New insight into the selectivity difference between Co and Ru catalysts for Fischer-Tropsch synthesis and the tuning of product selectivity

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Abstract: Ru and Co are two typical active catalysts in Fischer-Tropsch (FT) synthesis, and the selectivity control is a key challenge for both catalysts. By using CNT as a support, we confirmed that the Co catalyst exhibits higher CH_4 selectivity and lower heavier-hydrocarbon (C_{21+}) selectivity, whereas the Ru catalyst favors C_{21+} formation with lower CH_4 selectivity. Our studies suggest that the selectivity difference arises from the difference in hydrogenolysis of heavier hydrocarbons on the two catalysts. With the new insight, we succeed in tuning the FT selectivity by modulating the hydrogenolysis through modifying Ru or Co with Ir.

Keywords: Fischer-Tropsch synthesis, Selectivity control, Hydrogenolysis

1. Introduction

FT synthesis, which transforms syngas (CO/H_2) into hydrocarbon fuels or chemicals, has attracted much attention because of the rising interest in the utilization of non-petroleum carbon resources such as shale gas, coal and biomass to replace oil.[1] Fe, Co and Ru are typical active catalysts for FT synthesis. Co and Ru catalysts usually show higher C_{5+} selectivity and are suitable for liquid-fuel production. Co is more attractive for industrial application because of its lower cost. However, Co catalysts usually show higher selectivity of undesirable CH_4 than Ru catalysts. The understanding of the reason for the difference in selectivity between Co and Ru catalysts would provide an important clue for tuning the product selectivity via catalyst design.

Recently, we found that the hydrogenolysis of heavier hydrocarbons on a Co/Na-meso-Y catalyst is crucial to determining the product selectivity in FT synthesis.[2,3] It can be expected that Co and Ru catalysts may exhibit different behaviors in hydrogenolysis of heavier hydrocarbons, and thus may lead to different FT product selectivities. Here, we present our recent studies on the hydrogenolysis of n-$C_{16}H_{34}$, a model molecule of heavier hydrocarbons, on Co and Ru catalysts under H_2 and syngas atmospheres. The result enables us to propose that hydrogenolysis is a key to elucidating the selectivity difference between the two catalysts in FT synthesis. Furthermore, we succeed in tuning the FT selectivity on both Co and Ru catalysts by modifying the hydrogenolysis.

2. Experimental

Ru and Co nanoparticles supported on CNTs were typically prepared by an impregnation method. FT synthesis was performed on a fixed-bed flow reactor operated at 2 MPa with a H_2/CO ratio of 1:1. The conversion of n-$C_{16}H_{34}$ was performed under H_2 or H_2/CO atmosphere. The products were analyzed by gas chromatography. The selectivity was calculated on a molar carbon basis.

3. Results and discussion

We first compared the product selectivities of Co/CNT and Ru/CNT catalysts in FT synthesis. For better comparison, we controlled CO conversions of the two catalysts at a similar level (~30%). The selectivity of CH_4 on the Co/CNT was 12%, whereas it was only 1.6% on the Ru/CNT (Figure 1a). On the other hand, the Ru/CNT showed significantly higher selectivities of C_{10-20} and C_{21+} hydrocarbons than the Co/CNT catalyst.

To uncover the contribution of hydrogenolysis on product selectivity in FT synthesis, we performed the conversion of n-$C_{16}H_{34}$ under H_2 atmosphere. The result shows that the hydrogenolysis occurs on both Co/CNT and Ru/CNT catalysts under reaction conditions close to those used for FT synthesis. The n-$C_{16}H_{34}$ conversions exceeded 80%. However, the product distributions in the hydrogenolysis were quite different

(Figure 1b). The selectivity of CH_4 was much higher over the Co/CNT than that over the Ru/CNT. The other products were concentrated on C_{10}-C_{15} hydrocarbons on the Co/CNT, whereas C_2-C_{15} hydrocarbons were all formed with considerable selectivities on the Ru/CNT catalyst. This indicates that the mechanisms for the hydrogenolysis over the two catalysts are different. We propose that the hydrogenolysis of n-$C_{16}H_{34}$ on the Co/CNT proceeds via a mechanism of successive demethylation at the terminal C-C bond, forming CH_4 and a heavier fragment, whereas the Ru/CNT may adopt non-selective cleavage of C-C bonds.

