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The Effect of Crystalline phase of Sodium Molybdate on the Corrosion Inhibition for Carbon Steel

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Keywords：corrosion inhibition, sodium molybdate, electrochemical analysis.

ABSTRACT

This study is aiming at the effect of crystalline phase of sodium molybdate (Na_2MoO_4) on the corrosion inhibition of carbon steel. Our TGA result indicated three endothermic events, two of which corresponds to the transition of crystalline phase (i.e. the phase transformation from cubic to orthorrombic phase and from orthorrombic tohexagonal phase) and the last event is owing to the melting of Na_2MoO_4. Based on the weight-loss measurements, the efficiency of corrosion inhibition performed by Na_2MoO_4 with different crystalline phase differed as a result of different stacking orientation of MoO_4^{2-} on the test coupon. For example, the corrosion rate of carbon steel in the presence of MoO_4^{2-} with orthormobic phase was found at 0.01MPY which was 2.1 times better than that of commercial Na_2MoO_4 with cubic phase. This result was further supported by the PP (Polarization potential) and EIS (Electrochemical Impedance Spectroscopy) measurements in terms of the thermodynamic and kinetic viewpoints. Therefore, the corrosion inhibition capability of Na_2MoO_4 could be enhanced after appropriate thermal treatment. Further investigations by XPS are underway for examining the microstructure and chemical composition of MoO_4^{2-}-Fe^{2+} complex film possibly formed on the test coupon.

INTRODUCTION

Investigation of corrosion inhibition used in circulating cooling water system has been an important issue in industry for decades. Lots of works have dedicated to this field using various types of corrosion inhibitions such as Zn^{2+}, NO_2^-, MoO_4^{2-}, phosphonate, triazoleand etc. However, only few corrosion inhibitors could be put to practical use, as the relatively low cost and stability of corrosion inhibitor are critical to on-site operation and maintenance. For example, most of the green corrosion inhibitors suffer from low thermal tolerance, resulting to a short lifetime of corrosion inhibition because of possible thermal decomposition. In terms of this point, $MoO_4^{2-}$is alternative to most of corrosion inhibitors due to its relatively high stability and low environmental impact.

MoO_4^{2-} has been an efficient corrosion inhibitor for mild-steel since the first report was revealed at 1954. The following studies working on the corrosion inhibition of target metal by MoO_4^{2-} have confirmed the applicability and features of MoO_4^{2-}. MoO_4^{2-}, nowadays, is one of the most popular and efficient corrosion inhibitor in the practical use, which was exemplified by the case of the closed-loop cooling water system. Some reports also indicated that several complementary corrosion inhibitors such as nitrite and gluconate exhibit synergistic effect when coupled with MoO_4^{2-}. Investigation on this regard reveals that the performance of corrosion inhibition for carbon steel in the presence of MoO_4^{2-} and nitrite was enhanced by two-fold in comparison to the case with MoO_4^{2-} only. However, it seems that no study work on the effect of crystalline phase of $NaMoO_4$ on the ability toward inhibiting corrosion of carbon steel. In this study, we mainly evaluated the performance of corrosion inhibition contributed by the $NaMoO_4$ with different crystalline phases. In addition, the synthesis factors including synthesis temperature, synthesis time and stoichiometric ratio of NaOH to MoO_3 were also examined.

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EXPERIMENT AND METHOD

Characterization of dihydrated sodium molybdate

TGA was carried out under air from 30 to 1000℃ with a heating rate of 10℃ /min using a Thermal Analyst. XRD was performed within the range of 5-80^o using Cu K radiation at 2^o /min. FTIR spectra were also collected. Analyses were performed in the transmission mode in the 400-4000 cm^{-1} with a resolution of 2cm^{-1} and accumulation of 16 scans.

