

The influence of the calcination conditions on the catalytic activity of Bi_2MoO_6 in the selective oxidation of propylene to acrolein

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Abstract

The activity of Bi_2MoO_6 catalysts with small amounts of excess bismuth in the selective oxidation of propylene is strongly dependent on the calcination conditions. These catalysts show reasonable activities and high selectivities after calcination for a short period of time or after calcination at a moderate temperature. However, these catalysts become low active and low selective after calcination for a long period of time or after high temperature calcination. This difference is ascribed to relative low Bi/Mo-ratios at (parts of) the surface after calcination for a short period of time. The active surface becomes enriched with bismuth during prolonged calcination or reaction, resulting in a deactivation of the catalyst. The deactivated catalysts can be reactivated by reduction, this supports that the deactivation is due to a surface enrichment with bismuth. The dependence of the catalytic activity on the calcination conditions is likely one of the reasons behind the conflicting results on the activity of Bi_2MoO_6 found in the literature.

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1. Introduction

Bismuth molybdates form the base of commercial catalysts for propylene oxidation to acrolein, for propylene ammoxidation to acrylonitrile and for the oxidative dehydrogenation of butene to buta-di-ene [1,2]. The reactivity of the three model catalysts, Bi_2MoO_6 (γ -phase), $\text{Bi}_2\text{Mo}_2\text{O}_9$ (β -phase) and $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ (α -phase) in these reactions has been studied extensively in the literature [3–10]. Despite the large number of studies, there is still debate about the relative activity of these model catalysts. Most researchers agree that the $\text{Bi}_2\text{Mo}_2\text{O}_9$ phase is more active than the $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ phase [3–8]. However, the activity of Bi_2MoO_6 is disputed. Some researchers claim it to be the most active phase [3], some claim it to be much less active than the two other phases [4–6,10] and others find it to have an activity similar to $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ [7–9].

Several methods are used in the literature to synthesize the model catalysts: precipitation, solid-state reactions, spray-

drying and sol–gel methods. Within these methods, there are again a large number of variations like pH, concentrations and method of mixing of the bismuth and molybdenum solutions. Moreover, the conditions (temperature, duration and atmosphere) under which the bismuth molybdenum precursors are calcined to obtain the microcrystalline bismuth molybdenum oxide vary also greatly in different studies [11]. The influence of these different synthesis conditions on the activity has only rarely been mentioned in the literature [12].

The activity of Bi_2MoO_6 in the butene oxidation has been shown by Batist et al. to be strongly dependent on the conditions at which the catalyst has been prepared [13,14]. They explained this strong dependence partly by different oxygen coordination of molybdenum in the aqueous phase during the synthesis, and partly by the amount of bismuth at the surface of the catalyst. The second argument is supported by latter publications, which show that an excess of bismuth in Bi_2MoO_6 leads to a pronounced enrichment of the surface with bismuth. The result of this enrichment is a catalyst with a low activity and low selectivity [15–18]. This enrichment causes therefore the activity of the catalyst to be very sensitive to the

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ratio of bismuth and molybdenum in the catalyst, and thereby, also very sensitive to the preparation conditions.

We will focus on Bi_2MoO_6 in this article, since the activity of this catalyst is the most disputed issue in this context. During our previous work with bismuth molybdate catalysts in the propylene oxidation [19,20], we have observed that the activity of catalysts with a Bi/Mo-ratio close to 2 can be very sensitive to the calcination conditions. This dependence is, according to our knowledge, not reported previously and it could possibly explain some of the ambiguities on the activity of Bi_2MoO_6 catalysts found in the literature. This dependence will be the main issue of this paper, but we will start with a comparison of the activity of different samples with Bi/Mo around 2 prepared by co-precipitation and spray-drying. The results reported in this paper could also contribute to the general understanding of the catalytic activity of bismuth molybdate catalysts.

2. Experimental

2.1. Synthesis of catalysts

Co-precipitation and spray-drying were used to synthesize several batches of Bi_2MoO_6 catalyst. In the precipitation method, three solutions consisting of 0.49 M $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in 1.5 M HNO_3 , 0.035 M $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ in water and 4 M ammonia were mixed simultaneously using a peristaltic pump. The solutions were mixed simultaneously in order to assure the correct stoichiometric ratio between Bi and Mo during the mixing of the solutions. The pH of the mixture was kept between pH 3 and pH 6 by controlling the amount of ammonia during mixing. The final pH of the mixture was adjusted to 5 (P1, P4) or 5.5 (P2, P3, P5) and the mixture was filtrated after 2 h (P5), 6 h (P2, P3) or after 16 h (P1, P4).

In the spray-drying method, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ were dissolved in a nitric acid solution with a pH of lower than 1. The clear solution was spray-dried in a Büchi 190 spray-dryer with a 0.5 mm nozzle and a liquid feeding rate of 5 ml/min under a flow of heated air (700 l/min (STP) and 225 °C). Two samples were prepared by spray-drying, sample 1 had a Bi/Mo-ratio equal to 2.1 and sample 2 had a Bi/Mo-ratio equal to 2.0.

The amount of catalyst prepared per batch by precipitation and spray-drying was between 5 and 10 g. The samples were calcined in static air at temperatures between 350 and 550 °C for 10 h.

