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Enhanced Activity and Selectivity of Fischer−Tropsch Synthesis Catalysts in Water/Oil Emulsions

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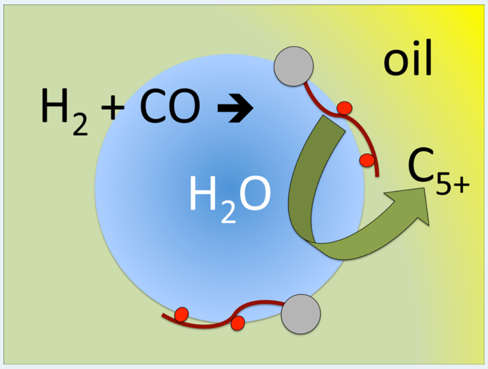
Supporting Information

ABSTRACT: Amphiphilic nanohybrid catalysts (Ru particles supported on carbon nanotube−metal oxide hybrids) enable the formation of water-in-oil emulsions and have a positive influence on the Fischer−Tropsch synthesis (FTS) activity and selectivity to desirable products in comparison with those obtained in single-phase solvents under the same reaction conditions. The reaction experiments were conducted at 473 K in a batch reactor that uses H_2/CO syngas as a feed at 2.0−3.5 molar ratio and 4136.85 kPa total pressure. One of the main effects observed when using the biphasic mixture instead of a single solvent is the spontaneous separation of products by solubility differences, which affect mass-transfer-dependent secondary reactions. Another positive effect of using the biphasic system arises from the enhanced FTS activity observed in the presence of condensed aqueous phase. Finally, the presence of an emulsion seems to improve the C_1/C_{5+} product balance, which can be explained by a dual-site model recently proposed in the literature.



KEYWORDS: *Fischer−Tropsch synthesis, emulsion, carbon nanotubes, nanohybrids, water*

1. INTRODUCTION

As a primary product, water is always present in the Fischer−Tropsch synthesis (FTS). It has long been acknowledged that water can significantly affect activity and selectivity,[1,2] but its effects largely depend on the specific metal chosen as the catalyst. For instance, it is recognized that in Fe-catalyzed FTS, water has an inhibiting effect on activity that can be attributed to catalyst oxidation.[3−5] In Co-catalyzed FTS, the effects are more complex and depend on the catalyst composition, nature of the support, and preparation method used. For example, in some of the studies involving Co catalysts, enhanced CO conversion[6,7] and lower methane selectivity[8] were observed in the presence of added water relative to the "dry" conditions. The water generated as a byproduct during FTS has also been observed to have similar effects.[9] The enhanced activity in the presence of water has been ascribed to a reduced energy barrier of the CO dissociation step due to water−CO interaction.[10−12] Alternatively, this enhancement has also been linked to oxidation of low coordination sites or surface reconstruction.[8] At the same time, the role of water in reducing methane selectivity has been explained in terms of a higher surface concentration of active carbon intermediates that lead to longer carbon chains.[8]

Another effect of water on Co catalysts is the enhanced production of alkenes, which is most probably due to the inhibition of secondary hydrogenation by competitive adsorption of water.[7] By contrast, other studies have reported inhibition in overall activity; however, in those cases, the Co particles were smaller than 4 nm and more susceptible to oxidation by water.[13] Additional considerations must be given to the effect of the support, which may affect the interaction with water. For example, on Co/SiO_2 catalysts, the addition of water vapor facilitates the formation of Co silicate, which inhibits the reduction of Co oxide and causes catalyst deactivation.[14] Similarly, when Al_2O_3 was used as a support, water addition was found to favor the formation of cobalt aluminate, which is difficult to reduce and also inhibits the activity.[15] Recent studies on Co/Al_2O_3, conducted at low conversions or on catalysts that have been preconditioned to minimize catalyst deactivation, showed the same positive effects of water as those mentioned above, that is, increased selectivity to long chain products and decreased selectivity to CH_4.[16,17] On a TiO_2 support, the interaction with Co does not seem to be enhanced by the presence of water. Thus, at low partial pressures, the effects of water on Co/TiO_2 catalyst are similar to those observed on unsupported Co.

At higher water partial pressures, the presence of a condensed water phase may complicate the situation because the transport of CO and H_2 might be enhanced in liquid water. As pointed out by Iglesia[18] and discussed further below, the presence of condensed water in the catalyst pores might

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increase the accessibility to regions in the catalysts that otherwise are mass-transport-limited.

Ru-catalyzed FTS is ideal to investigate the effect of water on catalyst activity because Ru has a high resistance to oxidation by water.[19−24] For example, in a recent study, Claeys and van Steen[25] used a Ru catalyst to investigate the FTS in a continuously stirred slurry reactor and found that the CO conversion increased with increasing water partial pressure. In addition, in agreement with the results observed on Co catalysts,[26−28] methane selectivity decreased and C_{5+} selectivity increased with increased water content. This behavior was ascribed to the inhibition of product desorption and promotion of chain growth by water. In this case, it was observed that the yield of products in the low carbon number range (C_3−C_7), which are not subject to secondary reactions, increased with water partial pressure. By contrast, secondary hydrogenation was inhibited by water, as demonstrated by higher alkene content.

