

Catalytic cracking of *n*-hexane over MoO₂

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Abstract

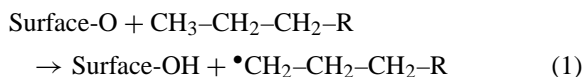
Catalytic cracking reactions of *n*-hexane over molybdenum oxide (MoO₂) grown on a polycrystalline molybdenum foil (~1 cm²) were studied in the temperature range 830–913 K at a low conversion (<2%). The *n*-hexane pressure was 7.3 Torr. The reactions were carried out in a batch reactor and no hydrogen or water vapor (steam) was used. The cracking products of *n*-hexane were mostly alkenes—ethylene (29 mol%), propylene (35 mol%), butenes (19 mol%) and pentenes (5 mol%)—along with small amounts of alkanes—methane (7 mol%), ethane (4 mol%) and propane (1 mol%). The apparent activation energy for the catalytic cracking of *n*-hexane was ~60 kcal/mol. The reaction rates were not deactivated over more than 5 h of use. Dehydrogenation and aromatization were also observed, but these reactions rates decreased as the gas inside the batch reactor reached an equilibrium. Auger and X-ray photoelectron spectroscopy studies suggested an oxycarbide form as the catalytically active phase. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Cracking; *n*-Hexane; Molybdenum

1. Introduction

Light olefins, ethylene and propylene, are valuable feedstocks in the chemical industry. The current technology for producing these olefins is by thermal cracking of a mixture of naphtha feeds and steam in an externally heated tube [1–3]. By controlling the contact time of the reactants, high ethylene and propylene yields are obtained. The use of catalysts could decrease the temperature needed for this endother-

mic dehydrogenation reaction and perhaps increase ethylene and propylene yields further. A variety of oxide materials have been tested for this purpose [4–10]. These studies [7–12] indicated that the catalytic reactions are initiated by hydrogen abstraction from hydrocarbons by an active oxygen species at the surface (Eq. (1)) followed by dissociation of the C–C bond at the β-position from the hydrogen-abstracted carbon (Eq. (2)):



In this study, we have tested an oxidized molybdenum foil as a model catalyst for catalytic cracking

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of *n*-hexane in the absence of hydrogen or water in the catalyst temperature range 830–913 K. The catalyst was produced by oxidation of a Mo foil in an ultrahigh vacuum chamber [13,14]. The *n*-hexane cracking produced ethylene and propylene with high selectivities (29 and 35 mol%, respectively). The methane selectivity was only 7 mol%. In the temperature range 830–913 K, the cracking reactions occurred through a catalytic pathway and not by gas-phase thermal cracking. X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) studies indicated that the catalytically active phase is a molybdenum oxycarbide that was formed during the reaction.

2. Experimental

The model catalyst preparation and catalytic reactions were carried out in an ultrahigh vacuum chamber (base pressure = 5×10^{-10} Torr) described in Fig. 1. The chamber was equipped with a retarding field analyzer (RFA) for AES, an argon ion gun for catalyst cleaning, a quadrupole mass spectrometer

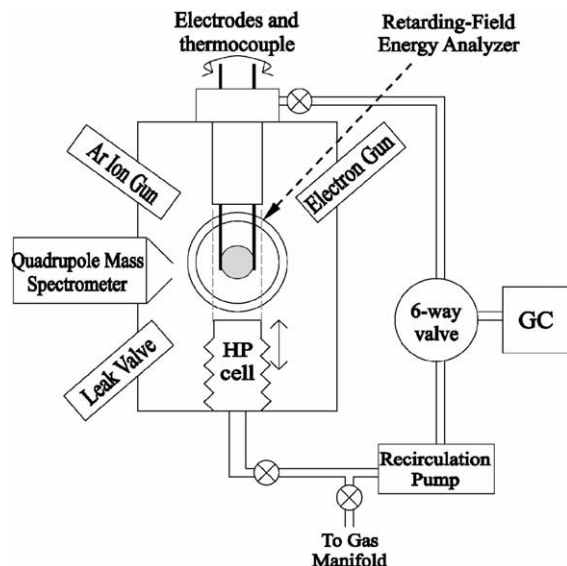


Fig. 1. Schematic diagram of the UHV system combined with an HP reaction system. Total volume of the HP reaction loop (cell + gas line) was 247 ml.

(Balzers QMG 421C) for residual gas analysis and a high-pressure (HP) cell for catalytic reactions. The total volume of the reaction cell and recirculation loop was 247 ml. The gas flow rate through a recirculation pump was 340 ml/min.