Evaluation of performance of corrosion inhibitor

The methods proposed in this study to evaluate the performance of the prepared corrosion inhibitors include weight-loss measurement, potentiodynamic polarization and electrochemical impedance spectrometry. The apparatus for weight-loss method was modified from jar-testing equipment. The test coupons were prepared by polishing with 240-grit papers and then cleaning with homemade cleaning reagent before being weighted by an electronic balance with a sensitivity of 0.1mg. The pretreated coupons were subsequently attached on paddle stirrers with specific acrylic clamps. Prior to the tests, the solutions were stirred at 200rpm for 30 min in order to achieve homogeneous dense films on the coupons. The efficiency of corrosion performance was calculated by weighting the coupons before and after the tests. The weight-loss experiments were performed in triplicate.

The Polarization studies were carried out in a CHI-electrochemical work station with impedance model 660A. Corresponding measurements were completed using a platinum sheet counter electrode and an Ag/AgCl reference electrode in a conventional three-electrode 300mL electrochemical cell. The scan rate was at 5 mV/s and the quiet time was 2s. Regarding the electrochemical impedance measurement, the spectra were recorded with sinusoidal potential wave of 5mV of amplitude applied at frequencies from 10^5 to 10^{-2} Hz. The impedance diagrams are given in the Nyquist representation.

RESULTS AND DISCUSSION

The effect of synthesis parameter of Na_2MoO_4 on the performance of corrosion inhibition

In this study, a preliminary experiment was carried out to examine the effect of synthesis parameters of Na_2MoO_4 on its corrosion inhibitor performance. Regarding the effect of synthesis temperature demonstrated in Table 1, it seems that the formation kinetics of MoO_4^{2-} is limited in case the synthesis temperature was enhanced to 90℃ that showed a yield of 50.9%. This result indicates that the alkaline conversion of MoO_3 to MoO_4^{2-} is an exothermal process. In other words, MoO_4^{2-} yield decreases as long as the synthesis temperature exceeds an allowed limit and our study found that the limit temperature of MoO_4^{2-} synthesis was at 60℃ (Table 1). The corrosion inhibition performances of the synthesized MoO_4^{2-} at three temperatures are also listed in Table 1. Interestingly, the normalized corrosion rate indicated that the synthesis temperature is a critical factor to affect the corrosion inhibition capability of MoO_4^{2-}. An increase in synthesis temperature of $Na_2MoO_4^{2-}$ from 30 to 90℃ appears to weaken the corrosion inhibition capability of MoO_4^{2-} by one order of magnitude (Table 1). However, no significant improvement of corrosion inhibition capability was found in terms of the effects of synthesis time and alkaline concentration, as determined by the weight-loss measurements (Data not shown). It can be concluded that the corrosion inhibition performance of Na_2MoO_4 is strongly dependent on the synthesis temperature rather than on the synthesis time and alkaline concentration. In addition, the corrosion inhibition performance of commercial Na_2MoO_4 (5.79E-3 MPY/ppm MoO_4^{2-}) is also second to that of the prepared Na_2MoO_4.

Table 1. Normalized corrosion rate as a function of synthesis temperature.

Synthesis Temperature (℃)	Yield (%)	Initial Conc of MoO_4^{2-} (ppm)	Corrosion rate (MPY)	Normalized corrosion rate (MPY/ppmMoO_4^{2-})
30	95.3	138.5	0.69	4.98E-3
60	94.7	119.9	1.05	8.75E-3
90	50.9	78.1	2.04	2.61E-2

Characterization of commercial Na_2MoO_4 $2H_2O$

Five endothermic events of Na_2MoO_4 were observed by TGA, as shown in Figure 1. The first peak can be designated as the loss of adsorbed water, which was followed by two phase transitions and melting process of Na_2MoO_4 occurring at 690℃. Two phase transitions taking place at 460℃ and 650℃ are owing to the phase transition from cubic to orthorrombic phase and from orthorrombic to hexagonal phase, respectively.