The exact way in which the presence of water facilitates the rate-limiting step of the FTS reaction has been a matter of interest during the past few years.[29,30] As mentioned above, rate enhancement due to water-assisted transport[18] is possible; however, the enhancement was also observed on very small catalyst pellets, which would exclude important intrapellet transport limitations. Therefore, an intrinsic kinetic enhancement has been proposed. Theoretical calculations have shown that CO dissociation has a much lower energy barrier when assisted by surface H.[29,30] Accordingly, it was proposed that water enhances the rate of the kinetically relevant CO activation by mediating the formation of COH* via a H-shuttling mechanism in which H* is transferred to a nearby H_2O molecule to form a short-lived $H_3O^{\delta+}$ intermediate that protonates the O of CO*.[31] The COH* thus formed undergoes $H^{\delta-}$ addition at the C, forming an *HCOH* intermediate and dissociates with nearby H_2O, which acts as a "H-shuttling mediator" in the kinetically relevant step. This mediating effect of water can also be responsible for the observed C_{5+} selectivity enhancement over Ru and Co catalysts when water is added.[31]

Within this context, it is interesting to investigate the changes in activity and selectivity when FTS is conducted in the presence of two liquid phases, organic and aqueous. We have recently conducted FTS in an emulsion system,[32] using nanohybrid catalysts that stabilize emulsion droplets by adsorbing at the liquid−liquid interface. Using an emulsion system for the FTS reaction exhibits some interesting advantages, such as the spontaneous product separation based on solubility differences, a higher catalyst tolerance against the presence of poisons, and an enhanced conversion in comparison with that obtained in organic single phase under the same conditions.

As described above, most FTS studies investigating the effect of water have concentrated on the addition of water vapor at varying partial pressures in the syngas feed. A recent FTS investigation[33] has revealed much higher CO conversions in liquid water than in common organic solvents. The incorporation of liquid water in the reaction system instead of water vapor presents different aspects to investigate. First, when varying amounts of condensed water are present, the equilibrium chemical potential of water remains unchanged. Thus, one should not expect changes in surface composition or intrinsic kinetics. By contrast, solubility and diffusivity of syngas and products may be greatly affected by the presence of varying amounts of condensed water. For example, syngas has diffusion coefficients in water that are three times higher than in typical hydrocarbon liquids.[34,35] Likewise, the diffusivities and solubilities of FTS products in water are very different from those in organic solvents. Therefore, the role of relative mass transfer rates is an important consideration when analyzing differences in rate among different media.

Finally, depending on the catalyst and support used, the biphasic system may adopt different configurations. As previously shown,[36] nanotube-based amphiphilic particles generate water-in-oil (w-in-o) emulsions with droplet sizes that depend on the water/oil volume ratio used. Partial oxidation of the nanohybrids with nitric acid produces functional groups on the carbon nanotube surface, thus enhancing the hydrophilicity of the nanohybrids. When the hydrophilic/hydrophobic balance is large enough, the emulsion can be reversed from w-in-o to o-in-w. The solvent−catalyst interaction affects not only the emulsion configuration but also the distribution of catalyst particles. For example, in our recent FTS study[32] over a Ru catalyst in an emulsion system, the majority of the Ru particles were located on the hydrophobic carbon nanotubes. Therefore, the catalyst resided preferentially in the oil side of the emulsion. In this sense, the support may play a more important role when the FTS is conducted in a biphasic liquid mixture than when it is conducted in the gas phase. In the present contribution, we have carried out a detailed examination of FTS over Ru catalysts in an emulsion system as well as in single-phase solvents. In addition to spontaneous separation of products in emulsion, significant enhancements in catalyst activity and product selectivity have been revealed; they are discussed in light of the kinetically promoting effect of water and the effect of emulsion on mass transfer of both reactant (syngas) and products.

2. EXPERIMENTAL SECTION

2.1. Materials. Catalysts were prepared by incipient wetness impregnation onto nanohybrid supports. Ruthenium(III) chloride hydrate (99.98%, Sigma-Aldrich) was dissolved in water and impregnated dropwise onto a determined amount of support. The impregnated samples were dried for ~12 h in a vacuum oven at 353 K, subsequently reduced in flowing H_2/Ar (1/10 volume ratio) at 673 K for 3 h, cooled to room temperature, and passivated in flowing O_2/He (1% O_2) for 2 h. The carbon nanotube-based nanohybrids, which consist of ~70 wt % multiwalled carbon nanotubes and the balance of Al_2O_3 and MgO, was prepared following established procedures,[37] in which the synthesis was carried out at 973 K in a vertical fluidized-bed reactor using ethylene as the carbon source and Fe−Mo as the catalyst prepared by incipient wetness impregnation of their precursor solution onto Al and Mg oxide supports.

Catalyst surface areas were determined by N_2 adsorption (BET, Micromeritics, ASAP 2000). Ru loadings were determined by inductively coupled plasma (ICP, Galbraith Laboratories). Estimation of average particle sizes was based on transmission electron microscope analysis (TEM) conducted on a JEOL 2000-FX unit.

