Fischer-Tropsch CO-Hydrogenation on SiO_2-supported Osmium Complexes

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Dedicated to Professor Helgard Raubenheimer on the occasion of his 65th birthday

The conversion of carbon monoxide with hydrogen was studied on a standard Os on SiO_2 catalyst at different reaction temperatures, in the range between 200 and 300 °C. Additionally, supported di- and triatomic organometallic Os complexes were tested for their activity in the Fischer-Tropsch synthesis at 220 °C. All compounds showed formation of hydrocarbons, indicating that the organo-osmium complexes are indeed active for C–C bond formation. Osmium as Fischer-Tropsch catalyst, however, is approximately 100 times less active compared to ruthenium. Very high methane selectivities ($>$ 90 C-%) were obtained as well as high olefin to paraffin ratios, in particular with the organometallic complexes tested.

Key words: Osmium, Fischer-Tropsch, Catalyst Activity, Catalyst Selectivity, Organometallic Complexes

Introduction

Fischer-Tropsch synthesis is the catalytic conversion of synthesis gas, a mixture of H_2 and CO, over a metallic catalyst yielding higher hydrocarbons [1]. All transition metals are active for the Fischer-Tropsch synthesis. Fe- and Co-based catalysts are commercially used, whereas Ru is known to be the most active catalyst for the Fischer-Tropsch synthesis [2].

However, very little is known about the use of Os as a catalyst for the Fischer-Tropsch synthesis. Fischer-Tropsch activity and selectivity on a heterogeneous Os on SiO_2 catalyst was first reported by Leconte *et al.* [3]. The catalyst, prepared by thermal decomposition of $Os_3(CO)_{12}$ on SiO_2, was tested at 250 – 300 °C and 1 bar (H_2/CO = 1 : 1), and the formation of C_1–C_5 hydrocarbons was observed. Odebunmi *et al.* [4] studied the Fischer-Tropsch activity of Al_2O_3-supported Os catalysts *ex* [$Os(CO)_5$] at different reaction temperatures ranging between 250 and 325 °C and a reaction pressure of 10 bar. They described the formation of C_1–C_7 hydrocarbons with methane being the preferred product ($>$ 70 C-%).

Several attempts using Os as homogeneous Fischer-Tropsch catalyst have been described in the literature [5 – 7]. Only oxygen-containing products, such as methanol or methyl formate, were observed. The activity of Os was lower than that of Ru.

Here we report a study on the Fischer-Tropsch activity and selectivity over a SiO_2-supported Os catalyst at different reaction temperatures. Additionally, the activity of di- and triatomic organometallic Os-complexes supported on SiO_2 is reported.

Experimental Section

Standard Os/SiO_2 catalyst

A standard Os/SiO_2 catalyst was prepared applying the incipient wetness impregnation technique. 0.0693 g of $(NH_4)_2OsCl_6$ (Anglo Platinum) was completely dissolved in 5 mL of water with stirring. Subsequently, the support material, SiO_2 (Davisil, grade 646, d_p = 200 – 250 μm, d_{pore} = 150 Å), was added and the sample was dried in a rotary drier at 60 °C and 300 mbar for 1 h, followed by drying at 110 °C for 4 h. The resulting Os-loading was 3 wt.-%.

Organometallic model catalysts

$Os_3(CO)_{12}$ was synthesized using a method described in the literature [8]. $Os(CO)_4(\eta^5\text{-}C_5H_5)_2$, however, was prepared using a modified procedure of that described in liter-

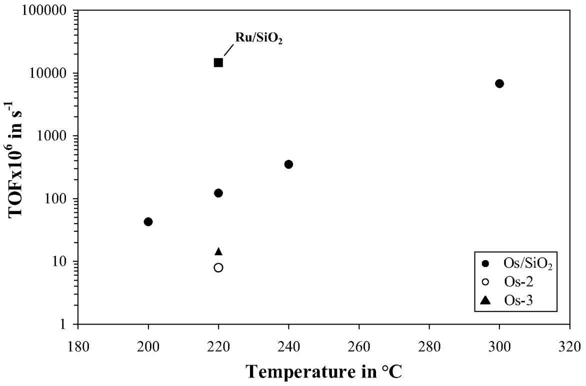

Fig. 1. Turnover frequencies as a function of reaction temperature obtained after 5 min runtime in the Fischer-Tropsch synthesis over Os/SiO_2, Os-2 and Os-3. For comparison purposes the turnover frequency for a Ru/SiO_2 catalyst at 220 °C is included. [P = 2 bar; GHSV = 7 mL(STP)/(min·g_{cat}); $(H_2/CO)_{in} = 2:1$].