2.2. Characterization of catalysts

The calcined samples were characterized by X-ray diffraction using a Philips X'pert diffractometer equipped with Co-source (wavelength of Co $K\alpha$ radiation: $\lambda = 1.79 \text{ \AA}$). An obliquely cut silicon disc was used as a sample support when the amount of sample was small (less than 0.5 g). The error introduced in 2θ by using a silicon disc was corrected by calculating the displacement of the sample by comparing the measured diffractogram with JCPDS-ICDD reference 84–0787 for Bi_2MoO_6 [21].

The surface area of the samples was measured by using a Sorptomatic 1990 from ThermoQuest. The samples were out-gassed overnight at 180 °C. The surface area was calculated by using the two-parameter BET model for adsorption points between $p/p^0 = 0.05$ and 0.33.

The surface composition was determined by XPS. The XPS spectra were recorded using an ESCA spectrometer equipped with an Al anode ($h\nu = 187.850 \text{ eV}$).

The bulk composition of the samples was determined by ICP. For this purpose, 20 mg of Bi_2MoO_6 sample was dissolved in 50 ml of 7.5 M nitric acid and afterwards diluted to 500 ml. Two or three solutions were made for each sample. The standard solutions were made from $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$.

2.3. Activity measurements

The catalysts were tested in a vertical down-stream quartz tube reactor with an internal diameter of 4 mm. The quartz tube was heated by an iron tube placed in a Carbolite oven. The grain size of the catalyst was between 200 and 500 μm and 0.05–0.1 g of catalyst was used. The reactant gasses, consisting of 5% O_2 in N_2 and 5% C_3H_6 in N_2 , were added in a ratio 1:1. The total gas flow varied between 20 and 60 $\mu\text{mol/s}$. The conversion was kept between 3 and 15%, to enable calculation of reaction rates from the results. The composition of the outlet gasses was determined by using an on-line Shimadzu 17A gas chromatograph with a thermal conductivity detector. The mole fraction of propylene, acetaldehyde and acrolein in the effluent gas was determined every 13 min on Carbowax 20 M on Chromosorb G and Chromosorb 101 packed columns in series. The mole fraction of carbonmonoxide and carbondioxide was determined on Carboxen 1000 and Porapak N packed columns in series. The latter analysis was not performed continuously.

The reaction rate for the formation of acrolein was calculated by assuming differential operation of the reactor. The reaction rate, r_w , based on the catalyst mass was calculated as:

$$r_w = F_{\text{tot}} \times \frac{Y_{\text{C}_3\text{H}_4\text{O}}}{m} \quad (1)$$

in which F_{tot} is the total mol flow (which is assumed to be constant during reaction), $Y_{\text{C}_3\text{H}_4\text{O}}$ the mole fraction of acrolein in the outlet stream and m is the catalyst mass. The reaction rate, r_s , based on the catalyst surface area was calculated as:

$$r_s = F_{\text{tot}} \times \frac{Y_{\text{C}_3\text{H}_4\text{O}}}{m \text{ SA}} \quad (2)$$

in which SA is the surface area of the catalyst.

The selectivity for the formation of acrolein was calculated as:

$$S_{\text{C}_3\text{H}_4\text{O}} = \frac{Y_{\text{C}_3\text{H}_4\text{O}}}{Y_{\text{C}_3\text{H}_6} - Y_{\text{C}_3\text{H}_{6,0}}} \quad (3)$$

in which $Y_{\text{C}_3\text{H}_6}$ and $Y_{\text{C}_3\text{H}_{6,0}}$ are the mole fraction of propylene in the outlet stream and in the inlet stream. The selectivity for the formation of acetaldehyde, carbonmonoxide and carbondioxide was calculated like the selectivity for acrolein, with the mole

fraction of carbonmonoxide and carbondioxide divided by 3 and the mole fraction of acetaldehyde divided by 1.5.

The sum of the selectivities for acrolein, acetaldehyde, carbonmonoxide and carbondioxide formation was between 95 and 105%. Determination of the acrolein selectivity with Eq. (3) becomes too inaccurate at low conversion, in these cases the selectivity to acrolein was calculated by:

$$S_{C_3H_4O} = \frac{Y_{C_3H_4O}}{Y_{C_3H_4O} + (2/3) \times Y_{C_2H_4O} + (1/3) \times Y_{CO} + (1/3) \times Y_{CO_2}} \quad (4)$$

The selectivity was also calculated by Eq. (4) for experiments that lasted for several days.

3. Results

3.1. Comparison of catalysts with Bi/Mo around 2

We have prepared five samples by precipitation and two samples by spray-drying. The first sample made by spray-drying (SD1) was prepared with Bi/Mo = 2.1, the second sample (SD2) had a Bi/MO-ratio of 2. The spray-dried samples have been calcined at 550 °C, while the calcination temperature of the samples made by precipitation has been varied.

Tables 1 and 2 show the activity, at a reaction temperature of 375 °C, as a function of calcination temperature for the different samples. Table 1 shows the rate of acrolein formation based on the catalyst mass (r_w), Table 2 shows the activity based on the surface area (r_s). The samples are ordered after increasing activity. The results show that there is a large variation in the activity for the samples calcined at 550 °C. The activity of sample SD2 with Bi/Mo=2 is about 10 times higher than the activity of SD1 with Bi/Mo=2.1. The activity of the samples made by precipitation (P1–P5) varies from 0.1 to less than 10^{-4} $\mu\text{mol}/(\text{m}^2 \text{ s})$.

