

Activity and stability studies of MoO₂ catalyst for the partial oxidation of gasoline

Oscar G. Marin Flores, Su Ha*

Washington State University, Department of Chemical Engineering, P.O. Box 642710, Pullman, WA, 99164-2710, USA

ARTICLE INFO

Article history:

Received 25 July 2008

Received in revised form 25 September 2008

Accepted 30 September 2008

Available online 11 October 2008

Keywords:

Isooctane

Partial oxidation

Molybdenum dioxide

Mars–van Krevelen

ABSTRACT

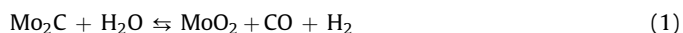
The present investigation is focused on the performance of molybdenum dioxide (MoO₂) as a catalyst for the partial oxidation of isooctane. Metallic character and high oxygen mobility exhibited by this oxide appear to enhance its catalytic activity, which can be explained in terms of the Mars–van Krevelen mechanism. An oxygen-to-carbon ratio (O/C) of 0.72 seems to stabilize the catalytic performance, which could reach H₂ yields of 78% and carbon conversions of 100%, at 700 °C and 1 atm, after 20 h on stream. In addition, the catalyst was tested for sulfur tolerance using thiophene as model sulfur compound. Our findings indicate that the catalytic activity is barely affected even at sulfur concentrations as large as 500 ppm, after 7 h on stream. Finally, the catalyst performance was compared to that of a nickel catalyst using premium gasoline as fuel. MoO₂ displayed a stable performance whereas the Ni catalyst deactivated due to coke formation.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Nickel (Ni) and noble metals are traditionally used as catalysts for hydrocarbon reforming processes, which suggest that the metallic characteristic may play an important role in the mechanism involved in such processes. Molybdenum dioxide (MoO₂) exhibits an unusual metallic electrical conductivity, which is not a common characteristic of metal oxides. This is attributed to its relatively high density of states observed in the valence band energy region. The existence of these free electrons is considered to enhance the catalytic activity of Mo⁴⁺ in MoO₂, unlike Mo⁶⁺ in MoO₃, where all the valence electrons of the metal are bonded to neighboring oxygen atoms [1]. The catalytic activity of MoO₂ for the isomerization of hydrocarbons has been interpreted in terms of a bifunctional (metallic–acidic) mechanism. According to this mechanism, the metallic sites existing on the dioxide are able to dissociate hydrogen and produce active hydrogen atoms, which bond with surface oxygen atoms to form Bronsted Mo–OH acidic functional groups [2].

Previous investigations [3–5] have reported that the formation of MoO₂ significantly affects the stability of molybdenum carbide (Mo₂C) for reforming processes. Thus, under strong oxidizing environments, such as a large steam to carbon ratio, the carbide phase transforms into dioxide according to the following expression:



Studies suggest that this phase transformation deactivates the carbide system. However, the experimental evidence obtained from these works was based only on the analysis of the bulk catalytic properties without investigating their surface compositions. For this reason, we strongly believe that the conclusions about the negative influence of the dioxide phase on the reforming reactions must be carefully examined prior to wide acceptance. Conversely, we have recently reported the presence of MoO₂ on the surface of active Mo₂C catalysts during the steam reforming of isooctane [6], which led us to conclude that the dioxide phase may play an important role in the steam reforming of liquid hydrocarbons.

An additional reforming process, partial oxidation, has been extensively studied employing transition metal oxides as catalysts [7–9]. Partial oxidation is a more cost effective and simpler reforming process, compared to steam reforming, as it requires no additional water. Even with these incentives, few investigations have been devoted to the partial oxidation of liquid hydrocarbons. Furthermore, no investigation has reported the use of MoO₂ for such systems. The lack of information regarding these topics has led us to focus our interest in the study of the MoO₂ performance for the partial oxidation of liquid hydrocarbons.

The objective of the present investigation is to understand how the various operating conditions affect the partial oxidation of gasoline over bulk MoO₂ catalyst. To simplify this study, isooctane (2,2,4-trimethylpentane) was used to model gasoline for our catalytic activity studies. The section 1 of this paper characterizes the physical properties of bulk MoO₂. The body of the present work combines thermodynamic analysis and experimental results to investigate the mechanistic process of MoO₂ toward the isooctane

* Corresponding author. Tel.: +1 509 335 3786.

E-mail address: suha@wsu.edu (S. Ha).

reforming reaction. Finally, the catalyst was tested to understand how the presence of sulfur compounds and coking precursors would influence their reforming activity and long-term stability.

2. Experimental

Experiments were performed in a 12 mm fixed-bed tubular (quartz) reactor. The liquid feed, consisting of either isoctane or premium gasoline, was vaporized at 200 °C and 350 °C, respectively. The vapor obtained was mixed along with air, employed as oxygen source for the partial oxidation, using a silicon carbide bed to enhance the mixing. Calibrated syringe pumps and mass flow controllers were employed to control the flow rates. The exit stream was cooled down to 5 °C to separate water, non-reacted fuel, and other possible condensable compounds from the off-gas. The dry gas product was analyzed using an SRI chromatograph to monitor H₂, CO, CO₂, and CH₄ concentrations. The GC columns used for this purpose were Molecular Sieve 13X and HyesepD. The carrier gas was a mixture of 10% hydrogen and 90% helium.

