Theoretical Insights into the Catalytic Effect of Transition-Metal Ions on the Aquathermal Degradation of Sulfur-Containing Heavy Oil: A DFT Study of Cyclohexyl Phenyl Sulfide Cleavage

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ABSTRACT: Steam injection is the most widely used technique for effectively reducing the viscosity of heavy oil in heavy oil production, in which in situ upgrading of heavy oil by aquathermolysis plays an important role. Earlier, transition-metal catalysts have been used for improving the efficiency of steam injection by catalytic aquathermolysis and achieving a higher degree of in situ oil upgrading. However, the unclear mechanism of aquathermolysis makes it difficult to choose efficient catalysts for different types of heavy oil. This theoretical study is aimed at deeply understanding the mechanism of in situ upgrading of sulfur-containing heavy oil and its catalysis. For this purpose, cyclohexyl phenyl sulfide (CPS) is selected as a model compound of sulfur-containing oil components, and, for the first time, a catalytic effect of transition metals on the thermochemistry and kinetics of its aquathermolysis is investigated by the density functional theory (DFT) methods with the use of the Becke three-parameter Lee–Yang–Parr (B3LYP), ωB97X-D, and M06-2X functionals. Calculation results show that the hydrolysis of CPS is characterized by fairly high energy barriers in comparison with other possible reaction routes leading to the cleavage of C−S bonds, while the heterolysis of C−S bonds in the presence of protons has a substantially lower kinetic barrier. According to the theoretical analysis, transition-metal ions significantly reduce the kinetic barrier of heterolysis. The Cu^{2+} ion outperforms the other investigated metal ions and the hydrogen ion in the calculated rate constant by 5−6 (depending on the metal) and 7 orders of magnitude, respectively. The catalytic activity of the investigated transition-metal ions is arranged in the following sequence, depending on the used DFT functional: Cu^{2+} ≫ Co^{2+} ≈ Ni^{2+} > Fe^{2+}. It is theoretically confirmed that transition-metal ions, especially Cu^{2+}, can serve as effective catalysts in aquathermolysis reactions. The proposed quantum-chemical approach for studying the catalytic aquathermolysis provides a new supplementary theoretical tool that can be used in the development of catalysts for different chemical transformations of heavy oil components in reservoirs due to hydrothermal treatment.

INTRODUCTION

Heavy oil and bitumen account for approximately 60−70% of total proved oil reserves all over the world.1 The highly efficient development of heavy oils has a great significance for meeting the increasing demand for energy. However, unlike conventional light oil, the development of these heavy reserves is more difficult and requires special recovery methods (mainly thermal methods) due to its high viscosity and low American Petroleum Institute (API) gravity.1 Steam injection is the most widely used technique for heavy oil production.2−4 In situ oil upgrading by the aquathermolysis reaction to reduce oil viscosity is among the main mechanisms in a steam injection process.3,5 It is widely accepted that the presence of heteroatoms (S, N, O) is one of the main reasons leading to the high viscosity of heavy oil because the heteroatomic links between hydrocarbon fragments, such as −O−, −S−, and −NH−, give rise to an increase in the molecular weight of oil components.6 These heteroatoms usually exist in resins and asphaltene molecules in the form of C−O, C−N, and C−S bonds.7 It is believed that the heat energy that steam passes to the hydrocarbons causes the cleavage of these heteroatomic bridges, which thus breaks large molecules into smaller ones, consequently reducing the viscosity and improving the flow properties of heavy oils.3 In the aquathermolysis reaction, the
weakest bonds are always cleaved first. The bond dissociation energies of the basic bonds C−H, C−C, C−N, and C−S are 96−99, 83−85, 69−75, and 66 kcal/mol, respectively, which means that the C−S bond is the one that can be cleaved most easily.6 It is believed that even a small fraction of bond breakage can lead to a huge improvement in the flow properties of heavy oils. However, to accelerate C−S bond cleavage reactions at steam injection conditions (500−600 K), some catalysts need to be used.