The most remarkable feature in the results, however, is that the activity of the low active samples depends strongly on the

Table 1
Reaction rate for acrolein formation at 375 °C based on catalyst mass, r_w ($\mu\text{mol}/(\text{g s})$), for different calcination temperatures

Temperature (°C)	P3	SD1	P1	P2	SD2	P4
Uncalcined	0.3		0.8			
350 °C	0.03					
450 °C	0.001		0.12	0.20		0.4
550 °C	0	0.007	0.005	0.07	0.08	0.11

Table 2
Reaction rate for acrolein formation at 375 °C based on catalyst surface area, r_s ($\mu\text{mol}/(\text{m}^2 \text{ s})$), for different calcination temperatures

Temperature (°C)	P3	SD1	P1	P2	SD2	P4
350	0.002					
450	0.0001		0.02	0.04		0.1
550	0	0.004	0.005	0.03	0.05	0.1

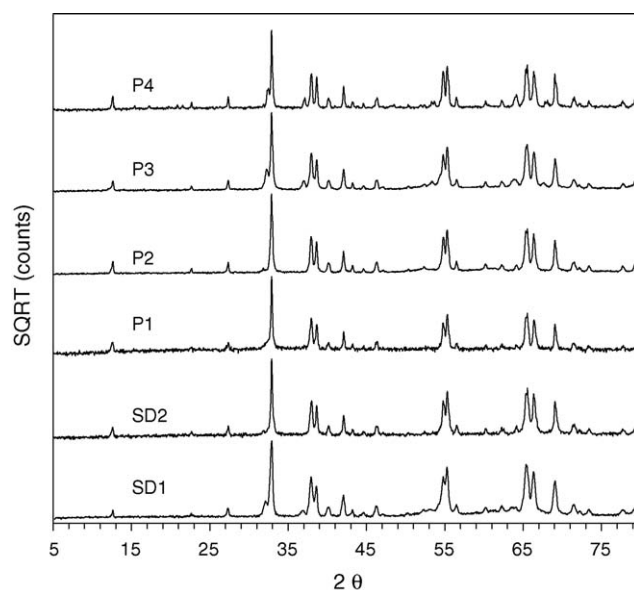


Fig. 1. XRD patterns of catalysts calcined at 550 °C.

calcination temperature. When the calcination temperature is decreased from 550 to 450 °C, the activity of sample P1 increases from 5×10^{-3} to 2×10^{-2} $\mu\text{mol}/(\text{m}^2 \text{ s})$, while the activity for sample P3 changes from no activity to 10^{-4} $\mu\text{mol}/(\text{m}^2 \text{ s})$. Calcination of this latter sample at 350 °C leads to an additional increase to 2×10^{-3} $\mu\text{mol}/(\text{m}^2 \text{ s})$. Such large increases in activity are not seen at all for samples P2 and P4.

Fig. 1 shows the XRD patterns for the samples after calcination at 550 °C, the intensity is displayed as the square-root of counts. All the diffraction peaks found for sample P2 and sample SD2 correspond to Bi_2MoO_6 (reference 84-0787). All the other samples have extra peaks around $2\theta = 32.5$ and 37.0° . However, sample P4 made by precipitation has a number of characteristics that are absent for the other samples: it has extra peaks at $2\theta = 15.4, 17.2, 20.9$ and 21.5° , the extra peak at 37.0° is sharper, it has a small double peak around 54° and the peak at 64° is more intense. All these characteristics are typical for $\text{Bi}_2\text{Mo}_2\text{O}_9$ and this means that sample P4 is polluted by $\text{Bi}_2\text{Mo}_2\text{O}_9$. Because of the absence of these characteristics, the other samples cannot be polluted by $\text{Bi}_2\text{Mo}_2\text{O}_9$, instead we ascribe the extra peaks to $\beta\text{-Bi}_2\text{O}_3$, which is the metastable tetragonal structure of Bi_2O_3 . The presence of $\beta\text{-Bi}_2\text{O}_3$ in Bi_2MoO_6 has also been reported by Buker and Greaves [22]. We have estimated the amount of $\beta\text{-Bi}_2\text{O}_3$ or $\text{Bi}_2\text{Mo}_2\text{O}_9$ in the samples from the ratio between the peak areas at 32.5° (mean signal for $\beta\text{-Bi}_2\text{O}_3$ and $\text{Bi}_2\text{Mo}_2\text{O}_9$) and 32.9° (mean signal for the Bi_2MoO_6). The results are given in Table 3.

