

Designing Heterogeneous Catalysts for Microwave Assisted Selective Oxygenation

Jia Sun,^[a] James S. Hayward,^[a] Michael Barter,^[b] Daniel R. Slocombe,^[b] and Jonathan K. Bartley^{*[a]}

Microwave dielectric heating is an emerging technology in heterogeneous catalysis. However, catalyst design in this field is not as well developed as when conventional heating is used. In this study the selective oxidation of propene to acrolein has been used as a model reaction to understand how the properties of bismuth mixed metal oxide catalysts can be tuned for use in microwave assisted catalysis. The role of the dielectric properties, that are crucial to enable the catalyst to be heated in the microwave electric field, were determined using cavity perturbation methods. Catalysts with a very high loss tangent

reached high temperatures leading to combustion products, whereas materials with a low loss tangent could not be heated and were inactive. Bi₂MoO₆ and BiVO₄ both showed promising performance during an initial screening and were investigated further. For Bi₂MoO₆, a partial substitution of molybdenum with vanadium resulted in the formation of Bi_{1-x/3}V_{1-x}Mo_xO₄, with a decrease in particle size and dielectric loss tangent, and the highest rate of acrolein production was found when x=0.6 at 15 W microwave power. Higher microwave power resulted in thermal runaway which decreased the activity of the catalyst.

Introduction

Although microwave-assisted heterogeneous catalysis has been studied since the 1990s, there are still considerable advances to be made in both catalyst and reactor design for processes to be commercialised.^[1] Studies of batch and flow processes have demonstrated significant advantages of microwave heating over conventional heating and include higher heating rates, selective heating of individual components (e.g. solvents, reactants or catalysts), the creation of microwave plasmas, and the formation of hot spots on the catalysts, which can lead to reduced reaction times or enhancements in activity or selectivity.^[2-5]

Whether a catalyst can be heated using microwave irradiation is related to the complex permittivity and permeability of the material. Dielectric heating by the microwave-

electric field depends on the complex permittivity, ϵ^* , which is defined as:

$$\epsilon^* = \epsilon' - j\epsilon''$$

Where ϵ' is the real component of the dielectric permittivity that relates to a material's ability to hold electrical energy and ϵ'' is the imaginary component of the dielectric permittivity, known as the dielectric loss factor, which relates to the material's ability to convert the electrical energy into heat. Similarly, magnetic heating in the microwave-magnetic field depends on the complex permeability, μ^* , which is defined as:

$$\mu^* = \mu' - j\mu''$$

Where μ' is the real component of the complex permeability and μ'' is the imaginary component of the permeability.

Most microwave assisted catalytic processes use dielectric heating and the loss tangent ($\tan \delta$) is frequently used in the literature to provide an indication of how the material can be penetrated by an electric field and how it dissipates the energy as heat. Therefore, a material with a high loss tangent is easily heated in the microwave electric field and can be calculated using:^[6]

$$\tan \delta = \frac{\epsilon''}{\epsilon'}$$

Many reactions that have been studied require high temperatures, and this has led to the use of catalysts that can be heated easily by the microwave-electric field, such as carbon, rather than single metal oxides that can be more difficult to heat. Wan and Ioffe have demonstrated this difference in dielectric properties by exposing metal oxides and carbon to pulsed microwave irradiation for two minute intervals, and

[a] J. Sun, J. S. Hayward, J. K. Bartley
 Cardiff Catalysis Institute
 School of Chemistry
 Cardiff University
 Cardiff
 CF10 3AT, UK
 E-mail: BartleyJK@cardiff.ac.uk

[b] M. Barter, D. R. Slocombe
 Centre for High Frequency Engineering, Cardiff University, CF10 3AT Cardiff, U.K.
 and
 School of Engineering
 Cardiff University
 Cardiff
 CF10 3AT, UK