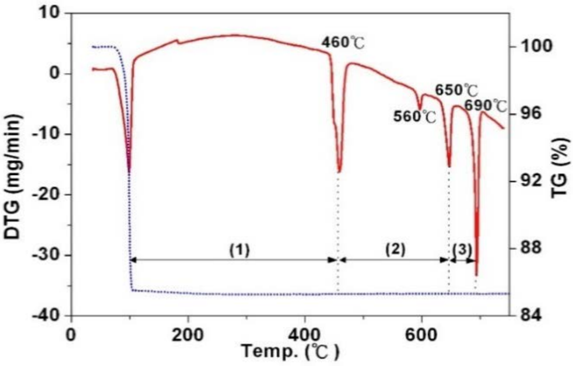

Fig. 1. Thermal gravity analysis of commercial Na_2MoO_4 $2H_2O$.

This result is consistent with that obtained from the previous study by Nakagaki et al. Based on the above result, two Na_2MoO_4 samples with thermal treatment temperatures at 500 and 675°C were prepared in order to examine the effect of crystalline phase of Na_2MoO_4 on its capability as a corrosion inhibitor. In the following statements, Na_2MoO_4-25°C Na_2MoO_4-500°C, and Na_2MoO_4-675°C were denoted as the commercial hydrated Na_2MoO_4 and Na_2MoO_4 with thermal treatment at 500 and 675°C, respectively. where *k* is defined as the steering ratio.

FTIR spectra have been used to analyze the microstructure of thermally treated Na_2MoO_4. FTIR spectrum of Na_2MoO_4-25°C Na_2MoO_4-500°C, and Na_2MoO_4-675°C are given in Figure 2 in which the frequencies of Mo-O stretching, O-H bending, and O-H stretching spike at around 816, 1440 and 3270cm^{-1}, respectively. No significant change on the IR spectra of was observed after thermally treating Na_2MoO_4. This result reveals that the crystalline structure of Na_2MoO_4 remains intact after thermal treatment. This result corresponds to the XRD patterns (not shown in this report) which demonstrate that, in the case of thermally-treated Na_2MoO_4, the presence of hydrated Na_2MoO_4 in addition to the anhydrous Na_2MoO_4. One interesting finding is that there is a slight decrease in Mo-O stretching frequency with increasing treatment temperature. This result reveals that the coordination of electrons presents on the oxygen of MoO_4^{2-} have changed, which appears to affect the corrosion inhibition capability of sodium molybdate.

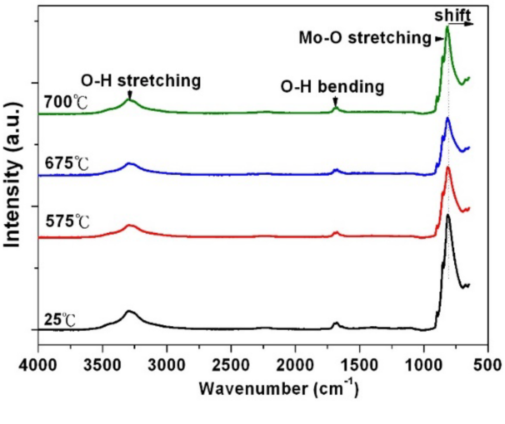

Fig. 2. FTIR spectra of commercial Na_2MoO_4 $2H_2O$ thermally treated at different temperatures.

Corrosion inhibition performance of Na_2MoO_4 $2H_2O$ with different crystalline phases

According to the experimental result of measured weight loss, the corrosion rate of carbon steel in the presence of Na_2MoO_4-25°C, Na_2MoO_4-500°C, and Na_2MoO_4-675°C are 0.25±0.09, 0.11±0.06, and 0.37±0.11MPY, respectively (Table 2). The corrosion inhibition of carbon steel in the case of Na_2MoO_4-500°C was better than that with commercial Na_2MoO_4 by more than twice. This result shows an enhanced corrosion inhibition capability of Na_2MoO_4 after appropriate thermal treatment which may be a breakthrough development for industrial use.

