Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2013, **23**, 44–45
Mendeleev Communications

Fischer–Tropsch synthesis in the presence of composite catalysts with different types of active cobalt

Lilia V. Sineva,*[a,b] Vladimir Z. Mordkovich[a,b] and Ekaterina Yu. Khatkova[a]

[a] *Technological Institute for Superhard and Novel Carbon Materials, 142190 Troitsk, Moscow Region, Russian Federation. Fax: +7 499 400 6260; e-mail: sinevalv@tisnum.ru*
[b] *INFRA Technology Ltd., 125009 Moscow, Russian Federation. Fax: +7 499 400 6260; e-mail: sineva@infratechnology.ru*

DOI: 10.1016/j.mencom.2013.01.016

The use of different types of active cobalt affects the basic parameters of the catalytic Fischer–Tropsch synthesis, including the yield of isoparaffins or olefins.

The Fischer–Tropsch process converts a mixture of CO and H_2 (synthesis gas) into a mixture of liquid and gaseous hydrocarbons:[1]

$$n\,CO + (2n+1)\,H_2 \rightarrow C_nH_{2n+2} + n\,H_2O \quad (1)$$

$$n\,CO + 2n\,H_2 \rightarrow C_nH_{2n} + n\,H_2O \quad (2)$$

Equations (1) and (2) show the formation of normal or isomerized paraffins and olefins, respectively. The challenge of contemporary Fischer–Tropsch reaction research is to develop techniques for controlling process parameters such as productivity of the catalytic bed, selectivity on liquid products (C_{5+}), the yield of specific groups of hydrocarbons, *etc*.[1–3]

In the Fischer–Tropsch catalysis, cobalt selectively produces normal alkanes with low oxygenate impurities.[1,3] Cobalt supported by impregnation is most commonly used in contemporary catalysts. However, skeletal cobalt (Raney cobalt) is unusual although it was suggested as a Fischer–Tropsch catalyst as early as 1934.[4]

The specific structure of Raney catalysts is responsible for high thermal conductivity, which is important in the highly exothermal Fischer–Tropsch reaction. However, the previous generations of Raney catalysts were characterized by a high concentration of an expensive active metal, a low specific activity and difficulties in storage and handling. For these reasons, the Raney catalysts for the Fischer–Tropsch synthesis have been forgotten for decades.

The aim of this work was to study the effect of active cobalt species in composite catalysts on the basic characteristics of the Fischer–Tropsch process.

The composite catalyst supports were prepared by paste extrusion. The paste samples contained 50 wt% highly dispersed aluminum metal powder, while the rest was the binder boehmite (20 wt%) and the H-form of zeolite Beta. In some cases, the pastes contained additionally 10 or 20 wt% highly dispersed Raney cobalt with a particle size of 2.8×0.9–12×7 μm and a specific surface area of 20 $m^2\,g^{-1}$ from Grace Davison Catalysts (Ra non-impregnated composite catalyst). The function of aluminum metal in this composite was to provide heat removal from active sites, while the function of Raney cobalt was to serve as an active component and provide additional thermal interface. Pastes were pressed by a piston extruder through a die with a diameter of 2.5 mm. The extrudates were kept in air, dried, calcined and then cut to 2.5–3 mm long granules.[5,6]

In contrast to the Ra catalysts, active sites in other samples were created by impregnation (Im impregnated catalyst on a composite support). Cobalt (10 or 20 wt%) was supported by impregnation from an aqueous solution of cobalt nitrate in one or two impregnation steps, respectively. The catalysts were calcined in an air flow (~1000 h^{-1}) at 250 °C for 1 h after every impregnation.[5,6]

The catalysts were activated and tested in a laboratory test rig for highly productive Fischer–Tropsch catalysts. The catalyst bed temperature was maintained by the circulation of pressurized preheated water through the reactor jacket. The circulating water pressure was 0.5–0.7 MPa higher than the boiling pressure at the reaction temperature. This provided efficient heat removal under stationary conditions and prevented undesirable hot spot development. In the latter case, the circulating water undergoes phase transition due to hot spot overheat, thus removes an excess heat and returns the bed into the stationary condition.