Many experimental and theoretical studies have been carried out to get a clear picture of the mechanism of decomposition of heavy oil in the aquathermolysis reaction.9−11 For this purpose, it is necessary to use model compounds for experiments or computer simulations owing to the fact that the complicated composition of heavy oil makes it difficult to understand the cleavage mechanism of the C−heteroatom bonds. Organic species containing aliphatic and aromatic fragments, as well as oxygen, sulfur, and nitrogen functional groups, are suitable model compounds for simulating the chemistry of thermal processes that takes place in natural environments. For example, thermolysis reactions of cyclohexyl phenyl ether, sulfides, and amines have been investigated under different reaction conditions in a series of experimental studies.10−13 As evidenced in the experiments, an acid-catalyzed carbocation mechanism operates for these systems at high temperatures in aqueous media.12−15 Gomes et al. used three different composite approaches (CBS-Q, G3, and G3MP2B3) to calculate the thermodynamic parameters of the conversion reactions of sulfur-containing compounds under the action of steam and heat.16 Vasil’iu et al. studied the thermal decomposition mechanism of thiophene both experimentally and theoretically and found that thiophene undergoes unimolecular decomposition by five pathways: C6H5S → (1) S==C=CH2 + HCCH, (2) CS + HCCCH2, (3) HCS + HCCCH2, (4) H2S + HCC—CCH, and (5) S + HCC—CH==CH2.17 Ur Rahman Memon et al. proposed that the thermal decomposition of thiophene was initiated by the homolytic C−S bond cleavage followed by ring opening and isomerization.18 Hore et al. conducted a study on thiophene and other five-membered ring compounds by laser pyrolysis. They proposed that transfer of 1,2-hydrogen is the most probable initiation stage in the decomposition of thiophene.19

Although many efforts have been made, there is still a long way to clearly understand the decomposition mechanism of heavy oil in the aquathermolysis process, especially catalytic aquathermolysis. With more and more problems being exposed during steam injection applications, such as low efficiency, high energy, and freshwater consumption to produce a big amount of steam, the use of catalysts to catalyze aquathermolysis is increasing and becomes a very important area recently.4,20 Transition-metal-based catalysts are the most widely used catalysts in the aquathermolysis process, including water-soluble inorganic metal salts; oil-soluble organic metal compounds; nano/microparticles of metal, metal oxide, or sulfide; etc.4,6

The study is aimed at theoretically calculating the kinetic and thermodynamic parameters of possible steps in the metal-catalyzed aquathermolysis of sulfur-containing heavy oil by density functional theory (DFT) methods and comparing them with the parameters of aquathermal processes that take place in the presence of H+ ions. To achieve these purposes, cyclohexyl phenyl sulfide (CPS) is selected as a model compound of sulfur-containing oil components, and its aquathermolysis mechanism and catalysis were investigated. As for catalysts, Fe, Co, Ni, and Cu were chosen as they are some of the most commonly popular and less expensive metal-based catalysts for the aquathermolysis process. Cyclohexyl phenyl sulfide is a typical model compound for simulating high-sulfur heavy oil components that are responsible for the cross-linking and high viscosity. A comprehensive ab initio study of different reaction pathways of aquathermolysis of cyclohexyl phenyl sulfide (CPS) also showed that the proton-catalyzed carbocation mechanism is a major route in the aquathermolysis of CPS in the presence of H+ ions, which has the lowest energy barrier for the cleavage of the C−S bond.21 The major final products of the reaction chain, in this case, are 1-methylcyclopenten and thiophenol, which agrees well with the experimental data.13 As for other thermal aquathermal processes, such as the homolytic cleavage with formation of radical products and the hydrolysis, their thermodynamic characteristics and energy barriers in the C−S bond cleavage are significantly less favorable.22 However, it should be noted that the delivery of H+ ions in the organic media of heavy oil components, in which the aquathermolysis processes take place, is difficult. The metal-based catalyst seems to be able to catalyze this process and promote its occurrence since some of them have been tested to be effective in improving the level of in situ upgrading in aquathermolysis processes. In this work, in which the calculation of catalytic aquathermolysis using DFT is attempted for the first time, Cu2+, Co2+, Ni2+, and Fe2+ were used as catalysts in the first step. In future work, more types of their compounds, oxides, sulfides, etc., will be calculated.

