

Scanning tunnelling microscopy for characterization of metathesis catalysts based on photogenerated $W(CO)_6/CCl_4$

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Abstract

We attempted to form a $W(CO)_6/CCl_4$ catalyst from the gas phase reaction of $W(CO)_6$ and CCl_4 by UV-irradiation and used this catalyst in a model metathesis reaction of 1-heptene. We analyzed both the intermediate volatile compounds using an on-line mass spectrometer and the structure of the solid polymer by FI-MS and DSC. Scanning tunnelling microscopy (STM) was used in order to study the structures of $W(CO)_6$ and photogenerated $W(CO)_6/CCl_4$ catalyst on HOPG. Color changes observed during UV-irradiation were considered to be an indication of the formation of the $W(CO)_6/CCl_4$ catalyst. The volatile compounds identified by mass spectrometry supported the formation of the catalyst. The mass spectra obtained with the field ionization mass spectrometer revealed that the catalyst may be in an oligomeric form with $[(CO)_4WC_2Cl_2]^+$ repeating units. Thermal transitions observed in the DSC thermograms indicated the existence of oligomeric chains. STM images clearly showed the structure of the $W(CO)_6$ molecules with some atomic level displacements. The STM images of the catalyst verified that the $W(CO)_6/CCl_4$ based metathesis catalyst is composed of oligomeric chains with four tungsten atoms.

Keywords: $W(CO)_6$; Photogenerated $W(CO)_6/CCl_4$ catalyst; STM

1. Introduction

The $W(CO)_6/CCl_4$ catalyst system photochemically generated by the reaction of $W(CO)_6$ and CCl_4 is a well known metathesis catalyst and has been studied by different groups [1–4]. They have attempted to identify the structure and the mechanisms of the metathesis reactions of this catalyst system. In order to find the role of catalyst in the metathesis reaction, Mol and coworkers have selected 2-pentene as a model

reaction and used several techniques including IR and FAB-MS spectroscopy, powder diffraction, thermal analysis and elemental analysis, and reported that photocatalytic metathesis of cis-2-pentene with the $W(CO)_6/CCl_4$ system showed a solid polymer formation [5]. Recently, Szymanska-Buzar has performed studies on photocatalytic systems containing $W(CO)_6$ and a halide of the group IV, XIII or XIV elements, and reported that the essential role is played by the donor–acceptor interaction between the tungsten hexacarbonyl (electron donor, D) and the halide AX_n (electron acceptor, A) in the initiation of the metathesis reaction [6]. They

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have also used a matrix-isolation technique, which was applied at low temperature, and therefore it was possible to show the structure of the deposits and to identify the intermediates in the metathesis reactions of different olefins by IR and UV-VIS spectroscopy [7–9].

Recently we have attempted to form a $W(CO)_6/CCl_4$ catalyst from the gas phase reaction of $W(CO)_6$ and CCl_4 by UV-irradiation and used this catalyst in a model metathesis reaction of 1-heptene [10]. We have analyzed both the intermediate volatile compounds using an on-line mass spectrometer and the structure of the solid polymer by FI-MS and DSC, the results of which are briefly given in this article. Here, for the first time, we also report the results of our studies aimed to identification of this catalyst system using scanning tunnelling microscopy (STM).

2. Experimental

2.1. Reagents

Tungsten hexacarbonyl ($W(CO)_6$) was purchased from Merck (Germany) and used as obtained. Carbon tetrachloride (CCl_4 , BDH, UK) was distilled three times under nitrogen. 1-heptene (Analar, UK) was refluxed for 4 h using metallic sodium and distilled under a nitrogen atmosphere. Both chemicals were kept under nitrogen until use. All other reagents were spectroscopic grade and were used as obtained.

