Fischer–Tropsch Catalysts

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Ruthenium Nanoparticles Supported on Carbon Nanotubes as Efficient Catalysts for Selective Conversion of Synthesis Gas to Diesel Fuel[**]

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Fischer–Tropsch (FT) synthesis is a key step for the transformation of nonpetroleum feedstocks, such as natural gas, coal, and biomass, into hydrocarbon fuels, such as ultraclean diesel fuel, by syngas (CO/H_2). FT synthesis has received renewed interest because of the worldwide demand for a decreased dependence on petroleum.[1,2] The hydrocarbon products in FT synthesis generally follow the Anderson–Schulz–Flory distribution, which is determined by the polymerization mechanism.[3] Such a distribution is unselective, and the development of novel FT catalysts which can selectively produce hydrocarbons in a certain range has attracted much attention.[4–8] To date, much attention has been paid to cobalt-based catalysts.[4] The use of mesoporous silica as a support for Co was reported to favor the formation of C_{10}–C_{20} hydrocarbons (diesel fuel fraction), and a C_{10}–C_{20} selectivity of 30–40% could be attained over a Co/SBA-15 catalyst.[9] As compared with Co, Ru catalysts possess higher intrinsic activity and can work under higher partial pressures of water or other oxygenate-containing atmospheres,[1,10,11] and the latter feature becomes particularly important for the conversion of syngas produced from biomass.[10] Thus, fundamental studies on Ru-based catalysts may provide important clues toward the development of efficient FT catalysts for the utilization of renewable biomass for hydrocarbon fuel production although the higher cost and lower availability of Ru may hinder its industrial-scale application.

Studies on Ru-based FT catalysts with controllable product distributions have to date been sporadic. Li and co-workers[12] recently found that the confinement of Ru nanoparticles in mesopores of SBA-15 caused an increase in $C_{\geq 5}$ selectivity to approximately 60%, but the confined Ru catalysts exhibited lower activity and higher CH_4 selectivity (over 20%). We have carried out systematic studies on the Ru-catalyzed FT synthesis with the aim to develop product-selective catalysts. Herein, we report our recent finding that Ru nanoparticles supported on carbon nanotubes (CNTs) show excellent selectivity for C_{10}–C_{20} hydrocarbons. The roles of the CNT support and the size of the Ru nanoparticles in determining the product selectivity were also investigated to gain an insight into the requirements for the rational design of FT catalysts with desirable product distributions.

Table 1 summarizes the catalytic performances of Ru catalysts on some typical supports for the conversion of syngas with a H_2/CO ratio of 1.0, which is close to the ratio produced from biomass.[13] In cases where metal oxides were used as supports, the product distribution was typically wide, and C_1–C_{40} hydrocarbons were formed. Heavy hydrocarbons ($C_{\geq 21}$) were suppressed over zeolite-supported Ru catalysts, and a higher selectivity toward C_5–C_9 hydrocarbons (52%) was obtained over the Ru/H-beta catalyst. Such a function of zeolite H-beta is to be expected because H-beta-supported cobalt catalyzes the production of C_5–C_9 hydrocarbons with good selectivity.[8,9b] However, the CNT-supported catalyst was not expected to restrain the formation of $C_{\geq 21}$ hydrocarbons. More significantly, Ru/CNT can produce C_{10}–C_{20} hydrocarbons with a selectivity as high as 60%; to our knowledge, the highest selectivity for the diesel fraction of

Table 1: Catalytic performances of various supported Ru catalysts.[a]

Catalyst	CO conv. [%]	Selectivity [mol%]				
		CH_4	C_2–C_4	C_5–C_9	C_{10}–C_{20}	$C_{\geq 21}$
Ru/SiO_2	32	6.8	10	20	39	24
Ru/TiO_2	20	14	36	22	22	5.7
Ru/ZrO_2	22	8.4	37	27	15	13
Ru/MgO	3.0	15	45	19	17	4.0
Ru/NaY	23	11	14	37	37	1.9
Ru/HY	25	12	13	41	31	3.0
Ru/H-beta	24	13	21	52	14	0
Ru/AC	11	20	20	22	26	12
Ru/graphite	20	2.9	12	25	55	5.8
Ru/CNT	34	8.3	9.1	21	60	1.9

[a] Reaction conditions: H_2/CO (1:1 ratio, flow rate = 20 mL min^{-1}, $P = 2.0$ MPa), catalyst (0.50 g; 3.0 wt.% Ru content), 533 K, 10 h.