2.2. Catalytic Activity Measurements. The FTS rates and selectivities were measured in a 100 mL stainless steel autoclave batch reactor (from Parr Instruments). In a typical experiment, 150 mg of catalyst and 30 mL of single phase or biphasic solvent were added to the reactor vessel. Three different solvents were used: decalin (anhydrous, ≥ 99% purity, Sigma-Aldrich), water (HPLC grade, Fischer Scientific), or a decalin/water mixture at a 2:1 ratio. The decalin/water mixture formed a water-in-oil emulsion upon stirring in the presence of the catalyst, as described in our previous study.[32] To reduce the catalyst, the reactor was sealed, purged, and pressurized with H_2 to 2757.90 kPa for a reduction period of 12 h at 523 K. After reduction, the system was cooled to room temperature, and the feed was introduced from a cylinder containing the premixed $H_2/CO = 3.5$ syngas (from Air Liquide) to first purge and then pressurize the reactor to a total pressure of 4136.85 kPa. The temperature was quickly raised to 473 K to conduct the FTS reaction in batch mode under a constant stirring speed of 700 rpm. After completing the reaction period, the resultant gas phase composition was identified and quantified on a gas chromatography−thermal conductivity detector (GC−TCD, Carle 400 AGC) with a built-in MultiCoat column and a gas chromatography−flame ionization detector (GC−FID, Varian CP-3800) with a Chrompack silica PLOT column (Catalog #8568, 60m x 0.32 mm ID). CO conversion was based on the quantification of its disappearance after the reaction. Liquid phase products were analyzed after filtration using GC−FID (Agilent 7890B) equipped with an Agilent G4513A auto sampler and a Phenomenex ZB-5 fused-silica column (60 m × 0.25 mm × 0.25 μm). For single water-phase runs, upon completion, decalin was added to the vessel, which was resealed and pressurized with 2068.43 kPa of nitrogen. Products were then extracted into decalin at 423 K for 2 h.

3. RESULTS

3.1. Catalyst Characterization. Figure 1a shows a TEM image of Ru particles (average size =2 nm) supported on the nanohybrid support. When these nanohybrids are placed in a decalin/water mixture without stirring, they tend to migrate toward the decalin/water interface (Figure 1b). Upon stirring with a sonicator, a stable emulsion is formed.[36] As shown in Figure 1d, the dark top part consists of water-in-oil emulsion, with decalin as the continuous phase, while the clear bottom part is the free aqueous phase. The optical microscopy image of the emulsion (Figure 1c) shows droplet sizes in the range of 1−5 μm.

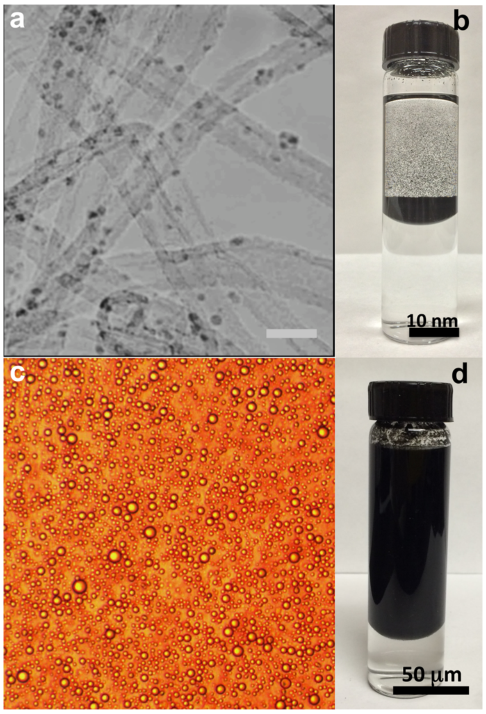


Figure 1. (a) TEM images of Ru supported on nanohybrid; (b) optical image of nanohybrids in decalin/water mixture before stirring; (d) emulsion formed upon stirring; (c) microscopy image of the emulsion.

3.2. FTS in Biphasic Liquid Mixtures of Varying Water/Decalin Ratio in a Batch Reactor. To quantify the initial catalyst activity in the water/decalin biphasic system, specific FTS reaction rates were measured at varying water/decalin ratios in a constant total volume of solvent. The CO conversion was kept below 20%, catalyst load = 100 mg, H_2/CO molar ratio = 2, and reaction period = 2 h. Figure 2 shows the evolution of FTS activity (expressed as TOF) together with the amount of CH_4 produced as a function of the amount of CO consumed. Depending on the amount of water added to the mixture and the reaction temperature (473 K), water may exist as vapor or as a condensed phase. As shown in the Supporting Information, the saturation vapor pressure at 473 K (dew point) is reached with addition of 0.5 mL of water. With further addition of water, a condensed phase is formed. As shown in the figure, the TOF increases, and the CH_4 selectivity decreases with increased water content, in agreement with previous studies conducted in the vapor phase.[31] An interesting point to emphasize is that the trend continues well beyond the threshold for appearance of liquid water. That is, although the chemical potential of water cannot increase beyond the saturation, the presence of increased amounts of liquid water seems to continue enhancing the TOF and suppressing the production of CH_4. It is reasonable to speculate that, with much less restrictions in the liquid phase, water may act as a more effective H-shuttle than when it is adsorbed on the surface. It must be noted that the contribution of the water−gas shift to CO consumption, although minimal,[32] was taken into account in the calculation of the TOF to ensure that only the FTS activity was considered (see Supporting Information).

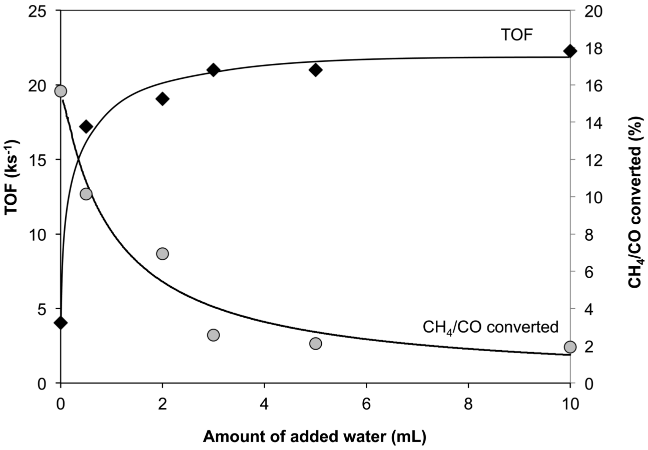


Figure 2. Evolution of TOF and methanation as a function of initial amount of liquid water added into decalin, keeping a total of 30 mL of solvent(s). Reaction condition: T = 473.15 K, t = 2 h, syngas ratio (H_2/CO) = 2.