2.2. Preparation and characterization of the catalyst

2.2.1. Preparation of the catalyst

The metathesis catalyst was prepared in a reaction system schematically shown in Fig. 1, which consists of the following parts: (A) the reaction vessel which is a pyrex flask (1 liter); (B) the feed-solution vessel; (C) a vacuum pump (Edwards ES 50, UK); (D) a pure nitrogen tank; (E) a mass spectrometer (Varian MAT, CH7,

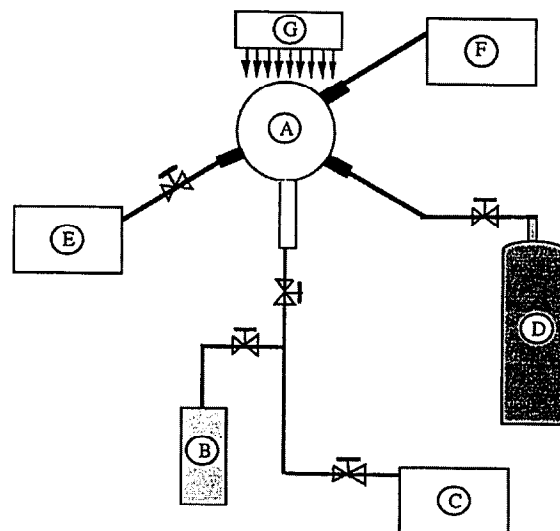


Fig. 1. The reaction system: (A) reaction vessel; (B) feed-solution vessel; (C) vacuum pump; (D) nitrogen tank; (E) mass spectrometer; (F) pirani gauge; (G) UV-light source.

Germany); (F) a pirani gauge (Edwards PRH 10, UK); (G) an UV-light source, i.e., a high mercury lamp of 200 Watt (Oriel 6137, Germany).

For preparation of the catalyst, the following steps were applied: first air in the system was displaced with pure nitrogen by flushing nitrogen through the reactor, and then pumping it down to a pressure of 1×10^{-2} Torr. The mixture of $W(CO)_6$ and CCl_4 was introduced to the reaction vessel, and the pressure of the vessel was kept constant at 1×10^{-1} Torr during the reaction period. Then, the reactions were initiated by applying UV-irradiation. After the desired period of time, which was about 30 min, the UV-irradiation was turned off, then the pressure in the reactor was slowly raised to atmospheric pressure by backfilling with pure nitrogen. The precipitate (i.e., the $W(CO)_6/CCl_4$ catalyst) formed on the inner surface of the reaction vessel was dissolved in methylene chloride (CH_2Cl_2), and subsequently used in the following tests. The volatile products formed during irradiation were identified simultaneously using a mass spectrometer.

2.2.2. Characterization of catalysts by FI-MS

In order to obtain the molecular ion peaks of the catalyst prepared in the previous step, a field ionization-mass spectrometer (JMS-HX110, Japan) was used. A drop of the catalyst solution was placed on the direct probe tip of the spectrometer, and then the mass spectra was obtained.

2.2.3. Characterization of catalysts by DSC

5 mg of the solid phase deposited on the inner surface of the reaction vessel was taken under nitrogen atmosphere, and was pressed in a sample capsule. The thermogram was then recorded using a differential scanning calorimeter (DSC, Mettler TA 3000, Germany) at a heating rate of 10°C/min, and in the temperature range 50–500°C. For comparison the thermogram of pure $W(CO)_6$ was also obtained under the same conditions.

2.2.4. Metathesis reactions and identification of products

Catalytic performance of the metathesis catalyst based on the $W(CO)_6/CCl_4$ produced in the previous step was investigated using 1-heptene. Briefly, after a UV-irradiation period (about 30 min), the volatile compounds were removed by applying vacuum, and by flushing with pure nitrogen. The 1-heptene was then introduced under the nitrogen atmosphere for about 10 min at room temperature. The metathesis reaction products were identified in the samples taken from the reaction vessel using gas chromatography (HP 5890 Series II with EPC, USA) and mass spectrometry (HP 5971, USA) which was described in detail elsewhere [10].

2.2.5. Scanning tunneling microscopy

The STM used in this work was constructed in our laboratory [11]. Mechanically, it consists of two main modules: a scanner and a coarse positioner. The scanner part is constructed with a PZT tube (EBL #3 PZT-5H, Staveley Sensors, CT) glued to an aluminum body. Electrical

connection of PZT is through a special connector. The tip holder is also glued to the interior of the PZT tube but isolated electrically. The coarse positioner is a magnetically driven slider which is fastened to the scanner. The whole system is mounted on a vibration isolation stage.

