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

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V. V. Ordomsky* and A. Y. Khodakov

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The aqueous-phase reforming (APR) and Fischer-Tropsch (FT) synthesis have been combined in a single biphasic reactor. The APR of glycerol over Pt/Al_2O_3 in the aqueous phase in the presence of acid leads to partial formation of syngas, which transforms in the organic phase over hydrophobic Ru/C into long chain hydrocarbons.

The development of new technologies for the production of fuels from renewable resources is currently one of the most challenging tasks. Biomass is one of the most interesting sources of liquid fuels. The technologies for liquid fuel synthesis such as biomass pyrolysis or biomass fermentation are either energy-consuming or complex multistep processes [1]. The most common Biomass to Liquid (BTL) technology involves gasification of biomass to syngas (CO and H_2) [2], which is further transformed into liquid alkanes by Fischer-Tropsch (FT) synthesis [3]. Biomass gasification is a complex multistage process with formation of syngas with low H_2/CO ratio and which contains different impurities (S-, N-compounds) and high amount of unburned residues like ash and condensates. The costly biomass gasification step might be substituted by recently uncovered aqueous-phase reforming (APR) process. The main advantages of APR compared to gasification are lower temperature (200-250 °C) and high selectivity to gaseous products (CO_2 and H_2) [4]. In addition, the APR operating conditions are similar to the conditions of low temperature FT synthesis. These reactions therefore, might be combined in one reactor. APR over Pt-Re/C and FT synthesis over Ru/TiO_2 were coupled earlier by Dumesic [5] et al. in two-bed reactor operating at 275 °C and pressure of 1-17 bar. The combined process however, has exhibited high methane selectivity (>30%) and high selectivity to CO and CO_2.

In this paper, we present a new strategy to enhance the efficiency of combined APR-FT process for synthesis of hydrocarbon fuels from biomass. This strategy is based on a biphasic reactor with location of the Ru/C hydrophobic catalyst for FT in the organic phase and location of Pt/Al_2O_3 hydrophilic catalyst for APR in the aqueous phase. The reactions occur in liquid phase which considerably eases the heat transfer. The experimental details are given in Electronic Supplementary Information (ESI).

Influence of the localization of Ru/C catalysts on FT synthesis
The carbon monoxide hydrogenation data over Ru/C catalyst located in aqueous or organic phases in an autoclave batch reactor are shown in Table 1. In agreement with reports [6-7], FT synthesis over ruthenium catalysts in the presence of water led to mostly C_4-C_7 light alkanes and oxygenates (aldehydes, alcohols). Only very low concentrations of C_8+ hydrocarbons were observed. Such a narrow hydrocarbon distribution might be explained by a higher probability of the chain FT termination in the presence of water. Indeed, it was shown previously [8] that addition of water during the FT synthesis over Ru catalyst results in a shift of hydrocarbon selectivity to lighter hydrocarbons.

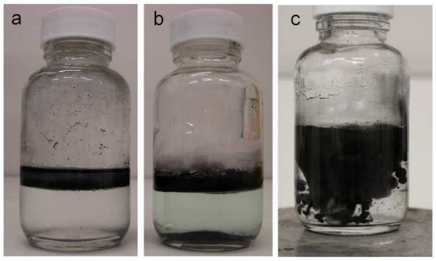

Fig. 1. Ru/C distribution between water and decane before (a),after APR-FT process (b) and during stirring (c)

To enhance selectivity to heavier hydrocarbons, Ru catalyst was placed in the organic phase (decane) which was located on the top of the aqueous phase in biphasic reactor. Figure 1 shows that hydrophobic Ru/C was totally localized in the organic phase before (Fig. 1a) and after reaction (Fig. 1b). During stirring with the same rate as in the reactor (600 rpm) the most part of organic phase was still on the top of the mixture with few large droplets of organic phase with Ru catalyst in aqueous phase. Interaction of the Ru/C catalyst with water for a short period of time at the reaction conditions in aqueous phase results in the loss of its hydrophobic properties due to the formation of hydrophilic groups on the surface. Due to the fact that Ru/C is still located in organic phase after tests aqueous phase does not interact directly with the catalyst. The same situation was observed in the combined processes of APR and FTS (Fig. 1). The CO conversion in this case was higher compared to the aqueous phase process (Table 1), which might be attributed to a

