTS with Ru/C in organic phase													
4	Pt/Al_2O_3	63	22	30.4	0.6	24.2	14.7	6.7	2.3	4.9	1.0	4.8	0.62
5	Pt/Al_2O_3+0.05M H_2SO_4	53	17	16.7	1.2	7.8	25.3	6.2	1.2	2.9	5.2	22.5	0.79
6	Pt/Al_2O_3+0.1M H_2SO_4	47	13	11.9	3.2	1.2	21.3	6.9	4.2	14.7	15.4	12.7	0.75

ASF distribution of Fischer-Tropsch products

The results can be described by Anderson-Schulz-Flory (ASF) statistics. As expected, the α coefficient of the products during CO_2 hydrogenation is quite low (0.76). At the same time, hydrogenation of CO in biphasic system leads to the standard α for CO hydrogenation over Ru based catalysts (0.84). The combination of APR and FTS in the presence of acid leads to the α coefficient (0.75-0.79) between α of the hydrocarbons during CO_2 and CO hydrogenation.

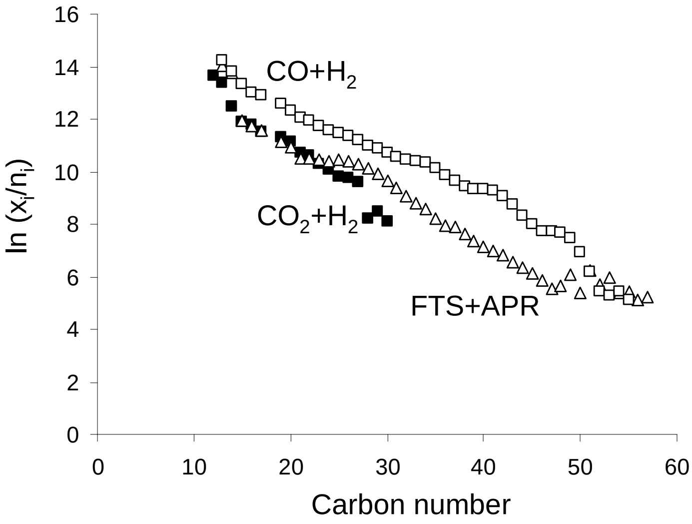

Fig. S1. ASF curves of hydrocarbons after CO and CO_2 hydrogenation and combined APR and FTS (reaction conditions are in Table 1, 2)