For STM studies, 10 μ l solution of the catalyst (containing 1 mg catalyst/ml methylene chloride) was deposited on to freshly cleaved highly oriented pyrolytic graphite (Union Carbide) and dried in vacuum. The STM was operated in air at atmospheric pressure with a tip-to-substrate bias of 150 mV and a tunnelling current of 1 nA. Etched tips of Pt/Ir (80:20) wires (0.5 mm in diameter, Digital Instruments, Santa Barbara, CA) were used in constant current mode.

3. Results and discussion

3.1. Formation of catalyst

In this work we produced a metathesis catalyst by gas phase reactions of $W(CO)_6$ and CCl_4 which was photoinduced by UV-radiation. A gray precipitate occurred on the inner surface of the reaction vessel approximately 8–10 min after the UV-radiation was turned on. The color of the precipitate then changed from gray to a brownish pale-yellow during the rest of the reaction. These color changes may be used as an indication of the formation of the $W(CO)_6/CCl_4$ catalyst. Similar color changes were also reported by others in reactions which were performed in solution rather than the gas phase [5].

Table 1
Volatile intermediate products identified with mass spectrometry

Compound	Determined mass (amu)
CO	28
Cl ₂	70
C ₂ Cl ₆	199
COCl ₂	98

Volatile intermediate products formed in the gas phase during irradiation, were also simultaneously identified using a mass spectrometer. The results obtained are summarized in Table 1. Reactions of $W(CO)_6$ and CCl_4 in liquid and gas phases have been discussed in detail elsewhere [10]. The data in Table 1 may be used for a brief discussion of the formation of the $W(CO)_6/CCl_4$ catalyst, as follows: CO in the gas phase is an indication of the loss of carbonyl groups from the reactants. Cl_2 and C_2Cl_6 are formed with the reaction of CCl_3 and Cl radicals which are the decomposition products of CCl_4 occurring during UV-irradiation. Formation of $COCl_2$ from the reaction of $W(CO)_6$ and CCl_4 , has also been reported by others, however, there is no clear explanation of the precise reaction mechanism [12,13]. The existence of all these compounds in the reaction medium may be considered as supporting the formation of the $W(CO)_6/CCl_4$ catalyst.

3.2. Characterization of catalyst

3.2.1. By FI-MS

In order to enlighten the molecular structure of the catalyst obtained from the reactions of $W(CO)_6$ and CCl_4 , by UV-irradiation, we obtained the mass spectra in a field ionization

mass spectrometer. A representative spectrum is given in Fig. 2. Details of these studies were given elsewhere [10].

As shown in this figure, the intensity observed between 388 and 393 amu may indicate isotopic distributions resulted from tungsten and chlorine atoms. By considering the mass distribution data and by using atomic mass data, we proposed a molecular ion consisting of one tungsten and two chlorine atoms, as follows: $[(CO)_4WC_2Cl_2]^+$. Note that this ion corresponds to a very unstable molecule, and it would be very difficult to obtain such a molecule from photoinduced reactions between $W(CO)_6$ and CCl_4 . Therefore this species cannot exist in the catalyst as a single molecule. However, the catalyst may contain oligomers which have this species as a repeating unit. Note that the peaks at 376 and 344.4 amu may correspond to loss of carbon and carbon dioxide from the species, respectively.

3.2.2. By DSC

Details of the thermal analysis of the reaction products were given elsewhere [10]. In Fig. 3 two representative thermograms, namely from pure $W(CO)_6$ and from the photo-induced catalyst material prepared in this study are given. The endothermic peak at $148^\circ C$ represents the

