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Oxidation of isobutene to methacrolein using bismuth molybdate catalysts: Comparison of operation in periodic and continuous feed mode

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Abstract

A series of bismuth molybdate catalysts were compared using a continuous feed of isobutene in air or a cyclic/pulse or gas–gas periodic flow mode, in which the oxide is first treated with air at the reaction temperature, followed by reaction of isobutene in nitrogen or argon in the absence of oxygen. For nonpromoted catalysts, in the continuous-feed mode, relatively low selectivities for methacrolein are observed and significant amounts of byproduct CO_2 are formed. In contrast, in the pulse mode, no CO_2 and almost 100% selectivity to methacrolein can be observed with nonpromoted $BiMoO_x$, especially for the initial reaction period. At realistic reaction temperatures, no carbon or carbon-containing product depositions are observed during the pulse mode, indicating that the very high selectivity observed is realistic for the nonpromoted catalyst under pulse conditions. The effect of Co and Fe as promoters on the catalytic performance was also investigated. The addition of Co and Fe leads to the observation of CO_2 also in the pulse mode along with some carbon deposition, although the selectivity to methacrolein remains significantly higher than that observed in the continuous-feed mode. Investigation of a more complex promoted catalyst representative of a commercial formulation [$BiMo_{12}Fe_2NiCo_7MgSb_{0.9}Ti_{0.1}Te_{0.02}Cs_{0.4}O_x$] also shows that CO_2 is observed in the pulse mode but, at much lower levels than observed with the less complex catalysts. However, in subsequent operation in the gas–gas periodic flow, the catalytic performance for this catalyst is almost identical in the continuous and pulse operations. It is concluded that, for pulse-mode operation, the best results, including almost total selectivity to methacrolein, are observed with the relatively simple nonpromoted binary oxides. In general, the first pulse-mode operation of these catalysts gives the highest yield of methacrolein and subsequent oxidation/reaction cycles gives lower yields. The origin of this effect was investigated using cyclic TPO/TPR and TPR/TPO analysis, revealing that the first TPR/TPO cycles are significantly different than subsequent cycles, likely due to the initial state of the catalyst surface.

Keywords: Isobutene; Methacrolein; Selective oxidation; Bismuth molybdate catalyst; Continuous flow; Pulse flow; Periodic flow; Reduction/oxidation; Temperature-programmed reduction/oxidation cycle; TPR/TPO cycle

1. Introduction

The selective oxidation of hydrocarbons remains a subject of intense interest, because this process is used in the large-scale synthesis of a number of chemical intermediates. For example, maleic anhydride is produced by the selective oxidation of n-butane using vanadium phosphate catalysts [1–4]. This reaction has become one of the most widely studied heterogeneously catalysed processes [5,6]. In addition, propene and isobutene are oxidised to acrolein and methacrolein, respectively, using bismuth molybdate catalysts [7,8]. Although relatively simple binary oxides are known to catalyse these reactions [e.g., $(VO)_2P_2O_7$ [5] and γ-Bi_2MoO_6 [7]], most often a complex array of promoters are added. For example, Co, Fe, and Mo are often added to commercial vanadium phosphate catalysts, although nonpromoted catalysts are used for this reaction, whereas bismuth molybdate catalysts are used commercially only in a promoted form and often in highly complex formulations, for example,

$BiMo_{12}Fe_2NiCo_7MgSb_{0.9}Ti_{0.1}Te_{0.02}Cs_{0.4}O_x$ [9]

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or

$Bi_{0.7}Mo_{12}W_{0.3}Fe_2Sb_{0.7}Ni_4Co_2ZnCe_{0.5}Si_5Cs_{0.5}K_{0.1}O_x$ [10].

In most cases, these catalysts are operated in a continuous-feed mode, in which the hydrocarbon is fed together with oxygen or air through a packed catalyst bed. In an alternative approach, Contractor et al. [11–15] have developed the riser/circulating fluidised bed (CFB) reactor for the oxidation of butane to maleic anhydride. This process is based on the observation that many oxides operate as oxidation catalysts by a Mars–van Krevelen mechanism [16]; that is, in the absence of a co-fed oxidant, the hydrocarbon reacts to give the selective oxidation product by reacting with lattice oxygen (O^{2-}). In the CFB process, butane is reacted with vanadium phosphate catalyst in the absence of air in a riser reactor. This allows the catalyst and hydrocarbon to remain in contact for a few seconds at the reaction temperature. Subsequently, the reaction products are recovered, and the catalyst is reoxidised in a fluidised bed by reaction with air.

Decoupling the reduction and reoxidation stages of the catalyst operation leads to improved process control; however, it does not lead to the elimination of the formation of CO_2 as an undesired byproduct of this reaction. In this process, the “catalyst” is acting as a stoichiometric oxygen carrier. Although work with CFB reactors has focused on the butane oxidation process, Du Pont and ElF Atochem have used a CFB process to oxidise propene to acrolein and acrylic acid [17,18].

Pulse (or periodic) flow reactors are attracting increased research attention for both gas–gas and gas–liquid reaction systems [19–26]. Therefore, the concepts are well developed for laboratory scale reactors, although to date there have been few studies on the effect of promoters under these conditions. In this paper we contrast the catalyst performance, in terms of activity and selectivity, for a series of bismuth molybdate for isobutene oxidation operated in both periodic- and continuous-flow modes, and comment on the role of promoters in these systems.

2. Experimental

2.1. Catalyst preparation

Bismuth molybdate binary oxide catalysts were prepared using a coprecipitation method. We describe the procedure used to prepare the $BiMoO_x$ material (the catalyst with a Bi:Mo ratio of 1:1); the amounts of the components used were adjusted to obtain other Bi:Mo mol ratios. $Bi(NO_3)_3{\cdot}5H_2O$ (25.8 g; Fisher Chemicals) was dissolved in nitric acid (108 ml, 5 M; Fisher Chemicals) at 25 °C to give solution A. $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (9.4 g; Fisher Chemicals) was dissolved in aqueous ammonia (108 ml, 5%; Fisher Chemicals) at 25 °C to give solution B. Solution A was added dropwise to solution B over 15 min at 25 °C with stirring. The pH was adjusted to 7 with 5% aqueous ammonia. The slurry was heated at 80 °C for 16 h to give a paste that was dried in air (100 °C for 24 h) and calcined at 480 °C for 12 h in static air at a temperature ramp rate of 1 °C min^{-1}.