The reactor for the Fischer–Tropsch synthesis was charged with 2.5 cm^3 of catalyst granules (2.5×2.5–3 mm). The catalyst was preactivated in pure hydrogen (3000 h^{-1}) at 400 °C (7 K min^{-1}) for 1 h.[5,6] Then, the catalyst was heated in a synthesis gas stream with increasing temperature from 170 to 228–234 °C by 3–10 °C steps every 6 h. The synthesis gas pressure was 2 MPa, and the gas-hour space velocity (GHSV) was 1000 to 4000 h^{-1}.

Optimum temperatures corresponding to maximal productivities were 228 °C for 20% Ra and 10% Ra + 10% Im and 233 °C for the others. The optimum temperature increased by 3 °C when GHSV was increased by 1000 h^{-1} for every sample.

All of the samples were active in the formation of liquid hydrocarbons with a chain growth probability (SFA coefficient[1]) of 0.65 to 0.81. Higher SFA coefficients were observed at lower syngas GHSVs.

The conversion of CO increased from 70 to 75–81% as the Co content was increased from 10 to 20 wt%. The rise in GHSV generally led to a decrease in CO conversion. In particular, the conversion of CO on samples with 20 wt% Co showed a maximum at 2000 h^{-1}; while the conversion of CO on samples with 10 wt% Co diminished from 70 to 41% when GHSV was raised from 1000 to 4000 h^{-1}.

The highest specific activity was detected with the Ra catalyst, which contained 10 wt% Co [Figure 1(*a*)]. When the Raney Co content was doubled, the activity decreased by a factot of 1.2–1.9. An increase in GHSV led to a deeper drop in activity. Thus, 10 wt% is the upper limit of reasonable Co concentrations in the catalyst. However, the addition of impregnated Co on top of already introduced 10 wt% Raney Co did not reduce the specific activity.

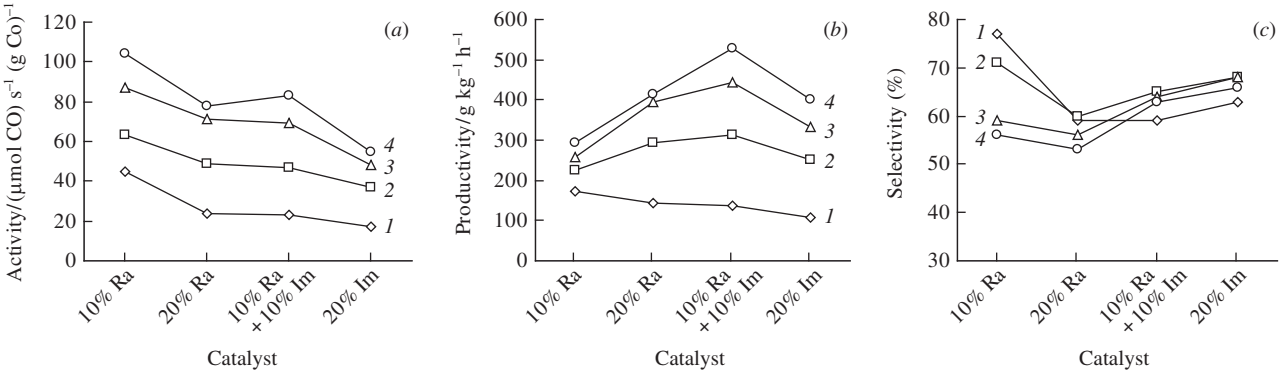

Figure 1 Effect of active metal on (*a*) the specific activity of Fischer–Tropsch catalysts, (*b*) the productivity of C_{5+} hydrocarbons and (*c*) selectivity for C_{5+} hydrocarbons. Gas flow rate of (*1*) 1000, (*2*) 2000, (*3*) 3000 and (*4*) 4000 h^{-1}.

Figure 1(*b*) shows the effect of active metal on the productivity of C_{5+} hydrocarbons. The increase in both total cobalt content and proportion of impregnated Co led to a decrease in the catalyst productivity at 1000 h^{-1}. However, a rise in the synthesis gas flow rate changed the behaviour, so that at higher GHSV the productivity of Im + Ra combination catalysts increased rapidly and manifested a noticeable maximum. Thus, a fourfold growth of the gas space velocity resulted in an increase in productivity: a twofold increase over the 10% Ra catalyst and a 3.8-fold increase over the 10% Ra + 10% Im catalyst.