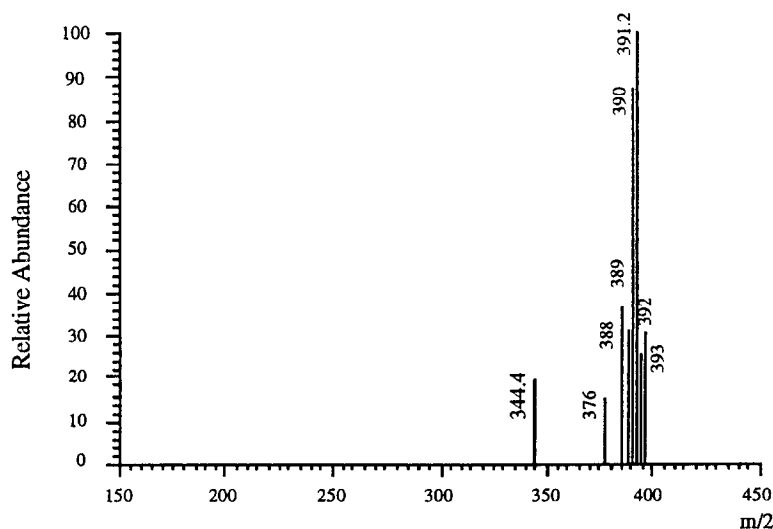


Fig. 2. FI-Mass spectrum of the $W(CO)_6/CCl_4$ catalyst.

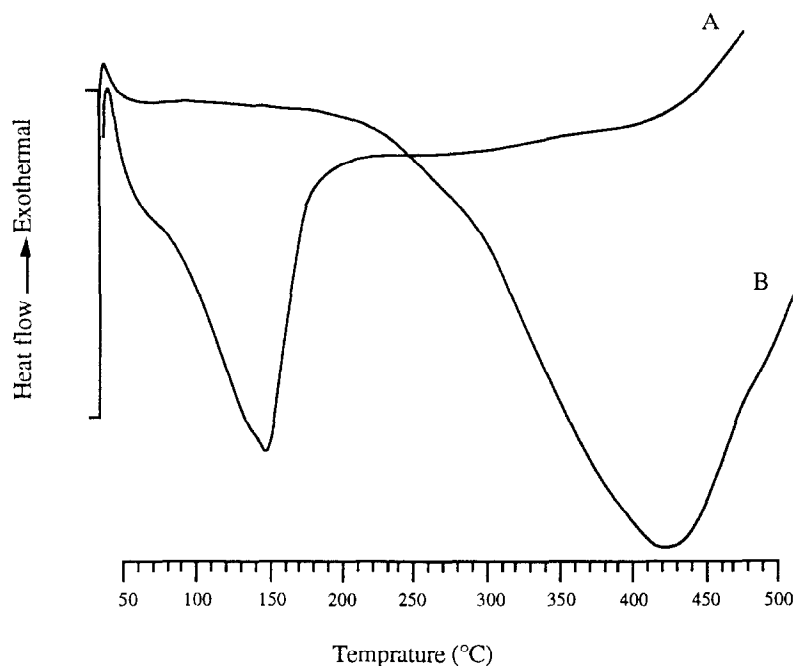


Fig. 3. DSC thermograms: (A) $W(CO)_6$, and (B) catalyst.

melting point of $W(CO)_6$ (Fig. 3A). Above 155 °C, $W(CO)_6$ starts to decompose. Since TGA data show that there is a loss in mass, we assumed that the thermal transition at 420 °C corresponds 'decomposition'.

3.2.3. Performance of catalyst in metathesis reactions

In order to show the catalytic activity of the $W(CO)_6/CCl_4$ based catalyst prepared in this study, the metathesis reaction of 1-heptene was