Cobalt-promoted bismuth molybdate catalysts were prepared as follows. Solutions A and B were used as described above. $Co(NO_3)_2{\cdot}6H_2O$ (3.9 g for $Co_{0.25}BiMoO_x$; 7.7 g for $Co_{0.5}BiMoO_x$; 15.4 g for $CoBiMoO_x$; Fisher Chemicals) was dissolved in water (35 ml) at 25 °C to produce solution C. Solution C was added dropwise to solution A over 5 min at 25 °C, and the mixed solution was then added dropwise to solution B over 10 min at 25 °C. The pH was adjusted to 7 with 5% aqueous ammonia, and the catalyst was recovered as described above. An iron-promoted bismuth molybdate catalyst ($Fe_{0.25}BiMoO_x$) was prepared similarly to the cobalt-promoted catalyst using $Fe(NO_3)_3{\cdot}9H_2O$ (5.4 g; Fisher Chemicals) dissolved in 5% aqueous ammonia (120 ml) as solution C. A multicomponent catalyst, $BiMo_{12}Fe_2NiCo_7MgSb_{0.9}Ti_{0.1}Te_{0.02}Cs_{0.4}O_x$, was prepared as described previously [9].

2.2. Catalyst characterisation

Various techniques were used to characterise the catalysts. Powder X-ray diffraction (XRD) was performed using an Enraf Nonius FR590 X-ray generator with a Cu-K_α source fitted with an Inel CPS120 hemispherical detector. Brunauer–Emmett–Teller (BET) surface area measurements, using nitrogen adsorption, were carried out with a Micromeritics ASAP 2000 instrument. Raman spectra were obtained using a Renishaw Ramanscope spectrograph fitted with a green Ar^+ laser ($\lambda = 514.532$ nm). Temperature-programmed oxidation (TPO) and temperature-programmed reduction (TPR) studies were carried out using a Micromeritics Autochem 2910 instrument with 0.1–0.2 g of catalyst. Thermogravimetric analysis (TGA) for the used catalysts was performed using a Perkin–Elmer TGA 7 thermogravimetric analyzer.

2.3. Catalyst testing

The oxidation of isobutene in the continuous-feed mode was done in a fixed-bed laboratory microreactor. The reactor was fabricated from stainless steel (4.4 mm i.d.) and operated at 1 bar pressure, containing catalyst (250- to 300-µm particles, 0.25 g) diluted with quartz (250- to 300-µm particles, 0.25 g). Isobutene, N_2, and air were fed to the reactor through mass flow controllers. For isobutene, typical continuous-feed flow conditions used 3.5 vol% isobutene in air (50 ml min^{-1}). The reaction products were analysed by on-line gas chromatography. Carbon mass balances for the continuous-feed mode were typically 98–100%. Two reactors were used for the pulse reaction studies. Initially, the same microreactor as that used in the continuous-flow mode was used. The catalyst was initially treated in flowing air (50 ml min^{-1}) at the reaction temperature for 30 min. Then 3.5 vol% isobutene in nitrogen (50 ml min^{-1}) was switched to pass over the heated catalyst. The reactant and products were analysed by on-line gas chromatography at regular time intervals, with the first interval occurring 10 s after switching isobutene/N_2 to pass over the catalyst. The void volume between the switching valve and the sample loop in the six-port sampling valve was ca. 3.2 ml; therefore, after ca. 3.8 s, the reactant/products reach the sample loop. After isobutene/N_2

flow for 2 min, air (50 ml min^{-1}) was switched to pass over and reoxidise the catalyst. In subsequent experiments, a specially designed gas–gas periodic flow reactor was constructed using a six-port sampling valve with a sample loop size of 250 µl to provide well-defined consecutive pulses, thereby ensuring considerably more control than that obtained using the standard microreactor. The reactor was located immediately downstream of the sample loop, so a well-defined pulse was injected onto the catalyst in a flow of helium carrier gas and then onto the gas chromatograph columns. The flow rates of air, argon, and isobutene were measured using calibrated mass flow controller, and the total flow rate of isobutene/air or isobutene/argon mixture was controlled at 50 ml min^{-1} through the sample loop. In the aerobic pulse-flow experiments, air and isobutene were measured and mixed together to pass through the six-port valve. In the anaerobic experiment, argon was used instead of air, and an isobutene/argon mixture was introduced into the reactor. After 30 min of isobutene/Ar introduction through the sample loop to the catalyst, a pulse of 250 µl O_2 was passed through the reactor to regenerate the catalyst. The flow of helium through the catalyst bed was maintained at all times. Both operations were carried out cyclically. Product analysis was carried out using gas chromatography with helium as a carrier gas using Porapak Q and Molecular sieve 13X columns and a thermal conductivity detector. All experiments were conducted several times, to ensure that reproducible data are reported.

3. Results and discussion

3.1. *Comparison of nonpromoted bismuth molybdate catalysts*

A series of bismuth molybdate catalysts were prepared using coprecipitation with varying Bi:Mo mol ratios (Bi:Mo = 1:12, 2:3, 1:1, 2:1, 3:1, 6:1) and characterised using powder XRD and laser Raman spectroscopy (see supplementary material). Bismuth molybdate catalysts have been extensively studied using these two techniques, and the materials prepared here were consistent with those used in earlier studies [27–38]. The phase composition and BET surface area for the catalysts with Bi:Mo ratios of 2:1, 2:3, and 1:1 are summarised in Table 1 (see supplementary material for other catalysts). The Bi:Mo = 1:1 material calcined at 480 °C in the present work comprises equal parts of γ-Bi_2MoO_6 and α-$Bi_2Mo_3O_{12}$. Calcination at temperatures above 600 °C formed β-$Bi_2Mo_2O_9$ [29,30]. These materials were used as catalysts for the oxidation of isobutene using the continuous-feed mode at 350–390 °C; the results are shown in Fig. 1. The catalyst containing γ-Bi_2MoO_6 was found to give the best results, in agreement with previous studies [37,38]. The catalysts were very stable under the continuous-feed mode, and after reaction, only traces (typically $<1\%$) of carbon or non-desorbed products were observed on the catalyst. Characterization of the catalysts after oxidation reaction using powder XRD and laser Raman spectroscopy found that their structures were unchanged. Normalising the catalytic performance to yield intrinsic activity data (mol isobutene converted $\text{m}^{-2}\,\text{h}^{-1}$, mol methacrolein formed $\text{m}^{-2}\,\text{h}^{-1}$) confirms that γ-Bi_2MoO_6 is the most active and selective catalyst in the continuous-feed mode (Fig. 2) and that with this material, selectivity to methacrolein is ca. 80% at 390 °C.

