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Adsorption thermodynamics of sulfur- and nitrogen-containing molecules on NiMoS: a DFT study

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Detailed adsorption thermodynamic data of organosulfur and organonitrogen molecules on NiMoS hydrotreating catalyst active sites were studied by density-functional theory (DFT) calculations. Initially, the adsorption of the molecules on the NiMoS edge surface is studied, and the most stable configuration for each molecule is identified. The changes in electronic energy and zero point vibrational energy upon the adsorption of different molecules on the NiMoS surface are calculated. The contribution of adsorbed molecules, as well as gas phase molecules, to changes in entropy and C_p values are obtained by calculating vibrational frequencies of adsorbed and free molecules. With these data, the changes in enthalpy, entropy, and free energy due to the adsorption on the NiMoS edge surface at different temperatures are determined. These data can be used to estimate the relative surface coverage of each type of species at different reaction conditions.

KEY WORDS: adsorption; hydrotreating; NiMoS; DFT; sulfur; nitrogen; HDS; HDN.

1. Introduction

Theoretical studies based on density-functional theory (DFT) have made significant contributions towards developing a fundamental understanding of hydrotreating catalysis and furthering the development of new highly active and selective hydrotreating catalysts [1]. For example, DFT calculations have provided new insights into the detailed surface structures of MoS_2-based hydrotreating catalysts [2–6]. Molybdenum exists as MoS_2 clusters in Mo-based sulfide catalysts, and previous calculations have indicated that during the incorporation of Ni (or Co) into molybdenum sulfide catalysts, the promoter atoms thermodynamically prefer to substitute molybdenum atoms on the edge planes of the MoS_2 layered structure [3]. Under typical sulfidation conditions, cobalt prefers to replace molybdenum on the (−1010) S-edge and nickel the (10–10) Mo-edge [4,6]. The incorporation of the promoter atoms decreases the binding energy of sulfur on the edge planes, thereby reducing the equilibrium sulfur coverage on the edge surfaces of promoted MoS_2 catalysts [2,3,6].

During the hydrotreatment of petroleum distillates, organosulfur and organonitrogen compounds are adsorbed and activated on hydrotreating catalyst surfaces, and mutual inhibitory effects have been observed between these groups of compounds due to competitive adsorption on catalytically active sites [7,8]. In deep hydrodesulfurization (HDS), inhibitory effects of basic nitrogen-containing compounds on HDS conversion are so severe that it becomes the dominant factor that prevents the complete HDS of 4,6-dimethyldibenzothiophene [9]. It has also been reported that basic and non-basic nitrogen compounds have different hydrodenitrogenation (HDN) reactivities, and the differences in HDN reactivity are partly due to their different adorptivities on catalyst active sites [10,11]. Detailed adsorption thermodynamic data of hydrotreating-relevant molecules on hydrotreating catalyst active sites can provide additional fundamental insight towards understanding competitive adsorption and inhibitory effects of the sulfur- and nitrogen-containing molecules in the hydrotreating processes.

Although there is no reliable method to directly measure these constants, it is possible to calculate the adsorption thermodynamic data of sulfur- and nitrogen-containing molecules on the well-defined active sites of hydrotreating catalysts by means of DFT calculations. Nickel-promoted molybdenum disulfide (NiMoS) is the most widely used HDN catalyst, and we have previously studied the surface structure of the nickel substituted (10–10) Mo-edge plane (Ni-edge) [6], the adsorption of H_2 and H_2S [12,13], and various nitrogen-containing compounds on NiMoS [14,15]. In the present work, the adsorption thermodynamic data of H_2, H_2S, NH_3, thiophene, pyridine, pyrrole, and aniline on the well-defined (10–10) NiMoS edge surface are calculated using a periodic supercell model. The thermodynamic results will facilitate the quantitative discussion of the com-

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petitive adsorption of theses molecules on the NiMoS edge surface, and allow an estimation of the relative surface coverage of each type of species at different reaction conditions.