It is worth noting that theoretical quantum-chemical studies of the kinetics and thermodynamics of these catalytic reactions are practically absent despite the fact that the current level of the development of quantum-chemical methods and computational power allows one to calculate parameters of complex chemical processes that take place in high-viscosity oil reservoirs under high pressures and temperatures. Therefore, the theoretical calculation method used in this work for studying the catalytic aquathermolysis can be a valuable supplement in the development of catalysts for different chemical transformations occurring in oil reservoirs under high-temperature conditions.

### THEORETICAL CALCULATIONS

Quantum-chemical calculations were performed using the Gaussian0922 and PRIRODA23 software packages.

The potential energy surfaces (PESs) of the reactions of CPS hydrolysis (reaction involving water molecules) were calculated using the DFT method with the Perdew–Burke–Ernzerhof (PBE) functional in the L1 basis set (PRIRODA). The PES values were scanned by varying the distance between the oxygen atom of the water molecule and the carbon atom of the C−S bond involved in the hydrolysis reaction at steps of 0.02 Å and by optimizing the geometry of reactants in each step (the calculations were started from a distance of 5 Å). The scanning process aimed at finding the PES region, in which the energy and geometry of neighboring intermediate states drastically change. In the next step, the Hessian matrix (the matrix of second-order derivatives of the energy with respect to atomic coordinates) of the intermediate structure immediately before and after the jump region was calculated using the PRIRODA software package. After that, the most negative frequency mode of the obtained structure is determined and a stationary point is searched along this frequency mode until
meeting convergence criteria for the energy between iteration points \((1 \times 10^{-7} \text{ a.u.})\) and for the vector of the Hessian-matrix partial derivatives \((5 \times 10^{-6} \text{ a.u.})\). This algorithm makes it possible to find the transition-state geometry with a single imaginary frequency mode that determines the reaction path in the intrinsic coordinates (IRC).

The energies of starting reagents and reaction products of the elementary stages of aquathermolysis reaction sequences involving the heterolytic cleavage with formation of the cyclohexyl carboxylation, as well as the chemical structure parameters, were calculated using the DFT method with the Becke three-parameter Lee–Yang–Parr (B3LYP) hybrid functional in the triple zeta valence polarization (TZVP) basis set within the integral equation formalism-polarizable continuum model (IEF-PCM) solvent reaction field model (embedded in Gaussian09 software).

The thermodynamic functions and parameters (electronic energy \(E\) and Gibbs free energy \(G\)) of reactants were calculated using Gaussian09 software by the DFT method (the B3LYP hybrid functional and the TZVP basis set). The energy changes of reactions were calculated by taking into account the calculated energies of reactants. The thermochemical characteristics of reactions at different temperatures were calculated at steps of 100 °C using different hybrid functionals (B3LYP, \(\omega\)B97X-D, and M06-2X).

## RESULTS AND DISCUSSION

Several reaction mechanisms were considered in previous ab initio theoretical studies of the reaction of aquathermolysis of cyclohexyl phenyl sulfide, namely, homolytic cleavage with formation of radical species, proton-catalyzed heterolytic cleavage, and hydrolysis.\(^{24}\) On the basis of these results and the results of experimental studies of the reaction products in the laboratory aquathermolysis process,\(^{13}\) we suggest that the heterolytic cleavage via ionic routes is also the most preferable mechanism involved in the transition-metal-catalyzed aquathermolysis processes of heavy oils, which we have studied recently under laboratory conditions.\(^{25–27}\) Even if the hydrolysis routes also involve ionic reaction schemes, they are characterized by rather high energy barriers according to the published results of ab initio calculations.\(^{24}\)