Figure 1(*c*) represents the selectivity for C_{5+} hydrocarbons *versus* the amount and type of cobalt. We also investigated the influence of active cobalt type on the yields of olefins and isoparaffins. The yield of the latter increased with the impregnated cobalt content of the catalyst. The concentration of Raney Co had no effect on isoparaffin formation. It is interesting that the Ra and Im catalysts showed very different behaviours at enhanced synthesis gas flow rates (Figure 2). Higher GHSV leads to a lower isoparaffin content in the case of Ra catalysts but exhibits no impact in the case of Im catalysts. This fact can be explained by a lower amount of contacts between Co and zeolite in the Ra catalysts. Higher GHSV (shorter contact time) results in a lower probability of hydrocarbon molecule transfer from cobalt to zeolite, where the isomerization probably takes place. This observation supports the theory that reaction (2) is a primary reaction of the Fischer–Tropsch process, while the paraffins are formed from olefins either by hydrogenation on metal centres (normal paraffins) or by isomerization on acid centres of zeolite (isoparaffins).[7–10]

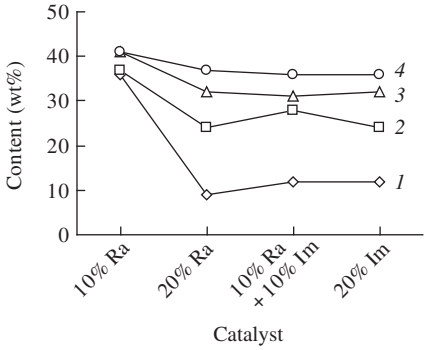

Figure 2 Effect of active metal in catalysts on the concentration of isoparaffins in the liquid product of the Fischer–Tropsch reaction. Gas flow rate of (*1*) 1000, (*2*) 2000, (*3*) 3000 and (*4*) 4000 h^{-1}.

More sophisticated dependences were observed for the yield of olefins at different types of active cobalt. In particular, the highest yield of olefins (11 g m^{-3}) was observed on the 20% Ra catalyst at 4000 h^{-1}, whereas the lowest one (0.5 g m^{-3}), on the 20% Im catalyst at 1000 h^{-1}.

In conclusion, skeletal cobalt was introduced into composite Fischer–Tropsch catalysts for the first time. The proposed technique allows one to utilize all possible advantages of this interesting form of active cobalt. The use of different types of active cobalt and their combinations in a composite granule makes it possible to control the productivity and selectivity of the Fischer–Tropsch synthesis and the yields of isoparaffins or olefins.

We are grateful to Dr. A. Malyschew (Sasol), who kindly provided us with the samples of boehmite.

This work was supported in part by the Russian Ministry of Education and Science (contract no. 16.552.11.7014).

References

1 *Fischer–Tropsch Technology. Studies in Surface Science and Catalysis*, eds. M. Dry and A. Steynberg, Elsevier, Amsterdam, 2004.
2 A. A. Khassin, *Gazokhimiya (Russian Gas Chemistry)*, 2008, no. 2, 28.
3 A. Y. Khodakov, W. Chu and P. Fongarland, *Chem. Rev.*, 2007, **107**, 1692.
4 F. Fischer and H. Meyer, *Ber.*, 1934, **67**, 253.
5 V. Z. Mordkovich, L. V. Sineva, I. G. Solomonik, V. S. Ermolaev and E. B. Mitberg, *RF Patent*, 2405625, B01J, 2010.
6 V. Z. Mordkovich, L. V. Sineva, I. G. Solomonik, V. S. Ermolaev and E. B. Mitberg, *RF Patent*, 2414300, B01J, 2011.
7 E. Iglesia, *Appl. Catal., A*, 1997, **161**, 59.
8 R. J. Madon and E. Iglesia, *J. Mol. Catal. A: Chem.*, 2000, **163**, 189.
9 H. Pichler, H. Schulz and M. Elstner, *Brennstoff-Chemie*, 1988, **48**, 78.
10 R. J. Gormley, V. U. S. Rao, R. R. Anderson, R. R. Schehl and R. D. H. Chi, *J. Catal.*, 1988, **33**, 193.

Received: 27th August 2012; Com. 12/3972