2. Methods

2.1. Catalyst model and DFT calculations

The structure of the fully-substituted NiMoS model was previously determined and optimized [6], and has been used in adsorption studies of hydrogen and nitrogen-containing compounds [12–15]. In the fully-substituted NiMoS model, all of the Mo atoms on the (10–10) metal edge of MoS_2 are replaced by nickel, and the surface tends to be uncovered by sulfur atoms at typical hydrotreating reaction conditions [6]. In the present study, a 2-MoS_2 supercell and a 6-MoS_2 supercell are used for all simulations (figure 1). Figure 1a is the 2-MoS_2 model which is repeated in the *x*-direction with a periodicity of two MoS_2 units, and figure 1b is the 6-MoS_2 model which is repeated in the *x*-direction with a periodicity of six MoS_2 units. For both models, the NiMoS slab consists of three layers of MoS_2 in addition to the top nickel layer, and the slabs are separated by vacuum layers of 15 Å in the *y*- and *z*-directions. The DFT calculations have been performed using Materials Studio DMol^3 from Accelrys® (version 3.2) [16]. The DNP basis sets [17] and GGA-PW91 exchange-correlation functionals [18] are used in all calculations. The real space cutoff radius is 4.5 Å. All electron basis sets are used for light elements, such as hydrogen, oxygen, and sulfur. Effective Core Potentials [19,20] are used to treat core electrons of molybdenum and nickel, and a *k-point* of [1× 1× 1] was used for the 6-MoS_2 model and [2× 1× 1] for the 2-MoS_2 model. Spin polarization was applied to all calculations.

2.2. Thermodynamic calculations

The adsorption of sulfur- and nitrogen-containing molecules on the NiMoS surface is expressed by the following equation:

$$\text{Surf} + \text{M(gas)} = \text{M-Surf.} \tag{1}$$

Surf represents NiMoS clean surface, M(gas) is the gas phase molecule, and M–Surf is the molecule adsorbed on the NiMoS surface. The adsorption energy (ΔE), enthalpy (ΔH), and free energy (ΔG) are defined by Eqs. (2), (3), and (4), respectively.

$$\Delta E = E_{\text{M-Surf}} - E_{\text{Surf}} - E_{\text{M(gas)}} \tag{2}$$

$$\begin{aligned}\Delta H &= H_{\text{M-Surf}} - H_{\text{Surf}} - H_{\text{M(gas)}} \\ &= (E_{\text{M-Surf}} + H_{T_{\text{corr}},\text{M-Surf}}) - (E_{\text{Surf}} + H_{T_{\text{corr}},\text{Surf}}) \\ &\quad - (E_{\text{M(gas)}} + H_{T_{\text{corr}},\text{M(gas)}})\end{aligned} \tag{3}$$

$$\Delta G = \Delta H - T\Delta S = \Delta H - T(S_{\text{M-Surf}} - S_{\text{Surf}} - S_{\text{M(gas).}}) \tag{4}$$

In Equation (2),$E_{\text{M-surf}}$, E_{Surf}, and $E_{\text{M(gas)}}$ are the ground state energies for the molecule adsorbed on the surface, the clean surface, and the free molecule, respectively. Similar notation is applied to the other thermodynamic properties. In Equation (3),$H_{T_{\text{corr}},\text{M-Surf}}$,$H_{T_{\text{corr}},\text{Surf}}$, and$H_{T_{\text{corr}},\text{M(gas)}}$ are enthalpy temperature corrections for the respective terms, as calculated by Equation (5);

