

PAPER • OPEN ACCESS

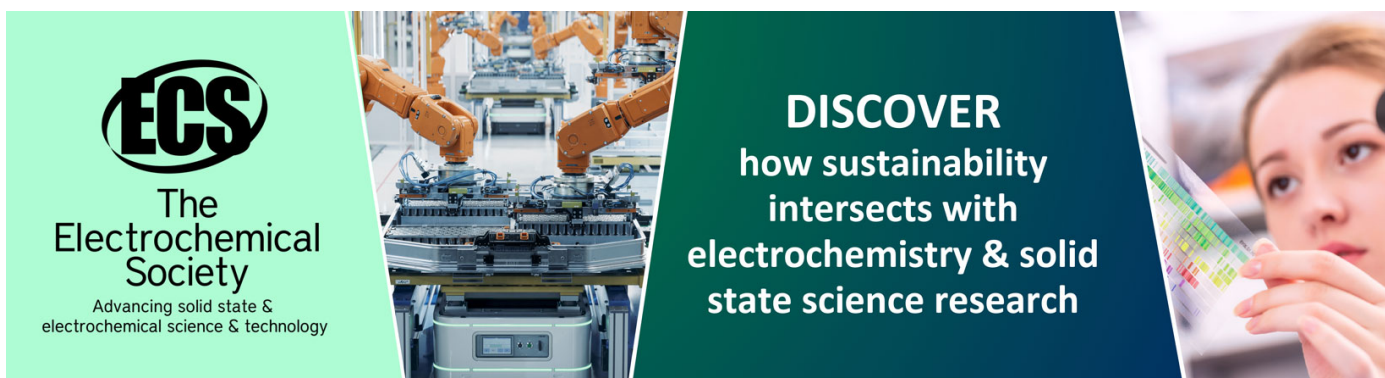
Influence of operating conditions on the main characteristics of a cobalt Fischer-Tropsch catalyst

To cite this article: R E Yakovenko *et al* 2021 *IOP Conf. Ser.: Earth Environ. Sci.* **808** 012041

View the [article online](#) for updates and enhancements.

You may also like

- [In situ characterization of Fischer–Tropsch catalysts: a review](#)
N Fischer and M Claeys
- [The “Innovation Liquid Energy” \(ger. “Innovation Flüssige Energie” - IFE\) Project: Development of a 1MW Power-to-Liquid Plant Based on Co-SOC Electrolysis and Fischer-Tropsch Synthesis](#)
Martin Hauth and Bernd Reiter
- [Performance of Bimetallic Fe and Co Catalyst Supported on HZSM-5 for Fischer-Tropsch Synthesis](#)
D H Ihsanti, Jimmy, Firman Kurniawansyah *et al.*



ECS
The
Electrochemical
Society
Advancing solid state &
electrochemical science & technology

DISCOVER
how sustainability
intersects with
electrochemistry & solid
state science research

Influence of operating conditions on the main characteristics of a cobalt Fischer-Tropsch catalyst

R E Yakovenko, A P Savost'yanov, N S Chistyakova, V G Bakun and S I Sulima

Platov South-Russian State Polytechnic University (NPI), 132, Prosveshcheniya street, Novocherkassk, 346428, Russia

E-mail: s_sulima@mail.ru

Abstract. Three stages of extraction of the contents of the porous space of cobalt catalysts, continuously operating for different periods of time (Time on stream (TOS) is from 40 to 800 h) in a Fischer-Tropsch fixed bed reactor, were performed to identify carbon-containing compounds using chromatographic analysis. At each stage of extraction, the surface of the samples under study was investigated by SEM and BET methods. It was determined that during operation, as a result of accumulation of linear alkanes in the pores of the catalyst with an average number of carbon atoms from 20 to 25 and a decrease in the specific surface area, the reaction rate reduces by 25-30 %. With the help of oxidative treatment, it was found that elemental carbon is contained in the porous space of the spent catalysts.

1. Introduction

The technology of processing gaseous carbon-containing raw materials into liquid hydrocarbons (GTL), which are the basis of synthetic motor fuels, is currently attracting increased attention of researchers. The Fischer-Tropsch synthesis (FTS), which is the main stage of this technology, proceeds at temperatures above 200 °C using solid heterogeneous catalysts, usually based on iron or cobalt [1]. Cobalt is preferred in terms of activity, selectivity for solid paraffins of linear structure, resistance to side reactions and oxidative deactivation [2].