A polycrystalline molybdenum foil (Goodfellow, 99.99%) with a surface area of about 1 cm^2 was cleaned by using repeated cycles of Ar^+ ion sputtering, oxygen treatment and annealing at 1003–1130 K until surface impurities, particularly carbon, were no longer detected in AES. A thin film of MoO_2 was formed on the Mo foil by exposure to oxygen of 3×10^{-5} Torr for 155 s at a sample temperature of 1130 K followed by subsequent annealing for 2 min under UHV at the same temperature [13,14]. AES taken after the oxidation reaction (e.g., see Fig. 6) showed the splitting of the 222 eV peak that is characteristic of the MoO_2 phase [14]. A stainless steel foil (area = 1 cm^2), cleaned and oxidized in the same way, was used to determine contribution from thermal cracking under the same reaction condition. AES of the oxidized stainless steel foil showed the presence of chromium oxide and iron oxide at the surface. *n*-Hexane (Fluka, 99.7%) was further purified by freeze-pump-thaw cycles. Ultrahigh purity oxygen (Praxair, 99.99%) and Ar (Air gas, 99.999%) were used as-supplied.

After the cleaning procedure, the sample was enclosed in the HP cell and exposed to a mixture of *n*-hexane (7.3 Torr) and argon. Argon was used as a make-up gas to keep the total pressure constant, 760 Torr. Then the Mo foil was resistively heated to a reaction temperature. The HP cell and the recirculation loop were kept at room temperature during the catalytic reaction test. The reaction was usually tested for 90–200 min, and the reaction products were analyzed using an online gas chromatograph (GC) (HP 5890A) every 10 min. Total conversion was kept low (less than 3%) in order to minimize secondary reactions that could occur in a batch reactor. Turnover number (TON, molecules/site) was calculated from the accumulated product amount with an assumption of 1×10^{15} surface sites per cm^2 . At the end of the reaction studies, the reaction mixture was pumped out at a catalyst temperature of 373 K. The HP cell was opened and an AES was immediately recorded. X-ray photoelectron spectra were collected, ex situ, using a Perkin Elmer 5000 spectrometer.

3. Results and discussion

3.1. *n*-Hexane reactions over MoO₂

Reaction pathways observed in the *n*-hexane reaction over MoO₂ include catalytic cracking, dehydrogenation and aromatization. The catalytic cracking products were C₁ (methane), C₂ (ethane and ethylene), C₃ (propane and propylene), C₄ (butanes and butenes) and C₅ (pentanes and pentenes). Dehydrogenation products were hexenes and hexadienes, whereas the aromatization product was benzene. In contrast to the studies of powder or supported catalysts, which showed a high isomerization activity [15–19], the MoO₂ model catalyst did not exhibit isomerization activity.

Fig. 2 shows the reaction accumulation curves of catalytic cracking, dehydrogenation and aromatization of *n*-hexane conversion over MoO₂ at 873 K. Dehydrogenation and aromatization reactions show deactivation within the reaction time, whereas catalytic cracking does not. The catalyst indicated no noticeable

deactivation for the cracking pathway even after 5 h of use (e.g., see Fig. 5a). Total conversion at 873 K was about 1.0% after 90 min of reaction time. At the catalyst temperature of 873 K, the selectivities for catalytic cracking (to C₁, C₂, C₃, C₄ and C₅), dehydrogenation (to hexenes), and aromatization (to benzene) were 16, 70 and 14%, respectively, after 90 min.

Fig. 3 shows the C₁ to C₅ cracking selectivity for *n*-hexane reaction using MoO₂ foil at 873 K. In the catalytic cracking reaction over MoO₂, the product distribution shows high selectivity toward alkenes and low selectivity toward alkanes. The selectivity for ethylene, propylene, butanes and pentenes was 29, 35, 19 and 5 mol%, respectively. The selectivity for methane, ethane and propane was 7, 4 and 1 mol%, respectively.

The apparent activation energy for the *n*-hexane cracking reaction over MoO₂ was calculated from the initial TOFs (calculated from first 20 min data), measured in the temperature range 830–913 K. The initial turnover rate for catalytic cracking reaction was in the range 0.0076–0.154 molecules/(site/s) under the reaction conditions. The temperature dependence of the