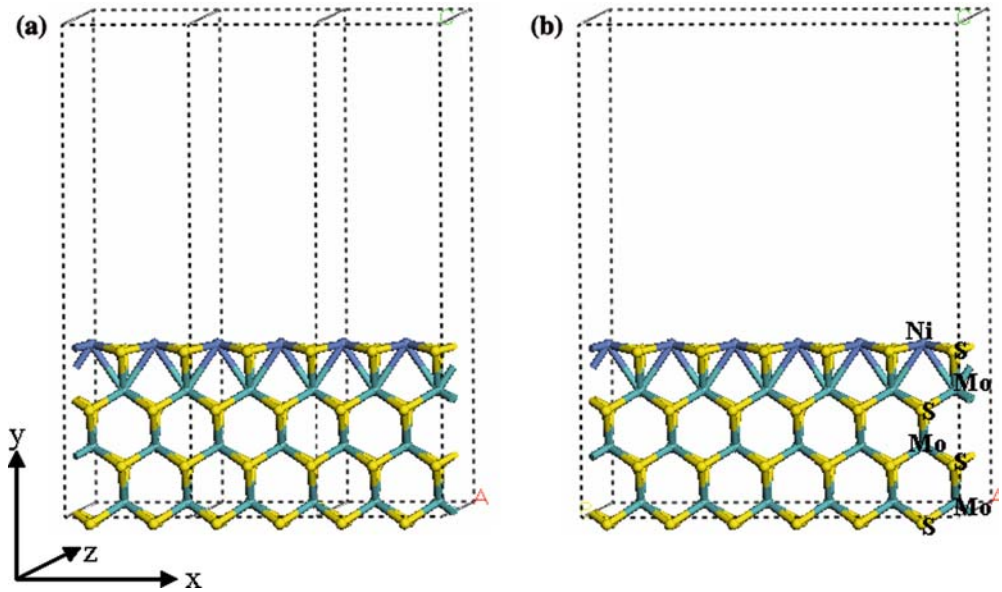

Figure 1. The NiMoS periodic model with a periodicity of (a) 2 MoS_2 and (b) 6 MoS_2 units.

$$H_{T_{\text{corr}}} = \text{ZPVE} + \int_0^T C_p \mathrm{d}T, \tag{5}$$

where ZPVE and C_p are the zero point vibrational energy and the heat capacity, respectively.

The molecule-adsorbed surface can be treated as the summation of the substrate and the adsorbed molecule, hence,

$$H_{T_{\text{corr}},\text{M-Surf}} = H_{T_{\text{corr}},\text{Surf}^*} + H_{T_{\text{corr}},\text{M}^*}, \tag{6}$$

where $H_{T_{\text{corr}},\text{Surf}^*}$ and$H_{T_{\text{corr}},\text{M}^*}$ are the temperature corrections for the enthalpies of the surface and the molecule of the molecule-adsorbed surface, respectively. Similar treatment has been used in calculating ZPVE change upon adsorption of hydrogen on MoS_2 edge surfaces by Cristol *et al*. [21]. The clean surface and the surface part of molecule-adsorbed surface are assumed to have the same ZPVE and C_p values. Thus, Equation (3) can be written as

$$\begin{aligned}\Delta H &= \Delta E + (H_{T_{\text{corr}},\text{Surf}^*} + H_{T_{\text{corr}},\text{M}^*}) \\ &\quad - (H_{T_{\text{corr}},\text{Surf}} + H_{T_{\text{corr}},\text{M(gas)}}) \\ &= \Delta E + \Delta\text{ZPVE} + \int_0^T \Delta C_\text{p} \mathrm{d}T,\end{aligned} \tag{7}$$

where ΔZPVE and ΔC_p are the differences in ZPVE and C_p of the molecules between the gas phase state and the adsorbed state on the NiMoS surface, respectively. Similarly, the entropy of the molecule-adsorbed surface can be expressed as the summation of the entropies of the substrate and the adsorbed molecule, where the substrate and the clean surface are assumed to have the same entropy. The entropy change for the adsorption of the molecule on the NiMoS surface is calculated as

$$\Delta S = S_{\text{M}^*} - S_{\text{M(gas)}}. \tag{8}$$

Thus, Equation (4) can be expressed as follows;

$$\Delta G = \Delta E + \Delta\text{ZPVE} + \int_0^T \Delta C_p \mathrm{d}T - T\Delta S. \tag{9}$$

ΔE values for the adsorption of different sulfur- and nitrogen containing molecules on the NiMoS surface are obtained by *ab initio* DFT calculations of total energies of the clean surface, molecule-adsorbed surface, and the free molecule. The enthalpy temperature corrections and entropies can be obtained by the calculations of normal mode frequencies of free and adsorbed molecules.

3. Results and discussion

The adsorption of H_2, H_2S, NH_3, thiophene, pyridine, pyrrole, and aniline on the (10–10) NiMoS edge surface was studied using different initial adsorption configurations; however, only the most energetically stable adsorption mode for each molecule is presented in figure2. For simple molecules, such as H_2, H_2S, and NH_3, the 2-MoS_2 model and the 6-MoS_2 model produce similar adsorption energetics. For pyridine, the vertical configuration on the edge surface also allows the use of the 2-MoS_2 model, which results in only 0.1 eV difference in the adsorption energy from using the 6-MoS_2 model. Therefore, the 2-MoS_2 model was used in calculating the vibrational frequencies of adsorbed molecules for these species with one molecule located on every two surface nickel sites (figure 2a –d). For thiophene, pyrrole, and aniline, the optimized geometries on the edge surface are either flat or titled, which requires a larger supercell to avoid significant interactions between the adsorbed molecules on the catalyst surface. Therefore, the 6-MoS_2 model is used for these molecules, with one molecule adsorbed on every six surface nickel sites (figure 2e –g).