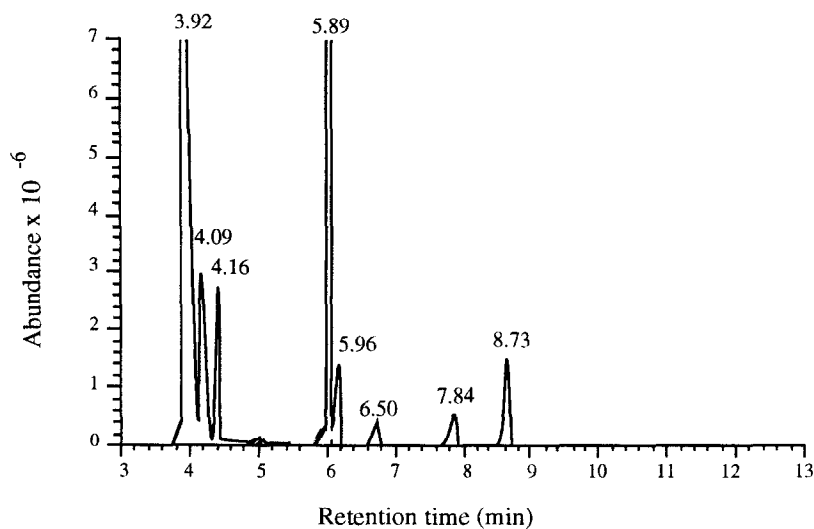


Fig. 4. A representative mass chromatogram of the metathesis reaction products of 1-heptene with the photoinduced $W(CO)_6/CCl_4$ catalyst.

Table 2
Relative amounts of metathesis products of 1-heptene determined by GC-MSD

Compound	Relative amount (%)
1-heptene	68.0
2-heptene	10.1
3-heptene	2.1
1-chloro, 2-pentene	8.8
5-Undecene ^a	4.7
6-Dodecene	6.3

^a Co-metathesis product.

investigated. The reaction products were identified by GC-MSD as described before, and given in detail elsewhere [10]. A representative chromatogram is given in Fig. 4 and the mass percent of each compound determined from this figure is presented in Table 2.

As shown in Table 2, the metathesis products of 1-heptene are a rather complex mixture of several compounds as reported in the related literature [7]. There is about 68% unconverted 1-heptene at the specific reaction conditions

given before. The isomerization reaction products (i.e., 2-heptene and 3-heptene) are about 12%. 1-chloro, 2-pentene, which is about 9%, is a typical halogen substitution product. 6-dodecene is the main product of the catalytic metathesis reaction of 1-heptene, which is about 6% of the yield. The existence of 5-undecene (about 5%), which is a co-metathesis product of 1-heptene and 2-heptene, indicates isomerization. All these reactions conclude that the $W(CO)_6/CCl_4$ based catalyst prepared in this study is behaving as an active metathesis catalyst.

3.3. STM Studies

For structural identification of the $W(CO)_6/CCl_4$ based catalyst prepared in this study, we used a novel technique, namely scanning tunnelling microscopy (STM), which is the main objective of this article.