Oxides of silicon, aluminum, titanium, and, less often, other elements are used as supports for Co-catalysts [3]. Promotion is carried out by introducing additives of noble metals (Pt, Re, Ru), oxides of aluminum, zirconium, manganese [4]. It is not only the improvement of catalytic properties that matters, but also the cost of modifying additives. The synthesis and studies of the Co-Al₂O₃/SiO₂ catalyst, which have been the subject of a number of recent publications [5-7], have shown its suitability for practical use, since high values of catalytic characteristics were established with optimal structural parameters of the active component and moderate mutual influence of "metal-support".

In industrial use, a long time of continuous operation of the catalyst is accompanied by a deterioration in its catalytic properties, which leads to reduction of the technical and economic indicators of production. In the scientific literature, various factors are indicated that are the cause of the decrease in the activity of the cobalt catalyst. Most often, this occurs due to the oxidation of the active component under the influence of reaction water [8], agglomeration of its crystallites during sintering due to high temperature [9], catalyst poisoning with catalytic poisons, in particular, sulfur compounds [10], carbon deposition of the porous space in the process of accumulation of particles of soot and other carbon-containing substances [11].



2. Materials and methods

The main parameters of the catalyst preparation process are shown in table 1.

Table 1. Catalyst preparation parameters.

Name	Meaning
Support	SiO ₂
Impregnating solutions	Co(NO ₃) ₂ , Al(NO ₃) ₃
Impregnation temperature, °C	70
Impregnation time, h	0.5
Drying temperature, °C	80-100
Calcination temperature, °C	350
Cobalt concentration, %	20
Aluminum concentration, %	1

The catalyst was loaded into a fixed bed reactor, reduced with hydrogen for 1 h at a temperature of 400 °C and a gas hourly space velocity (GHSV) of 3000 h⁻¹. The tests were carried out at a temperature of 160-230 °C, a pressure of 2.0 MPa, and GHSV of 1000 h⁻¹. The time of continuous testing ranged from 40 to 800 hours. The analysis of the reaction gases was conducted using a Kristall-5000 chromatograph. Liquid reagents were analyzed on an Agilent GC 7890 chromatograph.

The specific surface area of the catalysts (S_{BET}) was determined on a Micromeritics ChemiSorb 2750 instrument by the physical adsorption of argon at a temperature of minus 196 °C.

To study the substances accumulated on the inner surface of the catalysts, their extraction at a temperature of 60 °C for 0.5 h was performed in three stages using benzene (25 ml), into which a catalyst sample (0.5–0.6 g) was placed. The composition of the extract was investigated on an Agilent GC 7890 instrument. After drying, the surface of the catalysts was studied by electron microscopic images obtained by scanning electron microscopy (SEM) on a Hitachi SU8000 microscope.

3. Results

The effect of operating time on catalyst activity is shown in figure 1.

The change in the specific surface area at different stages of the extraction of substances accumulated on the catalyst surface is shown in figure 2.

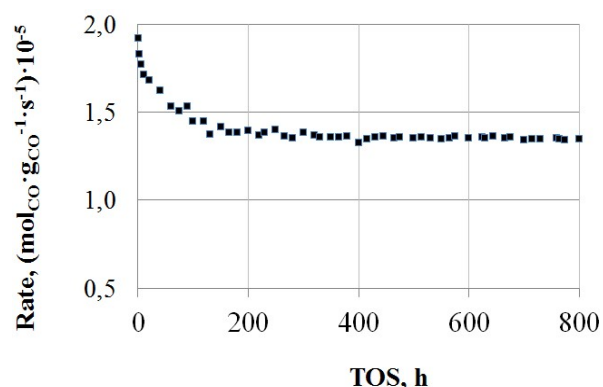


Figure 1. The dependence of the activity of the catalyst on the time on stream (TOS).

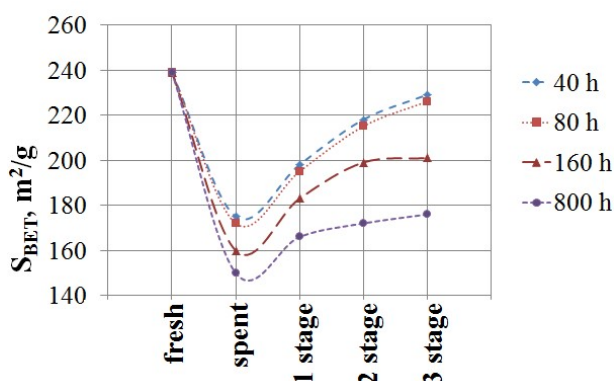


Figure 2. The change in the specific surface area during operation and different stages of extraction.

