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STUDIES ON THE REACTION OF OXYGEN WITH PREOXIDISED BISMUTH MOLYBDATE CATALYST

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Abstract

Transient techniques of gas adsorption chromatography (GAC) and temperature programmed desorption (TPD) were used to study the interaction of oxygen species with preoxidised bismuth molybdate supported silica catalyst. Results showed (i) that the adsorption of oxygen atom at low adsorption temperature may results in the atom to be physically adsorbed on the surface of the activated catalyst, consistent with an activation energy of 28 kJ mol^{-1} obtained from low temperature TPD, and (ii) that the amount of roughly 3.7 % of the total oxygen content has been desorbed in the coverage of more than a monolayer of chemisorbed oxygen in the TPD from ambient to 1173 K of the activated catalyst.

Abstrak

Teknik alihan iaitu kromatografi penjerapan gas (GAC) dan nyahjerapan terprogram suhu telah digunakan untuk mengkaji interaksi spesis oksigen dengan mangkin pra-teroksida bismut molibdena tersokong silika. Keputusan kajian menunjukkan (i) jerapan atom oksigen pada suhu rendah jerapan menyebabkan atom tersebut cuma terjerap secara fizikal pada permukaan mangkin teraktif, konsisten dengan nilai tenaga pengaktifan 28 kJ mol^{-1} diperolehi dari suhu rendah TPD, dan (ii) amaun sekitar 3.7 % dari keseluruhan kandungan oksigen telah berjaya dinyahjerap dalam liputan lebih dari ekalapis oksigen tererapkimia di TPD dari ambien hingga 1173 K pada mangkin teraktif.

Introduction

Selective conversion of unsaturated hydrocarbons to more valuable chemicals is an important process in the chemical industry. A number of intermediates such as acrolein, acrylic acid, acrylonitrile, and propylene oxide can be derived from propylene [1,2]. Catalysts that are selective for this transformation are of solid-state oxide systems including mixed iron-antimony oxide [2], molybdenum-antimony oxide [3], and bismuth-molybdenum mixed oxide [4,5]. These owing to the catalyst system itself that can store oxygen reversibly. Selective oxidation of the reactant can take place as a result of the oxygen stored in the catalyst. The abstraction of the oxidant resulted of the catalysts being reduced and the re-oxidation of the reduced sample is later taken over to restore the catalyst to its initial state (Mars - van Krevelen mechanism [6]). According to this mechanism, the oxidising agent is presumably O^{2-} from the lattice.

Indeed, this is what was observed by Grasselli *et al.* [7,8]. They studied the oxidation and ammoxidation of propylene to acrolein and acrylonitrile. Their Raman studies revealed that lattice oxygen is involved in the α-hydrogen abstraction and oxygen insertion into the intermediates. In another study by Keulks *et al.* [9], they used isotopic oxygen in the gas phase in their attempt to study the reactivity of the lattice oxygen in bismuth molybdate (Bi_2O_3-MoO_3). In the oxidation of propylene in the presence of ^{18}O, they found only 2 – 2½% of the oxygen atoms in the acrolein and carbon dioxide were isotopically labeled. The lacks of extensive incorporation of oxygen-18 into the reaction products suggest the involvement of lattice oxide ion in the surface reaction with participitation of many subsurface layers of the catalyst. Wragg *et al.* [10] also reported similar results using ^{18}O tracer over a bismuth molybdate catalyst. In a recent study by Moro-oka *et al.* [11], they used 99.1% $^{18}O_2$ tracer on a series of multicomponent bismuth molybdate catalysts. Their results indicated of the involvement of lattice oxide ion in the oxidation of propylene.

In this paper, experiments were carried out to obtain the nature of the selective oxidant present at the surface of the Bi_2MoO_6/SiO_2 oxide catalyst. The amounts of chemisorbed molecular oxygen and of lattice oxygen available along with their kinetics of availability at the surface for partial oxidation may also be determined. This was done by performing isothermal adsorption of oxygen at low temperature and temperature programmed desorption of oxygen of the preoxidised sample.

Experimental

Sample preparation

The Bi_2MoO_6/SiO_2 catalyst was prepared by an incipient wetness impregnation method [12].