Table 3 shows the results of the estimated content of $\beta\text{-Bi}_2\text{O}_3$ and $\text{Bi}_2\text{Mo}_2\text{O}_9$ and the Bi/Mo-ratio calculated from these percentages. The samples are ordered after decreasing Bi/Mo-ratio. The table displays also the Bi and Mo content measured by ICP. The results of the double measurements were within 5% of each other. The bismuth content is below the stoichiometric value for Bi_2MoO_6 and is almost the same for all the samples measured. As a result, the Bi/Mo-ratio calculated by using the bismuth

Table 3
Comparison of Bi/Mo-ratio determined by XRD, ICP and XPS for samples calcined at 550 °C

	Pollution	Bi/Mo	[Bi] (mmol/g)	[Mo] (mmol/g)	Bi/Mo	Bi/Mo from [Mo]	Bi/Mo
	XRD	XRD	ICP	ICP	ICP	ICP	XPS
P3	14% Bi ₂ O ₃	2.3	2.9	1.5	1.9	2.2	2.6
SD1	9% Bi ₂ O ₃	2.2	n.d.	n.d.	n.d.	n.d.	2.7
P1	3% Bi ₂ O ₃	2.1	2.9	1.6	1.8	2	2.4
P2	–	2	n.d.	n.d.	n.d.	n.d.	2.4
SD2	–	2	2.9	1.8	1.6	1.8	2.0
P4	11% Bi ₂ Mo ₂ O ₉	1.8	3.0	2.0	1.5	1.6	1.9

Stoichiometric values for Bi₂MoO₆: 3.3 mmol Bi/g and 1.6 mmol Mo/g.

and molybdenum measurements is below 2 for all samples. The molybdenum content in a bismuth molybdate sample is much more sensitive to differences in the Bi/Mo-ratio than the bismuth content, this is reflected in a larger variation between the results for the different samples. Therefore, and because of the low solubility of bismuth, the Bi/Mo-ratio is also calculated from the molybdenum content. The order in the Bi/Mo-ratios for the different samples calculated in this way correspond to the XRD-results; however, the values for the Bi/Mo-ratios are somewhat lower. We conclude from the XRD and ICP measurements, that P2 and SD2 are pure Bi₂MoO₆, P3, SD1 and P1 are polluted by β-Bi₂O₃ (P3 has the highest content, P1 the lowest) and sample P4 is polluted by Bi₂Mo₂O₉. It should be noted that the order in the Bi/Mo-ratios of the different samples in Table 3 corresponds to the order in activity in Table 2.

Table 3 displays also the Bi/Mo-ratio at the surface as measured by XPS. It shows that the Bi/Mo-ratio determined by XPS is higher than the ratio determined by XRD for samples P3, SD1, P1 and P2, while the two Bi/Mo-ratios are almost equal to each other for SD2 and P4. The XPS results show therefore that the samples that are polluted by β-Bi₂O₃ have a higher Bi/Mo-ratio at the surface than in the bulk. However, samples with a Bi/Mo equal or lower than 2, are not enriched with bismuth in the surface. This is in agreement with previous reported results [15–18]. Sample P2 does not show β-Bi₂O₃ in the XRD analysis; however, a Bi/Mo-ratio higher than 2 is measured for this sample by XPS.

The XRD and ICP analysis show that our samples made by spray-drying have approximately the intended Bi/Mo-ratio, while this is not the case for most of the samples made by precipitation. The latter should be ascribed to the loss of metal ions, especially molybdenum, during filtration. The loss of molybdenum was confirmed through the synthesis of P5. In this synthesis, the mixture was already filtrated after 2 h and the residue was analyzed for molybdenum and bismuth by ICP. No bismuth, but 14% of the molybdenum was found in the residue.

The results presented above confirm earlier reported results that show that the activity of Bi₂MoO₆ is very sensitive to the Bi/Mo-ratio [15–18]. A small excess of bismuth leads to a large enrichment of the surface with bismuth and thereby to a low activity. However, our results show that the activity of the catalysts with an excess of bismuth is very dependent on the calcination temperature. This dependence will be the issue of the remainder of this article.

3.2. Influence of calcination temperature on the crystallinity

Fig. 2 shows the XRD patterns for sample P3 after calcination at 350, 450, 500 and 550 °C, together with the pattern for SD2 calcined at 550 °C (pure Bi₂MoO₆). After calcination at 350 and 450 °C, all and only the reflections of the Bi₂MoO₆ structure are seen. The only difference with the pattern for the pure SD2 sample is the line broadening due to the smaller crystal size. The figure shows that the extra reflections displaying the presence of β-Bi₂O₃ are only seen after calcination at 500 °C. This means that it seems that pure Bi₂MoO₆ is obtained when sample P3 is calcined at a temperature of 450 °C or lower.

The same phenomenon is happening in a smaller degree for sample P4 with Bi/Mo lower than 2. Fig. 3 shows the XRD patterns for P4 calcined at different temperatures together with the pattern for pure Bi₂MoO₆. Also in this case, the pollution with Bi₂Mo₂O₉ is difficult to see when the sample is calcined at a low temperature.

3.3. Activity of uncalcined samples: influence of calcination temperature, duration and atmosphere on the activity

To investigate the influence of the calcination conditions further, the activity of uncalcined samples is measured. This means

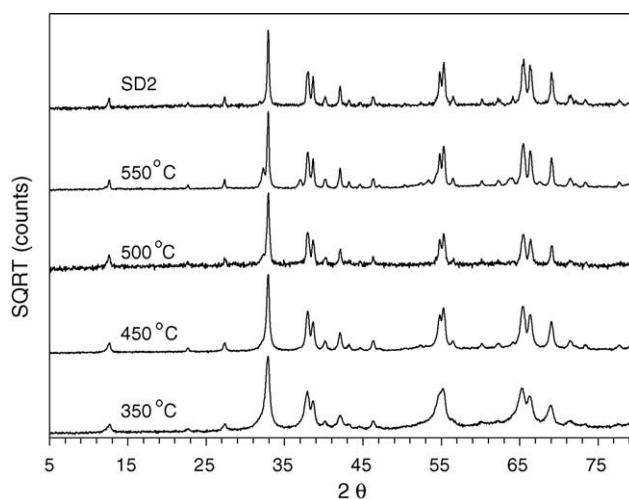


Fig. 2. Comparison of XRD patterns of sample P3 calcined at 350, 450, 500 and 550 °C with the XRD pattern of sample SD2 (pure Bi₂MoO₆) calcined at 550 °C.

