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Chemical vapour deposition (CVD) of molybdenum into medium pore H-zeolites

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Abstract. Several medium pore H-zeolites (HZSM-5, HIM-5, HTNU-9 and HZSM-11) were evaluated toward molybdenum deposition *via* chemical vapor deposition using Mo(CO)₆ as the molybdenum precursor. The deposition was through a high temperature adsorption of Mo(CO)₆ vapor onto dehydrated zeolites. The progress of deposition was monitored gravimetrically. *Ex-situ* infrared (FTIR) spectroscopy was employed to observe the interaction between Mo(CO)₆ and the zeolites during the deposition. X-ray photoelectron spectroscopy (XPS) was used to scrutinize the nature of molybdenum deposit within the zeolite. High temperature adsorption of Mo(CO)₆ vapor is an irreversible adsorption resulted in a molybdenum deposition onto the zeolites whereas the adsorption conducted at room temperature is a reversible one. Interaction of Mo(CO)₆ and the zeolites at high temperature led to the reaction of Mo(CO)₆ and hydroxyl group within zeolites i.e. silanol group and Brønsted acid site. The molybdenum dispersion within the zeolites was governed by the particle size of the zeolite. More concentrated molybdenum deposited on zeolite surface occurred on the zeolite with bigger particle size. The highest surface molybdenum deposition was observed on ZSM-11 surface as it has the biggest particle size.

1. Introduction

Molybdenum supported zeolite, especially medium pore zeolites, is an active catalyst toward light alkane activation such as methane conversion into aromatics and dehydrogenation of propane [1, 2]. The most applied method on the preparation of this material is wet impregnation using ammonium heptamolybdate solution [3]. A wide range of synthesis methods has been explored to gain a better catalyst. Some reviews claim that molybdenum introduced by wet impregnation result in catalyst for methane dehydroaromatization with highest activity [3,4].

The most crucial issue on the preparation of molybdenum-supported zeolite is the molybdenum dispersion throughout the zeolite. Conventional method cannot achieve a good molybdenum dispersion [5]. This is important since the reaction is believed to require close proximity of the active molybdenum phase to internal acid sites in the zeolite [6]. An improvement on the molybdenum dispersion was achieved by Sun *et al.* [7] by introducing ammonium heptamolybdate into Zeolite Socony Mobil-5 (ZSM-5) at high pH. Catalyst prepared had a higher performance attributed to a better diffusion of monomeric MoO₄²⁻ species at high pH into zeolite pore. The ability of an anionic molybdenum precursor to diffuse uniformly throughout an anionic zeolite framework is however unclear.



Mo(CO)₆ is an alternative precursor to be introduced into microporous framework. This uncharged organometallic precursor with significant vapor pressure at room temperature (~0.14 torr) is readily to be deposited in atomic level since it is a discrete molecule [8]. This method has been successfully applied to synthesize catalyst with high uniform molybdenum loading in large pore zeolite such as faujasite [9] and EMT [10]. Deposition of molybdenum into large pore zeolite conducted by room temperature adsorption of Mo(CO)₆ is used to synthesize an active catalyst but this protocol does not work in the zeolite with medium pore such as ZSM-5. Mo(CO)₆ with kinetic diameter more than 6 Å exceeds the notional pore diameter of a 10-ring zeolite such as ZSM-5. Therefore this molecule cannot diffuse into the medium pore zeolite by adsorption at room temperature [11]. This paper explained about the work on Molybdenum deposition on various medium pore zeolites, pore diameter of c.a. 5.5 Å, i.e. HZSM-5, HIM-5, HTNU-9 and HZSM-11, via chemical vapor deposition at elevated temperature using Mo(CO)₆ as the molybdenum precursor.

2. Experimental

2.1. Materials

ZSM-5 (Si/Al ratio: 40, zeolyst), TNU-9 (Si/Al = 13), IM-5 (Si/Al = 13) and ZSM-11 (Si/Al = 22) were synthesized at the University of Oslo. Al(NO₃)₃·9H₂O and Cabosil were used as aluminum and silicon source. The synthesis was conducted in a 52 mL Teflon liner steel autoclave. As synthesized zeolites were calcined at 550 °C for 5 hours in 50:50 oxygen and nitrogen. The calcined zeolites were treated with three-time ion exchange with excess 1M NH₄NO₃ for 2 hours at 70 °C. Calcination was applied at 550 °C for 5 hours to obtain H-form of zeolites Mo(CO)₆ was from Koch-Light Labs (Cat. Number 164115-69-9).

