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SELECTIVE NITRATION OF AROMATIC AND OLEFINIC HYDROCARBONS IN COKING LIGHT FRACTION VIA SODIUM NITRITE-BASED IONIC CATALYSIS

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This work examined the nitration reaction of the light fraction of coking, a petroleum refining by-product with a high proportion of aromatics and olefins, in the presence of sodium nitrite ($NaNO_2$), an ion-based catalytic system. The light fraction of coking is regarded as a promising feedstock for the synthesis of numerous functional derivatives and comprises a complex hydrocarbon mixture. The response was conducted with 59% nitric acid present at temperatures between 70 and 80 °C, and the mass ratio of the fraction to the acid was 1:1.5. A 61.5% product yield was achieved after two hours. Analysis of the impact of reaction parameters on product yield and selectivity revealed that C – NO_2 groups formed primarily.

O – NO_2 and other oxidized derivatives were generated in trace amounts, but the presence of C – NO_2 groups as the primary signals was confirmed by the analytical data. These results show that the $NaNO_2$ catalyst has a beneficial impact on the not only advances the reaction but also offers a safer and greener substitute for traditional mixed-acid systems. The findings imply that ion-based catalytic devices could be effective substitutes for complex hydrocarbon mixture modification.

Keywords: Light fraction of coking, Nitration, Ion-based catalysts, Sodium nitrite ($NaNO_2$), Green chemistry

INTRODUCTION

Nitration is one of the most important electrophilic substitution reactions in organic chemistry and is widely applied for the functional modification of hydrocarbons. Nitro-containing compounds are extensively used as key intermediates in the production of dyes, pharmaceuticals, agrochemicals, corrosion inhibitors, and energetic materials. Introduction of the nitro group significantly affects the chemical reactivity, polarity, and industrial value of hydrocarbon substrates, making nitration a strategically important transformation in petrochemical and fine chemical industries.

Traditional nitration processes are commonly carried out using mixed acid systems based on concentrated nitric and sulfuric acids. Although these methods provide high reaction rates, they are associated with several disadvantages, including low selectivity, formation of poly-nitrated and oxidized byproducts, strong corrosiveness, and serious environmental and

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safety concerns. In addition, the generation of large volumes of acidic waste limits the sustainability and industrial attractiveness of conventional nitration technologies. Therefore, the development of alternative nitration systems that are more selective, safer, and environmentally benign has become an important research direction.

In recent years, ion-based catalytic systems and nitrite-derived nitrating agents have attracted growing interest as greener alternatives to classical acid mixtures. Sodium nitrite ($NaNO_2$), in particular, enables controlled nitration under milder conditions and promotes selective C–NO_2 bond formation while suppressing excessive oxidation and undesired side reactions. Such systems are consistent with the principles of green chemistry and offer improved operational safety.

The light fraction of coking is a petroleum refining byproduct characterized by a complex mixture of aromatic and olefinic hydrocarbons. Owing to its high content of reactive components, this fraction represents a promising feedstock for chemical functionalization. However, selective nitration of such multicomponent systems remains insufficiently explored. This study investigates the selective nitration of the light fraction of coking using a sodium nitrite-based ionic catalytic system, aiming to achieve high selectivity and yield under relatively mild reaction conditions [1-4].

EXPERIMENTAL

As a by-product of petroleum refinement light coking flue gas is a complex mixture of hydrocarbons that is high in olefins and aromatics. It is a good feedstock for nitration reactions because of its versatile composition and high concentration of reactive elements.

Table 1. Main physicochemical indicators of the light fraction of coking

Property	Value
Density (20°C)	0.8635 g/cm³
Breakage indicator	1.4888
Dynamic viscosity	0.96 mm²/s
Average molar mass	196 g/mol
Aromatic and olefin composition	32%
Initial boiling point (IBP)	143–156°C
Final boiling point (FBP)	364–378°C
Distillation range (5%-95%)	It is wide.
Ignition temperature	57.5–67.5°C
Distillation output	≈99%

The physicochemical indicators shown in the table demonstrate that the light coking fraction is a reactive hydrocarbon mixture with a medium fraction and multiple components. Given its refractive index of 1. 4888 and density of 0. 8635 g/cm³ it is rich in both aromatic and aliphatic components. The light coking fractions good fluidity and uniform mixing in the reaction medium are indicated by its dynamic viscosity of 0. 96 mm²/s. According to its average molar mass of 196 g/mol the majority of its constituents are carbon chain compounds C_{10}–C_{14}.