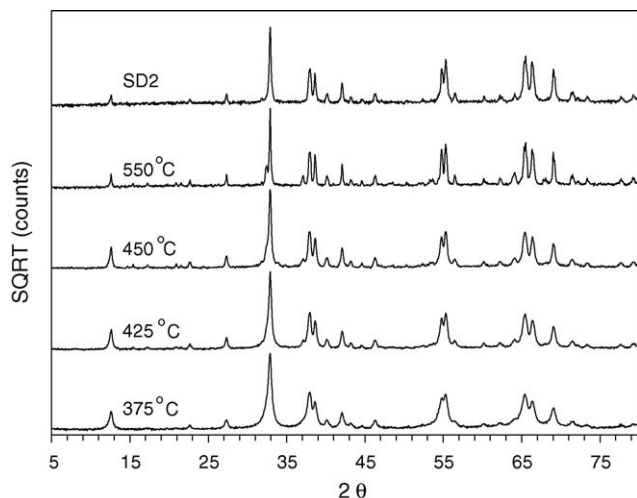


Fig. 3. Comparison of XRD patterns of sample P4 calcined at 375, 425, 450 and 550 °C with the XRD pattern of sample SD2 (pure Bi_2MoO_6) calcined at 550 °C.

that the uncalcined catalyst is heated in the reaction mixture consisting of 95% N_2 , 2.5% O_2 and 2.5% C_3H_6 . The left part (first 25 h) of Fig. 4 shows the activity, conversion and selectivity of sample P3 as a function of time, when it is heated in the reaction mixture to 375 °C. The heating rate was 5 °C/min and the final temperature is reached after 70 min. The figure shows that the activity increases during the calcination and reaches a maximum of $r_w = 0.3 \mu\text{mol}/(\text{g s})$ after 2 h at 375 °C. This maximum rate is 10 times higher than the rate measured after calcination at 350 °C for 10 h. The activity decreases rapidly after the maximum and is down to $0.06 \mu\text{mol}/(\text{g s})$ after 25 h. The decrease in activity is caused by a decrease in both the conversion and the selectivity. The selectivity reaches a maximum of 84% after 95 min, after 25 h the selectivity has decreased to about 50%. The maximum activities for the different uncalcined samples are given in Table 1.

Fig. 5 shows the activity at 375, 425 and 450 °C as a function of time for uncalcined P1 samples. The same pattern is seen as for

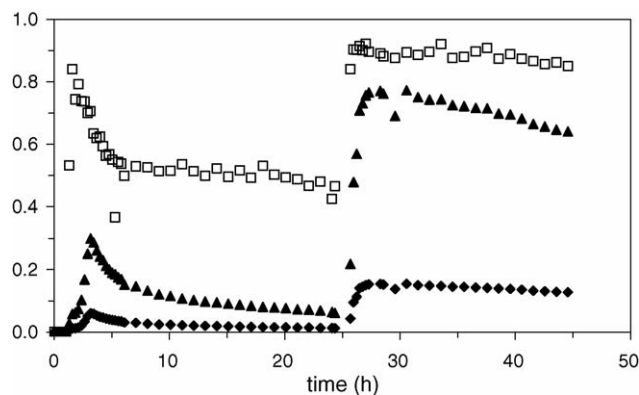


Fig. 4. (\blacktriangle) Rate for acrolein formation r_w ($\mu\text{mol}/(\text{g s})$), (\blacklozenge) conversion and (\square) selectivity of uncalcined sample P3 at 375 °C vs. time. The second part of the figure shows the results after reduction for 1 h in 5% of propylene in nitrogen.

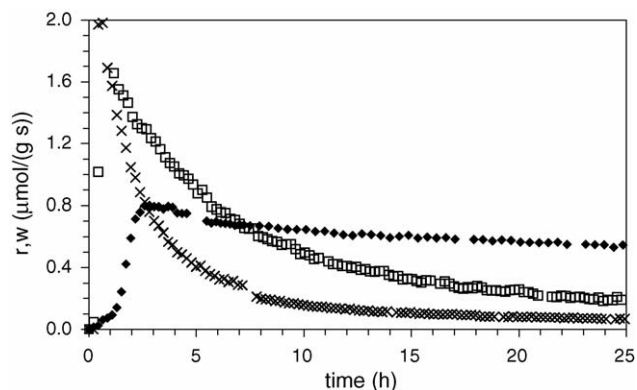


Fig. 5. Rate for acrolein formation r_w ($\mu\text{mol}/(\text{g s})$) of uncalcined sample P1 at (\blacklozenge) 375, (\square) 425 and (\times) 450 °C vs. time.