2.2. Synthesis

Deposition of molybdenum into the zeolites was performed in a vacuum microbalance. Prior to the deposition, the zeolites were dehydrated at 500 °C under vacuum condition. Freeze vacuum treatment was applied to Mo(CO)₆ for purification to be ready for deposition. Adsorption of Mo(CO)₆ vapor onto the zeolites was carried out at 120 °C to deposit molybdenum until reaching the required level of deposition. Subsequent evacuation followed the deposition to complete the decarbonylation accompanied by gradual heating at 120 °C, 200 °C and 300 °C. Room temperature deposition of molybdenum was also studied through a room temperature adsorption. Exposure of Mo(CO)₆ vapor onto the zeolites at room temperature was conducted until reaching saturation and stepwise desorption was conducted via evacuation and gradual heating treatment (room temperature, 100 °C, 200 °C and 300 °C).

2.3. Characterization

Study on the deposition process was carried out by means Fourier Transform Infrared (FTIR) spectroscopy. Pellet of the zeolites was mounted into a vacuum FTIR cell and dehydrated at 500 °C under vacuum condition. The pellet was exposed to Mo(CO)₆ vapor at room temperature or 120 °C followed by subsequent evacuation at room temperature, 100 °C, 200 °C and 300 °C. IR spectra were collected after each treatment with a Nicolet Nexus 870 FTIR spectrometer with a 4 cm⁻¹ resolution.

X-ray photoelectron spectroscopy (XPS) was employed to observe the molybdenum dispersion within the zeolites. The dispersion is defined as comparison of surface molybdenum concentration to the bulk molybdenum concentration whereas molybdenum concentration is the molar ratio of molybdenum to the silicon. Surface molybdenum concentration was obtained from XPS studies whereas bulk molybdenum concentration was determined gravimetrically. XPS spectra were collected at EPSRC XPS facilities at the University of Newcastle using Thermo k-Alpha instrument from Thermo Scientific.

3. Results and discussion

3.1. Molybdenum deposition

Gravimetric studies on the adsorption of Mo(CO)₆ vapor onto the zeolites (HZSM-5, HIM-5, HTNU-9 and HZSM-11) shows the reversibility of room temperature adsorption, where the uptake of Mo(CO)₆ vapour at room temperature with vapour pressure of 0.14 torr was about 1% weight for all zeolites. For brevity, typical graph on Mo(CO)₆ adsorption on the zeolite was represented by the adsorption on

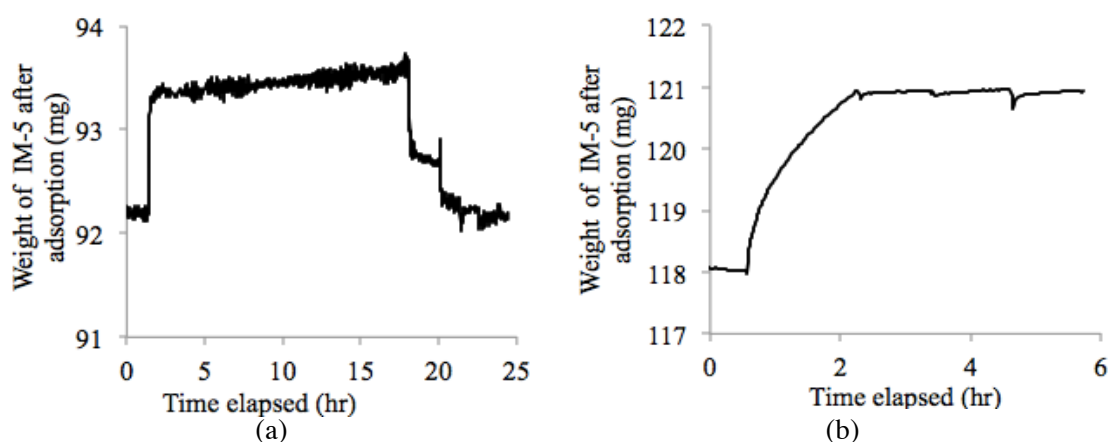


Figure 1. Weight-time profile of HIM-5 after adsorption of $\text{Mo}(\text{CO})_6$ into HIM-5 at (a) room temperature and (b) 120 °C