On the basis of these observations, we have chosen for the subsequent studies a mixture of 10 mL of water + 20 mL of decalin, which results in a maximum enhancement of catalyst activity and product selectivity. That is, the TOF does not significantly increase beyond this point. In addition, the relatively higher fraction of oil phase coupled with the dominant hydrophobicity of the nanohybrid facilitates the formation of a water-in-oil emulsion.[36]

The TOF values for the nanohybrid-supported Ru catalyst in decalin, emulsion, and aqueous media were quantified over 2-h reaction periods in the batch reactor, using 100 mg of catalyst at a conversion level below 30%. The data are summarized in Figure 3. As can be seen, the catalyst exhibited the lowest activity in the absence of added water, when single-phase decalin was used as a solvent. Much higher TOF values were obtained when the reaction media contained water. That is, the reactions conducted in emulsion and in water single phase resulted in activity increases of nearly 60%. The enhanced catalyst activity in the presence of water agrees well with our earlier results of FTS in emulsion[32] and with the promoting effects of water observed by others, as discussed above.

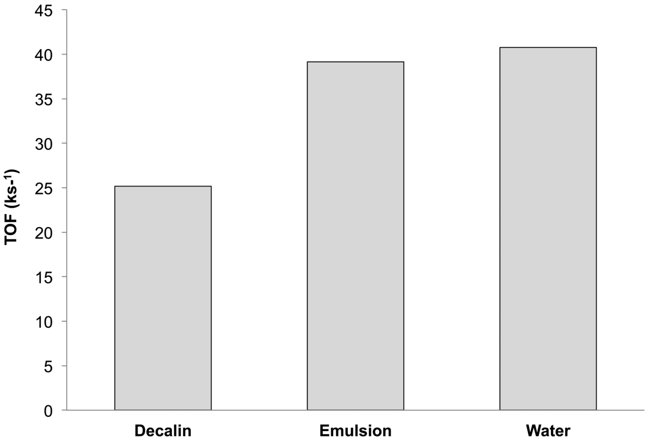


Figure 3. TOF of nanohybrid-supported Ru catalyst in different solvents. Reaction condition: $T = 473.15$ K, $t = 1$ h, syngas ration (H_2/CO) = 3.5.

3.3. Alcohols, Alkenes, and Alkanes Obtained in Single-Phase and Biphasic Liquid Mixtures.

Table 1 shows the different product distributions obtained at a similar conversion level (≈65%) in the three media. In particular, the fractions of alkanes, alkenes, and alcohols in C_6, C_{12}, and C_{18} products are compared. It is clearly seen that the products obtained in emulsion and single-phase water were higher in alcohol content than when conducted in single-phase decalin, especially for the low-carbon-number range (e.g., C_6). Another interesting observation is that the alkene/alkane ratio was lower in the single-phase water medium than in those containing the organic solvent.

At higher conversions, because of the high H_2/CO ratio employed in this study, secondary hydrogenation took over, and alkanes became the dominant products. That is, although alcohols and alkenes were observed at conversion levels of ≈65%, they disappeared as the conversion increased to 90%. To demonstrate this trend, the products of the run conducted at 65% conversion were subject to a postreaction hydrogenation (in pure H_2 at 473 K). The resulting product distribution was almost identical to that obtained at 90% conversion (See Supporting Information). The postreaction hydrogenation facilitates the analysis of the carbon chain length distribution, as shown below. Obviously, because the reaction was conducted in a batch reactor, the product selectivity reflects the cumulative reaction period and does not correspond to the instantaneous selectivity at the end of the experiment.

3.4. Chain Length Distribution in Single-Phase and Biphasic Liquid Mixtures.

Figure 4 compares the product carbon chain length distribution in terms of carbon molar fractions at the same conversion level of ≈65%. It can be seen that in decalin single phase, the highest fraction of carbon corresponds to the light gas products (C_1−C_4). This fraction is lower for the run conducted in single-phase water, and particularly, much lower for the run conducted in the emulsion. In fact, for this system, the fraction of lights (C_1−C_4) is the lowest, making the C_5−C_{12} range, the highest (i.e., >55%) and the broadly desirable FTS range (C_5−C_{20}) more than 76% of the products. Table 2 summarizes the above data numerically. The high selectivity to light products (C_1−C_4) in the absence of excess water could be explained on the basis of the concepts described above. That is, the production of CH* growth units, as well as chain growth rate, are relatively low without water acting as a mediator that enhances the chain growth. For reference, chain growth probability, defined as

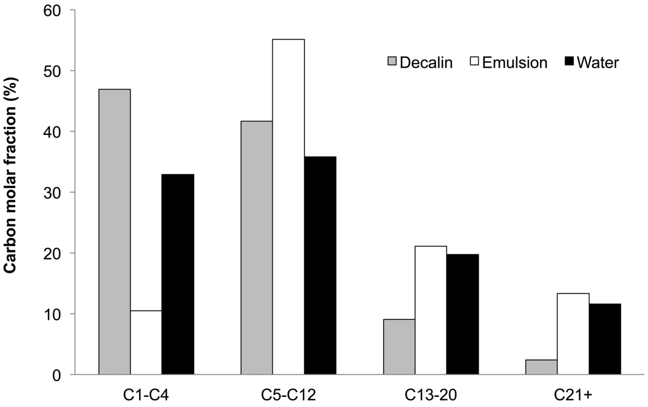


Figure 4. Product distribution obtained at a conversion of ≈65% in decalin, emulsion, and water. All reactions were conducted with 150 mg of catalyst under the same conditions of 4136.85 kPa initial syngas (H_2/CO = 3.5) and 473.15 K as indicated in the Experimental section.