To compare these two possible mechanisms, i.e., heterolytic cleavage and hydrolysis, which are most likely involved in the processes of aquathermolysis of CPS under conditions of catalysis by transition-metal ions, we have calculated thermodynamic characteristics of these processes using rigorous quantum-chemical approaches. The homolytic cleavage in this study was not considered since transition-metal ions hardly have catalytic effects on this process. Although the calculated energy barriers of the homolytic cleavage of C–S bonds in CPS at ambient temperatures (about 190 kJ/mol) were shown to be somewhat lower than the energy barriers of the heterolytic cleavage (about 290 kJ/mol) and be able further lowered under conditions of aquathermal treatment.\(^{24}\)
First, we have studied the hydrolysis of cyclohexyl phenyl sulfide in the uncatalyzed process and under conditions of catalysis with Fe$^{2+}$ ions using the DFT method within the PRIRODA software package. The relevant reaction routes are given in Scheme 1.

Two reaction paths for the hydrolysis process are considered: one path involves the formation of thiophenol and cyclohexanol as reaction products, and the second path leads to the formation of phenol and cyclohexanethiol (Scheme 1a). In the theoretical calculations of noncatalytic hydrolysis of CPS at 0 K, which were performed using the PRIRODA software package with the PBE functional in the L1 basis set, we have obtained transition states with a single imaginary frequency mode and determined both reaction paths in the IRC starting from a molecular pair comprised of CPS and one water molecule. The corresponding energy diagram is shown in Figure 1. As can be seen, the energy barriers calculated with respect to the energy of reagents are close to the published results obtained using the PRIRODA software package.

In the process of catalysis by Fe$^{2+}$ ions, the energy barriers of the hydrolysis process are noticeably lowered (Figure 2). However, we were not able to locate the first-order saddle point with a single imaginary frequency mode in the configuration space because of overcrowding of the reaction site and sudden rotation of the cyclohexyl moiety to avoid stereochemical tension. The latter fact leads to an abrupt change in the structural configuration of the transition state during scanning the vector of the Hessian-matrix second derivatives and impossibility to find a configuration with a single imaginary frequency mode. Consequently, the hydrolysis route with the formation of cyclohexanol cannot be considered as a preferable reaction route despite the fact that it was preferable under conditions of noncatalytic hydrolysis.

Thus, the calculation results demonstrate the catalytic effect of the transition-metal ion on the hydrolysis of cyclohexyl phenyl sulfide. Nevertheless, despite a substantial theoretical

### Table 1. Electronic Energy and Gibbs Free Energy Changes Calculated at $T = 298.15$ K by the B3LYP/TZVP DFT Method in the Gaussian09 Software Package for Elementary Steps and the Total Reaction Given in Scheme 2 under Conditions of Catalysis

| catalyst | $\Delta E_1$, kJ/mol | $\Delta G_1$, kJ/mol | $\Delta E_2$, kJ/mol | $\Delta G_2$, kJ/mol | $\Delta E_3$, kJ/mol | $\Delta G_3$, kJ/mol | $\Delta E_4$, kJ/mol | $\Delta G_4$, kJ/mol | $\Delta E_5$, kJ/mol | $\Delta G_5$, kJ/mol | $\Delta E_{tot}$, kJ/mol | $\Delta G_{tot}$, kJ/mol |
|----------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| H$_3$O$^+$ | -120.37             | -87.78              | 182.51              | 101.91              | -46.64              | -49.70              | 52.95                | 50.93                | -80.54              | -91.38              | 40.90               | -11.87              |
| Fe$^{2+}$ | 21.45               | 45.56               | 155.27              | 92.93               | -46.64              | -49.70              | 52.95                | 50.93                | -80.54              | -91.38              | 40.90               | -11.87              |
| Ni$^{2+}$ | 21.47               | 42.74               | 148.00              | 87.51               | -46.64              | -49.70              | 52.95                | 50.93                | -80.54              | -91.38              | 40.90               | -11.87              |
| Co$^{2+}$ | 19.99               | 39.10               | 146.60              | 86.36               | -46.64              | -49.70              | 52.95                | 50.93                | -80.54              | -91.38              | 40.90               | -11.87              |
| Cu$^{2+}$ | 2.65                | 17.75               | 112.48              | 60.53               | -46.64              | -49.70              | 52.95                | 50.93                | -80.54              | -91.38              | 40.90               | -11.87              |
catalytic effect of the iron(II) ions on the hydrolysis of cyclohexyl phenyl sulfide, the calculated energy barrier lowering is still not enough to surpass the energy characteristics of the direct heterolytic cleavage of the C=S bond with the formation of a cyclohexyl cation and phenyl sulfide. Considering these findings, we decided to study the latter process in more detail.