Table 1. CO hydrogenation over Ru/C in aqueous and organic phase (T=220 °C, 40 ml of water, 10 ml of decane, 0.5 g Ru/C, p(CO)=10 bar, P(H_2)=20 bar, 7h) and CO_2 hydrogenation in biphasic system over Ru/C in organic phase and Pt/Al_2O_3 in the aqueous phase with and without acid ((T=220 °C, 40 ml of water, 0.1 M H_2SO_4, 10 ml of decane, 0.5 g Ru/C, 0.5 g Pt/Al_2O_3, p(CO_2)=10 bar, P(H_2)=20 bar, 7h)

№	Catalyst in phase		CO/CO_2 conversion, %	Selectivity, mol. C%								Alfa
	Aqueous	Organic		CO_2/CO	CH_4	C_2	C_3	C_4	C_5-C_7	C_{8+}	Oxygenates	
$CO + 2 H_2$												
1	Ru/C	No phase	61	15.7	21	0.7	2.9	6.2	51.3	3.7	0.3	0.77
2	-	Ru/C	79	0.4	19	0.4	1.6	2.4	34.5	41	2.8	0.84
CO_2+ H_2												
3	Pt/Al_2O_3	Ru/C	57	-	59.6	4.1	3.0	3.3	12.2	7.8	1.8	-
4	Pt/Al_2O_3+H_2SO_4	Ru/C	66	0.7	26.8	2.5	1.4	1.4	23.9	26.4	2.6	0.76

much higher solubility of CO and H_2 in decane than in aqueous phase [9]. The product distribution in this biphasic system was also very different compared to syngas conversion in the aqueous phase. The formation of CO_2 by WGS reaction was significantly suppressed which was probably due to the lower concentration of water in organic phase. At the same time, the selectivity to C_8+ long chain hydrocarbons was significantly higher. It increased from 3.7 to 41 %. Thus, because of phase separation in the biphasic reactor, the influence of water on FT reaction rate and hydrocarbon selectivities seems to be not very significant for Ru/C catalyst located in the organic phase.

Selectivity shift of the glycerol APR to carbon monoxide in the presence of acid

Though CO is supposed to be the primary product [10-11], in the conventional APR process, most of glycerol is converted to H_2 and CO_2 [4]:

$C_3O_3H_8 + 3H_2O=3CO_2 +7H_2$.

Higher concentration of carbon monoxide in the APR products is required however for efficient liquid hydrocarbon synthesis using FT reaction.

Our experiments indicated that addition of H_2SO_4 to the aqueous phase significantly affected the selectivity of WGS reaction over Pt/Al_2O_3. Indeed, without acid addition, CO was almost fully converted into CO_2 and H_2 after 6 h in the batch reactor (Fig. 2) [12]. In the presence of H_2SO_4, less than 40 % of CO was converted into CO_2 for the same period of time (Fig. 2). At the same time, the reverse WGS reaction (CO_2+H_2 =CO+H_2O) almost was not observed in the aqueous phase without acid addition. Addition of acid to the aqueous phase under the same conditions leads to the CO_2 conversion of 1.5 % into CO. The presence of acid in the aqueous phase seems to affect the equilibrium of WGS reaction. The explanation of this fact needs additional study of WGS reaction in the presence of acids. The lower conversion of CO into CO_2 in the presence of acid could be explained, for example, by water protonation, interaction of acid with CO_2 or decrease of hydroxide concentration on the surface of the catalyst during WGS reaction. Thus, addition of acid to the aqueous phase during APR over Pt/Al_2O_3 leads to the increase in the concentration of CO in the reactor.