Table 1. Alkane/Alkene/Alcohol Fraction (%) for C6, C12, and C18 Products in Decalin, Emulsion, and Water, at a Conversion of ≈65%[a]

	C6			C12			C18		
	alkane	alkene	alcohol	alkane	alkene	alcohol	alkane	alkene	alcohol
decalin	43.9	26.0	30.1	51.6	28.7	19.7	46.6	43.1	10.3
emulsion	24.1	24.2	51.7	36.4	36.9	26.7	36.3	37.9	25.8
water	34.5	10.3	55.2	65.7	13.2	21.1	70.8	4.3	24.9

[a] All reactions were conducted with 150 mg of catalyst at the same conditions of 4136.85 kPa initial syngas (H_2/CO = 3.5) and 473.15 K, as indicated in the Experimental section.

Table 2. Product Distribution Obtained at a Conversion ≈65% in Decalin, Emulsion, and Water[a]

	product distribution(%)			
	C1−C4	C5−C12	C13−C20	C21+
decalin	46.9	41.6	9.1	2.4
rmulsion	10.5	55.1	21.1	13.3
water	32.9	35.8	19.7	11.6

[a] All reactions were conducted with 150 mg of catalyst under the same conditions of 4136.85 kPa initial syngas ($H_2/CO = 3.5$) and 473.15 K, as indicated in the Experimental section.

$$\alpha = \frac{R_p}{R_p + R_t}$$

where R_p and R_t are the rates of propagation and termination, respectively, was calculated on the basis of fitting with the Anderson−Shulz−Flory (ASF) equation[38] (see Supporting Information for more details). The α value was determined to be 73.5%, 80.9%, and 80.6% for decalin, emulsion, and water runs, respectively. It should be noted that in the derivation of the ASF equation, it is assumed that all products are from primary FTS reactions. However, this is not the case here, particularly operating at rather high conversion levels and in the liquid phase where products have long residence time and greater chance to undergo secondary conversion. Nevertheless, the comparison of α values serves as an additional support to the enhanced chain growth rate in the presence of water.

A point to note is that, being an FTS product, water is always present in increasing amounts as the conversion increases, even in the runs conducted in single decalin phase. In fact, the effect of inherently and cumulatively generated water is reflected in the larger factor by which the CO conversion increases with increasing reaction time comparing runs in single decalin phase with those in emulsion and single water phase (i.e., the X_{8h}/X_{2h} ratios shown in Supporting Information Table S2). These trends are in line with the concept of the promoting effect of water and with previous observations made in other studies.[9] Nevertheless, the amount of FTS-generated water was small in all cases and, in the runs conducted in decalin, it was clearly below that needed to reach the saturation vapor pressure. By contrast, this condition was present for both emulsion and single water phase (see Supporting Information). Therefore, the single decalin phase is addressed as "dry" conditions for qualitative discussion in this study.

3.5. Catalyst Deactivation in Single-Phase and Biphasic Liquid Mixtures.

Table 3 compares the evolution of the chain length distributions in the products obtained in the emulsion at various conversion levels with those obtained in the water single-phase reaction at comparable conversions. The differences are apparent: the C_1−C_4 selectivity not only was much higher in water single phase, but also increased considerably with conversion. By contrast, in the emulsion case, the C_1−C_4 selectivity increased only slightly. Likewise, the changes in the C_5−C_{20} fraction were minimal as conversion increased from 40% to 80%, as opposed to the large drop (from 53.7% to 35.7%) observed in single-phase water over a similar conversion span. It must be noted that the increase in conversion in the batch reactor is achieved by extending the reaction period. Therefore, it is important to take into account the deactivation of the catalyst that can take place as a function of reaction time. This effect was addressed in the following set of experiments.

In Figure 5a, we display the evolution of conversion as a function of time for the runs in single-phase water and in emulsion; each data point corresponds to a separate batch run. The estimation of the uncertainty level is based on repeated 6-h runs in each solvent medium, and it is expressed in terms of standard error. It should be noted that in the sealed batch reactor, the syngas pressure does not remain constant as the reaction progresses. Therefore, to compare the differences in activity under equivalent pressure conditions, we have plotted in Figure 5b the variation of slope (rate) obtained from Figure 5a as a function of conversion because at any given conversion, the syngas pressure is the same in all cases. That is, a higher rate at a given conversion reflects an intrinsically more active catalyst. Accordingly, the catalyst exhibits a much higher initial activity when run in single-phase water, but lower after a few hours. As discussed above, the higher initial activity in single-phase water could be ascribed to the promoting effect of water, that is, a higher diffusion coefficients of CO/H_2 in water; the unhindered access of water as H-shuttle to the catalyst surface; or both; but the lower catalyst activity observed at higher conversions (i.e., longer reaction times) in single-phase water reflect a faster catalyst deactivation. By taking together the evolution of carbon chain distribution and conversion rate with respect to conversion, one can see a clear link between the catalyst deactivation and the increase in selectivity to light products in both emulsion and water single phase.