Table 1
Catalyst properties

Catalyst	Phase composition	BET surface area ($\text{m}^2\,\text{g}^{-1}$)
Bi:Mo = 2:1	γ-Bi_2MoO_6 [27–34]	2
Bi:Mo = 2:3	α-$Bi_2Mo_3O_{12}$ [27,28,30]	2
Bi:Mo = 1:1	α-$Bi_2Mo_3O_{12}$ + γ-Bi_2MoO_6	2

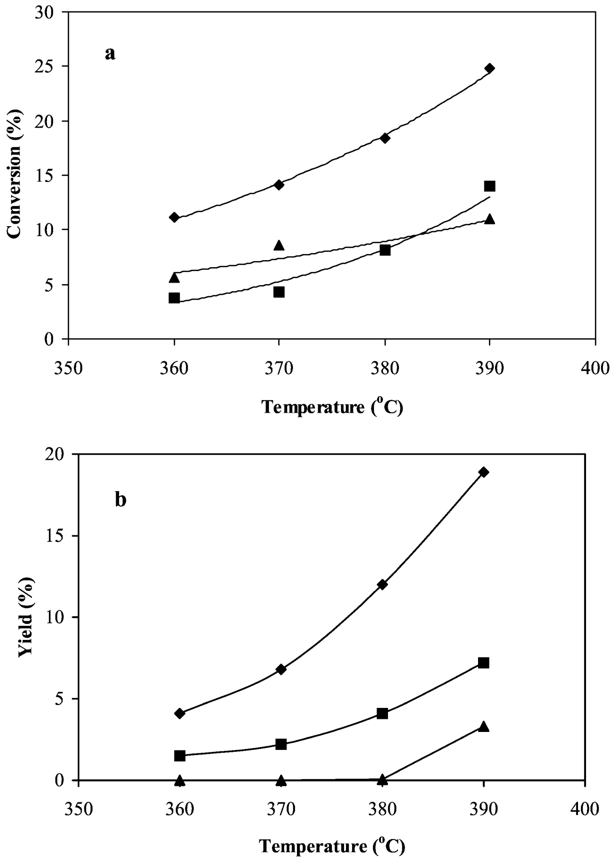

Fig. 1. Catalytic performance of bismuth molybdate catalysts in the continuous feed mode (3.5% isobutene in air): (a) isobutene conversion, (b) methacrolein yield. Key: (◆) Bi:Mo = 2:1, (■) Bi:Mo = 1:1, (▲) Bi:Mo = 2:3.

The catalysts were then evaluated in the pulse-feed mode using the same microreactor. In this case, the catalysts were initially oxidised in flowing air for 30 min at the required reaction temperature, in the 350–390 °C range. An oxidation of 30 min gave optimum results, with no further improvement observed when the catalysts were exposed to longer oxidation (up to 2 h). For the Bi:Mo = 3:1 and 6:1 materials, no methacrolein or CO_2 was observed in the pulse-mode operation at 359 and 379 °C, although some carbon deposition was observed (ca. 35–41% of the isobutene fed). However, for the other bismuth molybdate materials, operation in the pulse mode initially gave higher intrinsic activity for methacrolein formation in the pulse mode than in the continuous mode. Figs. 3–5 show the data at two temperatures; see supplementary material for the data at all temperatures investigated. Most significantly, for catalysts

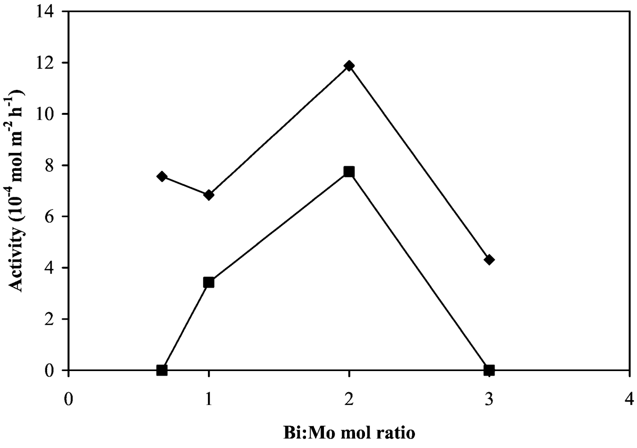

Fig. 2. Intrinsic activity data at 380 °C for bismuth molybdate catalysts operated in the continuous feed mode. Key: (◆) mol isobutene converted m^{-2} h^{-1}, (■) mol methacrolein formed m^{-2} h^{-1}.

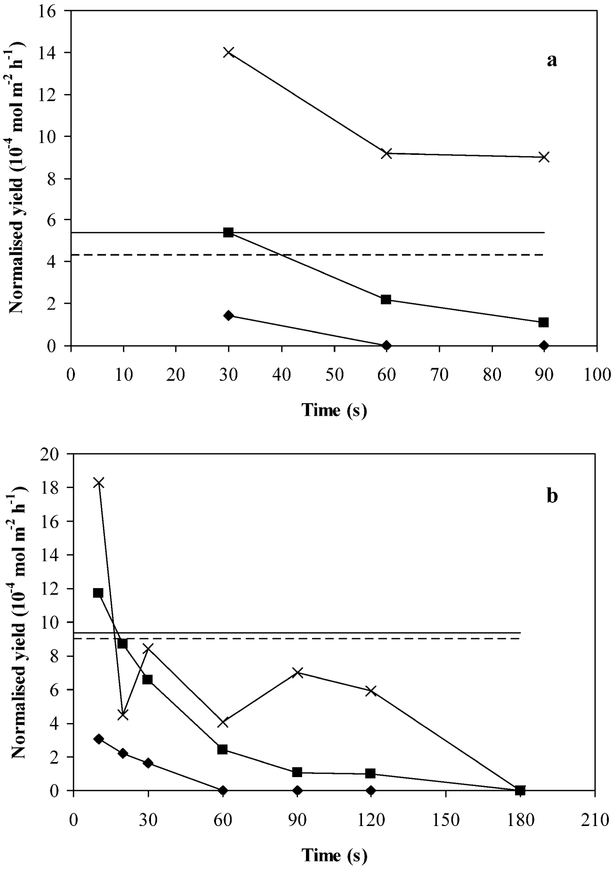

Fig. 3. Intrinsic activity data comparison for pulse and continuous feed modes for the Bi:Mo = 2:1 catalyst: (a) 365 °C, (b) 377 °C. Key: pulse mode: (◆) CO_2, (■) methacrolein, (×) carbon deposits. Continuous mode: (—) CO_2, (- - -) methacrolein.

with Bi:Mo mol ratios ⩽1.0, no CO_2 was observed in the pulse-mode operation, even at short reaction times.