The presence of 32% aromatic and olefin components in the light coking fraction as determined by the sulfonation analysis indicates that it is a good substrate for nitration and has high reactivity. Boiling point ranges are broad (IBP: 143–156°C FBP:. The complex and irregular structure of the ;ight fraction of coking is reflected in the steep distillation range (364–378°C). It is a reasonably dangerous substance as indicated by its flash point (57. 5–67. 5°C). e. flammable liquid. The distillation yield of approximately 99 percent suggests that this fraction is a useful substrate for post-reaction product separation and analysis.

In the 600–4000 cm^{-1} range spectral analyses were performed using a BRUKER ALPHA FT-IR spectrometer. Characteristic absorption bands verified that the light fraction of coking contained aromatic olefin and paraffin components.

RESULTS AND DISCUSSION

Using a BRUKER ALPHA FT-IR the light fraction of cokings infrared (IR) spectrum was captured. Spectrometer at wavelengths between 600 and 4000 cm-1 and Figure 1 displays the findings.

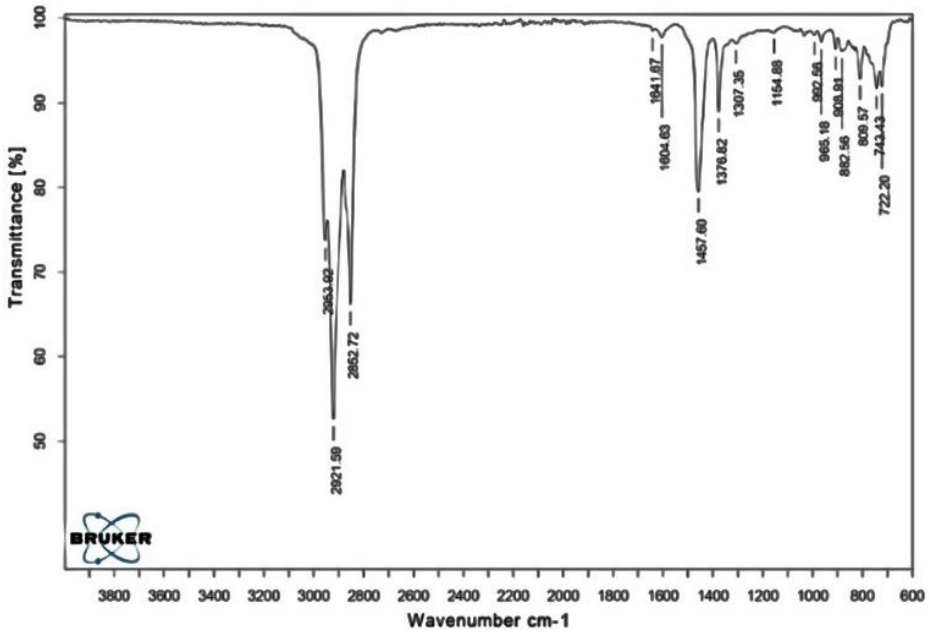

Figure 1. IR spectrum of the Light fraction of coking

Typical absorption bands in the spectrum were as follows.

- Deformation vibrations of CH_2 groups: 722, 1376, and 1457 cm^{-1}
- Stretching vibrations of CH_2 groups: 2852, 2921, and 2953 cm^{-1}
- Stretching vibrations of C = C bonds: 1641 cm^{-1}
- Stretching vibrations of C – C bonds in the benzene ring: 1604 cm^{-1}
- Deformation signals of aromatic C–H bonds in the benzene ring: 743, 809 and 882 cm^{-1}
- Deformation signals corresponding to C=C and C–C bonds: 908, 965, and 992 cm^{-1}

The complex mixture of aromatic olefin and paraffin components that make up the light fraction of coking are confirmed by these bands.