The changes in ground state electronic energy (ΔE) and zero point vibrational energy (Δ ZPVE) upon the adsorption of different molecules on the NiMoS surface are listed in table 1. The basic nitrogen-containing compounds have higher adsorption energy than the non-basic nitrogen compounds and sulfur-containing compounds; hydrogen has the lowest adsorption energy. The adsorption of these molecules on the NiMoS surface increases the ZPVE. This is because the adsorption of these molecules on the surface either generates new vibrational modes or increases the frequencies of some individual vibrations. For example, free molecular hydrogen only has a H–H stretching vibration mode with a frequency of 4370 cm^{-1}. The adsorption of H_2 on the NiMoS surface weakens the H–H bond, decreases the H–H stretching frequency to 3840 cm^{-1}, and also results in the formation of two Ni–H bonds which have asymmetric and symmetric vibrational frequencies of 1110 and 520 cm^{-1}, respectively. Additionally, three Ni—H_2 bending modes, which have frequencies of 320, 390, and 430 cm^{-1}, also contribute to the ZPVE. Thus, the ZPVE increases by 13.5 kJ mol^{-1}. Consequently, neglecting the contribution of ZPVE changes to the adsorption enthalpy may result in significant errors.

The changes in vibrational frequencies upon adsorption on the NiMoS edge surface also result in changes in $C_{\{\text{p}}$ and S values. In order to assess the accuracy of the calculations, we compared our calculated gas phase C_p values with the literature data for H_2, H_2S, NH_3, thiophene, pyridine, pyrrole, and aniline (figure 3). The discrepancies between the calculated and experimental literature data are about 1% for H_2 and H_2S, about 3% for thiophene, pyridine, and pyrrole, and approximately 4% for aniline. Table 2 presents the gas phase C_p and S values of these molecules at 525 and 650 K, which are typical hydrotreating reactor temperatures. Furthermore, the C_p and S values of the adsorbed molecules on the NiMoS edge surface were calculated, allowing for the calculation of ΔH, ΔS, and ΔG for the adsorption of these molecules on the NiMoS edge surface at different