Previously, both the experimental and theoretical studies confirmed that the acid-catalyzed mechanism of heterolytic cleavage of CPS with the formation of methycyclopentene and thiophenol as main products should be a major route in the aquathermolysis process. In addition, the mass spectral analysis of the reaction products of aquathermolysis of cyclohexyl phenyl sulfide shows that thiophenol is converted in significant amounts to secondary reaction products, such as the products of dimerization and reactions with intermediate cyclohexyl and methycyclopentyl carbocations.15 A general mechanism that explains the formation of these intermediates and reaction products in the proton-catalyzed aquathermolysis process of cross-linked cyclohexyl phenyl compounds has been proposed in the same study.15 On the basis of this mechanism, we propose the sequence of reactions (shown in Scheme 2) to study the catalytic action of H+ and iron(II), cobalt(II), nickel(II), and copper(II) ions in the heterolytic cleavage of C=S bonds in CPS.

Table 1 shows the calculated values of the electronic energy and Gibbs free energy changes for each step of the reaction sequence and for the total aquathermolysis reaction under conditions when an acid and different transition-metal ions are used as the catalyst. As can be seen from Table 1, the second step involving the heterolytic breakage of C=S bonds is the most energy-consuming step in the reaction mechanism. Hence, it can be considered as a rate-limiting step in the entire sequence of reactions. The obtained energy barrier values of the heterolytic cleavage of a prereaction complex of CPS with H3O+ are close to the published values.24 At the same time, this step is a barrierless reaction followed by subsequent rearrangement of the generated cyclohexyl cation into the more stable methycyclopentyl cation in the third exothermic reaction step.

Such an energy profile of the total reaction of CPS aquathermolysis allows one to consider the energy change in the second step as a kinetic barrier of the total reaction sequence. Hereinafter, the change in the electronic energy in the second step of the heterolytic aquathermolysis process is called “electronic energy of activation” and, accordingly, the change in the Gibbs energy is called “Gibbs energy of activation”. Consequently, it is the lowering of these activation parameters that determines the catalytic action of the proton and various transition-metal ions on the aquathermolysis reaction. As shown in Table 1, the calculated energy barriers of the heterolytic cleavage of the C=S bond under catalysis with transition metals at room temperature in most cases are somewhat lower than the energy barrier of the acid-catalyzed cleavage. Remarkably, the calculation results show that the Cu2+ ion may be substantially superior in catalytic activity not only to acids but also to the other transition-metal counterparts.

There is a well-known relationship between the standard rate constant ($k^0$) and the standard Gibbs free energy of activation ($\Delta^0 G^{\ddagger}$) in the transition state theory of monomolecular reactions.28

$$k^0 = \frac{k_B T}{h} \exp(-\Delta^0 G^{\ddagger}/RT) \quad (1)$$

where $k_B$ is the Boltzmann constant, $T$ is the temperature, $h$ is the Planck constant, and $R$ is the gas constant. In this study, the reacting mixture was considered as a quasi-homogeneous mixture with the even distribution of reactants, in which intermolecular interactions are intentionally neglected so that formula 1 for ideal gases can be applied for calculating the standard rate constant of the heterolytic cleavage of pre-reaction complexes (second step in Scheme 2). This simplified model was used in a comparative analysis of the relative reaction activities of the catalytic systems. For the analysis, the $k^0$ values are calculated using formula 1. In the calculations, $\Delta^0 G^{\ddagger}$ was considered to be equal to the $\Delta G_2$ values (Table 2) for the second rate-limiting step in the sequence of reactions shown in Scheme 2.