In this study the corresponding nitro compound was obtained by nitrating the light coking flue gas in the presence of ionic sodium nitrite ($NaNO_2$). It was determined how reaction conditions affected the yield and selectivity of the final product. [10]

At temperatures between 70 and 80 °C nitration reactions were conducted. The mass ratio of nitric acid to light fraction of coking was set at 1: 1. 5 (gram/gram) and the reaction was conducted with 59 percent HNO_3. The systems yield was 61. 5% after a 2-hour reaction time. The successful integration of the obtained products structure and functional groups was validated by IQ analysis [15-20].

The spectrum exhibited the following characteristic absorption bands:

- Deformation vibration of CH_2 groups: 1456 cm^{-1}
- Stretching vibrations of CH_2 groups: 2855, 2925, and 2954 cm^{-1}
- Stretching vibration of the O–NO_2 group: 1642 cm^{-1}
- Characteristic stretching signals of the C–NO_2 group: 1341, 1531, and 1549 cm^{-1}

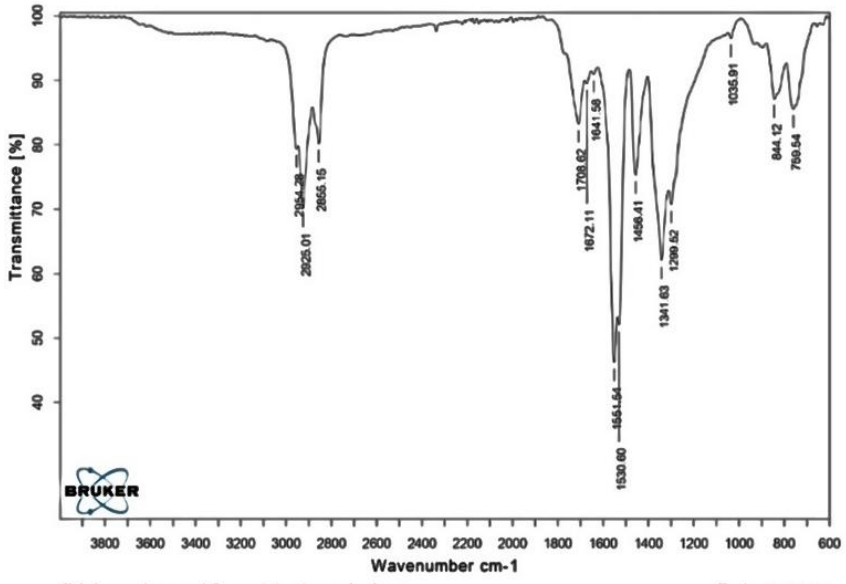

Figure 2. IQ spectrum of the nitro derivative obtained with $NaNO_3$

The spectrum also showed a weak absorption band at 1707 cm^{-1} that was associated with the carbonyl (C=O) group.

The NO_2 functional group has been successfully incorporated into the nitro products structure according to these spectral data. The structural features of the light coking fraction before and after nitration were further investigated by ^1H NMR spectroscopy using a BRUKER-Fourier spectrometer (300.18 MHz, $CDCl_3$).

The ^1H NMR spectrum of the untreated light fraction of coking exhibits resonance signals in the range of 0.71–1.05 ppm, attributed to methyl ($–CH_3$) protons, while signals observed at 1.05–1.50 ppm correspond to methylene ($–CH_2–$) groups of aliphatic chains. The resonance signals in the region of 1.50–2.13 ppm are assigned to protons of naphthenic rings. Signals appearing at 2.13–3.71 ppm are related to methylene and methine protons located in the α-position relative to aromatic rings and double bonds. The presence of olefinic protons is confirmed by signals at 4.60–5.95 ppm, whereas aromatic protons are observed in the range of 6.70–8.50 ppm.