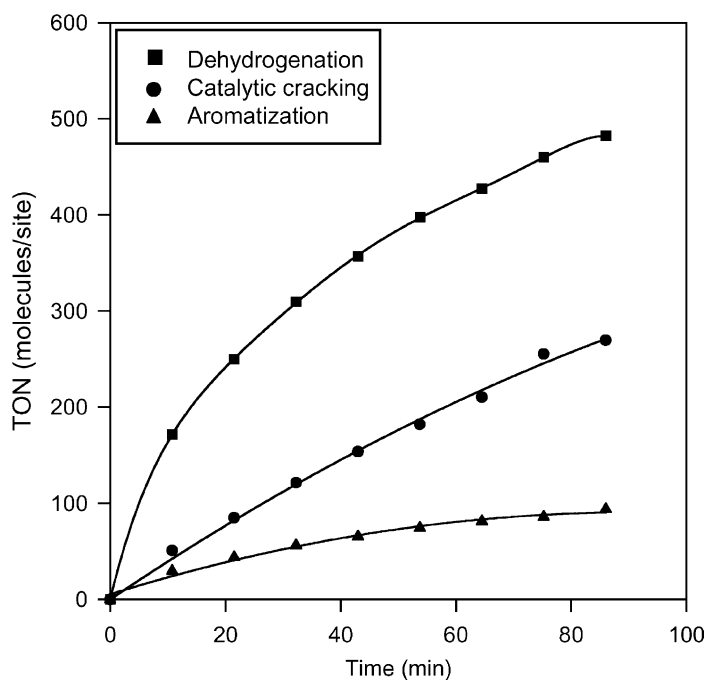


Fig. 2. Product accumulation plot for 7.3 Torr *n*-hexane reactions over MoO₂ foil at 873 K. Dehydrogenation and aromatization reactions showed deactivation, whereas catalytic cracking did not show any significant deactivation.

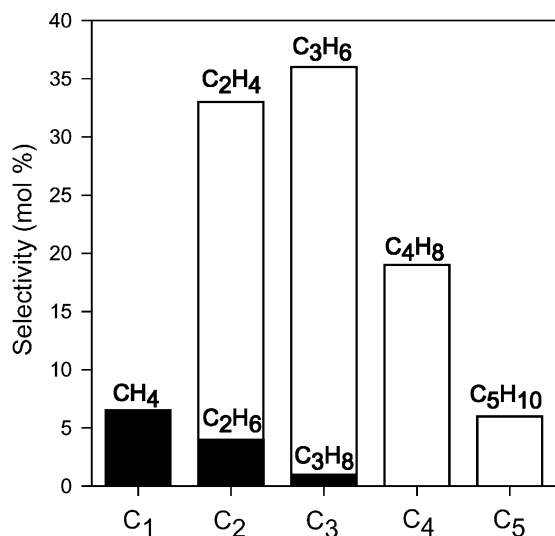


Fig. 3. Cracking products for *n*-hexane (7.3 Torr) reactions over MoO₂ at 873 K after 90 min.

n-hexane catalytic cracking reaction rates using MoO₂ foil is presented in an Arrhenius plot of \ln TOF vs. $1/T$ (Fig. 4). The slope of this plot gave an apparent activation energy of ~ 60 kcal/mol.

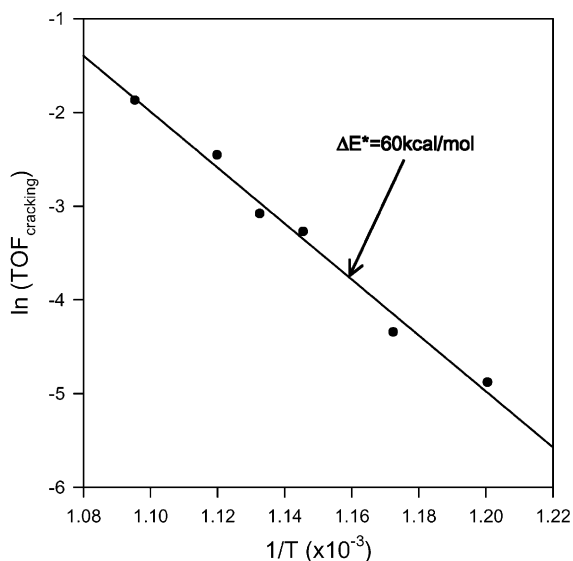


Fig. 4. Arrhenius plot— \ln (TOF_{cracking}) vs. $1/T$ —for catalytic cracking reactions of 7.3 Torr *n*-hexane over MoO₂. An apparent activation energy was calculated at ~ 60 kcal/mol from the slope.