Table 2. Corrosion rate, E_{corr} (corrosion potential) and I_{corr} and (corrosion current) of carbon steels with and without the presence of Na_2MoO_4.

Sample	**Corrosion rate (MPY)**	**E_{corr} (mv vs Ag/AgCl)**	**I_{corr} (A/cm^2)**	**β_a (mV/dec)**	**$-\beta_c$ (mV/dec)**
Blank	11.82	-396	5.50E-4	169.5	158.7
Na_2MoO_4-25℃	0.25±0.09	-380	2.23E-4	148.6	116.3
Na_2MoO_4-500℃	0.11±0.06	-375	2.13E-4	137.9	109.1
Na_2MoO_4-675℃	0.37±0.11	-383	2.34E-4	144.7	127.9

Further evidence is also available from PP and EIS analysis. In terms of the corrosion potential obtained from PP analysis (Figure 3), E_{corr} of carbon steel in the presence of Na_2MoO_4-25°C, Na_2MoO_4-500°C, and Na_2MoO_4-675°C are -0.380, -0.375, and -0.383V respectively. There is an anodic shift of E_{corr} of the carbon steel in the case of Na_2MoO_4-500°C, as compared to that of Na_2MoO_4-25°C. This result shows that the corrosion of carbon steel in the presence of Na_2MoO_4-500 is less thermodynamically favorable as compared to the case with commercial Na_2MoO_4. In addition, it was known that the anodic reaction is controlled predominantly, since more MoO_4^{2-} ions are transported to anodic sites. The same conclusion is available in terms of kinetic viewpoint that the I_{corr} obtained from polarization curve of Na_2MoO_4-25°C, Na_2MoO_4-500°C, and Na_2MoO_4-675°C are 2.23E-4, 2.13E-4, and 2.34E-6, respectively. In addition, either β_a orβ_c performed the lowest value as compared to other tested samples. This result is an indication of simultaneous anodic and cathodic inhibition of carbon steel corrosion by the addition of Na_2MoO_4-500°C. In other words, both anodic and cathodic reactions (i.e. corrosion of carbon steel and formation of hydrogen gas) are inhibited efficiently.

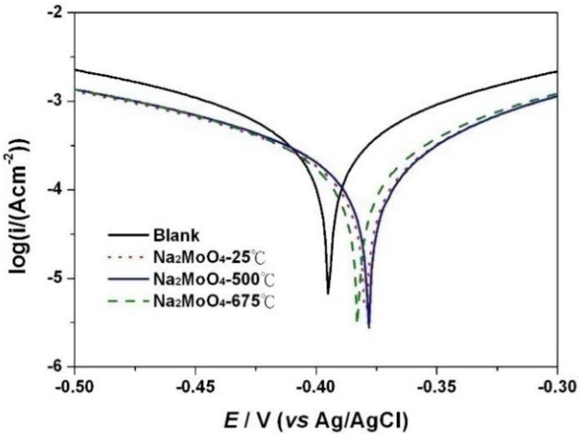

Fig. 3. Polarization curves of carbon steel without and with the presence of Na_2MoO_4-25°C, Na_2MoO_4-500°C, and Na_2MoO_4-675°C.

On the other hand, a decrease in the corrosion inhibition capability of Na_2MoO_4-675℃ could be as a result of an inhibiting effect by the hexagonal phase of Na_2MoO_4. After polarization, a brown layer was observed in several sections of the electrode surface, which was suspected that the precipitate observed could be $Mo(OH)_3$. From Equation 1, it is noted that the Mo(ш) ions formed through reduction, lead to the formation of $Mo(OH)_3$.

$$MoO_4^{2-} + 8H^+ + 3e^- \rightarrow Mo^{3+} + 4H_2O. \qquad (1)$$

Subsequently, the AC impedance spectra have also been utilized to detect the formation of film on the metal surface. As shown in Figure 4, AC impedance spectra obtained without the presence of corrosion inhibitor is different from the cases in the presence of MoO_4^{2-}. This result indicates the formation of protective film on the target coupon in case MoO_4^{2-} participates in the protection mechanism. However, detailed analysis on these spectra is not done because no free related software is available.