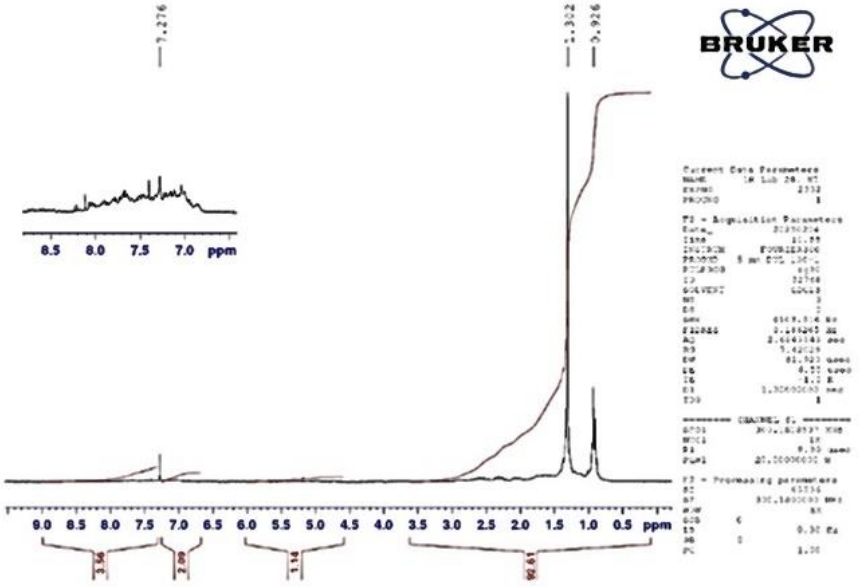

Figure 3. Untreated light fraction of coking

After nitration, the ^{1}H NMR spectrum of the nitrated light coking fraction shows noticeable changes. The methyl and methylene proton signals remain in the regions of 0.72–1.01 ppm and 1.01–1.49 ppm, respectively, indicating preservation of the hydrocarbon backbone. Resonance signals at 1.49–2.11 ppm correspond to naphthenic structures. A new set of signals observed in the range of 2.11–3.24 ppm is attributed to protons of CH–NO_2 fragments and α-positioned CH_2 and CH groups adjacent to aromatic rings, confirming the incorporation of nitro functionality. Aromatic proton signals are detected at 6.90–8.20 ppm, indicating that the aromatic framework remains largely intact after nitration.

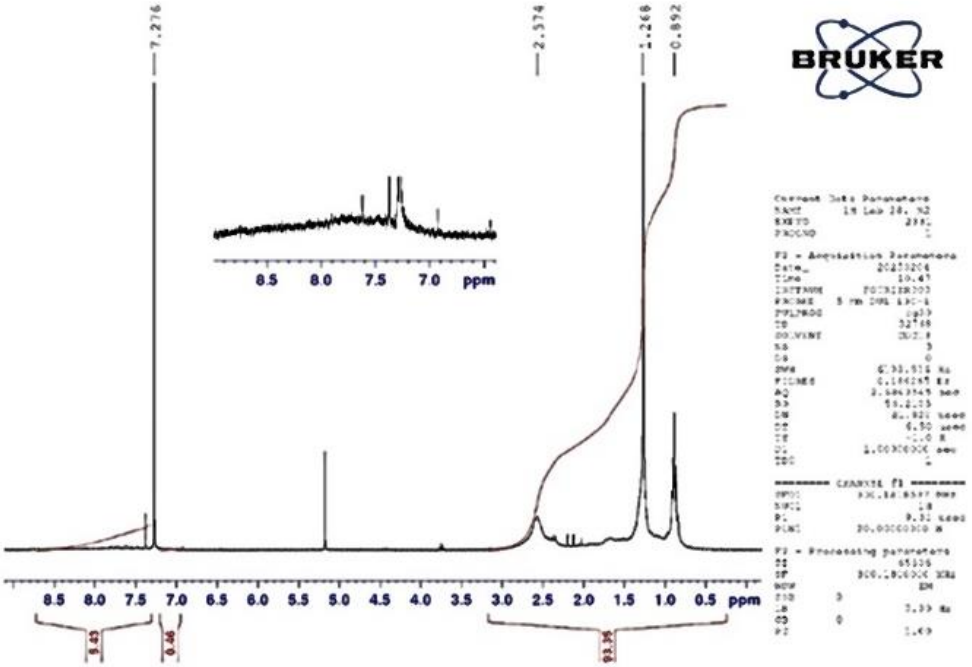

Figure 4. $NaNO_2$-catalyzed nitrated light fraction

The comparative analysis of proton distribution demonstrates that nitration predominantly affects the α-position of aromatic and olefinic structures, while the overall aromaticity degree remains nearly unchanged. These results confirm the selective formation of C–NO_2 bonds, in agreement with NMR spectroscopy data.