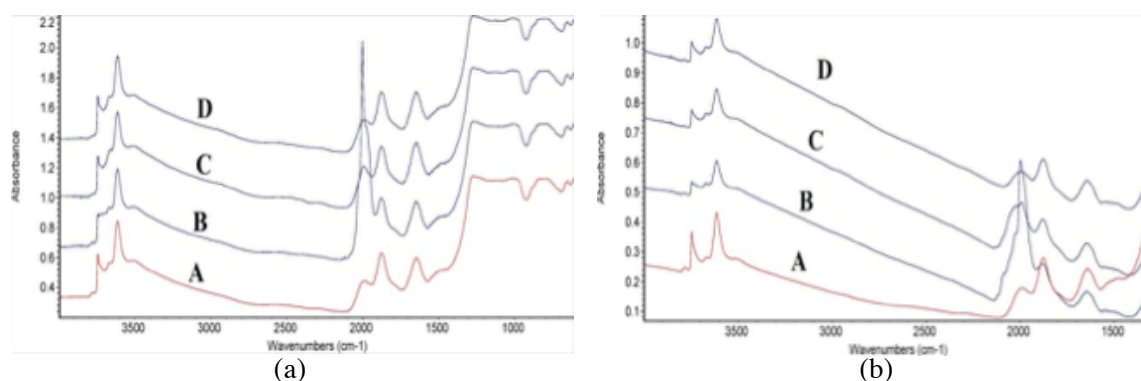


Figure 2. IR spectra of $\text{Mo}(\text{CO})_6$ adsorption into HTNU-9 at (a) room temperature for (A) outgassed zeolite, (B) exposed to $\text{Mo}(\text{CO})_6$, (C) evacuated at room temperature and (D) evacuated at 100 °C and (b) 120 °C for (A) outgassed zeolite, (B) exposed to $\text{Mo}(\text{CO})_6$, (C) outgassed at room temperature and (D) outgassed at 100 °C

HIM-5 (figure 1). The adsorbed molybdenum species was almost completely removed by outgassing at 100 °C. Evacuation performed at 300 °C restore the weight of the zeolite into original weight (figure 1a). The reversibility of room temperature adsorption was also confirmed by infrared spectroscopy (FTIR). Figure 2a is a sample of the studies i.e. room temperature adsorption of $\text{Mo}(\text{CO})_6$ onto HTNU-9. Exposure of $\text{Mo}(\text{CO})_6$ vapour onto HTNU-9 generates some vibration at 2137, 2119, 2083 cm^{-1} (shoulder), 2028 cm^{-1} (shoulder) and 1970 cm^{-1} (shoulder), as described in Ohta *et al.* [8] and Abdo and Howe [9]. These peaks are due to the vibration of carbonyl group of adsorbed $\text{Mo}(\text{CO})_6$, whereas the band at 2001 cm^{-1} refers to the vibration of free gas phase $\text{Mo}(\text{CO})_6$. The bands of adsorbed $\text{Mo}(\text{CO})_6$ in the $\nu(\text{CO})$ region show similar splitting to that seen for the molecule physically adsorbed on alumina [12] or silica [13] surfaces due to lowering of the octahedral symmetry. It also decreases terminal silanol peak at 3745 cm^{-1} whereas the vibration of Brønsted acid site at 3614 cm^{-1} remains unchanged. Evacuation at 100 °C restores the IR spectra of HTNU-9 into the origin [14].

In contrast to the room temperature gravimetric studies of $\text{Mo}(\text{CO})_6$ adsorption, exposure of the zeolites to $\text{Mo}(\text{CO})_6$ at its room temperature vapor pressure at 120 °C results in a larger and irreversible uptake. Figure 1b shows the molybdenum uptake on HIM-5 at 120 °C. A 2% uptake was achieved after 2 hours exposure and only a slight weight change on the subsequent outgassing at higher temperature. A longer exposure of zeolite at 120 °C to $\text{Mo}(\text{CO})_6$ vapor could be applied to achieve a higher molybdenum uptake and intermittently evacuating CO which was produced during the adsorption.