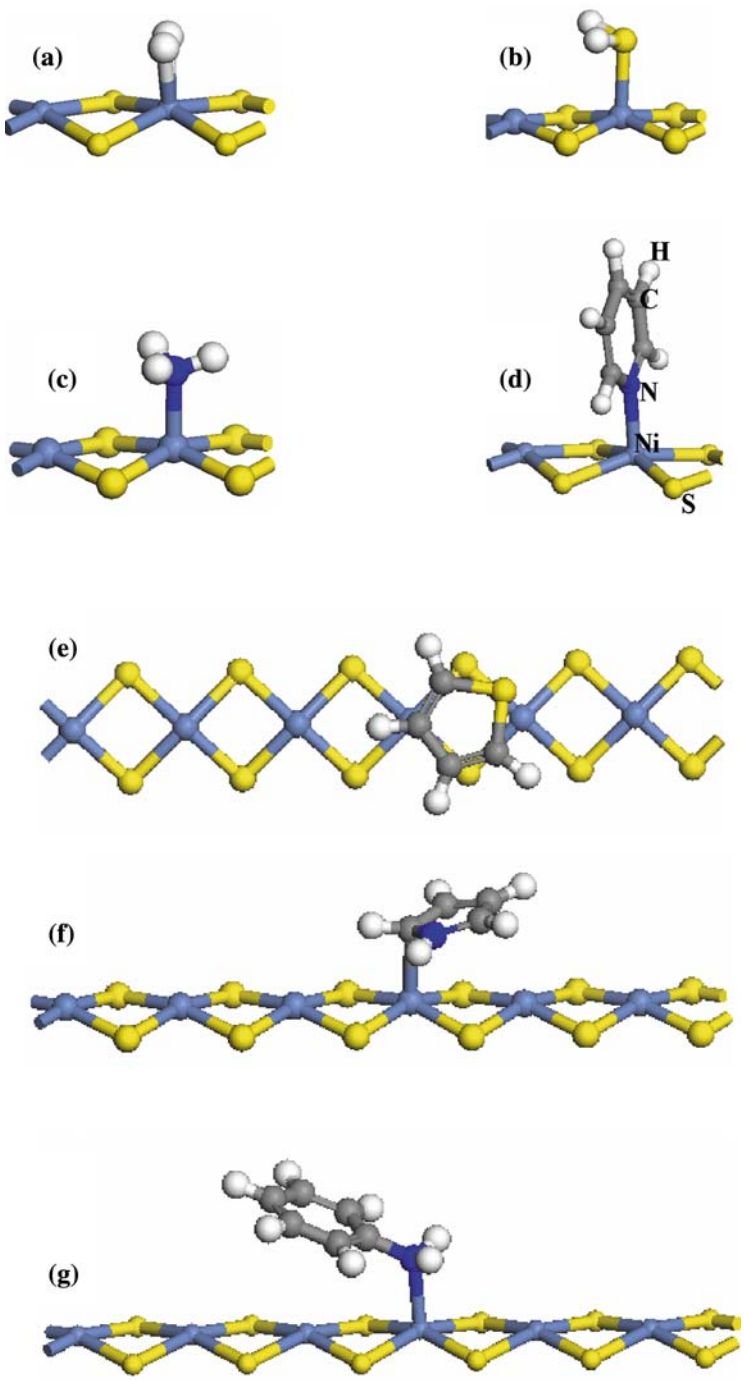

Figure 2. The optimized geometries of (a) H_2, (b) H_2S, (c) NH_3, (d) pyridine, (e) thiophene, (f) pyrrole, and (g) aniline on NiMoS.

temperatures. Table 3 lists the thermodynamic data at 525 and 650 K. The enthalpy changes for the adsorption of these molecules are all negative, which indicates the adsorption of these molecules on the surface are exothermic processes and also result in the loss of entropy of the molecules.

The entropy contributions from the adsorbed molecules are often neglected in thermodynamic calculations. From Tables 2 and 3, it can be clearly noted that the entropy loss due to adsorption is approximately 75% for H_2, and 70% for H_2S and NH_3. For these simple

Table 1
Energy and ZPVE changes upon the adsorption of molecules on the (10–10) Ni-edge surface of NiMoS

Molecules	ΔE, kJ mol^{-1}	Δ ZPVE, kJ mol^{-1}
H_2	−20.3	13.5
H_2S	−79.1	12.2
NH_3	−121.6	7.9
Thiophene	−48.2	2.7
Pyridine	−125.4	10.5
Pyrrole	−68.5	8.8
Aniline	−135.1	25.3

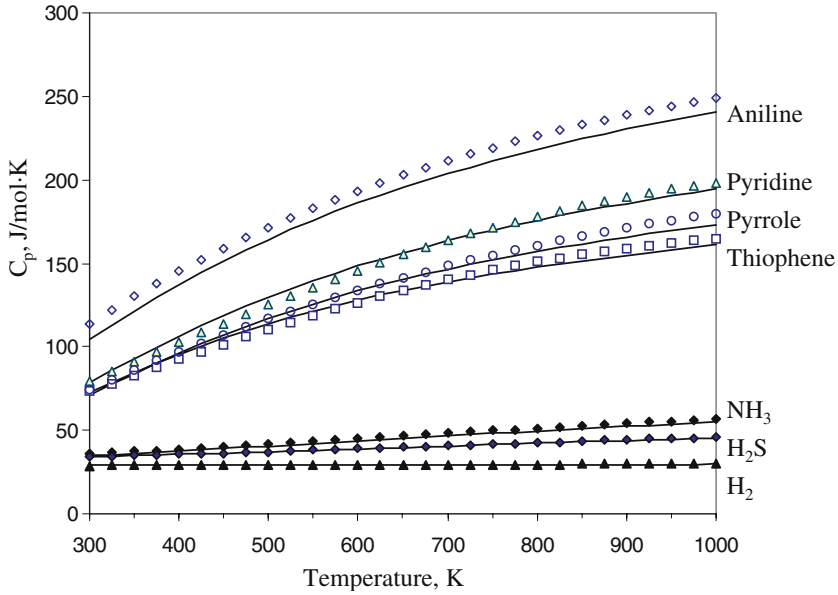

Figure 3. Calculated and experimental C_p values for gas phase H_2 and several S- and N-containing molecules. Solid lines are DFT calculated data, and scattered points are literature data from "Chemical Properties Handbook", Carl L. Yaws, 1999, McGraw-Hill.