The enhanced corrosion inhibition capability of Na_2MoO_4 after appropriate thermal treatment can be owing to the fact that the microstructure of thermally-treated Na_2MoO_4 results to a more compact and stackable layer formed on the target coupon than that caused by commercial Na_2MoO_4. In conclusion, a slight difference in crystalline lattice of Na_2MoO_4 likely leads to the formation of a different orientation of complex layer on the target coupon. This result appears to perform an enhanced ability toward inhibiting corrosion of carbon steel, as evidenced by the experimental results demonstrated in this study.

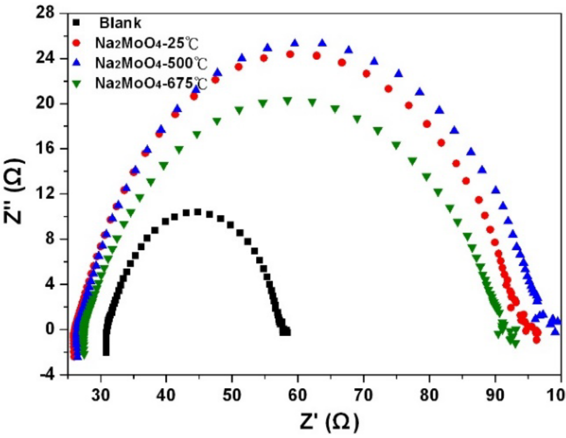

Fig. 4. Typical Niquist plots measured for carbon steel in 0.1N HCl without and with the presence of Na_2MoO_4-25℃, Na_2MoO_4-500℃, and Na_2MoO_4-675℃.

CONCLUSIONS

Investigation of the synthesis parameters and physical features of Na_2MoO_4 on its corresponding corrosion inhibition capability were performed through weight-loss measurements and electrochemical analysis. This study leads to some important findings as listed below:

(1) The corrosion inhibition performance of Na_2MoO_4 is independent on the synthesis parameters including synthesis temperature, synthesis time, and alkaline concentration.

(2) According to the result of weight-loss measurements and electrochemical analysis, Na_2MoO_4 with orthorhombic phase exhibits better corrosion inhibition performance than that with cubic and hexagonal phases by 2-3 times.

(3) There is an anodic shift of E_{corr} of carbon steel in the presence of Na_2MoO_4, which corresponds to the fact that MoO_4^{2-} function as an anodic inhibitor.

(4) A change on the microstructure of thermally treated Na_2MoO_4 is responsible for the enhanced corrosion inhibition capability, which could result to a more compact and denser Fe-MoO_4 complex film on the target coupon.

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鉬酸鈉晶相對碳鋼緩蝕的影響

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摘要

本研究旨在研究鉬酸鈉 (Na_2MoO_4)之晶相對於碳鋼緩蝕作用的影響。實驗之 TGA 結果表明三個吸熱狀態，其中兩個對應於晶相的轉變(即從立方相到正交相和從正交相到六方相的相變化)，最後一個狀態是由於 Na_2MoO_4 的熔化。根據失重量測，不同晶相的 Na_2MoO_4 的緩蝕效率因 MoO_4^{2-}在試樣上的堆積方向不同而異。例如，碳鋼在具有正交相的 MoO_4^{2-}存在下的腐蝕速率為 0.01MPY，是具有立方相的商用 Na_2MoO_4 的 2.1 倍。從熱力學和動力學的角度來看，PP (極化電位)和 EIS (電化學阻抗譜) 測量進一步支持了這一結果。因此，經過適當的熱處理，Na_2MoO_4 的緩蝕能力可以增強。本研究中另亦透過 XPS 進行更進一步的探討，可以檢查可能在試樣上所形成的 $MoO_4^{2-}Fe^{2+}$複合膜的微觀結構和化學成分。