SEM images of samples worked out at different time intervals are shown in figure 3.

The composition of the liquid obtained at different stages of extraction from the surface of the catalysts is shown in figure 4 in the form of molecular weight distribution (MWD) diagrams.

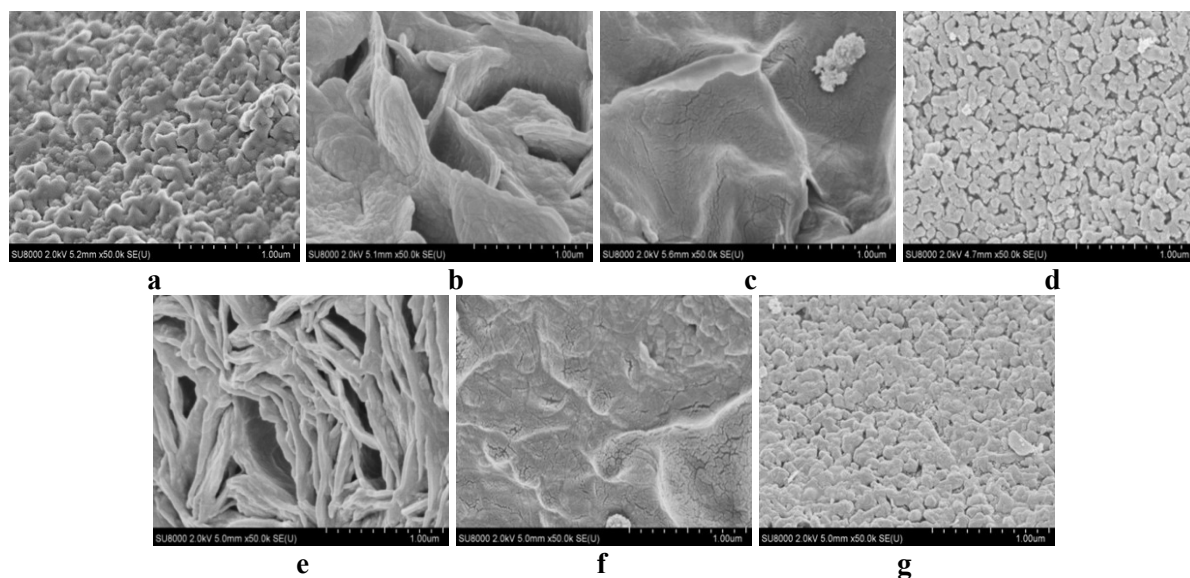


Figure 3. SEM images of the catalyst surface: a – fresh sample; b, c, d – sample after 40 h on stream with following three extraction stages; e, f, g – sample after 800 h on stream with following three extraction stages.