molecules, neglecting the entropy contribution of adsorbed molecules (by assuming the entropy loss is 100%) in calculating free energy changes at low temperatures (<300 K) might not cause significant errors, but at high temperatures they must be included in order to generate accurate results. For large organic molecules, such as thiophene, pyridine, pyrrole, and aniline, the entropy loss upon adsorption is about 50–60%, and thus the contribution of the adsorbed molecules cannot be neglected in calculating the free energy changes of adsorption, except at temperatures below 100 K.

Figure 4 plots the adsorption constant (lnK) versus $1/T$ over a temperature range of 300 and 650 K. These data can be used to estimate the relative surface coverage of each type of molecule at different conditions according to the Langmuir isotherm. In the presence of basic nitrogen compounds, such as NH_3, pyridine, and aniline, the catalyst surface is always dominated by these strongly adsorbed organonitrogen species, which will show strong inhibition effects on the reaction of other molecules, i.e. HDS. Since the adsorption enthalpies are much higher than that of other molecules, increasing reaction temperature will reduce their surface coverage relative to that of other molecules. Hydrogen has the lowest adsorption enthalpy, and thus increasing reaction temperature will increase its relative surface coverage.

4. Conclusions

Detailed adsorption thermodynamic data of several hydrotreating-relevant molecules on NiMoS active sites

Table 2
Calculated C_p and S values of gas phase molecules

Properties		C_p, J mol^{-1}K^{-1}	S, J mol^{-1}K^{-1}
H_2	525 K	29.1	152.6
	650 K	29.1	158.8
H_2S	525 K	37.5	231.7
	650 K	39.7	240.0
NH_3	525 K	41.3	222.9
	650 K	45.1	232.1
Thiophene	525 K	117.8	337.8
	650 K	156.3	364.6
Pyridine	525 K	134.7	348.5
	650 K	156.3	379.7
Pyrrole	525 K	121.4	330.1
	650 K	140.3	358.1
Aniline	525 K	170.1	393.1
	650 K	195.2	432.2

Table 3
Calculated thermodynamic data for the adsorption on the NiMoS surface

Properties		ΔH, kJ mol^{-1}	ΔS, J mol^{-1}K^{-1}	ΔG, kJ mol^{-1}
H_2	525 K	−12.0	−120.0	51.0
	650 K	−11.3	−118.6	65.9
H_2S	525 K	−67.7	−163.2	18.0
	650 K	−66.7	−160.4	37.6
NH_3	525 K	−107.6	−159.9	−23.7
	650 K	−108.2	−157.2	−6.0
Thiophene	525 K	−39.6	−161.2	45.0
	650 K	−37.1	−157.2	65.1
Pyridine	525 K	−111.8	−187.4	−13.5
	650 K	−109.8	−184.7	10.2
Pyrrole	525 K	−56.9	−186.4	41.0
	650 K	−55.0	−183.5	64.3
Aniline	525 K	−112.5	−243.6	15.4
	650 K	−110.3	−241.1	46.4

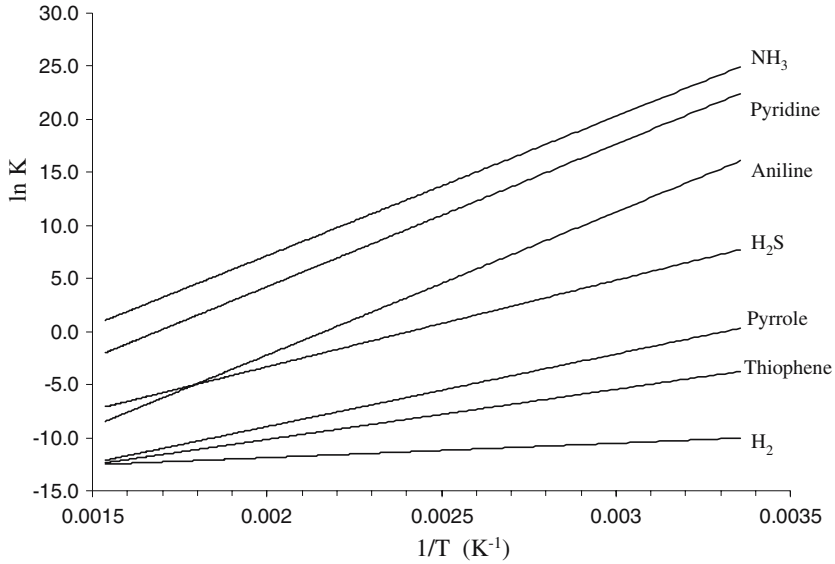

Figure 4. Plot of lnK vs. $1/T$. K is the adsorption constant and T is the reaction temperature.