In addition, almost no carbon or product deposition (within experimental error (±2% of isobutene fed)) was observed with $BiMoO_x$ catalyst during the pulse-mode operation. This observation is based on carbon mass balance data on reproducible experiments. The absence of deposited carbon was further confirmed by postreaction TGA and carbon analysis. These findings indicate that nonpromoted bismuth molybdate catalysts can give very high selectivity of methacrolein for short reaction times when operated in the pulse mode. However, it should be noted that because these catalysts are nonpromoted, their catalyst activity is relatively low compared with that of commercial promoted formulations [9]. For all catalysts, the catalytic activity decreased during exposure to the isobutene pulse.

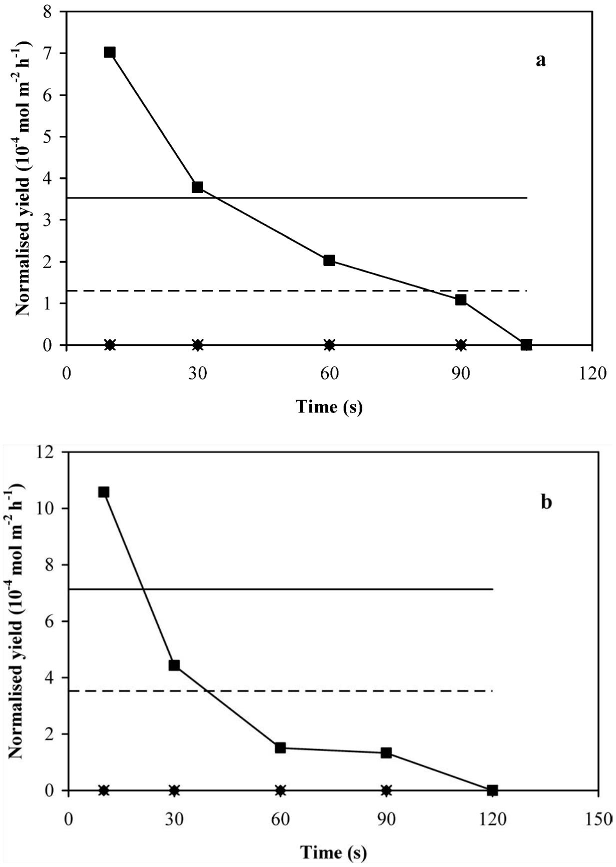

Fig. 4. Intrinsic activity data comparison for pulse and continuous feed modes for the Bi:Mo = 1:1 catalyst: (a) 359 °C, (b) 377 °C. Key: pulse mode: (◆) CO_2, (■) methacrolein, (×) carbon deposits. Continuous mode: (—) CO_2, (- - -) methacrolein.

The pulse-mode operation was investigated using a number of oxidation/reduction cycles; representative data for the Bi:Mo = 1:1 catalyst are given in Fig. 6. For all catalysts, the first oxidation/reduction cycle after catalyst calcination at 480 °C and exposure to air at the reaction temperature for 30 min gave higher activity for methacrolein formation than subsequent cycles. However, the catalytic performance for the second and subsequent oxidation/reduction cycles were always the same, and no deactivation was observed after a number of cycles.

A subsequent set of experiments used the gas–gas periodic flow reactor, in which the sample loop was used to introduce the pulse of reactants, to investigate the reactivity of Bi_2MoO_6 when the pulses could be more rapidly applied. A full analysis of the products was carried out. The effect of increasing the concentration of isobutene in the feed is detailed in Table 2. It is clear that the effect is replicated. Co-feeding isobutene/air produced much lower methacrolein selectivity in periodic flow

Table 2
Effect of isobutene concentration on the operation of a gas–gas periodic flow reactor at 360 °C using Bi_2MoO_6

Isobutene (%)	(Isobutene + air)/He			(Isobutene + Ar)/He/O_2			ΔS (%)[a]
	Conversion (%)	Selectivity (%)	Yield (%)	Conversion (%)	Selectivity (%)	Yield (%)	
1.3	90.0	31.1	28.0	57.4	72.2	41.4	41.1
3.4	83.4	49.6	41.4	36.3	80.8	29.3	31.2
8.6	68.8	65.6	45.1	23.8	81.7	19.4	16.1

[a] ΔS (%) denotes the selectivity enhancement when operated in (isobutene + Ar)/He/O_2 mode compared with that in (isobutene + air)/He mode.

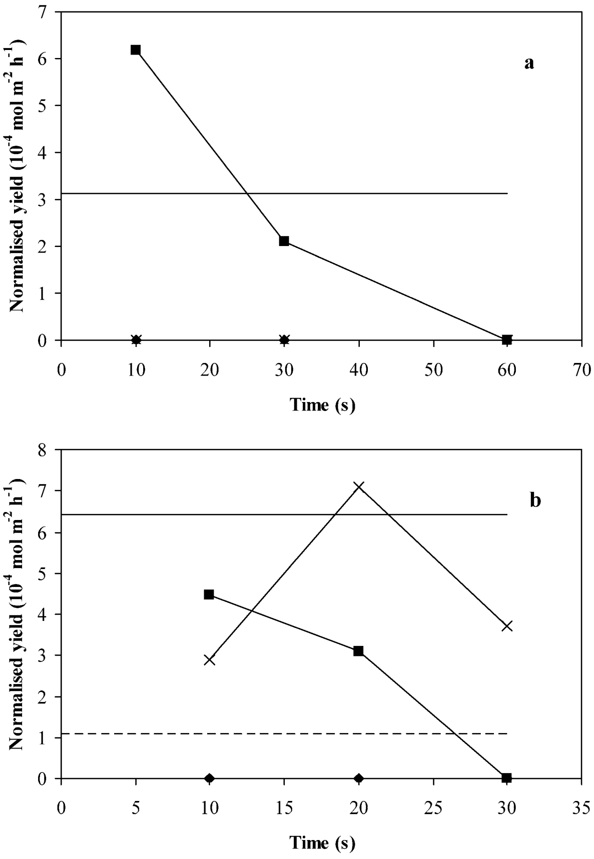

Fig. 5. Intrinsic activity data comparison for pulse and continuous feed modes for the Bi:Mo = 2:3 catalyst: (a) 359 °C, (b) 377 °C. Key: pulse mode: (◆) CO_2, (■) methacrolein, (×) carbon deposits. Continuous mode: (—) CO_2, (- - -) methacrolein.