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found that carbon reached 1283 °C, compared to <361 °C for metal oxides. During these experiments several single metal oxides such as Al₂O₃, ZrO₂, CeO₂, MoO₃ and TiO₂, that are common components of oxidation catalysts, failed to reach 100 °C.^[7] Catalysts based on these metal oxides are likely to be inactive, as reaction temperatures may be difficult to obtain with microwave heating, although mixed metal oxides, such as titanates, ferrites, vanadates and molybdates have different complex permittivity and permeability properties and are easier to heat than single metal oxides.^[8]

Selective oxidation reactions could potentially benefit from some of the advantages associated with microwave heating if the dielectric heating can be controlled. The catalyst bed can be selectively heated, as gas phase reactants are not heated in the microwave-electric field. This can lead to reduced energy costs over conventional heating, as calculated by Stankiewicz et al.,^[1] and improved selectivity as gas phase sequential reactions are suppressed. However, hot spots on the catalyst surface could lead to high temperatures and combustion products being formed. To achieve high selectivity in partial oxidation reactions, both the dielectric properties and active sites of catalysts need to be optimised. In this study we have investigated the performance of bismuth mixed metal oxide catalysts and their dielectric properties, to demonstrate the importance of the synergy between these two aspects of catalyst design, using propene oxidation as a model reaction.

Results and Discussion

Catalyst Screening

To gain a clearer understanding of the differences between conventional and microwave-assisted gas phase heterogeneous catalysis, a series of screening experiments were carried out.

Typical materials used for microwave electric field heating, such as activated carbon and silicon carbide were investigated and were found to reach very high temperatures, resulting in

full combustion to carbon oxides. Traditional propene oxidation catalysts, bismuth oxide containing mixed oxides, were also screened for comparison.

The bismuth-based metal oxides were synthesized using both a hydrothermal method (HT) and a sol-gel method based on the citric acid complexation (CA). These were tested as catalysts in the selective oxidation of propene under conventional heating at 400 °C and under microwave electric field heating at 25 W microwave power, respectively. The experimental results, as well as the specific surface area and dielectric parameters of each sample are shown in Table 1.

Most of the bismuth-based mixed metal oxides (except Bi₂Mo₃O₁₂ and Bi₂Mo₂O₉) showed good ability to be heated and could convert propene under microwave irradiation. Under conventional heating, the bismuth molybdate catalysts led to both higher propene conversion and higher acrolein selectivity, while under microwave heating, Bi₂Mo₃O₁₂ and Bi₂Mo₂O₉ cannot be well heated and Bi₂MoO₆ performed intermediately. BiVO₄ samples also performed well for both propene conversion and acrolein selectivity. Under conventional heating, bismuth molybdate samples showed a better performance than other bismuth-based materials. All the bismuth molybdate phases synthesized using the citric acid complexation method performed excellently in producing acrolein under conventional heating. However, in the microwave-electric field only Bi₂MoO₆ could be heated, showing promising activity, while Bi₂Mo₃O₁₂ and Bi₂Mo₂O₉ could not be heated and showed little activity.

The loss tangent was measured using a cavity perturbation technique.^[9] Both Bi₂Mo₃O₁₂ and Bi₂Mo₂O₉ were found to have very low loss tangents compared to Bi₂MoO₆ and only have limited ability to convert the microwave radiation to heat. The three samples were all prepared using the same synthesis method, but different molybdenum to bismuth ratios lead to different structures, which will cause them to have different dielectric properties.^[10]

BiFeO₃ and Bi₄Ti₃O₁₂ were found to have relatively high loss tangents, and could be heated in the microwave field, so are potentially good candidates for microwave-assisted heteroge-

Table 1. BET surface area, dielectric loss tangent and catalysts performance of bismuth mixed oxide catalysts under conventional heating at 400 °C and microwave heating using 25 W power. (Reaction conditions: 0.2 g of catalyst, propene:oxygen:nitrogen = 1 : 2 : 97, flow rate = 50 mL min⁻¹).