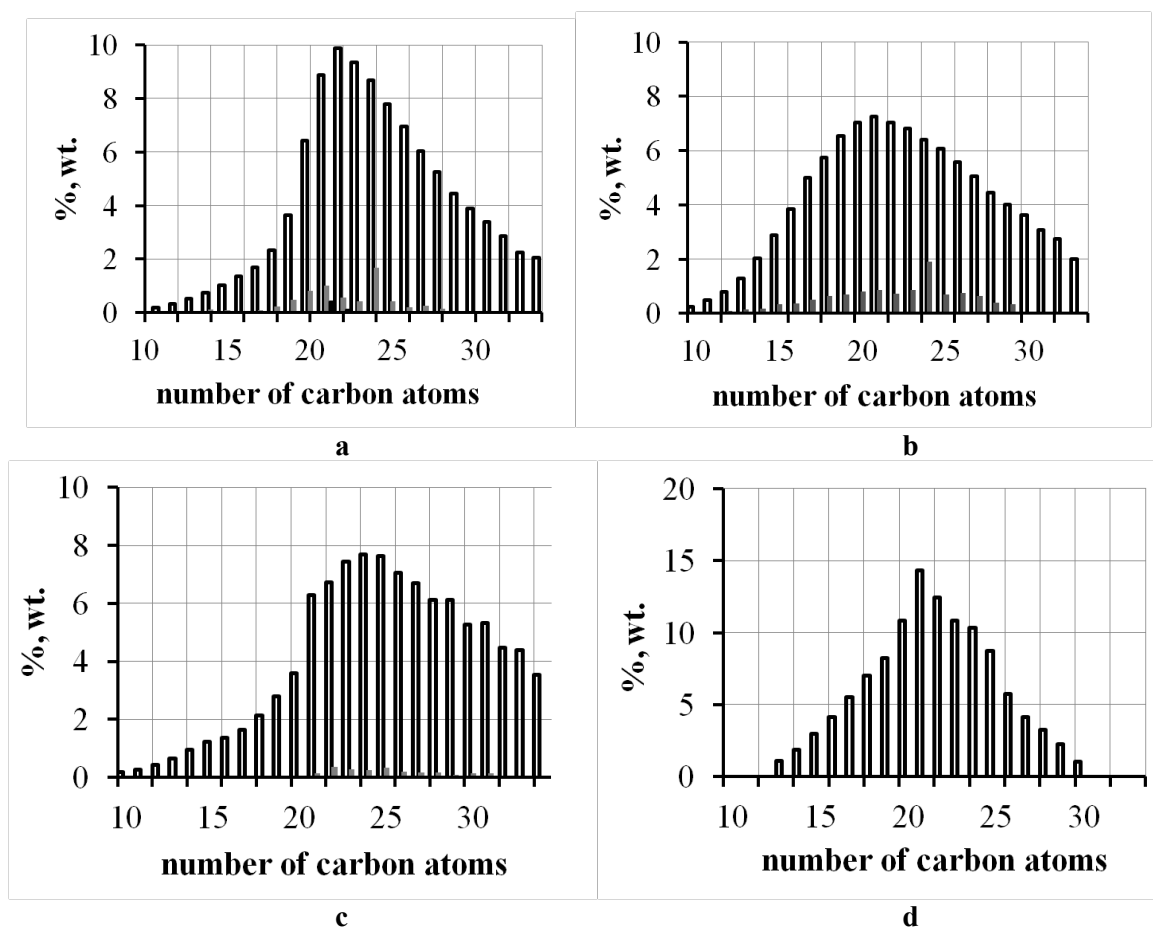


Figure 4. Composition of the organic extract obtained from spent catalysts: a – 40 h; b – 80 h; c – 160 h; d – 800 h (□ - after the 1st extraction; ▒ - after the 2nd; ■ - after the 3rd).

The parameters of the oxidative treatment of the catalyst are presented in table 2.

Table 2. Oxidation treatment parameters.

Parameter	Gas	Gas consumption, ml / min	Temperature, °C	TOS, h	Mass loss, %	Specific surface area, m ² /g	
						before treatment	after treatment
Meaning	O ₂	20	220	0,5	3,2	201	213

4. Discussion

The results of catalytic tests, presented in figure 1, show that the activity of the catalyst during continuous operation in the FTS reduces markedly. In the initial 40-50 hours on stream, the reaction rate decreases by about 25 %, in the next similar period, a decrease occurs by another 10 %. This is due to the accumulation of carbon-containing compounds on the catalyst surface. This is evidenced by the reduction in the specific surface area of the catalysts (figure 2), which occurs especially intensively at the beginning of process (up to 80 h), and during subsequent operation, the decrease in the area slows down.

The extraction of carbon-containing compounds leads to a noticeable increase in the specific surface area of the catalysts, which indicates the release of the porous space from the adsorbed synthesis products. This is evidenced by SEM images of the sample surface obtained at different stages of cleaning (figure 3). If the surface of the spent samples is covered with a large amount of impurities (figure 3, a), then after the 3rd stage of extraction, the image shows a similar picture with a fresh sample (figure 3, d). However, the surface cleaning of catalysts that have spent a longer time is less intensive, especially at the 2nd and the 3rd stages of the extraction, as shown in figure 2.

The composition of organic compounds extracted from the porous space of spent catalysts is shown in figure 4. It was found that most of the paraffin deposits from the surface of the samples are removed during the 1st extraction. The proportion of contaminants found in extracts at subsequent stages of purification is insignificant (figure 4, a-c) or none at all (figure 4, d).

As established by chromatographic analysis, on the surface of the catalysts in the course of continuous operation, accumulation occurs mainly of saturated hydrocarbons with a chain length of C₁₀-C₃₅. The highest concentration values in the MWD are for paraffins containing from 20 to 25 carbon atoms.

In general, the complete cleaning of the surface from accumulated hydrocarbon impurities with an increase in the operating time of the reactor requires fewer extraction stages (figure 4, a, d). This fact may indicate a correspondingly smaller amount of the aforementioned compounds adsorbed on the surface of the samples, with a longer operation.