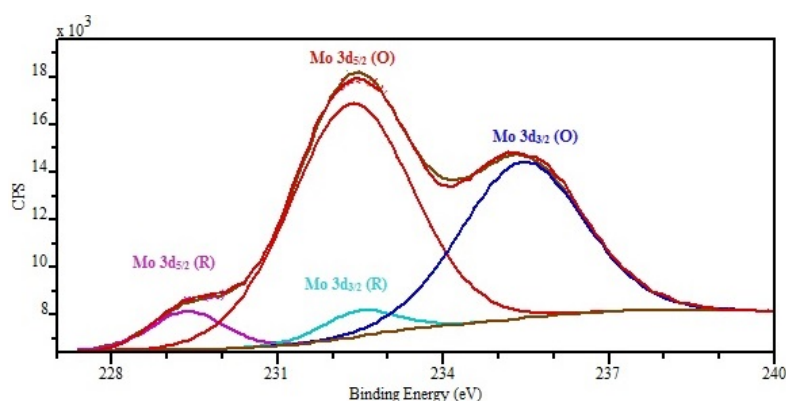


Figure 3. XPS spectra of molybdenum 3d of HZSM-5 with 2% molybdenum deposition

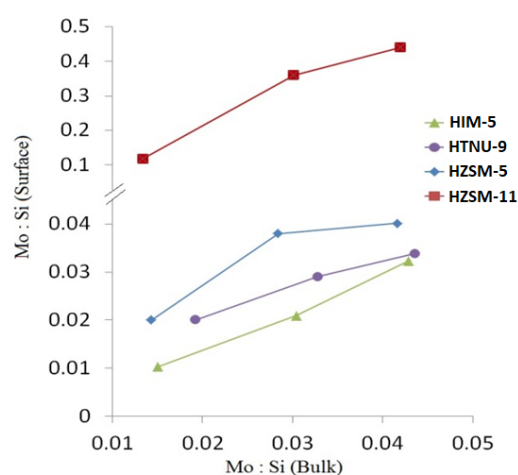


Figure 4. Comparison of surface and bulk molybdenum concentration determined by XPS and gravimetric analysis.

The success of molybdenum deposition by adsorption of $\text{Mo}(\text{CO})_6$ vapor at 120 °C was also supported by infrared spectroscopy studies (figure 2b). HTNU-9 exposed with $\text{Mo}(\text{CO})_6$ vapor at 120 °C gives peaks due to the vibration of carbonyl group of adsorbed $\text{Mo}(\text{CO})_6$. The peaks are at 2117 cm^{-1} (shoulder), 2089 cm^{-1} (shoulder), 2054 cm^{-1} (shoulder), 2026 cm^{-1} (shoulder) and 1975 cm^{-1} , whereas the peak at 1998 cm^{-1} shows the presence of gas phase $\text{Mo}(\text{CO})_6$ in the IR cell. Those peaks are in accordance with the results reported by Areán *et al.* [14]. Evacuation at 100 °C restores the IR spectra of HTNU-9 at the region of zeolite framework and leaves permanent decrease of Brønsted acid site peak at 3614 cm^{-1} and terminal silanol at 3745 cm^{-1} . This evidence supports the gravimetric studies that the high temperature adsorption leads to the deposition of molybdenum through its reaction with the Brønsted acid site and terminal silanol.

The interaction of molybdenum with Brønsted acid hydroxyl group of zeolites was convincingly shown by the IR spectra of deposited molybdenum at 120 °C as well as the interaction with surface silanol group of zeolite. Further characterization on the molybdenum dispersion was carried out by XPS. Figure 3 is the XPS spectra of molybdenum 3d of HZSM-5 with 2% of molybdenum deposition. A small amount of molybdenum with lower binding energy of 229.36 and 232 eV for $3d_{3/2}$ and $3d_{5/2}$ respectively is in lower oxidation state, such as molybdenum in MoO_3 or MoOOH , whereas most molybdenum is in higher oxidation state with binding energy of 232.33 and 235.43 eV for $3d_{3/2}$ and $3d_{5/2}$ respectively, these binding energies are close to the molybdenum in MoO_3 [15]. Concentration of molybdenum on zeolite surface obtained by XPS is compared to the bulk molybdenum concentration determined by gravimetric analysis is defined as the molybdenum dispersion over zeolites. The