CONCLUSION

The studys outcome was the successful nitration of coking light fraction in the presence of an ion-based catalyst based on $NaNO_2$. The products high content of C-NO_2 type functional groups was confirmed and a yield of 61. 5% was achieved. According to the tenets of green chemistry the low amount of O-NO_2 and other byproducts indicates that this method is a safer and more environmentally friendly substitute. ^{1}H NMR spectroscopy confirms that nitration of the light coking fraction occurs selectively while preserving the main hydrocarbon backbone. The emergence of signals attributed to CH–NO_2 and α-substituted CH/CH_2 groups indicates the formation of C–NO_2 bonds without significant loss of aromaticity. The largely unchanged aromatic proton region supports selective α-nitration, in agreement with IR spectroscopy results.

REFERENCES

[1] Abbasov, V.M.; Mammadov, E.A.; Dadashova, N.K.; Mursalov, N.I.; Aghamaliyeva, D.B.; Mammadov, A.M. The inhibition efficiency of nitrated cottonseed oil on corrosion of mild carbon steel in CO_2 medium, *Processes of Petrochrmistry and Oil Refining,* **2024,** v. 25 (3), pp.631-640, https://doi.org/10.62972/1726-4685.2024.3.631

[2] Abbasov, V.M.; Abuzarzada, A.H.; Mammadov, A.M.; Mammadova, R.R.; Azizbayli, E.I.; Adigozalova, R.Kh. Study of nitration reaction of 1-octene and DFT calculations, *Processes of Petrochrmistry and Oil Refining*, **2024,** v.25 (4), pp. 985-993, https://doi.org/10.62972/1726-4685.2024.4.985

[3] Abbasov, V.M.; Aghamaliyeva, D.B.; Azizov, R.E.; Musayeva, Ch. Z.; Ahmadbayova, S.F.; Rzayeva, S.G.; Mammadova, N.M. Investigation of nitrocompounds as precipitation inhibitors, *Processes of Petrochrmistry and Oil Refining*, **2025,** v.26 (2), pp. 321-327 https://doi.org/10.62972/1726-4685.2025.2.321

[4] Aliyeva, L.I.; Njafli, A.R.; Ayyubova, I.H.; Abdullayeva, L.E.; Environmentally friendly corrosion inhibitors: (review), *Processes of Petrochrmistry and Oil Refining*, **2024,** v. 25 (3), pp. 755-775, https://doi.org/10.62972/1726-4685.2024.3

[5] Eyyubova, E.J.; Nagiyev, Kh.J.; Chiragov, F.M. Adsorption study of Fe(III) ions by masc – 2 – amino – 4 – nitrophenol, *Azerbaijan chemical journal,* **2020,** v. 2, pp. 26-33, https://doi.org/10.32737/0005-2531-2020-2-26-33

[6] Abdullayeva, N.R.; Amiraslanova, M.N.; Aliyeva, L.I.; Afandiyeva, L.M. Preparation and study of the properties of alkylphenol-formaldehyde oligomers modified with imidazolines on the basis of synthetic petroleum acids and polyamines, *Processes of Petrochrmistry and Oil Refining*, **2023,** v. 24 (3), pp. 597-610, https://doi.org/10.36719/1726-4685/95/597-610

[7] Abbaszade, S.M. Research of the possibility of developing conservative liquids based on nitrolated oil distillates, *Processes of Petrochrmistry and Oil Refining*, **2023,** v. 24 (3), pp. 473-478, https://doi.org/10.36719/1726-4685/95/473-478

[8] Mukaiyama , T.; Hata , E.; Yamada, T.; Convenient and Simple Preparation of Nitroolefins Nitration of Olefins with Nitric Oxide, *Chemistry letters*, **1995,** v. 24 (7), **1995**, pp. 505–506, https://doi.org/10.1246/CL.1995.505

[9] Abbasov, V.M.; Mursalov, N.I.; Hasanov, E.K.; Kangarli, A.A.; Nabiyev, E.Y.; Azizov, R.E.; Gasimov, V. J. Exploration of the composition of amidoamine, synthesized through the nitrocombination of oleic acid and hexamethylenediamine, serves as a conservative liquid incorporated into T-30 oil distillate, *Processes of Petrochrmistry and Oil Refining,* **2023,** v. 24 (4), pp.706-713, https://doi.org/10.36719/1726-4685/96/706-713