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hydrocarbons reported for FT synthesis. The Ru/CNT-catalyzed reaction at 538 K over a longer period of time led to product selectivities which were not significantly changed from for reaction times of around 10 h; a C_{10}–C_{20} selectivity of 55 % was attained at a CO conversion of 37 % after about 120 h (see the Supporting Information, Figure S1).

Through H_2 temperature-programmed reduction (H_2-TPR) studies (see the Supporting Information, Figure S2), we have clarified that the Ru species in all of the catalysts except for Ru/zeolites (Table 1) are reduced almost completely to metallic Ru during the pretreatment (H_2 reduction at 573 K for 2 h). Moreover, the correlation of catalytic performances with the mean size of Ru particles in these samples (see the Supporting Information, Table S1) suggests that the peculiar C_{10}–C_{20} selectivity of the Ru/CNT catalyst is not only affected by the Ru particle size. Thus, the CNT support may play key roles in the selective formation of C_{10}–C_{20} hydrocarbons over the Ru/CNT catalyst. CNT catalyst supports have shown unique properties in other hydrogenation reactions.[6,14,15] It is proposed that the unique properties of the CNT in H_2 adsorption/spillover and electron transport may bring about positive effects in these catalytic reactions.[14c,15] H_2 temperature-programmed desorption (H_2-TPD) measurements for some typical supported Ru catalysts used in this work demonstrated that the H_2 desorption from the Ru/CNT occurred from lower temperatures than that from other catalysts (see the Supporting Information, Figure S3), which implies that the adsorbed hydrogen species on the CNT surface may be more active at the reaction temperature. Moreover, higher concentrations of adsorbed hydrogen occurred over the catalysts with CNT and zeolites H-beta and HY as supports, which showed lower $C_{\geq 21}$ selectivities. We speculate that these hydrogen species may contribute to the hydrocracking of heavy hydrocarbons ($C_{\geq 21}$) or the hydrocarbon chain terminating reactions.

CNT pretreatment played a key role in determining product distributions. When the CNT without pretreatment was applied, C_1–C_4 hydrocarbons were formed with much higher selectivity, possibly as a result of the remaining Ni catalyst, which was used for the CNT synthesis.[16] The pretreatment of CNTs with nitric acid significantly increased the selectivity towards $C_{\geq 10}$ and decreased that towards C_1–C_4 hydrocarbons (Table 2). Inductively coupled plasma (ICP) analyses showed that no Ni remained in the pretreated CNTs. The product distributions also depended on the concentration of HNO_3 used for the CNT pretreatment; the CNT pretreated with concentrated HNO_3 (68 %, typical treatment conditions) afforded a catalyst with remarkably higher C_{10}–C_{20} selectivity. Acidic functional groups, for example, carboxylic groups, may be formed on the CNT surface after HNO_3 pretreatment.[15] From NH_3-TPD measurements, we established that the pretreatment of CNT with concentrated HNO_3 led to the generation of acidity at the CNT surface. In the NH_3-TPD profile, in addition to the main NH_3 desorption peak around 460 K, owing to weak acid sites, a broad peak at 700–800 K was also observed for CNT pretreated with 68 % HNO_3 and for the corresponding Ru/CNT (see the Supporting Information, Figure S4), indicating the generation of medium-strength acidic sites. We have confirmed that the characteristics of Ru species (reducibility and particle size) are almost the same over a CNT support pretreated by HNO_3, with a range of concentrations (see the Supporting Information, Figures S5 and S6). Therefore, it is reasonable to consider that the acidic functional groups on the CNT surface may contribute to the high C_{10}–C_{20} selectivity by hydrocracking of heavier hydrocarbons.

To establish whether such hydrocracking reactions occurred, we investigated the effect of contact time, expressed as the ratio of catalyst weight to the total flow rate, on catalytic performances over the 3 wt % Ru/CNT catalyst. The result (see the Supporting Information, Figure S7) showed that, with increasing contact time, the selectivity towards $C_{\geq 21}$ decreases and that towards C_{10}–C_{20} increases. The decrease in $C_{\geq 21}$ selectivity corresponds well to the increase in C_{10}–C_{20} selectivity and suggests the conversion of heavier hydrocarbons into C_{10}–C_{20} over the Ru/CNT catalyst.