sample P3: the activity increases during calcination, it reaches a maximum and decreases afterwards. The maximum reached for sample P1 of $r_w = 0.8 \mu\text{mol}/(\text{g s})$ at 375 °C is somewhat higher than for sample P3. The deactivation, however, is much slower: after 25 h, the activity is $0.54 \mu\text{mol}/(\text{g s})$, which is nearly 70% of the maximum rate. At this stage, the activity of sample P3 was only 20% of the maximum rate. Such a large decrease is not even reached after 100 h for sample P1, where the activity is 35% of the maximum rate. The selectivity (as determined by Eq. (4)) decreased approximately from 95 to 85% during this 100 h period. At 425 and 450 °C, the deactivation of the catalyst is much faster. The activity is only 3% of the maximum activity after 25 h at 450 °C and the selectivity (Eq. (4)) has decreased from 90 to 65%.

Sample P1 has also been calcined in static air at 450 °C for 1, 4 and 25 h to see the influence of the calcination time on the surface area and on the activity. Table 4 shows the surface area, activity and selectivity of these samples. The results show that the surface area is almost independent on the calcination time, but the activity of the samples decreases strongly with increasing calcination time. The activity after 4 and 25 h of calcination is, respectively, 42 and 8% of the activity after 1 h of calcination. This rate of deactivation in static air is the same as under reaction conditions at 450 °C. Here, the activity decreases to, respectively, 0.32 and $0.07 \mu\text{mol}/(\text{g s})$ within 3 and 24 h after an activity of $0.7 \mu\text{mol}/(\text{g s})$ has been reached.

We have calcined sample P1 in the reactor in a mixture of 5% O_2 in N_2 at 450 °C for 24 h, to investigate the influence of the atmosphere on the deactivation. The activity of this sample, $0.10 \mu\text{mol}/(\text{g s})$, corresponds well with the activity of a sample calcined under reaction conditions after 25 h (see Fig. 5). The influence of the presence of water vapor on the deactivation has been tested by calcining a sample of P1 for 1 h in dry air and afterwards for 3 h in a mixture of approximately 1% water in nitrogen at 450 °C. The maximum activity of this sample is $0.20 \mu\text{mol}/(\text{g s})$ which is of the same order of magnitude as the activity of $0.49 \mu\text{mol}/(\text{g s})$ measured after 4 h under reaction. Comparing these values with the maximum activity of $2.0 \mu\text{mol}/(\text{g s})$ in Fig. 5, we could say that 90% of the activity is lost after calcination in 1% of water, while 76% of activity is lost during reaction.

Table 4
Surface area, rate for acrolein formation based on catalyst mass r_w ($\mu\text{mol}/(\text{g s})$) and selectivity at 375 and 450 °C for sample P1 calcined at 450 °C for different periods of time

Calcination time (h)	Surface area (m^2/g)	r_w (at 375 °C) ($\mu\text{mol}/(\text{g s})$)	r_w (at 450 °C) ($\mu\text{mol}/(\text{g s})$)	Selectivity (at 450 °C) (%)
1	6	0.27	0.69	70
4	6	0.12	0.29	70
25	5	0.02	0.07	55

Table 5
Reaction rate for acrolein formation at 375 °C based on catalyst mass, r_w ($\mu\text{mol}/(\text{g s})$), after reduction and ratio between reaction rate after and before reduction R , for different calcination temperatures

Temperature (°C)	P3		SD1		P1		SD2		P4	
	r_w	R	r_w	R	r_w	R	r_w	R	r_w	R
Uncalcined	0.77	12								
450 °C					0.40	3.3				
550 °C	0.19	∞	0.07	10	0.10	20	0.09	1.2	0.11	1.0

3.4. XPS-characterization at different stages of deactivation

The previous results show that the loss of activity is partly due to a decrease in selectivity. This decrease in selectivity implies that the surface composition changes during deactivation, in this case that the Bi/Mo-ratio increases, since surfaces with a Bi/Mo > 2 are known to be unselective [15–18]. We have measured the change in surface composition by measuring the Bi/Mo-ratio at the surface by XPS at different stages of deactivation. A sample of uncalcined P3 was taken out of the reactor when the maximum activity was reached at 375 °C (see also Fig. 4). The Bi/Mo-ratio for this sample was 2.4 which is somewhat lower than the value of 2.6 measured for a sample calcined at 550 °C. For P1, the Bi/Mo-ratio was measured after 2 h of calcination at 450 °C, the measured value of 2.3 is slightly lower than the value of 2.4 measured after calcination at 550 °C. Although the differences measured by XPS are small, they do agree with an increase in the Bi/Mo-ratio at the surface during deactivation.

3.5. Reduction experiments

It has been shown in the literature that the activity and selectivity of catalysts with Bi/Mo slightly above 2 can be increased by reduction, while the activity and selectivity of catalysts with Bi/Mo below 2 are unaffected [17,18,23]. The activation of the catalysts is ascribed to a lowering of the Bi/Mo-ratio at the surface, due to the formation of metallic bismuth [18,23,24].