3.2. Evidences for catalytic cracking of *n*-hexane over MoO₂

Even though the activation energy obtained is not much different from the typical activation energy for thermal cracking [20], we believe that the main reaction pathways over MoO₂ are catalytic because the cracking reactivity and selectivity varied when MoO₂ was replaced with an inert material. Fig. 5 compares the accumulation curves of 7.3 Torr *n*-hexane cracking products over the MoO₂ film and an oxidized stainless steel foil at 873 K. The oxide film on the stainless steel surface is known to be catalytically inert [6]. In the case of the oxidized stainless steel foil, the cracking rate started to decrease after 30 min and the amount of accumulated cracking products leveled off after 60 min of reaction time (Fig. 5b). In contrast, the cracking accumulation curve over MoO₂ showed no significant deactivation even after 5 h (Fig. 5a). The cracking product selectivity over oxidized stainless steel foil was also quite different from that over MoO₂ (insets to Fig. 5). MoO₂ foil produced mostly ethylene, propylene and butenes, while oxidized stainless steel preferentially produced butenes (57 mol%). These data indicated that the cracking reactions over MoO₂ are catalytic processes, not purely thermal processes.

When the *n*-hexane cracking reaction was attempted without oxidation of a polycrystalline Mo foil, the reaction rate was greatly reduced. After reaction, AES found that the Mo foil surface was covered with mostly carbon. The enhanced cracking after oxidation of the MoO₂ film suggested a catalytic role of the MoO₂ layer. Oxygen species of the oxide surface appeared to be involved in hydrogen abstraction from hydrocarbon, as shown in (Eq. (1)) [21,22].

3.3. Molybdenum oxycarbide as a catalytically active phase

AES was taken before and after each catalytic test to analyze any changes in the surface composition. The bottom spectrum in Fig. 6a presents a typical Auger spectrum for MoO₂ before an experiment, showing Mo MNN Auger transitions at 151, 163, 190 and 222 eV and an O KLL Auger transition at 510 eV. The 222 eV Auger transition shows a splitting characteristic of the MoO₂ phase [14]. Analysis of the sample

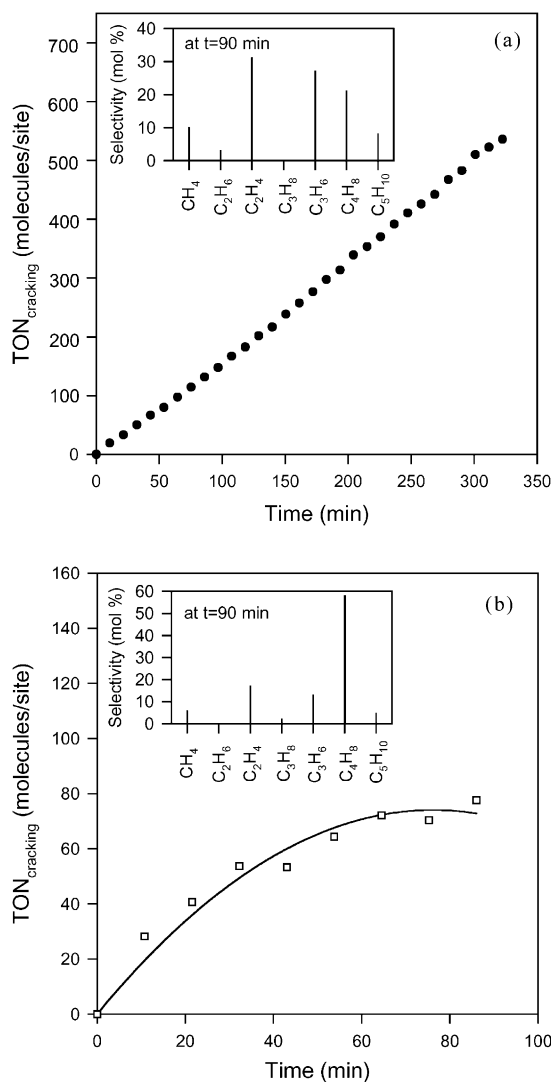


Fig. 5. Accumulation curves for catalytic cracking of 7.3 Torr *n*-hexane over (a) MoO₂ and (b) an oxidized stainless steel foil at 873 K. In both cases, the surface area was $\sim 1 \text{ cm}^2$. Inset shows the cracking selectivity after 90 min.

following a reaction of 7.3 Torr *n*-hexane catalyzed by MoO₂ after 90 min reveals the presence of carbon at 273 eV as well as oxygen on the surface (Fig. 6a, middle). The Mo Auger transition at 222 eV does not show the shoulder characteristic of the MoO₂ phase any longer, which suggests that the catalyst phase has been modified during the catalytic reaction. Some of the carbon can be readily removed as CO by flashing