For preliminary estimates, we analyzed the relative catalytic activities of different transition metals at room temperature (298.15 K). A comparison of the results given in Table 2 shows that these transition-metal ions (Fe2+, Ni2+, Co2+, and Cu2+) are able to significantly increase the rate of the aquathermal cleavage of organic sulfides. With the Cu2+ catalyst, the standard rate constant of the heterolytic cleavage step at 298.15 K is approximately 5 orders of magnitude higher than the rate constants of other studied catalytic systems.

To evaluate the catalytic activity of different transition-metal ions in the processes of heterolytic cleavage of C=S bonds under conditions of aquathermal treatment, standard Gibbs free energies of activation of the second step of CPS heterolysis shown in Scheme 2 were calculated at different temperatures using the DFT method with different functionals (Table 3). For Fe2+ and Co2+, their high-spin states were determined to be ground states at 0 K in the DFT calculations with the PBE functional and L1 basis set in the PRIRODA software.

### Table 3. Gibbs Free Energy Changes $\Delta^0 G^{\ddagger}$ (kJ/mol) for the Second Rate-Limiting Step of the Reaction Sequence Given in Scheme 2 with Different Catalysts and at Different Temperatures (Calculated Using the DFT Method with Corresponding Functionals in the Gaussian09 Software Package)

| T, K | Fe2+ $\omega B97X$-D | M06-2X | Co2+ $\omega B97X$-D | M06-2X | Cu2+ $\omega B97X$-D | M06-2X | Ni2+ $\omega B97X$-D | M06-2X |
|------|-----------------|--------|-----------------|--------|-----------------|--------|-----------------|--------|
| 0    | 152.90          | 193.71 | 204.20          | 146.32 | 185.65          | 198.25 | 146.32          | 198.25 |
| 100  | 134.59          | 173.71 | 181.58          | 127.84 | 168.17          | 180.97 | 127.84          | 168.17 |
| 200  | 114.13          | 152.21 | 160.85          | 107.01 | 148.18          | 162.51 | 107.01          | 148.18 |
| 300  | 93.57           | 130.97 | 139.86          | 86.00  | 127.80          | 144.30 | 86.00  | 127.80 |
| 400  | 73.04           | 110.00 | 118.81          | 64.98  | 107.34          | 126.37 | 64.98  | 107.34 |
| 500  | 52.59           | 89.29  | 97.77           | 44.03  | 86.90           | 108.71 | 44.03  | 86.90 |
| 600  | 32.25           | 68.84  | 76.81           | 23.19  | 66.54           | 91.31  | 23.19  | 66.54 |
| 700  | 12.03           | 48.63  | 55.95           | 2.46   | 46.26           | 74.17  | 2.46   | 46.26 |

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The difference between the energies of high- and low-spin states in the intermediate reaction complexes was 470 kJ/mol for Fe$^{2+}$ and 26 kJ/mol for Co$^{2+}$. As can be seen from Table 3, the B3LYP functional probably gives understated values of the free energy changes in comparison with the ωB97X-D and M06-2X functionals. The ωB97X-D long-range-corrected hybrid functional with empirical dispersion corrections has reported to provide satisfactory accuracy for thermochemistry, kinetics, and noncovalent interactions.29 The same is true with regard to the M06-2X functional of the Minnesota family.30 Despite the popularity of the B3LYP functional in quantum-chemical calculations, it may give less reliable results for the thermochemistry of transition-metal complexes. The Gibbs energy changes calculated in this study

Figure 3. Logarithmic temperature dependences of the half-life of the reaction of heterolytic cleavage of CPS with different catalysts determined from the appropriate standard Gibbs energies calculated using the DFT method with (a) B3LYP, (b) ωB97X-D, and (c) M06-2X functionals (dashed lines show reaction half-time levels corresponding to $t_{1/2} = 1$ h and $t_{1/2} = 1$ s).
with the use of the $\omega$B97X-D and M06-2X functionals are close to each other in most cases (see Table 3). Therefore, the later discussion is mainly based on the data obtained by the $\omega$B97X-D and M06-2X functionals.