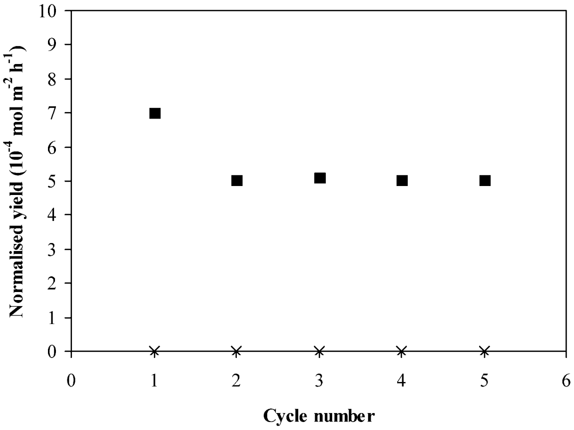

Fig. 6. Effect of oxidation/reduction cycles on the formation of methacrolein in the pulse feed mode for the Bi:Mo = 1:1 catalyst at 359 °C. Data are taken at 10 s in the reaction. Key: (■) methacrolein, (×) carbon deposits.

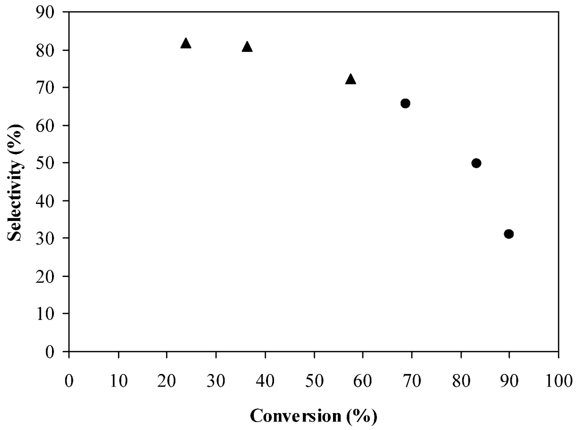

Fig. 7. Selectivity vs. conversion for isobutene oxidation at 360 °C over Bi_2MoO_6 catalyst operated in (isobutene + Ar)/He/O_2 and (isobutene + air)/He periodic flow mode. Key: (▲) (isobutene + Ar)/He/O_2 mode, (●) (isobutene + air)/He mode.

conditions, and an improved yield was also observed at the lower isobutene concentration. Indeed, the improvement in selectivity, denoted by ΔS, for the nonpromoted Bi_2MoO_6 was quite marked.

This result hides an interesting observation, however—namely, that selectivity is much more strongly influenced by isobutene conversion than by mode of operation. Thus Fig. 7 shows the data from Table 2 plotted as selectivity versus conversion. Unfortunately, there is no overlap of conversions in the two operating modes; nonetheless, a single curve can be drawn that passes through the two sets of data points with only a negligible (or, at best, small) improvement in selectivity. This result may suggest that the deposition of carbonaceous species is in competition with isobutene oxidation. The selectivity is then a function of the relative quantities of isobutene and methacrolein rather than the absolute quantities. The carbon mass balance in these operations is in the range 70–90%. In the pulse mode, the deposits are retained on the surface during the isobutene exposure and are oxidised to CO_x during the oxidation phase.

3.2. *Comparison of promoted $BiMoO_x$ catalysts*

A series of $BiMoO_x$ catalysts containing Co and Fe as additives was prepared with a Bi:Mo = 1:1 mol ratio. The materials were characterised by powder XRD and laser Raman spectroscopy (see supplementary material). Addition of Co to the materials did not result in any changes in the powder XRD pattern, whereas addition of Fe led to the forma-

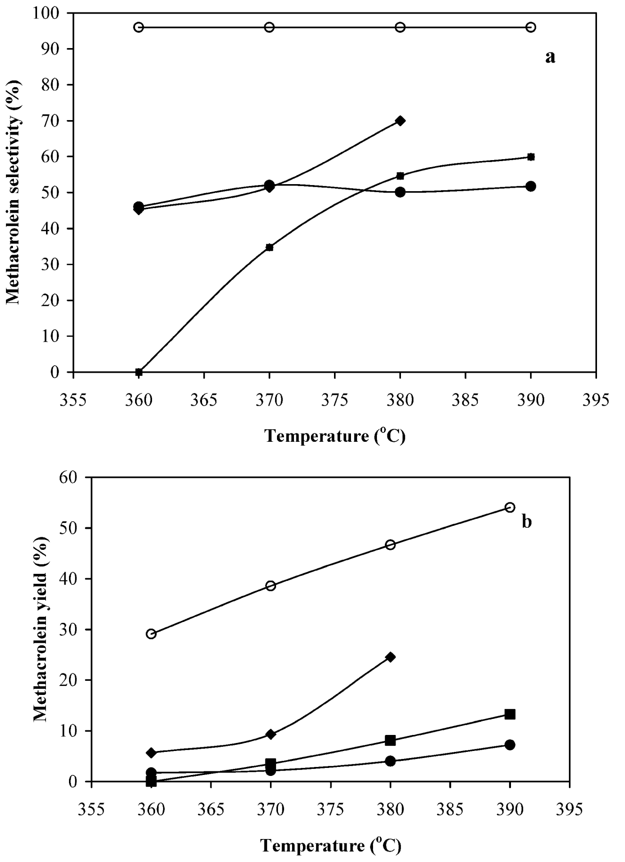

Fig. 8. Catalytic performance of non-promoted and promoted catalysts in the continuous feed mode (3.5% isobutene in air): (a) methacrolein selectivity, (b) methacrolein yield. Key: (●) $BiMoO_x$, (■) $Co_{0.25}BiMoO_x$, (◆) $Fe_{0.25}BiMoO_x$, (○) $BiMo_{12}Fe_2NiCo_7MgSb_{0.9}Ti_{0.1}Te_{0.02}Cs_{0.4}O_x$.