Alongside the CNT support, the size of Ru particles may also contribute to the selective formation of C_{10}–C_{20} hydrocarbons. Recent studies showed that both the activity and the $C_{\geq 5}$ selectivity over supported Co catalysts were dependent on the mean size of Co particles.[5,17] To clarify the effect on catalytic performance of the size of Ru particles, we have prepared Ru/CNT catalysts with mean Ru sizes varying from 2.3 to 10.2 nm, by using different post-treatment conditions after impregnation of Ru precursors onto the CNT pretreated by 68 % HNO_3 (see the Supporting Information for details, Figure S8). H_2-TPR and X-ray photoelectron spectroscopy (XPS) measurements have confirmed that ruthenium is in the metallic state in all of these samples. The typical TEM image and the corresponding Ru particle size distribution of the Ru/CNT sample with a mean Ru size of 7.4 nm are shown in Figure 1. Through TEM observations, we confirmed that the mean size of Ru particles did not undergo significant changes after FT synthesis (see the Supporting Information, Figure S9).Under the reaction conditions used, CO conversions changed only slightly, but the selectivity for C_{10}–C_{20} hydrocarbons varied significantly with the mean size of Ru particles (Figure 2). The optimum Ru particle size for C_{10}–C_{20} selectivity was approximately 7 nm. A C_{10}–C_{20} selectivity of 65 % was attained

Table 2: Catalytic performances of Ru catalysts supported on CNTs pretreated by HNO_3 with different concentrations.[a]

Conc. of HNO_3 [%]	Ru size [nm]	CO conv. [%]	Selectivity [mol %]				
			CH_4	C_2–C_4	C_5–C_9	C_{10}–C_{20}	$C_{\geq 21}$
–[b]	nd[c]	16	30	38	22	9.0	1.0
37	6.4	32	13	15	24	38	11
55	6.2	37	13	14	21	42	9.4
68	6.3	34	8.3	9.1	21	60	1.9

[a] Reaction conditions: H_2/CO (1:1 ratio, flow rate = 20 mL min^{-1}, P = 2.0 MPa), catalyst(0.50 g; 3.0 wt. % Ru content), 533 K, 10 h. [b] CNT was used without pretreatment. [c] Ru size was not measured because this sample contained Ni.

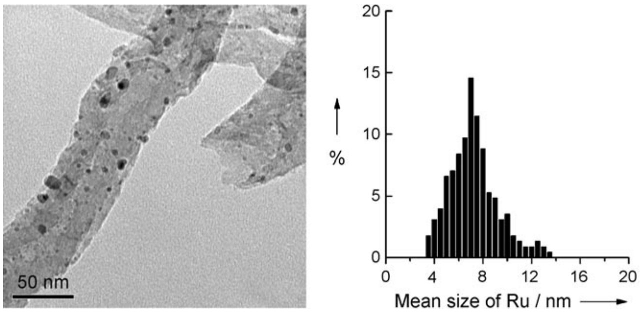

Figure 1. TEM micrograph and Ru particle size distribution for 3 wt% Ru/CNT, prepared by impregnation of $RuCl_3$ onto CNT followed by calcination at 573 K and subsequent H_2 reduction at 673 K.

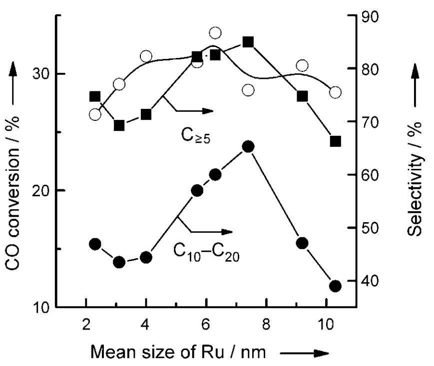

Figure 2. Effect of mean Ru particle size on CO conversion (○) and selectivity towards C_{10}–C_{20} (●) and $C_{\geq 5}$ (■) over the 3 wt% Ru/CNT catalysts. Reaction conditions: H_2/CO (1:1 ratio, flow rate = 20 mL min^{-1}, P = 2.0 MPa), catalyst(0.50 g), 533 K, 10 h.

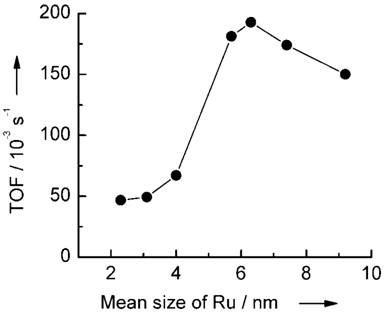

Figure 3. Dependence of TOF on the mean size of Ru particles.

under these conditions. The $C_{\geq 5}$ selectivity also reached a maximum at a mean Ru particle size of about 7 nm.