Sample pretreatment

The prepared sample was heated in helium stream of 25 $mLmin^{-1}$ at a pressure of 1 bar. The heat treatment in He stream was carried out in a stainless steel tube. The temperature was raised to 773 K at 5 $Kmin^{-1}$ and was held at that point for 1 hour before cooling down to ambient. This will decompose all precursor molecules in/on the catalyst. The He stream was later switched to an inert oxygen stream (25 $mLmin^{-1}$, 1 bar) in which the sample was treated in that environment at 673 K for 1 hour.

Characterisation of catalyst

The catalyst was characterized by the following analytical techniques. BET surface area was determined by using N_2 adsorption at 77 K, and the value obtained is 153 m^2g^{-1}. X-ray diffraction patterns were collected using Scintag XDS2000 (Scintag Inc., Sunnyvale, U.S.A.) equipped with CuK_α radiation as an X-ray source in the 2θ range 10 – 70°. TEM images were collected with Philips EM 400 operating at 120 KeV. Gas Adsorption Chromatography (GAC) was done by dosing nitrogen (10% N_2 in He) on the catalyst at 77 K. After about 10 minutes, the N_2 flow was switched to He flow and the nitrogen response on the mass spectrometer is monitored until it returns to the baseline value. While for Temperature Programmed Desorption (TPD), the oxygen was dosed into the cleaned catalyst surface. The active gas was then removed from the gas phase and replaced with helium and temperature was increased. As the temperature of the catalyst was increased at a known and constant rate, the surface species desorbs into the gas phase reaching a maximum in the rate of desorption at a characteristic temperature.

Results and Discussion

Isothermal oxygen adsorption over preoxidised Bi_2MoO_6/SiO_2

The adsorption isotherm of oxygen on preoxidised Bi_2MoO_6/SiO_2 at 195 K and its isothermal heat of adsorption were obtained by gas adsorption chromatography (GAC) [13].

A line shape of the detector response (mass spectrometer detector) during the oxygen gas adsorption chromatographic experiment is shown in Figure 1. A flow of helium is passed over the typical 0.2 g catalyst at 195 K, and after 2 minutes it was switched at point S_o to a O_2/He flow (10% O_2 in He, 1 bar). The time from S_o to t_o is the time to sweep out the dead volume of the system and at point t_1, the O_2 is seen to break through on the mass spectrometer. At the point S_1 the O_2/He flow was switched back to helium flow. The time difference $S_1 – t_3$ is the time to sweep out the dead volume of the system. Each point of the falling trailing edge of the eluted curve (i.e. the time difference $t_c – t_4$) is proportional to the differential of the adsorption isotherm i.e. to the differential of the number of moles adsorbed with respect to the gas phase concentration [14]. One can therefore do a stripwise integration i.e. horizontal integration of the eluted line shape, the area of the strip being proportional to the number of moles O_2 adsorbed while the height of each strip is proportional to the gas phase concentration O_2 to produce the isotherm shown in Figure 2.

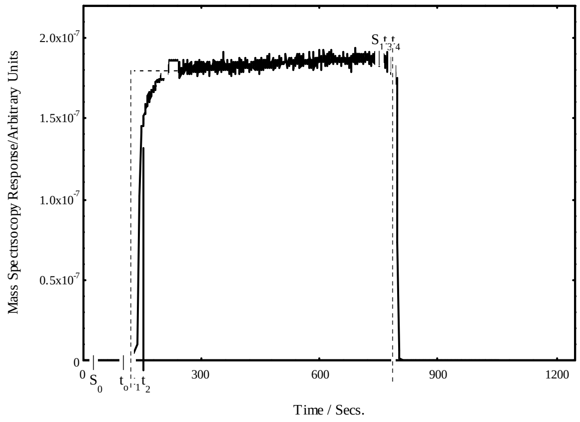

Figure 1. Adsorption isotherm of oxygen over Bi_2MoO_6/SiO_2 oxide catalyst at 195 K.