We conducted another set of experiments to assess the effects of the catalysts' deactivation. The FTS reaction was carried out for 6 h in two modes: continuously and in three 2-h stages. In the staged runs, each of the three 2-h periods was followed by reactor cool-down to room temperature, analysis, reactor purge, and reload of fresh syngas feed up to the original pressure (4136.85 kPa). After the 6-h continuous and staged runs, a 2-h run was conducted with fresh feed over the spent catalyst to compare the degrees of deactivation and selectivity changes caused by the two different operating modes in both emulsion and single-solvent media. As compared in Table 4, for the reaction conducted in the emulsion system, there was no significant difference between the TOF measured on the catalyst after a continuous 6-h run and that after the staged (3 × 2 h) runs. By contrast, the catalyst in single-phase water suffered a more severe deactivation during the continuous 6-h run than during the staged (3 × 2 h) runs. Table 4 summarizes

Table 3. Product Distribution at Different Level of Conversions in Emulsion and Water Single Phase

	product distribution (%)							
	emulsion				single water phase			
level of conversion	C1−C4	C5−C12	C13−C20	C21+	C1−C4	C5−C12	C13−C20	C21+
low conversion	10.6	55.4	21.2	12.8	30.8	32.2	21.5	15.5
medium conversion	11.0	55.2	21.3	12.5	48.8	29.8	13.6	7.8
high conversion	15.0	50.3	22.0	12.7	56.6	21.4	14.3	7.7

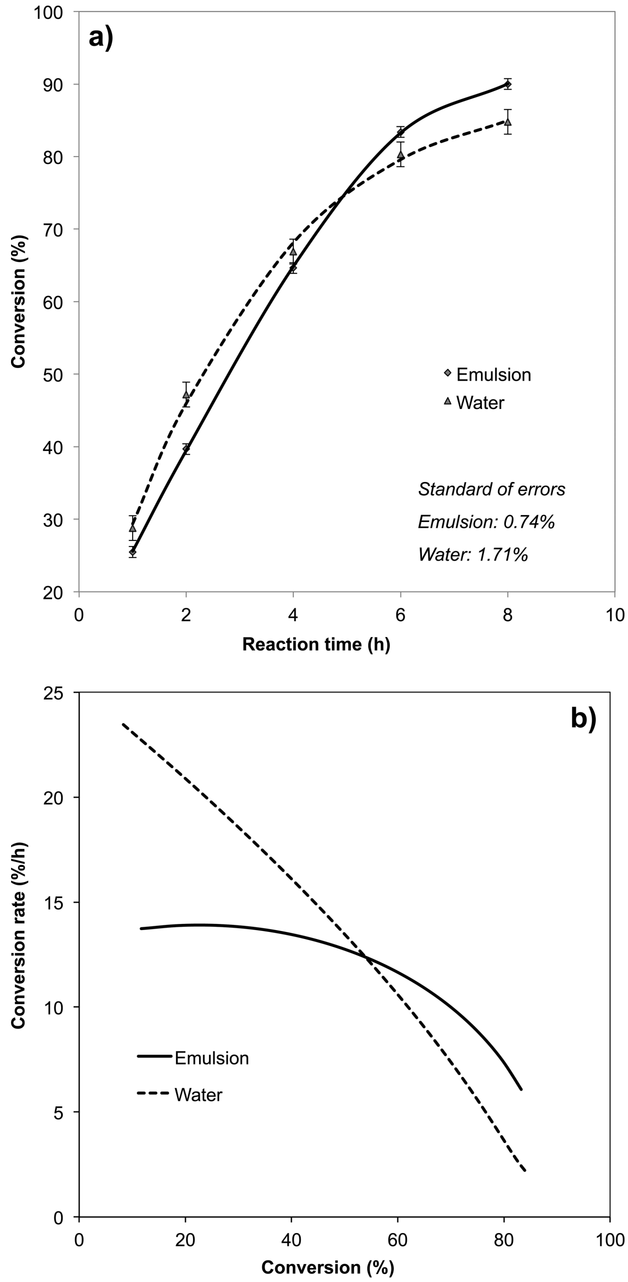


Figure 5. CO conversion vs reaction time in emulsion and water phase, with each data point from a separate run (standard of errors was based on repeated 6-h runs in emulsion and water and assuming the same extent of errors for the rest of the data points) (a), and CO conversion rate vs conversion in emulsion and water phase, analytically obtained by taking derivatives of the curve of CO conversion vs reaction time with respect to reaction time (b).

the differences in TOF and C_1−C_4 selectivity for the runs after the continuous and staged runs in emulsion and single-phase water. It can be seen that although the two comparative runs in water gave similar CO conversions, the run with the stronger deactivation (i.e., after the continuous run) led to much higher selectivity to gas phase products (C_1−C_4). Here again, the direct link mentioned above between the extent of deactivation and selectivity to light products is clearly evident.