Catalyst ^[a]	S.A. (m ² g ⁻¹) ^[b]	ε'	tan δ	Conventional heating		Microwave heating		
				Conversion (%) ^[c]	Selectivity (%) ^[d]	Temperature (°C) ^[e]	Conversion (%) ^[c]	Selectivity (%) ^[d]
Bi ₂ MoO ₆ (HT)	17	1.0012	0.0560	5	24	490	82	1
Bi ₂ MoO ₆ (CA)	8	1.0013	0.0483	35	61	389	29	69
Bi ₂ Mo ₂ O ₉ (CA)	6	1.0009	0.0174	11	89	120	3	0
Bi ₂ Mo ₃ O ₁₂ (CA)	8	1.0001	0.0133	16	87	105	2	0
BiVO ₄ (HT)	24	1.0010	0.0324	13	24	397	23	49
BiVO ₄ (CA)	17	1.0013	0.0283	10	21	345	17	45
Bi ₄ Ti ₃ O ₁₂ (HT)	9	0.0013	0.0494	20	1	377	86	2
BiFeO ₃ (HT)	81	1.0011	0.1111	17	1	364	26	0

[a] Catalysts prepared using hydrothermal synthesis (HT) or citrate sol-gel method (CA). [b] Catalyst surface area. [c] Conversion of propene. [d] Selectivity to acrolein. [e] Catalyst bed temperature at 25 W.

neous catalysis studies. However, they were not selective to acrolein, even at low conversion, under both conventional and microwave heating. It can be seen from these initial experiments that, in addition to the ability to be heated, a promising candidate as a selective oxidation catalyst must also have a good catalytic performance to produce the target products. Although catalysts produced using the hydrothermal method were initially more active, they deactivated quickly under reaction conditions (Table 1). This was attributed to the lack of a calcination step during the synthesis that is crucial to form a stable catalyst for microwave heating.

Catalyst Characterization

Having identified Bi_2MoO_6 and BiVO_4 as promising candidates, a series of bismuth molybdate vanadate samples were prepared using the sol-gel methodology with different ratios of molybdenum to vanadium. The samples were denoted as $\text{Bi-Mo}_a\text{-V}_b$, where a and b are the percentage ratios of molybdenum and vanadium in the materials. The XRD patterns of the materials with different Mo:V ratios, are shown in Figure 1.

The XRD patterns showed that without vanadium the orthorhombic Bi_2MoO_6 was the main phase produced, combined with a small amount of $\text{Bi}_2\text{Mo}_2\text{O}_9$. When 10% vanadium was introduced ($\text{Bi-Mo}_{90}\text{-V}_{10}$) the orthorhombic Bi_2MoO_6 remains although splitting of the peak at $2\theta = 28^\circ$ is observed. This splitting is due to V^{5+} cations replacing an equivalent number of Mo^{6+} cations at the orthorhombic sites which creates O vacancies in the structure.

As more vanadium is added ($\text{Bi-Mo}_{80}\text{-V}_{20}$, $\text{Bi-Mo}_{70}\text{-V}_{30}$ and $\text{Bi-Mo}_{60}\text{-V}_{40}$) two patterns are observed that can be assigned to the orthorhombic Bi_2MoO_6 which is noted by the reflection marked (131) in Figure 1; and tetragonal structured $\text{Bi}_{1-x/3}\text{V}_{1-x/3}\text{Mo}_x\text{O}_4$ which is identified by the reflections at (101) (112) (116)