were obtained by DFT calculations. In these calculations, the changes in zero point vibrational energy and the contributions of adsorbed molecules to changes in entropy and C_p values, as well as the electronic energy changes, are considered by calculating vibrational frequencies of adsorbed and free molecules. From these calculated thermodynamic data, one can predict that basic nitrogen molecules always dominate the catalyst surface, and thus, organonitrogen compounds would show stronger inhibition than other bulk fluid molecules. Increasing reaction temperature will reduce the relative surface coverage of the strongly adsorbed basic nitrogen compounds, and increase the surface coverage of hydrogen on the catalyst surface. The calculated thermodynamic quantities and the adsorption strength of organosulfur and organonitrogen compounds will expectedly change using different catalyst surfaces, and specifically as a function of Ni substitution in the Ni-MoS edge plane, due to differences in energetics and surface structures, i.e. sulfur coverage. The effect of Ni substitution in NiMoS (10–10) edge planes on the adsorption of organosulfur and organonitrogen compounds will be the focus of future studies.

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References

[1] H. Topsøe, B. Hinnemann, J.K. Nørskov, J.V. Lauritsen, F. Besenbacher, P.L. Hansen, G. Hytoft, R.G. Egeberg and K.G. Knudsen, Catal. Today 107 (2005) 12.
[2] L.S. Byskov, J.K. Nørskov, B.S. Clausen and H. Topsøe, J. Catal. 187 (1999) 109.
[3] P. Raybaud, J. Hafner, G. Kresse, S. Kasztelan and H. Toulhoat, J. Catal. 190 (2000) 128.
[4] H. Schweiger, P. Raybaud and H. Toulhoat, J. Catal. 212 (2000) 33.
[5] M. Sun, J. Adjaye and A.E. Nelson, Appl. Catal. A. 263 (2004) 131.
[6] M. Sun, A.E. Nelson and J. Adjaye, J. Catal. 226 (2004) 32.
[7] C.N. Satterfield, M. Modell and J.A. Wilkens, Ind. Eng. Chem. Process Des. Dev. 19 (1980) 154.
[8] G.C. Laredo, A. Montesinos and J.A. De los Reyes, Appl. Catal. A 265 (2004) 171.
[9] M. Egorova and R. Prins, J. Catal. 224 (2004) 278.
[10] S. Shin, K. Sakanishi, I. Mochida, D.A. Grudoski and J.H. Shinn, Energy Fuels 14 (2000) 539.
[11] D. Ferdous, A.K. Dalai and J. Adjaye, Energy Fuels 17 (2003) 164.
[12] M. Sun, A.E. Nelson and J. Adjaye, Catal. Today 105 (2005) 36.
[13] M. Sun, A.E. Nelson and J. Adjaye, J. Catal. 233 (2005) 411.
[14] M. Sun, A.E. Nelson and J. Adjaye, Catal. Today 109 (2005) 49.
[15] M. Sun, A.E. Nelson and J. Adjaye, J. Catal. 231 (2005) 223.
[16] B. Delley, J. Chem. Phys. 113 (2000) 7756.
[17] A.D. Becke, J. Chem. Phys. 88 (1988) 2547.
[18] J.P. Perdew and Y. Wang, Phys. Rev. B 45 (1992) 13244.
[19] M. Dolg, U. Wedig, H. Stoll and H. Preuss, J. Chem. Phys. 86 (1987) 866.
[20] A. Bergner, M. Dolg, W. Kuechle, H. Stoll and H. Preuss, Mol. Phys. 80 (1993) 1431.
[21] S. Cristol, J.F. Paul, E. Payen, D. Bougeard, S. Clémendot and F. Hutschka, J. Phys. Chem. B 104 (2000) 11220.