[10] Aliyeva, F. Kh.; Mammadova, F.A. Study of the operational properties of compositions based on nitrogen-containing derivatives of mono-and diesters of alkenyl succinic acids, *Processes of Petrochrmistry and Oil Refining,* **2024,** v. 25 (3), pp.942-951, https://doi.org/10.62972/1726-4685.2024.3.942

[11] Alimadatli, N.Y. Summary of research on the development reagents based on nitrogen-containing organic compounds for the oil and gas extraction and processing industry at the institute of petrochemical processes (IPCP), *Processes of Petrochrmistry and Oil Refining,* **2025,** v. 26 (3), pp.639-656, https://doi.org/10.62972/1726-4685.2025.3.639

[12] Abbasov, V.; Abbaszade,S.; Ismailov,T.; Tahirova,F.; Aliyev, T.; Abbasova, Kh. Nitration behavior of aromatic and olefin-enriched coking light fraction with ionic catalytic systems, *Turan-fundamental sciences symposium*, **2025**, pp.154, https://turansymposium.yildiz.edu.tr/abstract-e-book/

[13] Mammadbayli, E.H.; Talybov, A.G.; Hasanova, K.F.; Babayeva, V.H.; Efendiyeva, K.M. Alkylation of morpholine, piperidine, diethylamine and benzylamine with propylene oxide in aqueous medium, *Processes of Petrochrmistry and Oil Refining,* **2025,** Special issue, pp. 302-312, https://doi.org/10.62972/1726-4685.si2025.1.302

[14] Abbasov, V.M.; Aghamaliyeva, D.B.; Abbasov, M.M.; Talibov, A.H.; Amirli, F.A.; Afandiyeva, L.M.; Aghamaliyev Z.Z. Exploratıon of the antıbacterıal effect of dıpentylammonıum (Z) – 3 – carboxylate complex, *Processes of Petrochrmistry and Oil Refining,* **2024,** Special issue (No. 1), pp.199-205 https://doi.org/10.62972/1726-4685.si2024.1.199

[15] Xosilova, Z. Nitrat va nitritlarning organizmdagı fiziologik jarayonlarga ta'sirıı (adabiyotlar tahlili). *ACTAA NUUz,* **2025,** v.3 (3.1), pp.104 – 107, https://doi.org/10.69617/nuuz.v3i3.1.7390

[16] Talybov ,A.; Mamedbeyli , E.; Abbasov , V.; Abdullayev , Y.; Kochetkov. K. Synthesis of substituted N-Alkylamines in aqueous media. *Green and Sustainable Chemistry*, **2013,** v. 3 (1), pp. 31-35, http://dx.doi.org/10.4236/gsc.2013.31006

[17] Friedrich, K.L.; Souza, A.R.; Fia,R.; Leal, C.D.; Araújo, J.C.; Siniscalchi, L.A.B. Nitratation in pilot-scale bioreactors fed with effluent from a submerged biological aerated filter used in the treatment of dog wastewater, *Environmental Technology,* **2021,** v. 42, pp. 3852 – 3862, https://doi.org/10.1080/09593330.2020.1742796

[18] Casiello, M.; Caputo, D.; Fusco, C.; Cotugno, P.; Rizzi, V.; Dell'Anna, M.M.; D'Accolti, L.; Nacci, A. Ionic-Liquid Controlled Nitration of Double Bond: Highly Selective Synthesis of Nitrostyrenes and Benzonitriles, *EurJOC,* **2020,** v.37, pp. 6012 – 6018, https://doi.org/10.1002/ejoc.202001027

[19] Gottuso, A.; Kobielusz, M.; Macyk, W.; Fedel, M.; Parrino, F. Advancing nitrate radical chemistry through electro – assisted photocatalytic cleavage of olefins, *Materials Today Sustainbility,* **2025,** v. 32, 101263 , https://doi.org/10.1016/j.mtsust.2025.101263

[20] Nong, J.; Cao, Z.; He, Q.; Zhang, Y.; Chen, J.; Wang, Y. A versatile, tunable method for $NaNO_2$ / HX(Cl or Br) – mediated radical dihalogenation or nitration of olefins, *Green Chemistry,* **2025,** v.27 (46), pp. 14883 – 14898, https://doi.org/10.1039/d5gc04596g