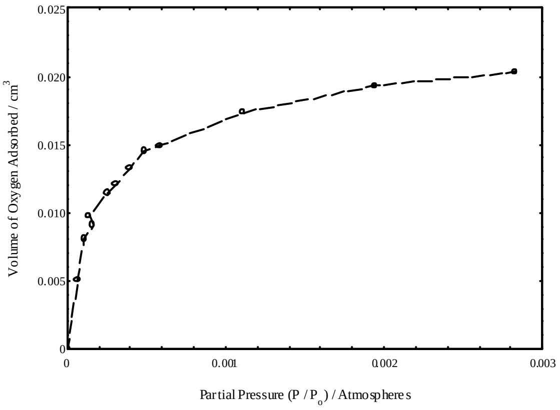

Figure 2. Low temperature oxygen chemisorption of Bi_2MoO_6/SiO_2 oxide catalyst at 195 K.

The curve is a characteristic of Langmuir adsorption isotherm. The adsorption of O_2 on the surface of Bi_2MoO_6/SiO_2 catalyst at equilibrium can be represented as below (Equation 1).

$$O_2\,(g) \quad + \quad Bi_2MoO_6\,(\text{surface}) \quad \underset{k_d}{\overset{k_a}{\rightleftharpoons}} \quad O_2{-}Bi_2MoO_6\,(\text{surface}) \qquad 1$$

where O_2 is the gaseous adsorbate, Bi_2MoO_6 is a vacant site on the surface, O_2-Bi_2MoO_6 represents an adsorbed molecule of O_2 or an occupied site on the surface, and k_a and k_d are rate constants for adsorption and desorption, respectively. The fractional coverage (θ) of the Bi_2MoO_6/SiO_2 by adsorbed O_2 is given by Equation 2.

$$\theta = \frac{K_p}{1 + K_p} \quad \text{or} \quad \theta = \frac{K[O_2]}{1 + K[O_2]} \qquad 2$$

where $K = k_a/k_d$, p is the partial pressure/atm and $[O_2]$ is concentration of O_2/mol. If $\theta = V/V_m$ where V_m is volume corresponding to monolayer coverage, equation 2 can be re-written as Equation 3 as shown below.

$$\frac{[O_2]}{V} = \frac{[O_2]}{V_m} + \frac{1}{KV_m} \qquad 3$$

The plot of $[O_2]/V$ against $[O_2]$ gives a straight line of slope $1/V_m$ and intercept $1/KV_m$ as shown in Figure 3. The least square line has an intercept at $[O_2] = 0$, $7.93 \times 10^{-7}$and a slope, $1/V_m$ of 0.45. So the volume of monolayer V_m can be obtained from the slope as 2.22 cm^3. This corresponds to a coverage of 3.6×10^{13} molecule cm^{-2} or an area of 28 $Å^2$ per O_2 molecule. This large value of area must be due to the adsorption of gaseous oxygen occurring on the catalyst specific defects.

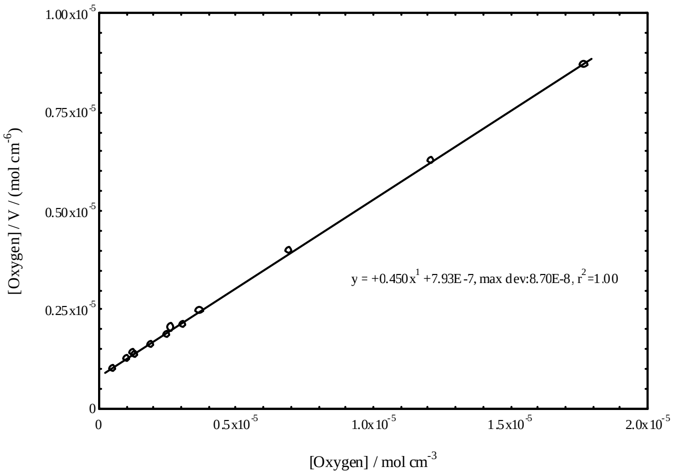

Figure 3. Linearisation of the eluted curve of the adsorption isotherm of oxygen at 195 K

The normally assumed value of the desorption pre-exponential (A_d) is 10^{13} s^{-1} and since the adsorption of O_2 species is probably non-activated, the adsorption A-factor will equal the standard collision number. If the units of the adsorption A-factor are in $cm^3mol^{-1}s^{-1}$ the standard collision number has a value of 10^{13} $cm^3mol^{-1}s^{-1}$. Therefore $A_a \approx A_d$ in volume and the value of enthalpy of adsorption can be gathered from Equation 4.

$$K = \exp(\Delta H / RT) \qquad 4$$

$$\text{so that,} \quad \Delta H = RT \ln K$$
$$= 8.314 \times 195 \times 17.85$$
$$= 29 \text{ kJ mol}^{-1}$$

This value of enthalpy of adsorption of O_2 species on the catalyst is within the range of physisorption.