According to the DFT/$\omega$B97X-D and DFT/M06-2X methods, the calculated values of the Gibbs energy of activation decrease, with an increase in the temperature from 300 K (ambient temperature) to 700 K (close to temperatures achieved under conditions of aquathermal treatment of heavy oil reservoirs), by a factor of 3–4 in the case of a catalytic system based on Fe$^{2+}$, by a factor of about 3 for Co$^{2+}$, by a factor of 4 to 38 for Cu$^{2+}$, and by a factor of 2–2.5 for Ni$^{2+}$. Cu$^{2+}$ significantly outperforms its counterparts in catalytic activity, as can be seen from the calculated Gibbss energies of activation. The investigated transition-metal ions can be arranged in the following descending order by their catalytic action: Cu$^{2+} >$ Co$^{2+} \approx$ Ni$^{2+} >$ Fe$^{2+}$.

The kinetic patterns of catalytic cleavage of CPS are more clearly illustrated by corresponding kinetic constants calculated using eq 1. Based on the calculated standard rate constants (Table 4), all of the investigated transition-metal catalytic systems significantly accelerate the reaction rate at 500–600 K. This temperature range is usually achieved in reservoirs during the steam injection process for heavy oil recovery, which means that these metals have potential in catalyzing aquathermolysis processes in a real steam injection project in the oilfield. In the case of Cu$^{2+}$, a relatively high kinetic constant is obtained even at $T = 400$ K (see Table 4).

Figure 3 shows the logarithmic temperature dependences of the half-life of the reaction of heterolytic cleavage of CPS bonds for different catalysts, which are determined under the assumption of first-order decay by the following expression: $t_{1/2} = \ln 2 / \kappa$. As noted above, activation parameters $\Delta^\circ G^\circ$ calculated by the DFT/B3LYP method are most likely significantly understated. For this reason, the half-life of the reaction corresponding to $t_{1/2} = 1$ h achieved with this functional seems to be improbable in the temperature range of about 225–300 K for the different catalytic systems, let alone a half-time of $t_{1/2} = 1$ s can be obtained for different transition metals in the temperature range of 260–340 K (see Figure 3a). A half-life of 1 h and 1 s with the $\omega$B97X-D functional can be achieved for different catalytic systems in the temperature range of 310–375 and 350–430 K, respectively (Figure 3b). These simulation results obtained with the $\omega$B97X-D functional seem to be more reliable. In comparison to the $\omega$B97X-D functional, the M06-2X functional gives somewhat higher values ($t_{1/2} = 1$ h and $t_{1/2} = 1$ s in the temperature ranges of 340–410 and 400–470 K, respectively) (see Figure 3c).

To understand the reasons for a substantial difference in the catalytic activity of Cu$^{2+}$, Mulliken population analysis of charge densities on relevant atoms of the prereaction complexes is performed, as well as bond lengths and highest occupied molecular orbital (HOMO)—lowest unoccupied molecular orbital (LUMO) gaps of these complexes are compared (Table 5). The analysis shows that Cu$^{2+}$ has significant differences in the charge distribution, M–S bond length, and HOMO–LUMO gap compared to those for other ions. At the same time, there is no direct relationship between the reference data on the ionic radii$^{31}$ and the considered parameters for transition metals under study. As can be seen from Table 5, the effect of increased catalytic activity of Cu$^{2+}$ in comparison with the other metals is determined by a shorter M–S bond length, a substantial distribution of the positive charge to S, and a larger HOMO–LUMO gap in the prereaction complex. The Mulliken population analysis shows a significant positive charge on the S atom and a less negative charge on the C atom of the cyclohexyl ring in the prereaction complex with Cu$^{2+}$ compared to the other metals, which should facilitate the elimination of the cyclohexyl cation in the cleavage reaction. There are no significant differences in the C–S bond lengths of the prereaction complexes with different metals; however, this bond in the starting CPS was noticeably shorter in length (1.845 Å). The found HOMO–LUMO gaps of the prereaction complexes requires further analysis beyond the scope of this study but allow us to make a preliminary conclusion that lower gaps for complexes with Ni$^{2+}$, Co$^{2+}$, and Fe$^{2+}$ give rise to their greater stability through delocalization of the energy when compared to the complex with Cu$^{2+}$. The less stability of the prereaction complex with Cu$^{2+}$ explains its higher reactivity and enhanced catalytic activity of Cu$^{2+}$ in the cleavage of C–S bonds.