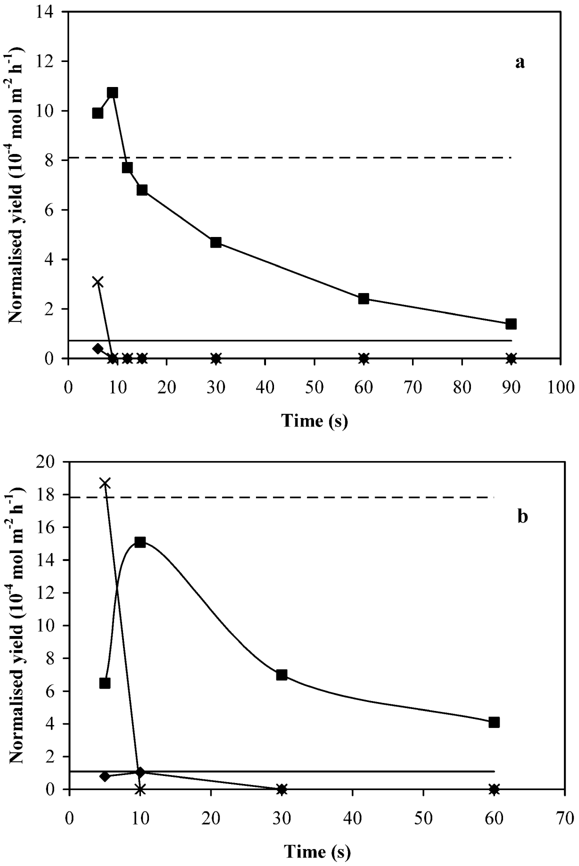

Fig. 9. Intrinsic activity data comparison for pulse and continuous feed modes for $BiMo_{12}Fe_2NiCo_7MgSb_{0.9}Ti_{0.1}Te_{0.02}Cs_{0.4}O_x$ catalyst: (a) 347 °C, (b) 382 °C. Key: pulse mode: (◆) CO_2, (■) methacrolein, (×) carbon deposits. Continuous mode: (—) CO_2, (- - -) methacrolein.

tion of a new phase, $Bi_3FeMo_2O_{12}$. The materials were investigated as catalysts for the oxidation of isobutene in the continuous mode; the results are shown in Fig. 8 (see supplementary material for all of the data). As expected, addition of the Co and Fe promoters enhanced the catalytic performance. Data are also given for the more complex multicomponent catalyst, $BiMo_{12}Fe_2NiCo_7MgSb_{0.9}Ti_{0.1}Te_{0.02}Cs_{0.4}O_x$ [9]; with this commercial formulation, methacrolein yields were significantly enhanced and the selectivity to methacrolein was ca. 96% for all temperatures investigated.

These catalysts were also investigated in the pulse-feed mode in the same way as the nonpromoted catalysts; the data are given in Table 3 and Fig. 9. Introduction of Co or Fe into $BiMoO_x$ led to the formation of CO_2 as well as methacrolein in the initial exposure of the catalyst to isobutene in the pulse mode. This is in contrast to the nonpromoted catalyst (Fig. 4), where no CO_2 was observed during the pulse-mode operation. However, the formation of CO_2 was much less than that observed in the continuous-feed mode. At low temperature with Co-promoted $BiMoO_x$ catalysts, there was no deposition of carbon within the limits of experimental error, but at higher temperatures, carbon deposition was observed (see supplementary material). Significant levels of carbon deposition were observed with the Fe-promoted catalyst. The data for the complex promoted catalyst $BiMo_{12}Fe_2NiCo_7MgSb_{0.9}Ti_{0.1}Te_{0.02}Cs_{0.4}O_x$ [9] show that the initial methacrolein yield in the pulse mode was low and increased through a maximum with continuing exposure to isobutene (Fig. 9). It is clear that this catalyst was significantly more active than the relatively simple promoted formulations; however, CO_2 was still observed at the initial isobutene exposure time, but not at similar reaction times for the equivalent nonpromoted formulation $BiMo_{12}O_x$ (see supplementary material), although, superficially, the observed methacrolein selectivity was similar to that seen in the continuous mode.

In a subsequent set of experiments, the gas–gas periodic flow reactor was used to investigate the reactivity of $BiMo_{12}Fe_2NiCo_7MgSb_{0.9}Ti_{0.1}Te_{0.02}Cs_{0.4}O_x$ in a similar way as was done for Bi_2MoO_6 (Table 2). The effect of increasing the isobutene concentration in the feed is characterised in Table 4. No carbon loss was found within experimental error. Clearly, this effect was replicated using the microreactor under pulse-flow conditions as well. Co-feeding isobutene/air gave only marginally lower methacrolein selectivity and slightly higher isobutene conversion, so that the overall yields were almost identical. This confirms that for the optimised promoted catalyst, the benefits of operating in a pulse-flow mode are very limited. In contrast, the nonpromoted $BiMoO_x$ catalyst led to lower conversion in a pulse-flow mode but gave almost total selectivity to methacrolein within experimental error.

Table 3
Comparison of the operation of $BiMoO_x$ and promoted $BiMoO_x$ catalysts in the pulse and continuous feed modes

Catalyst	Time (s)[a]	Normalised yield (10^{-8} mol s^{-1} m^{-2})					
		358 °C			376 °C		
		CO_2	Methacrolein	Carbon	CO_2	Methacrolein	Carbon
$BiMoO_x$	10	0	19.5	0	0	29.4	0
	30	0	10.5	0	0	17.3	0
	60	0	5.6	0	0	4.2	0
	90	0	3.0	0	0	3.7	0
	120	0	0	0	0	0	0
	Continuous	9.8[b]	3.6	0	19.8[c]	9.8	0
$Co_{0.25}BiMoO_x$	10	3.6	15.9	0	6.2	23.0	2.1
	30	0	5.8	0	0	7.8	1.0
	60	0	0	0	0	0	0
	Continuous	8.9[b]	0	0	22.0[c]	11.1	0
$Fe_{0.25}BiMoO_x$	10	2.0[d]	8.2	8.1	3.2[e]	11.3	10.7
	30	0	4.2	11.5	0	4.5	3.1
	60	0	2.0	3.6	0	2.3	0
	90	0	0	0	0	0	1.3
	Continuous	9.4[b]	4.8	0	13.8[f]	8.2	0

[a] Pulse mode data collected at specified times during 2 min isobutene feed (3.5 vol% isobutene in N_2, 50 ml min^{-1}); continuous mode data collected at 360, 370, 380, 390 °C using 3.5 vol% isobutene in air (50 ml min^{-1}).

[b] Continuous mode data collected at 360 °C.

[c] Continuous mode data collected at 380 °C.

[d] Pulse mode data collected at 355 °C.

[e] Pulse mode data collected at 370 °C.

[f] Continuous mode data collected at 370 °C.

Table 4
Effect of isobutene concentration on the operation of a gas–gas periodic flow reactor at 360 °C using $BiMo_{12}Fe_2NiCo_7MgSb_{0.9}Ti_{0.1}Te_{0.02}Cs_{0.4}O_x$

Isobutene (%)	(Isobutene + air)/He			(Isobutene + Ar)/He/O_2			ΔS (%)[a]
	Conversion (%)	Selectivity (%)	Yield (%)	Conversion (%)	Selectivity (%)	Yield (%)	
1.3	97.5	87.1	84.9	96.9	91.2	88.4	4.1
3.4	97.2	89.4	86.9	96.6	92.9	89.7	3.5
8.6	96.4	91.9	88.6	92.8	95.9	89.0	4.0

[a] ΔS (%) denotes the selectivity enhancement when operated in (isobutene + Ar)/He/O_2 mode compared with that in (isobutene + air)/He mode.