ature [9, 10]. Thus, instead of using $OsCl_3 \cdot nH_2O$ as starting compound, 2 g of $(NH_4)_2OsCl_6$ was used. It was added to 60 mL of ethanol in a 200 mL autoclave (Parr). The autoclave was pressurized with CO to 70 bar, followed by gradual heating to 175 °C. After keeping the autoclave at 175 °C and under continuous stirring for 8 h, it was slowly cooled to r. t. overnight. $[Os(CO)_3Cl_2]_2$ was obtained as a pale yellow solid with 59 % yield. The further reaction steps, including the syntheses of the intermediates $[Os(CO)_2H(\eta^5\text{-}C_5H_5)]$ and $[Os(CO)_2(\eta^5\text{-}C_5H_5)]^+PF_6^-$ as well as the formation of the desired product $Os_2(CO)_4(\eta^5\text{-}C_5H_5)_2$, were all known in the literature. Since completion of our work, an improved synthesis of $Os_2(CO)_4(\eta^5\text{-}C_5H_5)_2$ has been reported [11].

These catalyst precursors were deposited on SiO_2 *via* dissolution in acetone and impregnation of the support (Os-loading: 3 wt.-%). The solvent was removed by gently blowing N_2 over the mixture at r. t. for 5 h. The di- and triatomic model catalysts are denoted Os-2 and Os-3, respectively, in the following.

Fischer-Tropsch experiments

CO hydrogenation was performed in a fixed bed reactor at 2 bar at different temperatures with a H_2 to CO ratio of 2.0 (space velocity: 7 mL(NTP)/min/g_{cat}; 0.4 g catalyst loaded in the reactor). Prior to Fischer-Tropsch testing, the standard Os/SiO_2 catalyst was activated *via* hydrogen reduction (30 mL(NTP)/min, 300 °C for 5 h; heating rate: 2 °C min^{-1}), whereas the organometallic model catalysts were used without pre-treatment. Due to their limited thermal stability rapid heating to the reaction temperature was applied with the organometallic model catalysts *via* dipping the U-tube shaped reactor into a preheated silicon oil bath. Details of the reactor set-up have been described elsewhere [12].

Table 1. Activity and selectivity obtained after 5 min runtime in the Fischer-Tropsch synthesis over different tested model catalysts. [T_{rxn} = 200 – 300 °C; P = 2 bar; GHSV = 7 mL(NTP)/min/g_{cat}; $(H_2/CO)_{in} = 2:1$].

Sample	T_{rxn} (°C)	$TOF \times 10^6$ [a] (s^{-1})	$S(CH_4)$ [b] (C-%)	Olefin content (mol-%) C_2 [c]	C_3 [d]	p_g [e]
Os/SiO_2	200	42.6	91.7	54.2	45.5	0.69
	220	121.5	92.6	43.9	49.2	0.61
	240	350.0	95.1	32.0	43.8	0.63
	300	6775.2	98.8	43.0	61.3	0.60
Os-2	220	7.9	94.7	79.8	97.4	0.21
Os-3	220	14.7	99.8	89.4	98.5	0.08

[a] Turnover frequency of volatile organic compounds [(C_1–C_7 hydrocarbons (Os/SiO_2) or, respectively, C_1–C_4 hydrocarbons (Os-2, Os-3)]; [b] methane selectivity in C_1–C_7 hydrocarbons for standard catalyst (Os/SiO_2) and in C_1–C_4 hydrocarbons for supported organometallic compounds (Os-2, Os-3); [c] molar content of ethene in C_2 hydrocarbons; [d] molar content of propene in C_3 hydrocarbons; [e] chain growth probability in C_4–C_7 hydrocarbons for the standard catalyst (Os/SiO_2) and in C_1–C_2 hydrocarbons for supported organometallic compounds (Os-2, Os-3).

Off-line sampling of the product stream, to which a reference gas stream containing an organic and inorganic compound (cyclohexane and nitrogen) was fed for quantification purposes, has been achieved applying the ampoule sampling technique developed by Schulz *et al.* [13]. Product analysis was conducted on a gas chromatograph adapted to the ampoule sampling technique employing a flame ionization detector (Varian 3400).