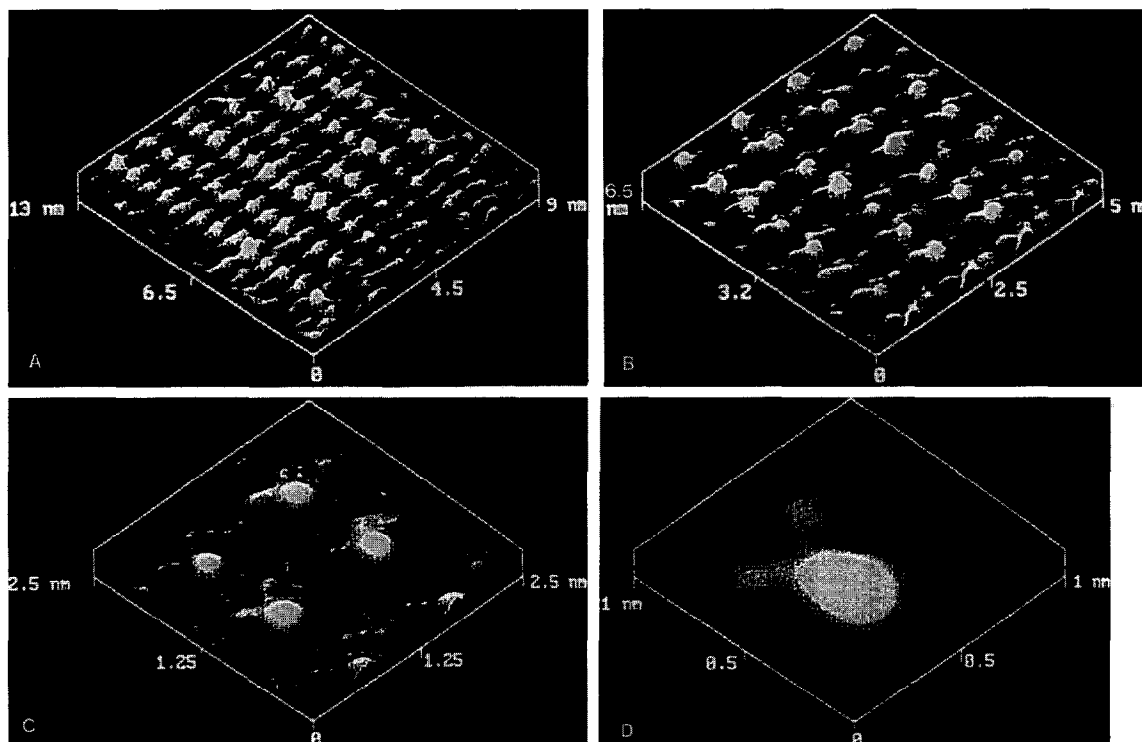


Fig. 5. Representative STM images of $W(CO)_6$ molecules on HOPG. (A) Scan area: $130 \times 90 \text{ \AA}$; (B) Scan area: $65 \times 50 \text{ \AA}$; (C) Scan area: $25 \times 25 \text{ \AA}$; and (D) Scan area: $10 \times 10 \text{ \AA}$. Tunnelling current: 0.05 nA and bias voltage: 200 mV.

In this study, for comparison we obtained STM images of both pure $W(CO)_6$ and the $W(CO)_6/CCl_4$ based catalyst deposited on highly oriented pyrolytic graphite (HOPG) substrate. Fig. 5 gives the images of $W(CO)_6$ on HOPG surfaces at different magnifications. In the largest scan ($130 \times 90 \text{ \AA}$) (the lowest magnification) given in Fig. 5A, long-range ordering of molecules is evidenced as rows. On narrowing the scan range to $65 \times 50 \text{ \AA}$ and then to $25 \times 25 \text{ \AA}$, the increased resolution distinguishes rows of parallel oriented molecules (Fig. 5B, C). The rows are subdivided into discrete units of molecules, in which we assume that each unit corresponds to one single $W(CO)_6$ molecule (Fig. 5D). The size of each brighter blob in Fig. 5D is about 2.80 \AA which is very close to the atomic diameter of a tungsten atom (i.e., 2.82 \AA). Therefore we also assume that the bright oval in the front is a tungsten atom in each cell, while the CO groups appear as a fainter bright in the back. Note that it is not possible to distinguish the carbon and oxygen atoms separately on these images. From these images, the distance between two tungsten atoms was measured as about 8.2 \AA (the distance between the centers of two neighbor tungsten atoms measured directly from the STM images). Note that in a closest packed structure of $W(CO)_6$ molecules, assuming that there is no direct bond between two tungsten atoms, this distance is expected to be 6.38 \AA , by considering intermolecular distances obtained by elec-

tron diffraction (with a W–C of 2.06 \AA and a C–O of 1.13 \AA) [14].

In order to show the atoms of $W(CO)_6$ on the HOPG surface, a profile of the surface corrugation was taken along the line LM exemplified in Fig. 6A. As seen in the height–distance curves there are two different peak sizes (Fig. 6B). We calculated average heights of these two peaks by using more than 20 similar corrugations of the same surface. The average height of the larger peak was about 2.80 \AA which corresponds to the size of a tungsten, while the smaller one was in the range of $1.05\text{--}1.50 \text{ \AA}$, which is the size range of carbon and oxygen atoms.