However, even after the removal of these substances, the surface area of the catalysts remains much smaller compared to the S_{BET} of a fresh sample. It can be assumed that this is due to the accumulation in the catalyst pores of either heavy hydrocarbons such as C₃₅₊ ceresin or molecular carbon, the particles of which block small pores and are not removed by extraction. Taking into account the fact that ceresin is readily soluble in benzene, it can be concluded that the presence of elemental carbon in the porous space is more probable. Further cleaning of the catalyst surface was possible to carry out using oxidative treatment with oxygen (table 2). A decrease in the mass and an increase in the surface area of the sample indicates the possible oxidation of carbon and its removal from the porous space in the form of CO₂.

5. Conclusion

Time on stream (TOS) up to 800 h affects the activity of the cobalt catalyst on a silicate support promoted with aluminum oxide, the composition and nature of carbon-containing impurities on its surface. The reaction rate drops sharply at the initial stage of operation, then this decrease slows down.

During the operation of the reactor, solid products of FTS accumulate in the porous space of the catalysts, their composition is represented by C₁₀-C₃₄ n-alkanes, the highest concentrations of hydrocarbons are found in compounds in the range from 20 to 25 carbon atoms.

Some of the impurities on the surface of the samples in an amount of about 3 % of the catalyst mass are presented in the form of soot-like particles of elemental carbon, which are not recovered during the extraction process. Removal of these impurities by oxidative treatment allows a marked increase in the surface area of the catalyst.

Acknowledgments

The work was carried out within the framework of the state task for R & D, application number 2019-0990, received with the support of the Ministry of Education and Science of the Russian Federation.

References

- [1] Qi Z, Chen L, Zhang S, Su J and Somorjai G A 2020 A mini review of cobalt-based nanocatalyst in Fischer-Tropsch synthesis. *Applied Catalysis A: General* **602** 117701
- [2] Botes F G, Niemantsverdriet J W and van de Loosdrecht J 2013 A comparison of cobalt and iron based slurry phase Fischer-Tropsch synthesis. *Catalysis Today* **215** 112-20
- [3] Munirathinam R, Pham Minh D and Nzihou A 2018 Effect of support and its surface modifications in cobalt-based Fischer-Tropsch synthesis. *Industrial & Engineering Chemistry Research* **57** 16137-61
- [4] Moradi G, Basir M, Taeb A and Kiennemann A 2003 Promotion of Co/SiO₂ Fischer-Tropsch catalysts with zirconium. *Catalysis Communications* **4** 27-32
- [5] Zhang Y, Nagamori S, Hinchiranan S, Vitidsant T and Tsubaki N 2006 Promotional effects of Al₂O₃ addition to Co/SiO₂ catalysts for Fischer-Tropsch synthesis. *Energy & Fuels* **20** 417-21
- [6] Savost'yanov A P, Yakovenko R E, Sulima S I, Bakun V G, Narochnyi G B, Chernyshev V M, and Mitchenko S A 2017 The impact of Al₂O₃ promoter on an efficiency of C₅₊ hydrocarbons formation over Co/SiO₂ catalysts via Fischer-Tropsch synthesis. *Catalysis Today* **279** 107-14
- [7] Prasongthum N and Reubroycharoen P 2015 Preparation of Co/SiO₂-Al₂O₃ fiber catalyst by electrospinning for Fischer-Tropsch synthesis. *Key Engineering Materials* **659** 221-25
- [8] Okoye-Chine C G, Moyo M, Liu X and Hildebrandt D 2019 A critical review of the impact of water on cobalt-based catalysts in Fischer-Tropsch synthesis. *Fuel Processing Technology* **192** 105-29
- [9] Sadeqzadeh M, Chambrey S, Piché S, Fongarland P, Luck F, Curulla-Ferré D, Schweich D, Bousquet J and Khodakov A Y 2013 Deactivation of a Co/Al₂O₃ Fischer-Tropsch catalyst by water-induced sintering in slurry reactor: Modeling and experimental investigations. *Catalysis Today* **215** 52-9
- [10] Visconti C G, Lietti L, Tronconi E, Forzatti P, Zennaro R and Rossini S 2010 Detailed kinetics of the Fischer-Tropsch synthesis over Co-based catalysts containing sulphur. *Catalysis Today* **154** 202-9
- [11] Carvalho A, Ordonsky V V, Luo Y, Marinova M, Muniz A R, Marcilio N R and Khodakov A Y 2016 Elucidation of deactivation phenomena in cobalt catalyst for Fischer-Tropsch synthesis using SSITKA. *Journal of Catalysis* **344** 669-79