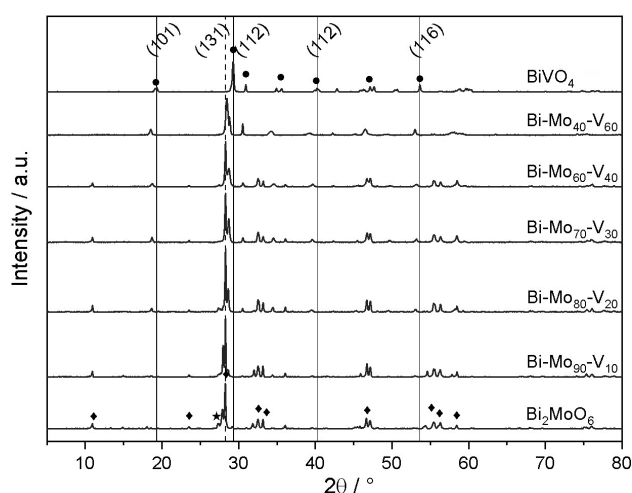


Figure 1. The XRD patterns of the synthesised bismuth molybdate, bismuth vanadate and bismuth molybdate vanadate materials with different Mo:V ratios. Samples are denoted $\text{Bi-Mo}_a\text{-V}_b$, where a and b are the percentage ratios of molybdenum and vanadium in the materials. Key: $\blacklozenge = \text{Bi}_2\text{MoO}_6$; $\star = \text{Bi}_2\text{Mo}_2\text{O}_9$; $\bullet = \text{BiVO}_4$.

(121) and (116). This $\text{Bi}_{1-x/3}\text{V}_{1-x/3}\text{Mo}_x\text{O}_4$ solid solution has been reported previously,^[10-12] where Mo^{6+} cations replace an equivalent number of V^{5+} cations at the tetrahedral sites, leaving vacancies evidenced by the splitting of the peaks at $2\theta = 19^\circ$, 29° , 47° , and 53° .^[11] $\text{Bi-Mo}_{40}\text{-V}_{60}$ contains only tetragonal structured $\text{Bi}_{1-x/3}\text{V}_{1-x/3}\text{Mo}_x\text{O}_4$ with $x=0.4$ and complete substitution of molybdenum with vanadium shows a pattern that can be indexed to tetragonal BiVO_4 .

Using the reference intensity ratios (RIR) from the International Centre for Diffraction Data PDF database, based on the intensity of the reflections in the powder pattern compared to corundum (I/Ic), the relative amounts of each phase could be estimated, and these are shown in Table 2. Although the use of RIR can only be considered semi-quantitative, some general observations can be made from the analysis. The relative amount of the tetragonal phase was seen to increase with increasing vanadium content. The stoichiometry suggests that excess bismuth will be present when the $\text{Bi}_{1-x/3}\text{V}_{1-x/3}\text{Mo}_x\text{O}_4$ tetragonal phase is formed, so it is likely that an X-ray amorphous bismuth rich phase was also formed in samples with a high vanadium content. Crystallite size and lattice constants for the bismuth molybdate vanadate samples were calculated and are shown in Table 3. The loss tangents of the materials were found to be strongly influenced by crystallite size and for both the orthorhombic structured Bi_2MoO_6 and tetragonal structured $\text{Bi}_{1-x/3}\text{V}_{1-x/3}\text{Mo}_x\text{O}_4$ the crystallite sizes were found to decrease with increasing vanadium content.

The dielectric properties of the materials (Table 4) were measured using a cyl- ϵ cavity operating at 2.5 GHz in the TM_{010} mode. The dielectric constant (ϵ') did not show significant change for the materials with different V:Mo ratios, while replacing Mo with V led to changes in the dielectric loss (ϵ''). The dielectric loss initially increased with vanadium addition and reached a maximum value with 40% vanadium. The dielectric loss started to decrease at higher vanadium content and was considerably lower for the pure BiVO_4 phase. The loss tangent of the bismuth molybdate vanadate catalysts is shown in Figure 2.

The loss tangent of the samples increased as the molybdenum was partially substituted with vanadium to a maximum when the vanadium content was 40% ($\text{Bi-Mo}_{60}\text{-V}_{40}$). When the

Table 2. Relative amounts of the phases present in bismuth molybdate vanadate materials prepared with different Mo:V ratios calculated from the XRD patterns in Figure 1 using ICDD relative intensity ratios.