Representative STM images (obtained at different magnifications) of the $W(CO)_6/CCl_4$ based catalyst prepared in this study are given in Fig. 7. Quite different structures are observed comparing with the images of $W(CO)_6$ molecules given in Fig. 5. Structures consisting of four ‘blobs’ are clearly observed. The size of each blob (i.e., a brighter oval) is about 2.5 \AA , which is smaller than that observed for the size of the bright feature in $W(CO)_6$. This is expected because the oxidation state of tungsten in $W(CO)_6/CCl_4$ is different from that in $W(CO)_6$. It seems that these could be oligomer chains containing about four tungsten atoms. The tungsten atoms are laterally separated from each other by a distance of 3.5 \AA which is in good agreement with the distance of a tungsten–tungsten bond length which is approximately

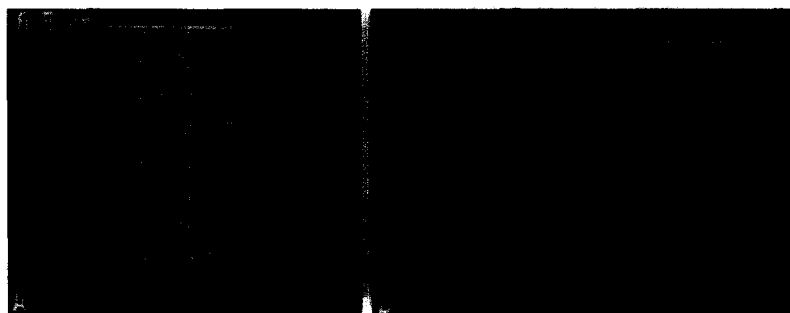


Fig. 6. A representative STM image of $W(CO)_6$ molecule on HOPG. (A) Scan area: $65 \times 50 \text{ \AA}$; Tunnelling current: 0.05 nA and bias voltage: 200 mV . (B) Profile of z -deflection along the line LM on the image given in Fig. 6A.