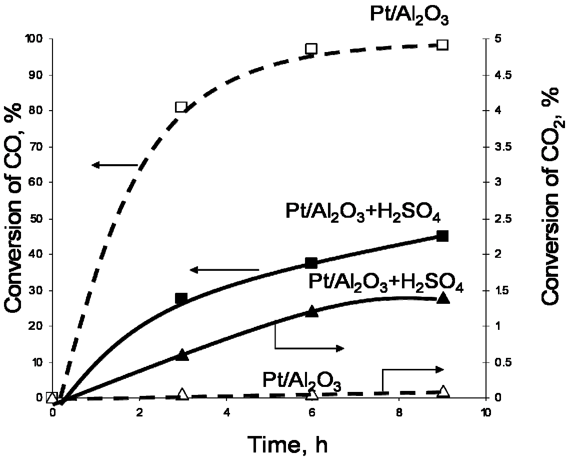

Fig. 2. Time dependence of CO (T=220 °C, 40 ml of water, p(CO)=5 bar., mcat=0.5 g) and CO2 conversion (T=220 °C, 40 ml of water, p(CO)=5 bar., p(H_2)=5 bar., m_{cat}=0.5 g) in aqueous phase over Pt/Al_2O_3 and Pt/Al_2O_3 in the presence of sulfuric acid (0.1 M)

The effect of addition of sulphuric acid on the reaction selectivity was studied for APR of glycerol (Table 2). Without addition of acid, 55 % of glycerol after 7 h of the reaction was converted into mostly H_2, CO_2 and oxygenates. The selectivity to H_2 was relatively high (68 %) and consistent with previous report [4]. Only trace amounts of CO were detected. The main oxygen containing products were ethylene glycol, propanol, ethanol, methanol and propanediol. These products are intermediates in APR and might be further converted into H_2 [13].

The effect of acid addition on the product distribution in glycerol APR was more pronounced with higher acid concentrations (Table S1, ESI†). Addition of H_2SO_4 up to 0.1 M concentration leads to decrease in CO_2 selectivity from 36 to 20 % and H_2 from 68 to 33 %. The selectivity to CO remained however relatively low (2.3 %). At the same time, the selectivity to ethane and propane increased from 3.1 to 27 % and from 1.9 to 16 %, respectively. Previously it was shown that addition of acid catalysts (e.g. aluminosilicate and zeolite) during APR of sorbitol and xylitol over Pt catalysts led to higher yield of lighter hydrocarbons [14, 15]. Interestingly, in the present work the increase in lighter hydrocarbon fraction coincided with the decrease in amount of oxygenates (Table 2). This could be due to hydrogenation of lighter alcohols to alkanes under these conditions. The remaining oxygenates were derivatives of dioxalane which probably resulted from glycerol dehydration. Note that mostly alkanes with the carbon number lower than in the parent biomass-derived hydrocarbons were detected. Indeed, the selectivity to C_5-C_7 hydrocarbons was significantly lower than the selectivity to C_2-C_3 (Table 2).

To check our hypothesis about possible conversion of CO_2 to CO in the presence of added acid, CO_2 hydrogenation was studied in biphasic system over Pt/Al_2O_3 located in aqueous phase and Ru/C located in organic phase with and without acid addition (Table 1). Note that CO is more reactive in the presence of hydrogen: its hydrogenation over Ru catalysts generally yields long chain hydrocarbons. Carbon dioxide hydrogenation in the biphasic reactor without addition of acid to the aqueous phase leads to CH_4 with the selectivity of 60 %.

Table 2. APR of glycerol over Pt/Al_2O_3 without acid and in the presence of H_2SO_4 (T=220 °C, 40 ml of water with 5 g glycerol, 0.5 g Pt/Al_2O_3, $p(N_2)$=5 bar, 7h) and combined process of APR of glycerol over Pt/Al_2O_3 (after treatment with H_2SO_4 – Pt/Al_2O_3 (H_2SO_4) and in the second cycle Pt/Al_2O_3+H_2SO_4-II) and FTS over Ru/C (T=220 °C, 40 ml of water with 5 g glycerol, 0.1 M H_2SO_4, 0.5 g Pt/Al_2O_3, 10 g decane, 0.5 g Ru/C, $p(N_2)$=5 bar, 7h)

№	Aqueous phase	Conv. Glycerol, %	S_{H2}, %	Selectivity, mol. C%									Alfa
				CO_2	CO	CH_4	C_2	C_3	C_4	C_5-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+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													
3	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
4	Pt/Al_2O_3+ 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
5	Pt/Al_2O_3+H_2SO_4-II	53	17	13.2	2.3	3.2	22.5	9.3	6.4	17.4	13.2	9.8	0.79
6	Pt/Al_2O_3 (H_2SO_4)	71	19	29.1	0.1	28.2	16.1	7.9	2.4	2.9	0.3	5.6	0.7