Table 4. Data of 2-h FTS Reactions Following 6-h Staged or Continuous Reaction Periods in Emulsion and Single Water Phases

reaction media	parameters	after three 2-h runs (100 mg catalyst)	after one 6-h run (150 mg catalyst)
emulsion	TOF ($\times 10^{-3}$ s^{-1})	26.0	26.5
	CO conversion (%)	19.0	29.4
	gas fraction (%)	9.3	13.4
single water phase	TOF ($\times 10^{-3}$ s^{-1})	31.4	20.8
	CO conversion (%)	23.2	23.9
	gas fraction (%)	13.6	22.6

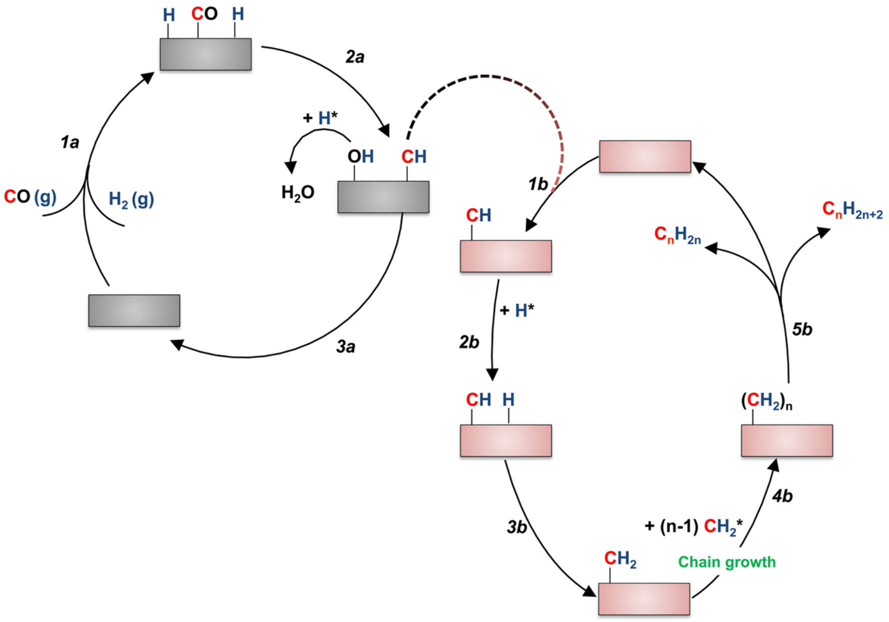
4. DISCUSSION

4.1. Effects of Reaction Media on Relative Alcohol/Alkene/Alkane Contents. As noted above, when the FTS was conducted in emulsion and in single-phase water media, the products were higher in alcohol, especially for low carbon numbers (e.g., C_6). This enhanced alcohol/alkene is likely due to secondary alkene hydration accelerated by the presence of water. At the same time, if alcohols are formed as primary products, it is possible that dehydration is less efficient in the presence of excess water. The enhancement of the alcohol/alkene ratio is especially pronounced for the low-carbon-number products because short alcohols preferentially partition in the water phase and, as a result, have a lower concentration in the oil phase. Of course, as emphasized by Madon and Iglesia,[39] reaction rates depend on the thermodynamic activity (i.e., chemical potential) of reactants and products rather than concentrations. However, when the reaction or selectivity is affected by the rate of mass transfer, solubility may affect selectivity, which seems to be the situation in this case.

On the other hand, the lower alkene/alkane ratio in the single-phase water medium can also be explained by the role of relative mass transfer rates. Alkenes have very low solubility in water. Therefore, when they are produced in the water medium, they cannot dissolve into the aqueous phase, and they would tend to remain on the catalyst surface, forming a separate phase, most probably a surface thin film. As a result, readsorption and secondary hydrogenation should be more effective than when an organic phase is in direct contact with the catalyst, which would allow a fast removal from the region around the catalyst. Obviously, these solubility effects of the solvent medium indicate that the system should not be in phase equilibrium (i.e., same chemical potential in each phase), but rather, should have concentration gradients that significantly alter the product selectivity.

4.2. Effects of Reaction Media on Catalyst Deactivation and Product Chain Length Distribution. Although the very high selectivity to light products (C_1−C_4) obtained in single-phase water seems to contradict the concept of water acting as a mediator that enhances chain growth, the series of experiments on catalyst deactivation in single-phase and biphasic liquid mixtures reconcile the proposed explanation with this apparent contradiction. As mentioned above, these experiments clearly indicate a link between the catalyst deactivation and the increase in selectivity to light products

Scheme 1. Overall FTS Process on the Catalyst Surface[a]



[a] CO dissociates into CH species on site 1 (2a), which migrate onto site 2 (1b) for chain growth (4b). In water, the higher diffusion coefficients and unhindered accessibility of water to the surface results in a high initial production rate of CH species. In addition, hydrocarbon molecules cannot desorb as readily as in emulsion (5b). Therefore, the catalyst deactivates quickly in water and slowly in emulsion because of better synchronization between sites 1 and 2.

in both emulsion and water single phase. In fact, the relationship between catalyst deactivation and increased selectivity to light products has been previously observed in vapor-phase FTS.[40,41] The important issue that needs to be addressed is the difference in the extent of deactivation between the two media.

A potential deactivation path that has been frequently considered[42,43] is the sintering of the metal clusters; however, TEM examination of the catalyst spent in the two media during 8-h reaction periods revealed the same extent of particle growth in both media (see Supporting Information). Therefore, sintering cannot account for the observed differences in rate of deactivation. Another potential reason for catalyst deactivation could be the loss of active metal species;[44] however, ICP results indicate that the Ru content was identical after 8-h reaction in the two media (3.0 wt %), from the original 3.5 wt % on the fresh catalyst.