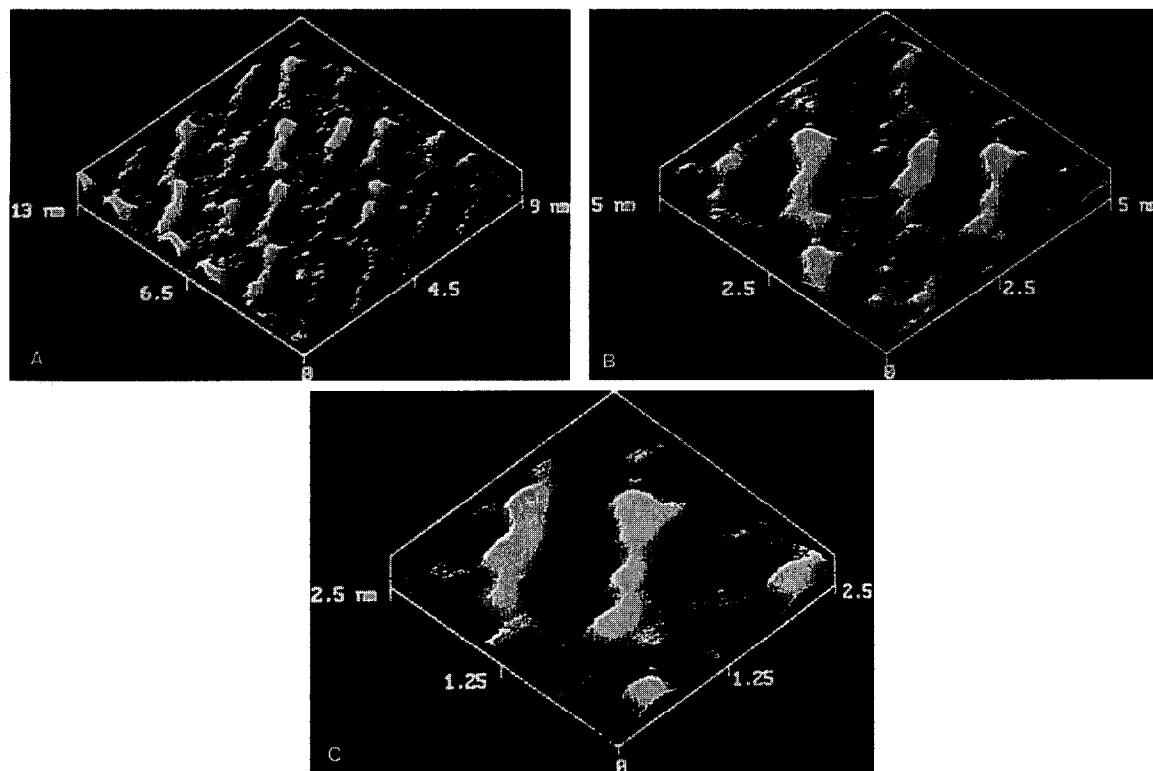


Fig. 7. Representative STM images of a $W(CO)_6/CCl_4$ based catalyst on HOPG. (A) Scan area: $130 \times 90 \text{ \AA}$; (B) scan area: $50 \times 50 \text{ \AA}$; (C) scan area: $25 \times 25 \text{ \AA}$; tunnelling current: 0.05 nA and bias voltage: 200 mV.

3.5 Å [15]. The number of the fainter bright regions is much less in the catalyst structure compared to the original $W(CO)_6$ molecule, which may be an indication of the loss of CO groups during the catalyst formation reaction.

However, it is difficult to say anything conclusive about the chlorine atoms on the oligomer chains. They should be in the structure according to the results of FI-Mass spectra discussed before. Maybe they are hidden at the back of

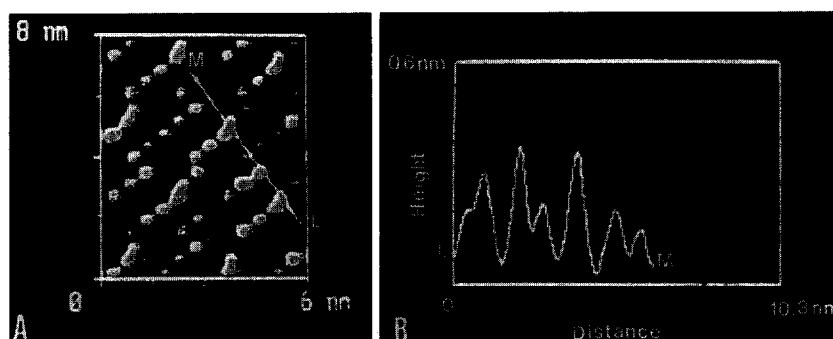


Fig. 8. A representative STM image of a $W(CO)_6/CCl_4$ based catalyst on HOPG. (A) Scan area: $80 \times 60 \text{ \AA}$; tunnelling current: 0.05 nA and bias voltage: 200 mV. (B) Profile of z -deflection along the line LM on the image given in Fig. 7A.

the chains, therefore we cannot see them in the STM images.

Fig. 8A, B, show a representative image of the $W(CO)_6/CCl_4$ based catalyst on HOPG and the profile of z -direction along the line LM, respectively. As seen here, there are peaks with different sizes (Fig. 8B). The relatively higher amplitude is about 2.50 Å which roughly corresponds to the size of a tungsten in $W(CO)_6/CCl_4$, as discussed in the previous paragraph. The smaller peaks are in the range of 1.00–1.85 Å, which is the size range of carbon–oxygen–chlorine atoms, which may be interpreted as an indication of the incorporation of chlorine atoms in the catalyst structure.

4. Conclusion

In this study we were able to produce a $W(CO)_6/CCl_4$ based metathesis catalyst by a photo-induced gas phase reaction of $W(CO)_6$ and CCl_4 . Color changes observed during UV-irradiation were considered as an indication of the formation of the $W(CO)_6/CCl_4$ catalyst. The volatile compounds identified by mass spectrometry supported the formation of the catalyst. The mass spectra obtained with the field desorption mass spectrometer revealed that the catalyst may be in an oligomeric form with $[(CO)_4WC_2Cl_2]^+$ repeating units. A thermal transition observed in the DSC thermograms also indicated the existence of oligomeric chains. STM images clearly showed the structure of the $W(CO)_6$ molecules with some atomic level displacements. The STM images of the catalyst veri-

fied that the $W(CO)_6/CCl_4$ based metathesis catalyst composed of oligomeric chains usually with four tungsten atoms. The profile of z -direction obtained by tracking on STM images suggested the incorporation of chlorine atoms in the catalyst structure.

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