No CO was observed. Very small amounts of hydrocarbons with different chain length were detected under these conditions. In the presence of added acid, the main product was still methane; the selectivity to long-chain hydrocarbons however remarkably increased (Table 1). It confirms our suggestion about positive effect of added acid on the yield of carbon monoxide in WGS reaction. Even small amount of formed CO will be continuously extracted by decane and transformed into hydrocarbons.

Combination of APR and CO/CO_2 hydrogenation a single biphasic reactor

The catalytic data obtained for the combined APR and carbon monoxide hydrogenation is shown in Table 2. The combination of APR and FT synthesis was studied in the biphasic batch reactor. Similarly to CO_2 hydrogenation, Pt/Al_2O_3 catalyst was located in the aqueous phase and Ru/C was in the organic phase. The process without addition of acid to aqueous phase led to the formation of methane and light alkanes. Methane might be the product of glycerol hydrogenolysis in the aqueous phase [16] or CO_2 hydrogenation [17]. Note that the presence of Ru/C in the organic phase led to significant decrease in the oxygenate fraction in the products. This might be due to hydrogenation and hydrogenolysis of oxygenates in the presence of hydrogen over Ru/C. Small amount of long chain hydrocarbons (1 % of C_8+) were also detected.

Addition of sulphuric acid to the aqueous phase resulted in major changes in selectivity patterns. Methane formation was significantly suppressed, while hydrocarbon selectivity shifted to long chain hydrocarbons (Table 2, Table S1, ESI†). Higher selectivity to long chain hydrocarbons in FT synthesis can be attributed to higher fraction of carbon monoxide produced during APR of glycerol in the presence of acid. Indeed, the CO_2 selectivity decreases from 30 to 12 % which might be due to the enhancement of the reverse water gas shift reaction (Table 2). The selectivity to C_5+ hydrocarbons calculated on basis of carbon atoms of converted glycerol was around 30 %. The increase in the selectivity to hydrocarbons is accompanied by a decrease in the selectivity to oxygenates and light hydrocarbons (methane, ethane). This is the result of the continuous consumption of hydrogen for FTS, which leads to decrease of the hydrogen consumption for hydrogenolysis.

The effect of sulfuric acid addition could be also explained by modification of the catalyst. In order to check influence of sulphuric acid on the active sites, Pt/Al_2O_3 catalyst was treated by 0.1M H_2SO_4 under the reaction conditions (T=220 ˚C, t=7h). Then, the catalyst was washed by water afterwards and used again in the biphasic reaction of glycerol transformation without addition of acid. The catalytic results were similar to those measured for untreated sample showing high selectivity to CH_4 and CO_2 (entry 6, Table 2). This suggests that the change in the selectivity could be related to the influence of H_2SO_4 on WGS equilibrium rather than to the modification of catalyst structure.

Pt/Al_2O_3 could also deactivate during combined process by products of condensation of oxygenates. In order to check the extent of deactivation the catalyst was extracted after reaction (entry 4). The catalytic performance of the spent catalyst was tested in the second cycle (entry 5). The catalyst showed the product distribution similar to the results in the first cycle.

In the current work, decane was used as a solvent for APR-FT experiments. In order to exclude possible formation of hydrocarbons due to hydrogenolysis of decane, APR-FT experiment was conducted at the same conditions but without glycerol. The amount of hydrocarbons formed from decane would correspond to only 0.9 % selectivity to C atoms. This suggests that the solvent is not involved in the APR or FT reactions.

The hydrocarbon distributions obtained in CO, CO_2 hydrogenation and combined APR-FT processes are shown in Fig. S1, ESI†. The distribution curves followed Anderson-Schulz-Flory (ASF) statistics. The apparent chain growth probability (α) was a function of the operating conditions. Hydrogenation of CO in biphasic system (Table 1) led to the chain growth probability of 0.84. The α was lower (0.76) for carbon dioxide hydrogenation in biphasic reactor. The intermediate chain growth probability of 0.75-0.79 and process selectivity of 30% to C_5+ hydrocarbon products were observed in the combination of APR and FT synthesis in the presence of acid (Fig. S1, ESI†).