The MoO₂ catalyst was purchased from Alfa Aesar. The catalyst sample was supported by a quartz wool plug placed inside the reactor. Spent samples were analyzed by powder X-ray diffraction (XRD) on a Philips diffractometer that employs Co K α radiation with an iron filter. XPS spectra were obtained with an AXIS-165 manufactured by Kratos Analytical Inc. using an achromatic MgK α (1254 eV) X-ray radiation with a power of 210 W. The binding energy was calibrated against the 4f_{7/2} line of clean Au to be at 84 eV. A pass energy (PE) of 80 eV was used to acquire all survey scans. At this PE the energy resolution was about 1.2 eV. The high-resolution spectra of Mo3d were acquired at PE of 40 eV with an energy resolution of about 0.8 eV. The base pressure of the XPS analyzing chamber was 1.0 \times 10⁻⁹ Torr. Before performing any XPS analysis, the powdered samples were pressed into pure indium (99.99% pure) in order to minimize the effects of charging. The curve fitting of high-resolution spectra was performed using a least-squares fitting program. Mo3d spin-orbit pair intervals were set at 3.13 eV, and an area ratio of 0.666 was used. To prevent further oxidation between the end of the experiment and the XPS or XRD analysis, the samples were cooled down to room temperature inside the reactor under helium. BET surface area measurements were performed using a Coulter SA-3100 automated characterization machine. The data was analyzed in terms of hydrogen yield and carbon conversion, which were calculated as follows:

For isoctane as fuel:

$$H_2 \text{ yield} = \frac{2 \times n_{H_2}^{out}}{18 \times n_{C_8H_{18}}^{in}}$$

$$C \text{ conversion} = \frac{n_{CH_4}^{out} + n_{CO}^{out} + n_{CO_2}^{out}}{8 \times n_{C_8H_{18}}^{in}}$$

For premium gasoline (C₇H₁₃) as fuel:

$$H_2 \text{ yield} = \frac{2 \times n_{H_2}^{out}}{13 \times n_{Gas}^{in}}$$

$$C \text{ conversion} = \frac{n_{CH_4}^{out} + n_{CO}^{out} + n_{CO_2}^{out}}{7 \times n_{Gas}^{in}}$$

3. Results and discussion

3.1. Characterization

XRD analysis was employed to examine the bulk structure of the dioxide. MoO₂ displays a distorted rutile structure with

monoclinic symmetry, whose unit cell parameters were found to be: $a = 5.59 \text{ \AA}$, $b = 4.84 \text{ \AA}$, $c = 5.62 \text{ \AA}$, and $\beta = 121.23^\circ$. These values agree with those found in previous studies [10].

The surface analysis involved two different techniques: BET and XPS measurements. BET surface area measurements yielded a surface area of barely 4.5 m²/g. XPS analysis was used to determine the composition of the oxide surface. The results indicated that the most abundant elements on the oxide surface were Mo (23%), C (29%), and O (48%). Further analysis was performed to obtain the spectrum of each element. These results can be seen in Fig. 1.

The catalyst surface appears to be a mixture of three different molybdenum oxide phases. The Mo3d spectrum (Fig. 1(A)) indicates that Mo hexavalent (232.73 eV, 53%) shows the highest concentration, followed by Mo pentavalent (231.16 eV, 29%), and finally Mo tetravalent (229.46 eV, 18%). The de-convolution of the

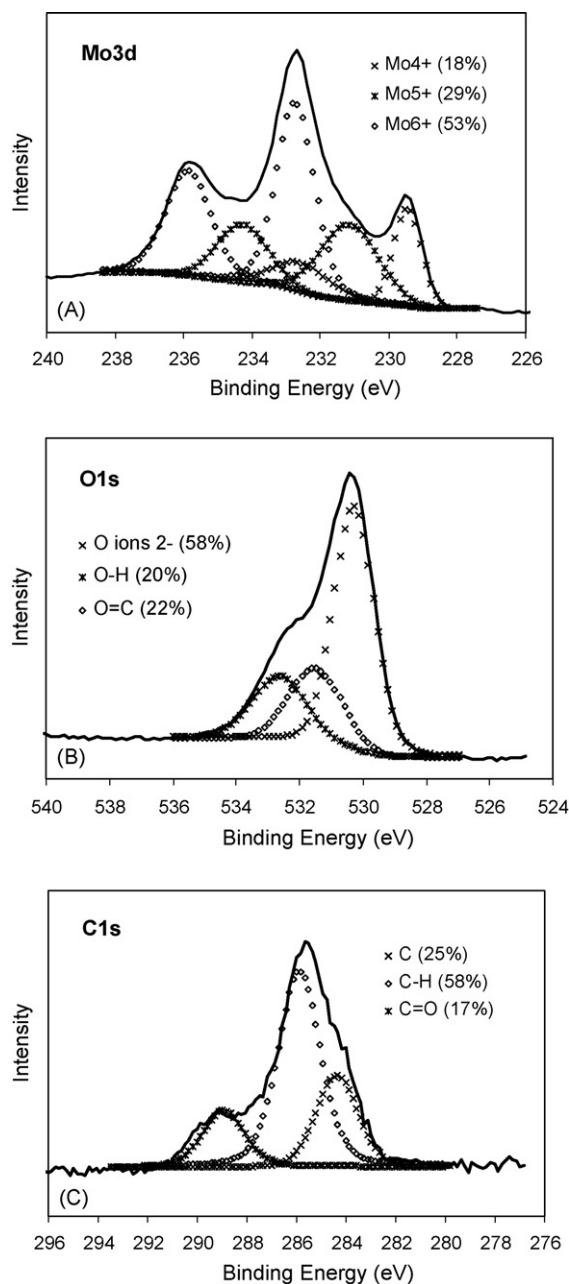


Fig. 1. XPS spectra of fresh MoO₂: (A) the Mo3d spectrum, (B) the O1s spectrum and (C) the C1s spectrum.

Download English Version:

<https://daneshyari.com/en/article/43161>

Download Persian Version:

<https://daneshyari.com/article/43161>

[Daneshyari.com](https://daneshyari.com)