By contrast, the recently proposed dual-site model[45−47] is consistent with the observations presented in this work. This model contemplates two distinct surface sites (1 and 2) on the FTS catalyst. Site 1 is responsible for CO dissociation, and site 2 is responsible for chain growth. Our observations would indicate that during the initial stages of reaction in single-phase water, the higher diffusion coefficients and unhindered accessibility of water to the surface results in a high initial activity. However, the hydrocarbon products are not removed efficiently by the water solvent and tend to stay on the catalyst surface, causing the deactivation of site 2 (responsible for chain growth) and enhancement of light products. If the amount of single-carbon species (C*) produced greatly exceeds the consumption capability of site 2, excess C* species may form carbonaceous deposits that further deactivate the catalyst.

In the emulsion system, the rates on sites 1 and 2 remain more balanced. First, the mass transfer rate of syngas to the surface may be limited as a result of the lower diffusion coefficients in oil. Then the formation of C* species on site 1 may not greatly exceed the C* consumption on site 2, as in the case of single-phase water. Second, and perhaps more important, in the emulsion medium, the hydrocarbon products can more readily desorb from the catalyst surface into the oil as a result of their higher solubility in the oil phase. As a result, site 2 can be kept free and available for continued chain growth. Therefore, contrary to the case of single-phase water, the emulsion can preserve both sites active by keeping a relative balance between them. The above concept is summarized in Scheme 1. One might expect direct evidence for carbonaceous deposits by temperature-programed oxidation or hydrogenation; however, it is apparent that significant site deactivation may occur with even small amounts of carbon, especially considering the low Ru loading in the catalyst. Similar conclusions have been drawn in a recent study.[17]

The continuous and staged runs provide further investigation into the differences in deactivation between the emulsion and single-solvent systems and lend more support to the concepts presented above. In the emulsion system, the activity of sites 1 and 2 remains well balanced, but it becomes unbalanced in the single-phase water medium. Therefore, the catalyst activity does not change significantly with time in the former case, but it does in the latter. During the 6-h continuous run in water, the hydrocarbon product that cannot dissolve in the solvent and accumulates as a film over the catalyst causes a more pronounced deactivation. However, the formation of the deactivating film on the surface may be disrupted in the staged run, when the reaction is stopped and restarted intermittently. That is, the process of cooling, depressurizing, and incorporating a new feed may cause the removal of the accumulated species on the catalyst. Thus, the catalyst deactivation may not be as severe as during the continuous 6-h run in water solvent. In line with these results, previous transient isotopic tracing studies on Co catalysts[8] have demonstrated that the enhanced

CO dissociation by the presence of water generates an increase in surface coverage of single-carbon species (C*), which is not paralleled by a similar increase in the consumption of these C* species. As a result, this imbalance causes a “carbon crowding”.

5. CONCLUSIONS

The use of Ru/carbon nanotube nanohybrid catalysts for Fischer−Tropsch synthesis (FTS) in a water/decalin biphasic system exhibits several advantages. First, the unique amphiphilic character of the carbon nanotubes enables the formation of water-in-oil emulsions that enlarge the water/oil interfacial area and enhance the interfacial mass transfer. Second, the FTS rate enhancement typically observed in the presence of water vapor is clearly apparent in aqueous single-phase and biphasic emulsion systems. In addition, the FTS rate continuously increases with the addition of water beyond the dew point, which shows that the presence of liquid water further enhances activity. Third, the nanohybrid catalysts yield the highest fraction of products in the C_5−C_{20} range and the lowest in the C_1−C_4 range when they are used in emulsion. Single-phase solvents result in higher selectivity to the less desirable C_1−C_4 range. Fourth, the runs in the emulsion system keep a low selectivity to the less desirable C_1−C_4 products for longer time than the runs in single-phase solvents.

As recently proposed, the activity promotion by water might be due to its role as H-shuttle, which thus enhances the H-assisted CO dissociation. On the basis of these concepts, our results would indicate that water could accomplish its role as H-shuttle more effectively in the liquid phase than as an adsorbed molecule. With higher mobility and a larger number of degrees of freedom, water in the liquid phase may find more possibilities to accommodate the H atom at energetically favorable configurations than on the adsorbed state. In addition, in comparison with a water molecule in the gas phase, the one in the liquid phase has more opportunities to interact more effectively with a given adsorbate (*H) because the residence time in the vicinity of the surface is much longer. Therefore, although the surface chemical potential should not increase beyond the dew point, the FTS activity continuously increases.

On the other hand, the desirable product selectivity toward the C_5−C_{20} range can be explained in terms of the two-site FTS model. In the emulsion, the formation rate of C* species on site 1 does not greatly exceed the C* consumption and chain growth rates on site 2. When the imbalance occurs, the chain growth sites deactivate and the selectivity to C_1−C_4 products increases because there is a direct link between the extent of deactivation and the selectivity to light products. In the emulsion medium, the hydrocarbon products can more readily desorb from the catalyst surface into the oil because of their higher solubility in the oil phase. By contrast, in the single water phase, the hydrocarbons remain on the surface and deactivate the catalyst faster. At the other end, in the single organic phase, the promoting effect of added water is missing, so the selectivity to longer chains decreases.

ASSOCIATED CONTENT

Supporting Information

Calculation of water vapor during reduction and reaction steps, TOF, GC settings and chromatographs, calculation of alcohol/alkene equilibrium ratios in alkene hydration, fittings to ASF and chain growth probability calculations, Figures corresponding to Tables 1 and 3, TEM images of fresh and spent Ru-on-nanohybrid catalyst, table corresponding to Figure 1, CO conversions of 2- and 8-h reactions in different reaction media, summary of FTS reactions in this study. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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