It is tempting to suggest that nonpromoted catalysts could be successfully operated for isobutene oxidation in the pulse- or gas–gas periodic flow mode, but several factors mitigate against this being a commercial possibility. First, the activity of the nonpromoted catalysts is much lower per unit area of catalyst compared with that of the promoted commercial formulations, and, consequently, the gains made in improved selectivity are unlikely to be sufficient to offset the higher costs associated with the inherently more complex pulse mode of operation. Second, the promoters provide a structural function [5] in that they lead to higher surface areas for the active catalysts (e.g., $BiMoO_x = 2$ $m^2\,g^{-1}$, $Co_{0.25}BiMoO_x = 4$ $m^2\,g^{-1}$, $BiMo_{12}Fe_2NiCo_7MgSb_{0.9}Ti_{0.1}Te_{0.02}Cs_{0.4}O_x = 6$ $m^2\,g^{-1}$), and, consequently, promoted catalysts will always exhibit superior catalyst performance in terms of methacrolein yield for this reaction. Nonetheless, the overall potential benefits of operation of nonpromoted and promoted bismuth molybdate catalysts in the pulse mode are small relative to the cost penalties associated with the more complex reaction. Hence, for this reaction, there is likely to be no performance benefit in using pulse or riser reactor technology. It is clear that the time-integrated activities of the low-activity nonpromoted $BiMoO_x$ catalysts are significantly impaired by operation in the pulse mode, even though selectivities are substantially higher. Although these results are only of academic interest, they may provide useful clues as to how the elusive goal of total reaction selectivity (i.e., 100% atom efficiency) can be obtained in heterogeneous oxidation reactions.

3.3. *Investigation of the first and subsequent pulses using TPR/TPO*

Since the initial studies of Robertson et al. [39] using TPR, TPR/TPO have been used to characterise the oxides used in redox reactions. Monts and Baiker [40] carried out a definitive study of TPR methodology and established the optimum conditions under which this characterisation technique should be used. To date, most researchers have used single TPR or TPO analysis for catalyst characterisation. This can be of great value in determining the optimum catalyst reduction or calcination temperatures, but for redox reactions, in which the catalyst cycles between reduction and oxidation, single TPR/TPO determinations may not be representative. The observation that the first pulse-mode operation with bismuth molybdate catalysts

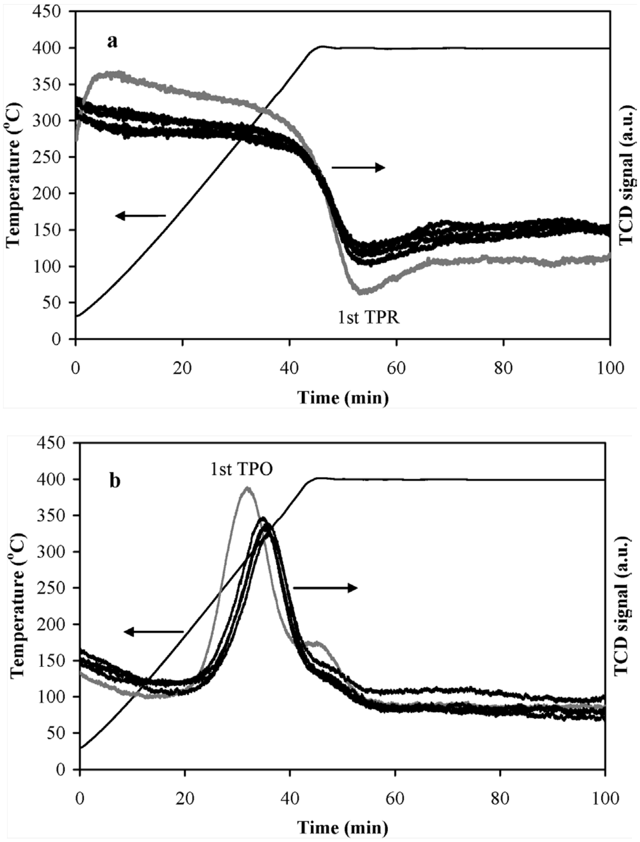

Fig. 10. Characterisation of Bi_2MoO_6 catalyst using 5 TPR/TPO cycles. Grey lines show the first TPR or TPO profiles: (a) TPR, (b) TPO. Conditions: 10 °C min^{-1}. TPR: 10% H_2/Ar, 50 ml min^{-1}. TPO: 10% O_2/He, 50 ml min^{-1}.

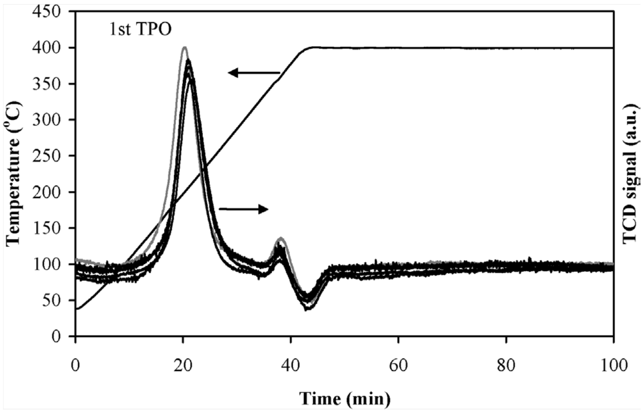

Fig. 11. TPO characterisation of Bi_2MoO_6 catalyst using 5 TPR/TPO cycles. Grey line shows the first TPO profile. Conditions: 10 °C min^{-1}. TPR: 4% isobutene/He, 50 ml min^{-1}. TPO: 10% O_2/He, 50 ml min^{-1}.