To gain further information about the effect of Ru particle size on catalytic activity, we compared the turnover frequency (TOF) for CO conversion over the Ru/CNT catalysts with different sizes of Ru particles. The TOF was calculated on the basis of the CO conversion rate at a shorter contact time (to ensure CO conversions < 10%) per surface Ru atom. The dispersion of Ru in each catalyst was measured by using a H_2–O_2 titration technique.[18] The value of Ru dispersion thus measured was in agreement with that estimated from the size of Ru particles (see the Supporting Information, Table S2). The TOF increased significantly with the mean size of Ru up to approximately 6 nm and then decreased only slightly with further increases in Ru particle size (Figure 3).

Bezemer et al.[5] reported that the TOF for CO conversion over Co supported on carbon nanofibers increased with Co size up to roughly 8 nm and then remained almost unchanged with further size increases. Borg et al.[17] recently reported a volcano-like curve when the $C_{\geq 5}$ selectivity was plotted versus the size of Co particles supported on Al_2O_3. The maximum $C_{\geq 5}$ selectivity was obtained at a Co size of 7–8 nm. Herein, we have demonstrated that the smaller Ru particles (less than 6 nm) are less active in FT synthesis than larger Ru particles. Bell and co-workers reported that the TOF for CO conversion over Ru/Al_2O_3 was also decreased by increasing the Ru dispersion from 0.3 to 0.75.[19a] However, they found that the situation over Ru/TiO_2 with strong metal–support interactions was more complicated. Although it seemed that the Ru/TiO_2 catalyst with a Ru size of approximately 1.5 nm exhibited higher TOF, they clarified that the appropriate covering of the Ru particles by amorphous TiO_x actually determined the TOF.[19b,c] We have demonstrated herein that both the TOF for CO conversion and the product selectivities depend on the size of Ru particles, and that a Ru/CNT catalyst with a mean Ru particle size of roughly 7 nm can provide the highest selectivities towards C_{10}–C_{20} and $C_{\geq 5}$ hydrocarbons. It is still difficult to make a straightforward interpretation of these phenomena because FT synthesis comprises a large number of elementary steps, such as dissociation, insertion, and hydrogenation. These steps may require the combination of different sites,[5] and may lead to the unique dependence of TOF and product distributions on Ru particle size.

In summary, we have found that Ru/CNT is a highly selective Fischer-Tropsch catalyst for the formation of C_{10}–C_{20} hydrocarbons. The unique adsorbed hydrogen species and the acidic functional groups on CNT surfaces may both play roles in mild hydrocracking of heavier hydrocarbons to C_{10}–C_{20}. Both the C_{10}–C_{20} selectivity and the TOF for CO conversion depend on the mean size of Ru particles, and the Ru/CNT catalyst with a mean Ru size of approximately 7 nm exhibits the best C_{10}–C_{20} selectivity and relatively higher TOF.

Experimental Section

Multiwalled carbon nanotubes (CNTs) with outer diameters of 20–60 nm and inner diameters of 3–5 nm were prepared by an established method.[16] The CNTs were typically pretreated in concentrated HNO_3 (68 wt%) at 413 K under refluxing conditions to remove amorphous carbon and the remaining Ni catalyst and to create functional groups, such as carboxylic groups, for anchoring metal precursors.[15] The Ni content was 5.5 wt% before pretreatment and our ICP analyses showed that no Ni remained in the CNT after treatment with HNO_3. Ru catalysts on various supports were typically prepared by impregnating the supports with an aqueous solution of $RuCl_3$, followed by drying at 323 K under vacuum. After calcination in air at 573 K for 2 h, the sample was subjected to reduction by H_2 at 573 K for 2 h. Different post-treatment conditions were applied to the preparation of Ru/CNT catalysts with different mean Ru particle sizes (2.3–10.2 nm; see the Supporting Information for details). Catalysts were characterized by XRD, N_2-physisorption, XPS, TEM, H_2-TPR, H_2-TPD, and H_2–O_2 titration techniques.

Fischer–Tropsch synthesis was performed on a fixed-bed flow reactor, typically operated at 2 MPa. The catalyst loaded in the reactor was pretreated in H_2 gas flow at 573 K before reaction. After the reactor was cooled down to the reaction temperature (typically 533 K), syngas with a 1:1 H_2/CO ratio was introduced into the reactor. Argon, at a concentration of 4% in the syngas, was used as an internal standard for calculation of CO conversion. The products were analyzed by gas chromatography. The selectivity was calculated on a carbon basis.

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