Catalyst	Bi_2MoO_6 ^[a]	BiVO_4 ^[b]	$\text{Bi}_2\text{Mo}_2\text{O}_9$ ^[c]
Bi_2MoO_6	92.63	0	7.37
$\text{Bi-Mo}_{90}\text{-V}_{10}$	87.63	0	12.37
$\text{Bi-Mo}_{80}\text{-V}_{20}$	79.46	21.54	0
$\text{Bi-Mo}_{70}\text{-V}_{30}$	63.86	35.14	0
$\text{Bi-Mo}_{60}\text{-V}_{40}$	56.76	43.24	0
$\text{Bi-Mo}_{40}\text{-V}_{60}$	0	100	0
BiVO_4	0	100	0

[a] ICDD reference pattern 72-1524. [b] ICDD reference pattern 72-1524. [c] ICDD reference pattern 72-1524.

Table 3. Crystallite size and lattice constants for bismuth molybdate vanadate materials with different Mo:V ratios, calculated from the XRD patterns in Figure 1.

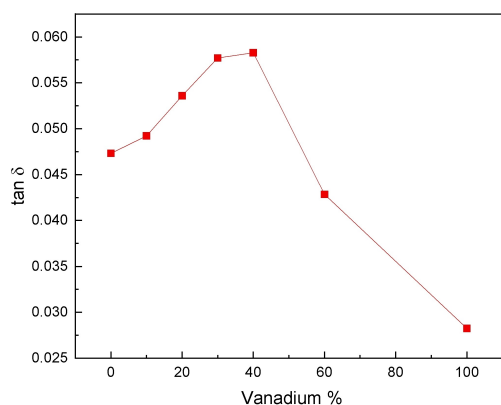
Catalyst	Crystallite size (nm)	Lattice parameters							
		Phase ^[a]	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	α (°)	β (°)	γ (°)	volume (Å ³)
Bi ₂ MoO ₆	607	O	5.50	16.20	5.49	90	90	90	490
	394	M	11.94	10.82	10.87	90	89.81	90	1534
Bi–Mo ₉₀ –V ₁₀	599	O	5.50	16.20	5.48	90	90	90	489
	665	M	11.90	10.79	11.85	90	90.62	90	1521
Bi–Mo ₈₀ –V ₂₀	588	O	5.50	16.20	5.48	90	90	90	489
	442	T	5.21	5.21	11.69	90	90	90	317
Bi–Mo ₇₀ –V ₃₀	580	O	5.50	16.20	5.48	90	90	90	489
	352	T	5.19	5.19	11.69	90	90	90	315
Bi–Mo ₆₀ –V ₄₀	536	O	5.51	16.18	5.48	90	90	90	488
	289	T	5.17	5.17	11.82	90	90	90	317
Bi–Mo ₄₀ –V ₆₀	270	T	5.21	5.21	11.72	90	90	90	317
BiVO ₄	381	T	5.10	5.10	11.58	90	90	90	301

[a] O = Orthorhombic, T = Tetragonal, M = Monoclinic.

Table 4. Dielectric and physical properties of the bismuth molybdate vanadate catalysts.

Catalyst	S.A. (m ² g ⁻¹) ^[a]	ϵ'	ϵ''
Bi ₂ MoO ₆	8	1.0013	0.04738
Bi–Mo ₉₀ –V ₁₀	9	1.0012	0.04927
Bi–Mo ₈₀ –V ₂₀	10	1.0010	0.05364
Bi–Mo ₇₀ –V ₃₀	10	1.0010	0.05776
Bi–Mo ₆₀ –V ₄₀	10	1.0009	0.05833
Bi–Mo ₄₀ –V ₆₀	14	1.0010	0.04289
BiVO ₄	17	1.0013	0.02828

[a] Catalyst surface area.