We have reduced our samples for 30–60 min in a flow of 5% of propylene in nitrogen. The second part of Fig. 4 shows the result for reduction of sample P3 at 375 °C. The activity after reduction is 2.5 times higher than the maximum activity and 12 times higher than the activity immediately before reduction. The reduction leads also to a much higher selectivity (about 90%) and a more stable catalyst. The activity of the samples after reduction and the increase obtained by reduction for the different samples is shown in Table 5. It can be seen that the reduction

leads to a strong increase in activity for the low active samples, while the activity of the active samples is hardly influenced by the reduction. It can also be seen that the activity of all samples calcined at 550 °C have the same order of magnitude after reduction. In accordance to the results of Mitchell et al. and of Alsdorf et al., XRD and DSC measurements show that reduction of the samples leads to the formation of metallic bismuth [18,23]. The bismuth particles are several hundreds Ångstrom large, as estimated from the line width of the XRD peak of metallic bismuth at $2\theta = 31.7^\circ$. The DSC measurements show that typically 3–5% of the bismuth is reduced to metallic bismuth.

The P1 catalysts that are calcined at 450 °C for 1, 4 and 25 h (see Table 3) were reduced at 450 °C. Fig. 6 shows the activity at 450 °C of these samples after reduction. The figure shows that all these catalysts have approximately the same activity, and that they also deactivate with approximately the same rate after reduction. This means that, although the catalysts had very different activities before the reduction, the catalysts (surfaces) are very similar after reduction. The deactivation of the catalyst happens according to a typical pattern: first a relative slow deactivation at constant high selectivity, afterwards

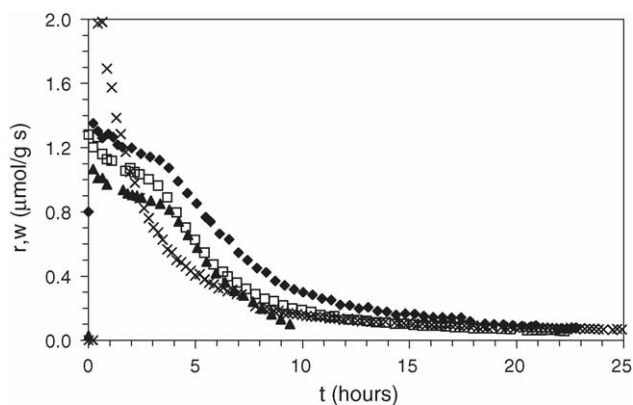


Fig. 6. Rate for acrolein formation r_w ($\mu\text{mol}/(\text{g s})$) at 450 °C after reduction of samples of P1 that were calcined at 450 °C for (♦) 1, (□) 4 and (▲) 25 h, and rate for acrolein formation for (×) uncalcined sample P1 vs. time.

a faster deactivation together with a decrease in selectivity. The deactivation of the uncalcined sample at 450 °C (see Fig. 5) is compared with the deactivation of the reduced samples at 450 °C in Fig. 6. This comparison shows that the uncalcined sample deactivates with approximately the same rate as the reduced samples in the second deactivation stage.

4. Discussion

Our and previous reported results show that bismuth molybdate catalysts with Bi/Mo larger than 2 are enriched with bismuth at the surface [15,17,18]. This results in samples which have normally low activities and low selectivities. However, after calcination at a low temperature or for a short period of time, these samples show relative high activities and high selectivities. These samples deactivate during calcination and this means that the activity is very dependent on the calcination conditions. This dependence of the activity on the calcination conditions is very likely one of the reasons for the conflicting results found in the literature about the activity of Bi_2MoO_6 . The fact that significant amounts of pollution (either $\beta\text{-Bi}_2\text{O}_3$ or $\text{Bi}_2\text{Mo}_2\text{O}_9$) cannot be seen by XRD after calcination at temperatures up to 500 °C, makes this effect even more important.

The strong deactivation of samples with $\text{Bi/Mo} > 2$ is accompanied by a loss of selectivity. Together with the XPS results, this shows that the Bi/Mo-ratio at the catalytic active surface increases during the calcination. This change in Bi/Mo-ratio at the surface is shown to be an activated and relative slow process. The question is, what is happening during this deactivation process?

One of the reasons for the increase in the Bi/Mo-ratio at the surface could be the loss of molybdenum from the surface. The loss of molybdenum due to the sublimation of molybdenum compounds is a well-known cause for the deactivation of the $\text{Fe}_2(\text{MoO}_4)_3$ catalyst in the methanol to formaldehyde synthesis. This sublimation is known to be strongly enhanced by the presence of water due to the formation of the relative volatile $\text{MoO}_2(\text{OH})_2$ compound [25,26]. The loss of molybdenum from $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ has been reported recently by Yanina and Smith [26]. However, the loss of molybdenum cannot explain the fact that catalysts with Bi/Mo significantly higher than 2 in the bulk, do show high initial activities and selectivities. Furthermore, we have shown that the rate of deactivation is approximately the same when the catalyst is under reaction conditions (final water content maximal 0.4%), under a dry O_2 in N_2 flow, or when it is calcined in static air. Calcination in a 1% water–air mixture leads to a somewhat higher deactivation (90% of the maximum activity is lost) than under reaction conditions (76% of the activity is lost) after 4 h at 450 °C. According to the results of Yanina et al. and to previous results on the $\text{Fe}_2(\text{MoO}_4)_3$ catalyst, the presence of water should have a very strong influence on the deactivation [25,26].