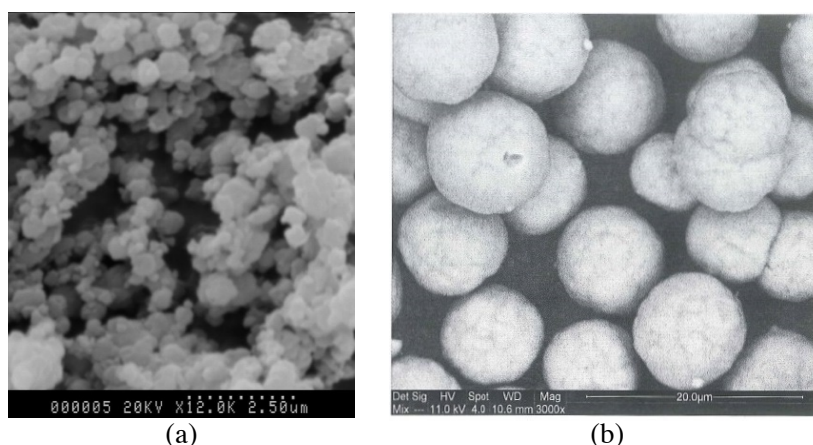


Figure 5. Electron micrograph of (a) HZSM-5 and (b) HZSM-11

molybdenum dispersion over zeolites is presented in figure 4. From XPS and gravimetric characterization on the Mo/H-zeolites, the highly dispersed molybdenum should show a uniform molybdenum concentration throughout the zeolite grain. Figure 4 shows the comparison of molybdenum concentration on the zeolite surface and bulk zeolite. HIM-5, HTNU-9, and HZSM-5 have good molybdenum dispersion into bulk, whereas HZSM-11 has surface molybdenum concentration about 10 fold of the bulk concentration. It is suggested that this difference is caused by the difference of the zeolite particle size. IM-5, TNU-9 and ZSM-5 are in hundreds nanometer where as ZSM-11 has particle size about 10 μm as shown in figure 5. A smaller particle size allows the diffusion of molybdenum easily throughout the zeolite particle whereas a bigger one gives an obstruction to molybdenum to reach the inner part of the zeolite particle lead to the accumulation on the zeolite surface.

4. Conclusions

Adsorption of $\text{Mo}(\text{CO})_6$ onto H-zeolites (HZSM-5, HIM-5, HTNU-9 and HZSM-11) conducted at room temperature is reversible whereas adsorption at 120 $^\circ\text{C}$ is irreversible and leads to the molybdenum deposition onto the zeolite. Deposition of molybdenum is through decomposition of adsorbed $\text{Mo}(\text{CO})_6$ and reaction of molybdenum with Brønsted acid site and terminal silanol of zeolites. Molybdenum dispersion over zeolites is governed by particle size of zeolites i.e. zeolite with bigger particle size has more molybdenum on the surface than smaller particle size.

Acknowledgements

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References

- [1] Wang L, Tao L, Xie M, Xu G, Huang J and Xu Y 1993 *Catal. Lett.* **21** 35–41
- [2] Solymosi F, Németh R, Óvári L and Egri L 2000 *J. Catal.* **195** 316–25
- [3] Ismagilov Z R, Matus E V and Tsikoza L T 2008 *Energy Environ. Sci.* **1** 526–41
- [4] Atta A Y, Shuwa S M, Naser J T and Jibril B Y 2015 *Asian J. Chem.* **27** 307–12
- [5] Hassan A and Sayari A 2006 *Appl. Catal. A* **297** 159–64
- [6] Ha V T T, Tiep L V, Meriaudeau P and Naccache C 2002 *J. Mol. Catal. A-Chem* **181** 283–90
- [7] Sun C, Yao S, Shen W and Lin L 2008 *Catal. Lett.* **122** 84–90
- [8] Ohta T, Cicoira F, Doppelt P, Beitone L and Hoffman P 2001 *Chem. Vap. Deposition* **7** 33–7
- [9] Abdo S and Howe R F 1983 *J. Phys. Chem* **87** 1713–22
- [10] Bécue T, Manoli J M, Potvin C, Djéga-Mariadassou G and Delamar M 1997 *J. Phys. Chem B* **101** 6429–35
- [11] Yong Y S and Howe R F 1986 *Stud. Surf. Sci. Catal.* **28** 883–9
- [12] Brenner A and Burwell Jr R L 1978 *J. Catal* **52** 353–63
- [13] Kurhinen M, Venäläinen T and Pakkanen TA 1994 *J. Phys. Chem* **98** 10237–42

- [14] Areán C O, Palomino G T, Platero E E and Mentrui M P 1997 *Dalton Trans.* **19** 873–9
- [15] Weckhuysen B M, Rosynek M P and Lunsford J H 1998 *Catal. Lett.* **52** 31–6