**Figure 2.** Loss tangent of bismuth molybdate vanadate catalysts synthesised with different amounts of vanadium partially substituted for molybdenum

vanadium content is greater than 40% the loss tangent dropped sharply. From the XRD results (Figure 1, Table 2), with 0–40% vanadium substitution, all catalysts contain orthorhombic structured Bi₂MoO₆, and this starts to decrease as the vanadium content increases further. This could be related to

the larger loss tangent of Bi₂MoO₆ compared to the other bismuth molybdate phases (Table 1) that is crucial for the catalyst to convert the microwave radiation into heat. It has previously been reported that introducing defects in a dielectric material will increase the loss tangent as the ions are non-uniformly distributed so that they break the periodic arrangement of charges in the crystal.^[13,14] The increasing number of defects in the sample associated with the substitution of molybdenum with vanadium could also result in increased loss tangents for the higher loadings.

Catalyst Testing

To investigate the performance of the catalysts, reactions were carried out under microwave and conventional heating at 15 W microwave power or 400 °C respectively.

Mo:V Ratio

Figure 3 shows the propene conversion over the bismuth molybdate vanadate catalysts with different vanadium content under microwave heating.

Partial substitution of molybdenum with vanadium improves the activity of catalysts under microwave heating, and the catalyst with 40% vanadium was found to give a significant enhancement over the bismuth molybdate, with the propene conversion increasing from 10% to 64%. When the vanadium content increases above 40%, the catalyst starts to become difficult to heat as the loss tangent reduces, and the conversion dropped below 10%. The propene conversion showed a positive correlation with the temperature of the catalyst bed. According to the dielectric parameters given in Figure 2 and Table 4, the 40% V sample has the largest loss tangent among

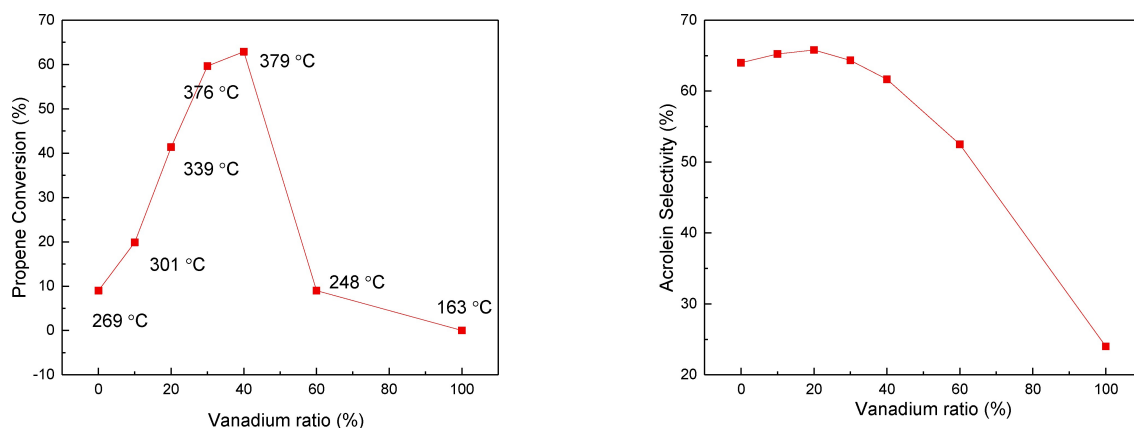


Figure 3. Propene conversion and acrolein selectivity over the bismuth molybdate vanadate catalysts under microwave heating (15 W input power, 0.2 g of catalyst, propene:oxygen:nitrogen = 1:2:97, flow rate = 50 mL min⁻¹). The temperature labels on the points are the catalyst bed temperatures.

the samples, which means that sample can convert the microwave energy into heat more effectively than other materials and reaches a higher temperature, leading to higher conversion.

Figure 3 also shows the acrolein selectivity at 15 W microwave power. Catalysts with vanadium content from 0–40% all displayed a good acrolein selectivity of more than 60%, with the best acrolein selectivity of 65% achieved by the material containing 20% V. However, it is difficult to compare the selectivity between different samples, because there is more than one factor that can affect the selectivity, for example, the structure of the catalyst, the conversion and the temperature the catalyst bed can achieve. To have a clearer understanding of the influence of vanadium substitution, conventional tests was also carried out at a fixed temperature of 400 °C, which is similar to the highest bed temperature measured at 15 W microwave power (Figure 4).