The relatively high initial activities and selectivities can instead be explained by relatively low initial Bi/Mo-ratios at the catalytically active surface. This means that after a short period of calcination (parts of) the surface is not or hardly enriched with bismuth, resulting in an active and selective catalyst. This

means that the bismuth that is in excess, is initially located in the bulk of the catalyst or that is concentrated in larger particles of bismuth oxide on the surface. Extensive surface studies, which are beyond the scope of this work, would be required to solve this latter question. The excess bismuth merges during calcination or reaction with the active parts of the surface, leading to a deactivation of the catalyst.

The deactivated catalyst can be reactivated by reduction, while the activity of the active samples is hardly influenced by reduction. Catalysts that are deactivated in different degrees before reduction get approximately the same activity and deactivation behavior after reduction. Combined with the results of van Oeffelen et al. and Mitchell et al., this supports our opinion that the deactivation is due to an increase in the Bi/Mo-ratio at the catalytically active surface [17,18]. The comparable activities after reduction show that the properties of the surface after reduction are not determined by the properties of the catalytically active surface before the reduction, but rather by the properties of a much larger part of the catalyst that is reduced.

Catalysts having different Bi/Mo-ratios in the bulk obtain also approximately the same activity after reduction. This shows that reduction creates surfaces with a composition that is more or less independent on the bulk composition, or surfaces where the activity is more or less independent on the surface composition ($\text{Bi/Mo} < 2$). The slow initial deactivation at a high and stable selectivity after reduction, is an indication that the Bi/Mo-ratio at the catalytically active surface is below 2 after reduction. The reduction leads to the formation of metallic bismuth [18] and, due to the low melting point of 271 °C of bismuth, to the formation of bismuth particles [23,24]. The formation of these particles will lead to a decrease in the Bi/Mo-ratio in the remaining surface, making this part of the surface active and selective. After reduction, the bismuth particles are re-oxidized and merge with the active part of the surface, leading to a deactivation [23]. The comparable rate of deactivation of the reduced samples in the second stage, and of the deactivation of the uncalcined samples indicates that the processes by which excess bismuth is polluting the active parts of the surface are similar in both cases.

We have shown that relative large amounts of excess bismuth and molybdenum cannot be seen by XRD as $\beta\text{-Bi}_2\text{O}_3$ and $\text{Bi}_2\text{Mo}_2\text{O}_9$ when the samples are calcined at temperatures below 500 °C. A reason for this could be that the areas of crystalline $\beta\text{-Bi}_2\text{O}_3$ and $\text{Bi}_2\text{Mo}_2\text{O}_9$ formed at low temperatures are not large enough to be seen by XRD. Comparing the temperatures where $\beta\text{-Bi}_2\text{O}_3$ is observed by XRD with the much lower temperatures where deactivation occurs, it is clear that XRD visible $\beta\text{-Bi}_2\text{O}_3$ is not a prerequisite for the deactivation. Spectroscopic methods like Infrared and Raman, may be more suitable for detecting these impurities [27].

When we compare the activity of pure Bi_2MoO_6 at 375 °C (0.08 $\mu\text{mol}/(\text{g s})$ or 0.05 $\mu\text{mol}/(\text{m}^2/\text{s})$ for sample SD2) with the activities of pure $\alpha\text{-Bi}_2\text{Mo}_3\text{O}_{12}$ (0.09 $\mu\text{mol}/(\text{g s})$ or 0.06 $\mu\text{mol}/(\text{m}^2/\text{s})$) and pure $\beta\text{-Bi}_2\text{Mo}_2\text{O}_9$ (0.08 $\mu\text{mol}/(\text{g s})$ or 0.07 $\mu\text{mol}/(\text{m}^2/\text{s})$) synthesized by spray-drying, we can conclude that all three model catalysts have comparable activities. This conclusion was also found in our previous work [20]. The comparable activities makes that the ordering after activity is

difficult, and can therefore easily be influenced by factors like small amounts of impurities in the catalyst and uncertainty in the determination of the surface area.

5. Conclusions

The activity and selectivity of Bi_2MoO_6 catalysts, in the selective oxidation of propylene to acrolein, are very sensitive to the presence of small amounts of excess bismuth. This excess leads to a surface enrichment with bismuth, and thereby to a low active and low selective catalyst. However, such catalysts with a Bi/Mo slightly above 2, do show reasonable activities and selectivities after calcination at moderate temperatures and/or for a short period of time. These catalysts lose their activity after calcination at a higher temperature or for a longer period of time. This makes that the activity and selectivity of these catalysts are strongly dependent on the calcination time and temperature. The above mentioned dependences are most likely to be some of the main reasons behind the conflicting results reported in the literature on the activity of Bi_2MoO_6 .

The reasonable initial activities of catalysts with a Bi/Mo slightly above 2, are ascribed to relative low Bi/Mo-ratios at parts of the surface after calcination for a short period of time. The excess bismuth merges with the active parts of the surface during calcination, leading to the deactivation of the catalyst. The sublimation of molybdenum from the catalyst may play a minor role in the deactivation process.

In accordance with literature, the deactivated samples can be reactivated by reduction, while the activity of the active samples is hardly affected by reduction. This reactivation is a result of the formation of bismuth particles leading to a decrease in the Bi/Mo-ratio at other parts of the surface. The deactivation during calcination and after reduction occur at similar rates indicating that these deactivation processes are similar.

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