The amount of oxygen adsorbed in equilibrium with 10% O_2 in the gas phase can also be determined by measurement of the frontal uptake (Figure 1). Its value is 8.50 x 10^{-5} mol or 5.1 x 10^{19} molecule g^{-1} on 0.2 g of catalyst corresponding to a coverage of 3.3 x 10^{13} molecule cm^{-2}. This value is in good agreement with that obtained above by linearisation of the Langmuir isotherm.

Temperature programmed desorption of oxygen from fresh oxidised Bi_2MoO_6/SiO_2.

Adsorption temperature 77K

The pretreated catalyst was cooled to 77 K under the oxygen stream and left at that temperature for 30 minutes. The oxygen flow was then switched to a helium flow (25 mLmin^{-1}, 1 bar) and temperature was raised to 298 K (5 Kmin^{-1}), following oxygen (m/z = 32) on the mass spectrometer. The oxygen desorption spectrum obtained is shown in Figure 4. Only one desorption peak is observed with a distinct peak maximum at 101 K. The desorption activation energy was obtained by solution of Redhead equation (Equation 5).

$$\frac{E_d}{RT_m^{\,2}} = \frac{A}{\beta} \exp \frac{E_d}{RT_m} \qquad 5$$

Where E_d is the desorption activation energy (kJmol^{-1}), A is the desorption A-factor (10^{13} s^{-1}, assumed), R is the gas constant (J $K^{-1}mol^{-1}$), β is the heating rate (Ks^{-1}) and T_m (K) is the temperature of the peak maximum.

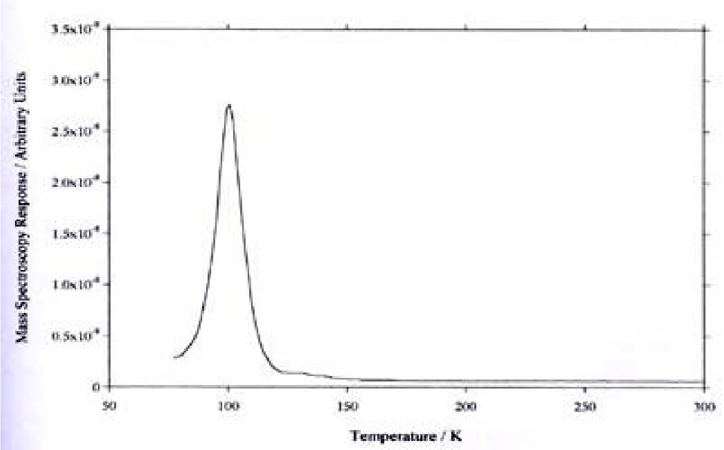

Figure 4. TPD of oxygen from 77 to 298 K from a preoxidised Bi_2MoO_6/SiO_2 catalyst after exposure to O_2 at 77 K

The activation energy obtained for the peak maximum at 101 K is 28 kJmol^{-1}. This is the upper limit of physisorbed energies and could signify a specific adsorption site. Significantly, no other chemisorbed or lattice oxygen is observed here. The calculation of the area under the peak gives the number of oxygen species desorbed while ramping the temperature up from 77 to 298 K as 5.0 x 10^{19} molecule g^{-1} (Table 1). This is exactly the same amount that was obtained when the oxygen was adsorbed at low temperature (195 K), which was 5.12 x 10^{19} molecule g^{-1}. This confirms that the oxygen molecules when adsorbed at low temperature are apparently only physically adsorbed on the fully oxidised Bi-Mo/SiO_2 catalyst surface, possibly at specific defect sites.

Table 1. Amounts of oxygen desorbed on temperature programmed desorption over fresh Bi_2MoO_6/SiO_2 oxide. Adsorption temperature 77 K.