Under conventional heating, replacing molybdenum with vanadium also improved catalyst activity and acrolein selectivity. The trend is very similar to the microwave tests, with the highest conversion under conventional heating observed with 40% V and a drop in conversion as the vanadium content

increased. However, it is interesting that at low vanadium content the catalysts showed poor activity, despite the higher temperature than observed under microwave heating and that the catalysts with 20–40% V showed higher conversion despite the lower measured bed temperature. It should be noted that under microwave heating the temperature was measured remotely using an IR camera that is not as accurate as the thermocouple inserted into the bed during conventional heating and could underestimated bed temperature. However, it is clear that the dielectric properties are not the only factor in determining activity under microwave heating, and the nature of the active sites on the catalysts is also important. The acrolein selectivity also showed a similar trend to the microwave heating results, with high selectivity at low vanadium content that dropped when the vanadium content was above 20%.

The results of conventional tests at 400 °C confirm that temperature is not the only factor responsible for the performance of bismuth vanadate molybdate catalysts, and the composition and structure of catalysts also play an important role. The trends observed under conventional heating are consistent with previous research investigating the influence of

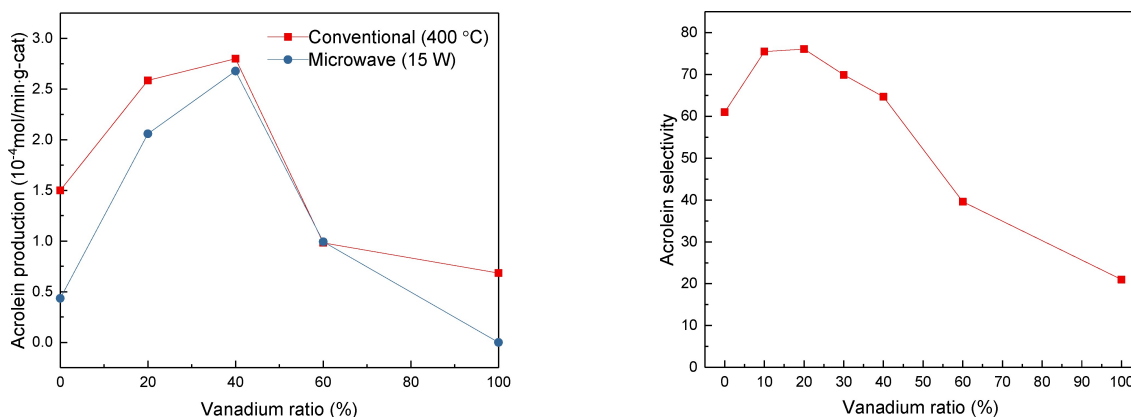


Figure 4. Propene conversion and acrolein selectivity over the bismuth molybdate vanadate catalysts under conventional heating (400 °C, 0.2 g of catalyst, propene:oxygen:nitrogen = 1:2:97, flow rate = 50 mL min⁻¹).

vanadium content on catalyst activity^[11,15] and selectivity.^[11] These previous studies investigated the kinetics of propene oxidation over bismuth molybdate vanadate mixed metal oxide catalysts and found that, with increasing vanadium content, the formation of tetragonal $\text{Bi}_{1-x/3}\text{V}_{1-x}\text{Mo}_x\text{O}_4$ will facilitate the production of carbon oxides, which leads to the drop in acrolein selectivity.

Microwave Power

The catalyst containing 40% V was demonstrated to be the most efficient catalyst at converting microwave radiation into heat, with a high selectivity to acrolein. This catalyst was used to understand the impact of heating on the performance, and this was further investigated under microwave heating at different powers from 2.5 to 25 W (Figure 5).