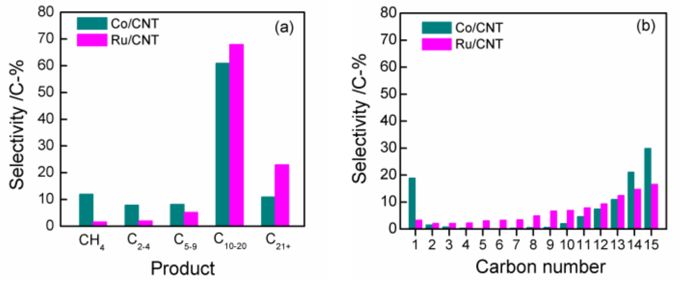

Figure 1. Product distributions in (a) FT synthesis and (b) n-$C_{16}H_{34}$ hydrogenolysis over the Co/CNT and Ru/CNT.

We further studied the hydrogenolysis of n-$C_{16}H_{34}$ under syngas atmosphere, i.e., under the true FT reaction conditions. The analyses of our results revealed that CO conversions (FT synthesis) did not alter significantly in the presence of n-$C_{16}H_{34}$ over both catalysts, but the conversion of n-$C_{16}H_{34}$ changed due to the presence of CO. The hydrogenolysis for the Co/CNT was only slightly changed under H_2/CO atmosphere, but a remarkable decrease in n-$C_{16}H_{34}$ conversion was observed for the Ru/CNT under H_2/CO. In other words, the hydrogenolysis on the Ru/CNT was remarkably inhibited under the true FT reaction conditions, although the presence of CO did not significantly affect that on Co/CNT. Our studies suggest that such a difference may stem from the difference in CO chemisorption on the two catalysts. The stronger chemisorption of CO on the Ru/CNT catalyst decreases its hydrogenolysis ability under FT synthesis conditions, resulting in its higher C_{21+} selectivity and lower CH_4 selectivity. On the other hand, the higher CH_4 selectivity on the Co catalysts arises from the significant hydrogenolysis of heavier hydrocarbons via demethylation mechanism under FT reaction conditions.

With this new insight, we carried out catalyst design to modulate the CO chemisorption by modifying the Co and Ru catalysts. We found that the addition of Ir into Ru or Co nanoparticles loaded on CNTs could regulate the CO chemisorption, and thus was capable of changing the hydrogenolysis ability. The formation of Ru-Ir alloy (Figure 2) suppressed the CO chemisorption, and thus enhanced the hydrogenolysis. As a result, the C_{21+} selectivity decreased and the C_{10-20} selectivity increased to as high as ~75%. This the highest value reported for the diesel fuel selectivity in FT synthesis. On the other hand, the formation of Co-Ir alloy promoted the CO chemisorption, thus suppressing the hydrogenolysis. Hence, the CH_4 selectivity decreased significantly to <3% and the C_{5+} selectivity increased from 83% to 94% over the Ir-modified Co/CNT catalyst. The product distribution on the $Ir_{0.04}$-Co/CNT catalyst was similar to that on the Ru/CNT catalyst.

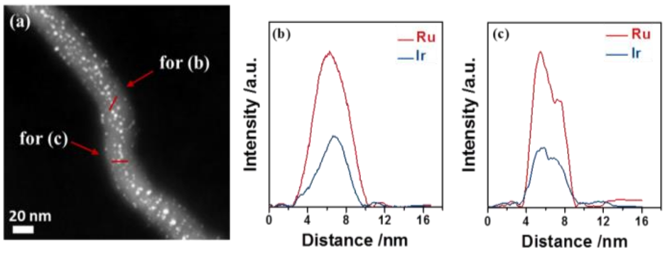

Figure 2. TEM image in dark field (a) for Ru-Ir/CNT and line-scan EDS analyses (b and c) across the nanoparticles in TEM image.

4. Conclusions

We uncovered that the difference in the hydrogenolysis on Co and Ru catalysts is a key to elucidating their selectivity difference in FT synthesis. The higher CH_4 selectivity of the Co catalyst arises from the hydrogenolysis, whereas the hydrogenolysis is inhibited on the Ru catalyst due to the strong CO chemisorption under FT reaction conditions. The control of hydrogenolysis by modification of Ru or Co with Ir can successfully tune the FT product selectivity.

References

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