Species	Peak maximum temperature, T_m / K	Desorption activation energy, E_d / kJ mol^{-1}	Amount evolved / molecule g^{-1}
O_2	101	28.0	5.0 x 10^{19}

Adsorption temperature 298 K

A second temperature programmed desorption was carried out on a freshly oxidised Bi_2MoO_6/SiO_2 oxide catalyst having undergone pretreatment as described earlier. This new batch of catalyst was then cooled down to room temperature under oxygen stream and after some time later the oxygen flow was switched to a helium flow (25 mLmin^{-1}, 1 bar) and temperature programming from room temperature up to 1173 K (at a heating rate of 5 Kmin^{-1}) following the oxygen signal on the mass spectrometer. The experiment would detect the desorption of chemisorbed oxygen species, having desorption energies more than 80 kJ mol^{-1} and of lattice oxygen.

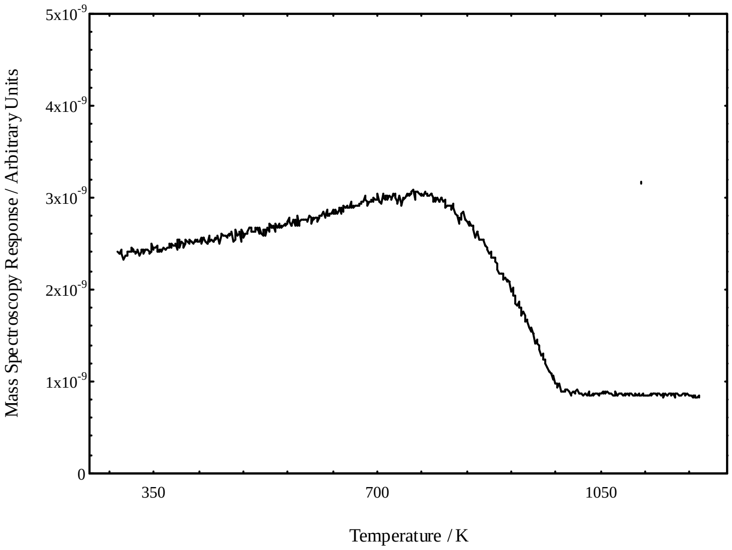

Figure 5. TPD of oxygen from room temperature to 1173 K from a preoxidised Bi_2MoO_6/SiO_2 catalyst after exposure to O_2 at room temperature

In this second oxygen desorption spectrum, shown in Figure 5, absolutely no significant peaks are observed here. However, a broad hump ranging from ambient going constantly up until at bout 800 K and at which point decreasing abruptly to 995 K, is observed. The amount of oxygen evolved was determined by calculating the area under the broad hump and is shown in Table 2. The value obtained is 7.0 x 10^{20} O_2 molecule g^{-1} or 1.4 x 10^{21} O atom g^{-1} which on a catalyst whose surface area is 153 m^2 g^{-1} would correspond to a coverage of 9.2 x 10^{14} atom cm^{-2}. Assuming there are approximately 10^{15} atoms cm^{-2} on the surface of Bi_2MoO_6/SiO_2 catalyst and that the proportion of oxygen ions on the surface is roughly stoichiometric, then the surface oxygen ion population is 6.7 x 10^{14} ions cm^{-2}. So, a coverage of 9.2 x 10^{14} atom cm^{-2} would correspond to more than a monolayer of chemisorbed oxygen. It is therefore lattice oxygen species, the amount desorbing being ~ 3.7 % of the total oxygen content of the catalyst (3.8 x 10^{22} O atom g^{-1}).

Table 2. Amounts of oxygen desorbed on temperature programmed desorption over fresh Bi_2MoO_6/SiO_2 oxide. Adsorption temperature 298 K.

Species	Peak maximum temperature / K	Desorption activation energy / kJ mol^1	Amount evolved / molecule g^{-1}
O_2	No clear maximum	Unobtainable	7.0 x 10^{20}

Conclusions

1. Oxygen atoms were found to be physically adsorbed on the surface of activated catalyst at low adsorption temperature and the adsorption may occur on the catalyst specific defect sites as shown by the large area per molecule of O_2 molecules covered.

2. Temperature programmed desorption from ambient to 1173 K of the activated catalyst removed 3.7 % of the total oxygen content from the catalyst.

3. The TPD result suggests that these oxygen molecules are probably the selective ones due to the fact that these oxygen species originating from the lattice of the catalyst.

Acknowledgements

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