### CONCLUSIONS

In summary, using the DFT methods, it is confirmed that the hydrolysis is not a kinetically preferred process among the possible reaction routes in the aquathermolysis process of the model reagent (CPS), while the reaction sequence involving the heterolytic cleavage of C–S bonds with formation of the cyclohexyl carboxylate has a substantially lower kinetic barrier in the rate-limiting step. The results of simulation of the thermochemistry and kinetics that transition-metal ions, such as Cu$^{2+}$, Fe$^{2+}$, Co$^{2+}$, and Ni$^{2+}$, noticeably reduce the kinetic barrier of the hydrolysis of CPS. Moreover, transition-metal ions more substantially reduce the kinetic barrier of the heterolytic thermal cleavage of CPS in comparison with the acid-catalyzed process verified by the DFT calculation results obtained with the B3LYP, $\omega$B97X-D, and M06-2X functionals. Also, the estimates of the half-lives of the reaction for ideal gas conditions show that relatively short half-lives in the heterolytic cleavage of CPS can be achieved with transition metals in the temperature range of 400–500 K. All of these results confirm theoretically that transition-metal ions can

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Table 5. Ionic Radii of Metals under Study and Calculated Parameters of Prereaction Complexes with These Metals (See Scheme 2)$^{a}$

| M$^{2+}$ | Ionic radius, Å | S–M bond length, Å | S–C bond length, Å | Mulliken atomic charge on S | Mulliken atomic charge on M | Mulliken atomic charge, C | HOMO–LUMO gap, eV |
|---------|----------------|--------------------|-------------------|-----------------------------|-----------------------------|-------------------------|-------------------|
| Fe$^{2+}$ | 0.78 | 2.624 | 1.879 | 0.010 | 0.943 | −0.176 | 5.712 |
| Co$^{2+}$ | 0.745 | 2.561 | 1.880 | 0.010 | 0.956 | −0.194 | 5.719 |
| Ni$^{2+}$ | 0.69 | 2.506 | 1.880 | 0.017 | 0.918 | −0.199 | 5.728 |
| Cu$^{2+}$ | 0.73 | 2.420 | 1.884 | 0.188 | 0.689 | −0.003 | 5.882 |

*Notes: Ionic radii are taken from ref 31; C is the carbon atom of the cyclohexyl ring in the C–S bond; the B3LYP/TZVP method is used in calculations.*
serve as effective catalysts in the downhole upgrading of high-sulfur heavy oil under conditions of superheated steam injection. In general, the catalytic activity of the investigated transition-metal ions can be arranged in order $\text{Cu}^{2+} \gg \text{Co}^{2+} \approx \text{Ni}^{2+} \gg \text{Fe}^{2+}$. In terms of the rate constant, the $\text{Cu}^{2+}$-based catalytic system outperforms the other metals by more than 5 orders of magnitude.

The first time use of the DFT calculation for catalytic aquathermolysis not only gives important information about how to promote aquathermolysis reaction in steam injection process but also provides a valuable theoretical calculation method as a supplement in developing catalysts for different chemical transformations occurring in oil reservoirs under high-temperature conditions, as well as in other industrial areas.

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■ ABBREVIATIONS

CPS, cyclohexyl phenyl sulfide; DFT, density functional theory; B3LYP, Becke three-parameter Lee−Yang−Parr; PES, potential energy surface; PBE, Perdew–Burke–Ernzerhof; IRC, intrinsic reaction coordinate; TZVP, triple zeta valence polarization; IEF-PCM, integral equation formalism-polarizable continuum model

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