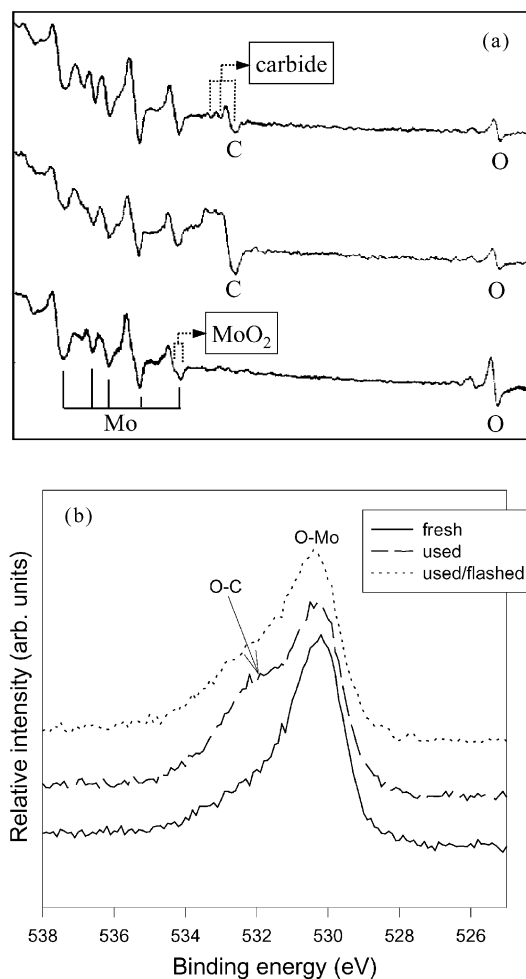


Fig. 6. (a) AES spectra of the MoO₂ catalyst before reaction (bottom), after reaction (middle), and after heating to 1193 K (top). (b) XPS spectra of O 1s, obtained ex situ, of a fresh MoO₂ catalyst (bottom), a catalyst used for cracking reaction at 873 K (middle), and a catalyst used for cracking reactions at 873 K followed by heating to 1193 K (top). Spectra are offset for comparison.

to 1193 K. After flashing, an undulating feature of the carbon peak appeared (Fig. 6a, top spectrum), indicating the presence of carbidic carbon species as well as oxygen species at the film surface.

Fig. 6b compares the O 1s XPS spectra of three different samples: freshly oxidized MoO₂ catalyst (bottom), catalyst surface used for *n*-hexane reactions at 873 K (middle) and catalyst surface flashed to 1193 K after reaction at 873 K (top). Noticeable

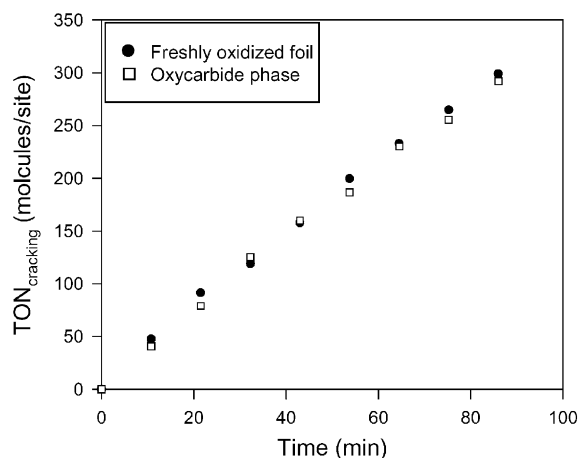


Fig. 7. Product accumulation curve for *n*-hexane cracking reactions at 873 K. Filled circles are the data for the clean MoO₂ surface, and open circles for the restart reaction with the used catalyst.

difference in O 1s spectra was observed between fresh and used surfaces. The fresh surface showed one peak located at 530.2 eV, which was attributed to oxygen bonded to Mo metal. The O 1s photoelectron spectra of the two other sample surfaces show a second 1s peak at 532.2 eV which was assigned as oxygen species bound to carbon [13,17,19,23]. The results from Auger and XPS spectra implied that the surface species formed during the catalytic cracking reactions are a molybdenum oxycarbide (MoO_xC_y) phase.

Fig. 7 compares the *n*-hexane cracking activities of two catalysts: clean MoO₂ phase and the oxycarbide phase produced after reactions of MoO₂ with *n*-hexane. The cracking activity of the oxycarbide catalyst was the same as that of the MoO₂ catalyst from the beginning on the initially clean sample. This result implied that the oxycarbide phase is formed at a very early stage of the reaction.

4. Conclusions

We have shown that MoO₂ film formed by Mo oxidation can catalytically crack *n*-hexane, selectively producing small olefins in the absence of hydrogen or steam. The major products were ethylene, propylene and butenes. The apparent activation energy for the catalytic cracking was ~60 kcal/mol. The active

surface phase for catalytic cracking appeared to be MoO_xC_y which was formed by initial reactions of MoO₂ with *n*-hexane and was highly resistant to deactivation.

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