Thus, the combination of APR and FTS results in glycerol transformation into hydrocarbons with C_5+ selectivity about 30 % and CO_2 transformation with C_5+ selectivity about 50 %. In order to further increase selectivity both the catalysts and reaction parameters should be optimized. The acid might be proposed which would not dehydrate alcohols to olefins but shift the equilibrium in the direction of CO formation. A close contact between aqueous and organic phase could be beneficial for fast consumption of produced CO and H_2 before their participation in hydrogenation in aqueous phase. This might be achieved by application of emulsion type system with surfactants for closer contact between aqueous and organic phase.

Conclusions

A combination of APR with FT synthesis in a biphasic reactor under the same operating conditions led to the direct synthesis of long chain hydrocarbons from glycerol. In this reactor, APR occurs over a hydrophilic Pt/Al_2O_3 catalyst in aqueous phase, while FT synthesis is catalysed by a hydrophobic Ru/C catalyst in organic phase. Addition of sulphuric acid to the aqueous phase led to higher yield of carbon monoxide in the APR process and in a 5- fold increase in C_5+ selectivity (up to 30%) in the combined process.

Notes and references

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
Fax:+330320336236;Tel:+330320436953
Email: Vitaly.Ordomsky@univ-lille1.fr

Electronic Supplementary Information (ESI) available: [Preparation of catalysts, catalytic tests, WGS in the presence of acid, APR and APR-FTS]. See DOI: 10.1039/c000000x/

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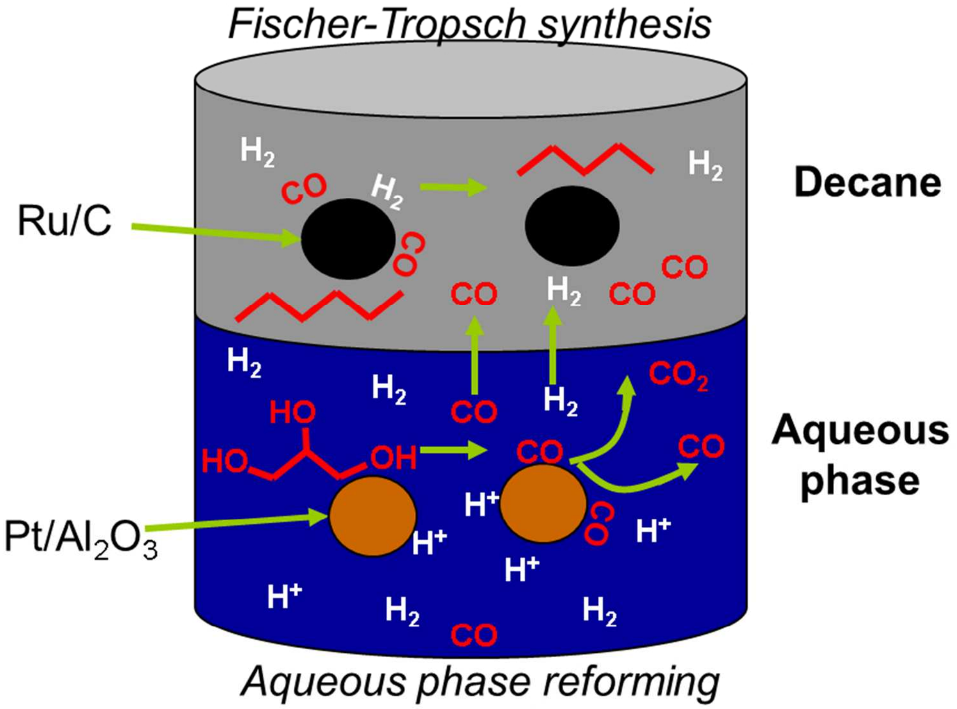

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Combination of aqueous-phase reforming of glycerol and Fischer-Tropsch synthesis in a single biphasic reactor in the presence of acid leads to formation of long chain alkanes.