Results and Discussion

The Fischer-Tropsch activity was expressed in terms of turnover frequencies (TOF), based on product formation rates per metal surface area present after pre-treatment in hydrogen. The metal surface area was determined from an average Os-crystallite size of 6.0 nm obtained by means of transmission electron microscopy (TEM). Catalyst activities obtained after 5 min runtime at the different reaction temperatures for Os/SiO_2 and at 220 °C for Os-2 and Os-3 are illustrated in Fig. 1 (for corresponding data see Table 1). For comparison purposes the TOF of a corresponding 3 wt.-% Ru/SiO_2 catalyst at 220 °C is included. C_1–C_7 hydrocarbons were formed on the standard Os/SiO_2 catalyst. The organometallic model catalysts, Os-2 and Os-3, showed formation of C_1–C_3 hydrocarbons and are thus displaying Fischer-Tropsch activity. The same observation has been described in the literature on organometallic Ru complexes, stating that 2 adjacent metal atoms can promote Fischer-Tropsch chain growth [14, 15]. The activation energy

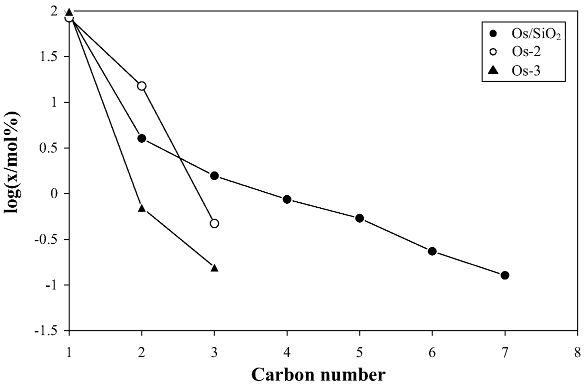

Fig. 2. Anderson-Schulz-Flory distribution of the organic product obtained after 5 min runtime in the Fischer-Tropsch synthesis over Os/SiO_2, Os-2 and Os-3. [T_{rxn} = 220 °C; P = 2 bar; GHSV = 7 mL(STP)/(min·g_{cat}); $(H_2/CO)_{in}$ = 2 : 1].

of the Fischer-Tropsch synthesis over Os/SiO_2, calculated from an Arrhenius plot, was 115 kJ mol^{-1}, which is in good agreement with activation energies reported for conventional Fischer-Tropsch catalysts in the literature [16]. It must be noted that the catalyst activity is significantly lower (approx. 100 times) compared to Ru supported on SiO_2 under the same reaction conditions [12].

Methane is known to be the thermodynamically most stable Fischer-Tropsch product. Generally, with Os very high methane selectivities were obtained ($>$ 90 C-%). Correspondingly, very low chain growth probabilities in the range C_1–C_2 (as determined from Anderson-Schulz-Flory distributions, see Fig. 2) of around 10 to 20 % were determined for the organometallic model catalysts. A similar value is obtained for Os/SiO_2 in this carbon number range. For Os/SiO_2 larger chain growth probabilities are obtained at higher carbon numbers, *i. e.* approximately 60 % in the range of C_4–C_7. A similar effect has been described in the literature on Al_2O_3-supported Ru Fischer-Tropsch catalysts [14, 15], and it was attributed to the formation of different kinds of reactive sites on the catalyst surface, *viz.* methane and chain growth sites.

Olefins are normally the main primary organic products in Fischer-Tropsch synthesis. In the absence of olefin re-adsorption the olefin content per carbon number is typically between 60 and 80 mol-% [17]. Observed olefin contents on the organometallic model catalysts were significantly higher (80 – 98 mol-%) than those obtained for the standard Os/SiO_2 catalyst (40 – 60 mol-%). This may indicate that re-adsorption of olefins in the complexes did not occur, while secondary olefin reactions may have occurred over the standard Os/SiO_2 catalyst. Alternatively, the primary selectivity of olefin *versus* paraffin formation may be affected by the catalytic site, *viz.* small complexes of 2 to 3 atoms *versus* large agglomerates of atoms in the crystallites of the Os standard catalyst. The relatively low olefin contents obtained with the Os/SiO_2 standard catalyst could then be an indication that the step of β-hydrogen elimination to form olefins is not as facile as with Co, Fe and Ru catalysts where normally higher olefin contents are obtained [17].

Conclusions

A standard Os/SiO_2 catalyst appeared to be approximately 100 times less active compared to SiO_2-supported Ru, understood to be the most active metal for Fischer-Tropsch synthesis. Fischer-Tropsch hydrogenation activity and C–C chain growth was investigated for two supported organometallic Os-complexes. Generally, very high methane selectivities were obtained with all tested catalysts. Additionally, the chain growth probability obtained for the organometallic model catalysts was found to be very low, indicating that C–C bond formation is not preferred on these systems.

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