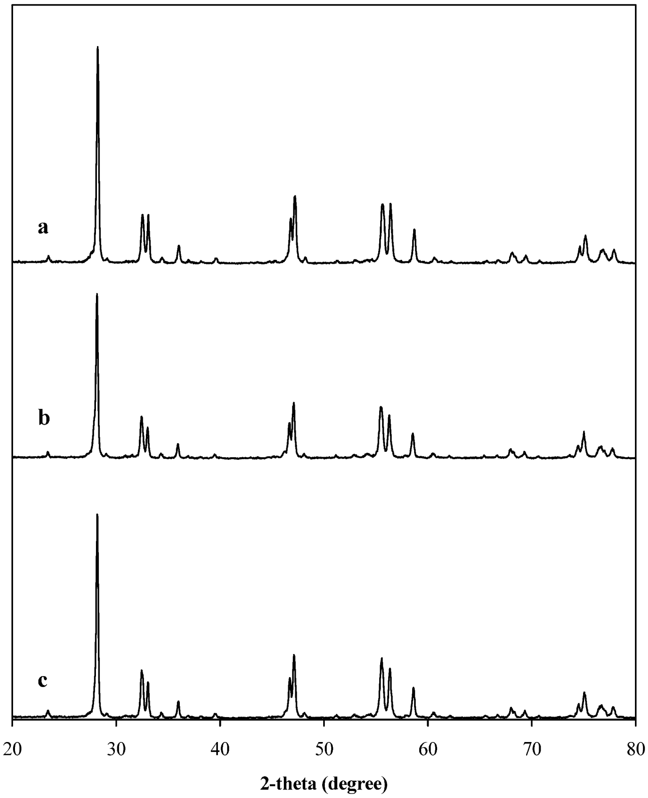

Fig. 12. Powder X-ray diffraction patterns for Bi_2MoO_6 catalyst: (a) fresh calcined catalyst, (b) after TPR_1/TPO_1, (c) after $TPR_1/TPO_1/\ldots/TPR_5/TPO_5$.

always gave a higher intrinsic activity for methacrolein formation than subsequent pulses (Fig. 6) prompted us to investigate TPR/TPO cycles as a means of characterising the redox behaviour of the γ-Bi_2MoO_6 catalyst. We investigated five cycles of TPO/TPR or TPR/TPO using dilute H_2 (10% H_2 in Ar) or dilute isobutene (4% isobutene in He) as the reducing agents and dilute O_2 (10% O_2 in He) as the oxidant. In these experiments, the temperature was ramped to 400 °C and held constant there. Typical data for this cyclic TPR/TPO study are shown in Fig. 10 for H_2 used as the reducing agent and in Fig. 11 for isobutene used as the reducing agent. The data for the TPR cycles with isobutene are complicated by the reaction of isobutene with the catalyst; hence only the TPO data are shown. However, in both cases, the initial TPR and TPO are significantly different from the subsequent TPR/TPO. Characterisation of the catalysts after H_2-TPR/TPO cycles using powder XRD (Fig. 12) show subtle changes in intensity in the 32° and 56° regions. Laser Raman spectroscopy (Fig. 13) shows no significant difference between the first and subsequent oxidation cycles. However, significant differences between the first TPR/TPO cycle and subsequent cycles were observed with all of the nonpromoted and promoted bismuth molybdate catalysts reported in this study and appears to be a consistent effect. These data indicate that single TPR and TPO determinations may not be appropriate for the characterisation of catalysts to be used in redox processes or cyclic operations using pulse reactors, such as the circulating fluidised bed reactor [11–15]. The observation that the first TPO determination is different from subsequent TPO cycles is consistent with the enhanced activity for methacrolein formation observed with the first isobutene pulse (Fig. 6). It is clear that reoxidation of the catalyst cannot restore the initial catalyst surface present after the calcination step of the preparation. In the present study, we used 480 °C as a calcination temperature. The pulse mode experiments were carried out with a maximum temperature of 390 °C; thus the TPR/TPO studies with a maximum temperature of 400 °C are consistent with the catalytic studies. However, to determine whether the effect is due

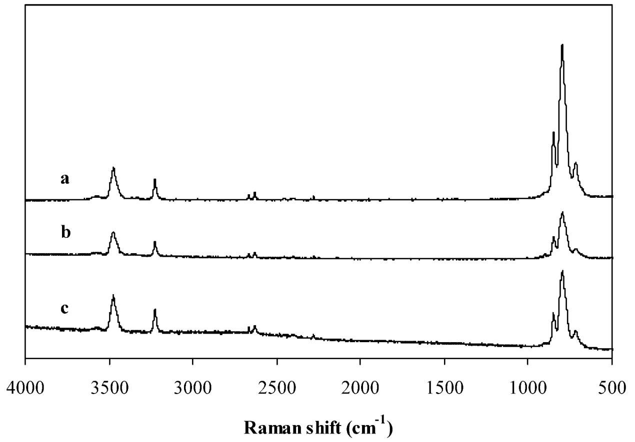

Fig. 13. Laser Raman spectra for Bi_2MoO_6 catalyst: (a) fresh calcined catalyst, (b) after TPR_1/TPO_1, (c) after $TPR_1/TPO_1/\ldots/TPR_5/TPO_5$.

to a higher calcination temperature, a series of TPO/TPR cycles were conducted with a maximum temperature of 500 °C. Again, the first TPR and TPO cycles were significantly different than the subsequent cycles. Thus the effect observed for the enhanced catalytic formation of methacrolein with the first pulse of isobutene is not related to the temperature at which the catalyst is reduced/oxidised. The origin of this effect remains unclear, but if it can be understood someday, then it may be possible to prepare catalysts with significantly improved intrinsic activities that are of generic importance for redox reactions in the pulse mode of operation.

4. Conclusion

A comparison of promoted and nonpromoted bismuth molybdate catalysts for the oxidation of isobutene to methacrolein has shown that the performance of the relatively noncomplex nonpromoted $BiMoO_x$ catalyst can be significantly improved by operation in the pulse mode. Significantly, almost total selectivity to methacrolein can be observed during the short duration of the pulse experiments. Promoted catalysts tend to yield greater deposition of carbon or reaction products during the pulse mode of operation, which significantly decreases the overall selectivity of these catalysts. We conclude that the complex catalysts designed specifically for use in the continuous mode are not well suited for use in the pulse mode of operation, and hence there is no potential benefit to be gained by operating the promoted bismuth molybdate formulation with a riser reactor [11–15] or gas–gas periodic flow reactor for this reaction. It is apparent that bismuth molybdate catalysts that are not particularly selective in the continuous-feed mode can be operated with improved performance in the gas–gas periodic-flow mode, but the potential gains are far outweighed by the complexity and cost of operating such a process on a commercial scale.

Overall, the complex promoted catalysts are superior to the nonpromoted catalysts because of their higher activities and higher surface areas. Interestingly, our results for this reaction indicate that the riser reactor technology could allow the use of relatively low-activity nonpromoted catalysts with high selectivity. However, commercially, these benefits would likely be outweighed by the complexity of operating a riser reactor.

Using TPO/TPR or TPR/TPO cycles has been shown to be informative. In most cases, the first TPR or TPO cycle is significantly different than subsequent cycles, although there is no effect on the bulk structure. This is consistent with the observation that the first pulse reaction cycle for isobutene oxidation gives significantly higher yields of methacrolein.

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Supplementary material

Powder XRD patterns, laser Raman spectra and some catalytic test data are provided.

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