The acrolein production initially increased as the input power increased but then decreased at higher power input, with the best acrolein production rate achieved at 15 W. At low power (<7.5 W), the catalyst bed temperature is low, and little propene was converted. This is because the catalyst cannot absorb enough energy from the microwave to reach the reaction temperature. As the input power is increased, the propene conversion and acrolein production both experienced sharp rises with maximum conversion and acrolein yields achieved at 15 W. At high power (>15 W), the temperature of the catalyst bed increased sharply and reached high temperature >600 °C in a very short time, and then decreased dramatically. The spike in temperature is a sign of thermal runaway that can occur at high power under microwave heating.^[16] This phenomenon has been discussed by Zhang and Hayward in their review of the applications of microwave-assisted heating in the field of environmental-related heterogeneous catalysis and concluded that there is a critical power value for peak performance.^[16] When the input power is less than the critical power, the sample will heat to a steady temperature, but for input powers above critical power, the temperature will continue to rise uncontrollably. In thermal runaway, the sample temperature can keep on rising until the sample melts or decomposes.

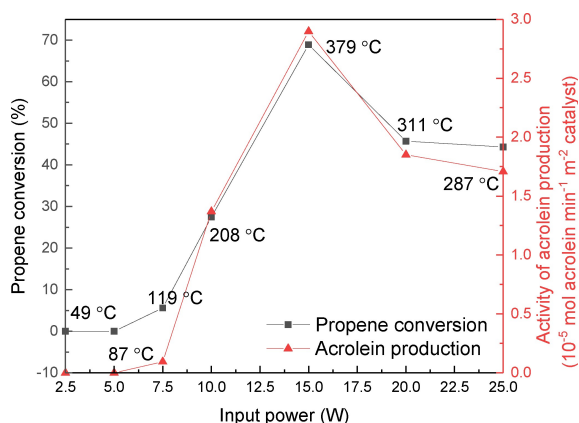


Figure 5. Propene conversion and rate of acrolein production over the

Following the temperature spike the power was stopped and the catalyst bed allowed to cool. When the reaction was restarted a steady catalyst bed temperature was reached in the next run (Figure 5 – 20 W and 25 W) although the observed conversion, yield and temperature were lower than at 15 W input. This is attributed to the temperature spike in the first run causing sintering or a phase change in the catalyst that led to a change in the dielectric properties of the sample. Further dielectric measurements could be taken to investigate this hypothesis, although after thermal runaway the catalyst could not be recovered from the reactor tube for further characterisation in this study.

Comparison of Conventional and Microwave Heating

The most promising catalyst from the microwave-assisted process, containing 40% V, was also tested under conventional heating conditions (Figure 6). As expected, under conventional heating the propene conversion increased with increasing temperature, whilst the highest acrolein production rate was achieved at 450 °C, as at higher temperature the selectivity to CO and CO₂ starts to increase over the tetrahedral phase bismuth molybdate vanadate mixed metal oxide catalysts in line with previous studies.^[11,15]

Ikawa has suggested a correlation between the acrolein selectivity and the bandgap of the catalyst.^[15] They studied a scheelite structured $\text{Bi}_{2-x/3}\text{Mo}_x\text{V}_{1-x}\text{O}_{12}$ ($x=0-1$) catalyst and found that the bandgap of this catalyst decreased with increasing V content. From these experiments they proposed that when the bandgap of the catalyst falls below 2.1 eV, the intrinsic selectivity to acrolein decreases rapidly and then decreases further with increasing propene conversion. This is attributed to the high activity of oxygen atoms at the catalyst surface leading to oxidation of the intermediate from which acrolein is formed and the sequential combustion of acrolein to CO₂.

Under microwave heating, the highest acrolein production rate of around $2.9 \times 10^{-5} \text{ mol acrolein min}^{-1} \text{ m}^{-2} \text{ catalyst}$ was achieved at 15 W input power with a measured catalyst bed

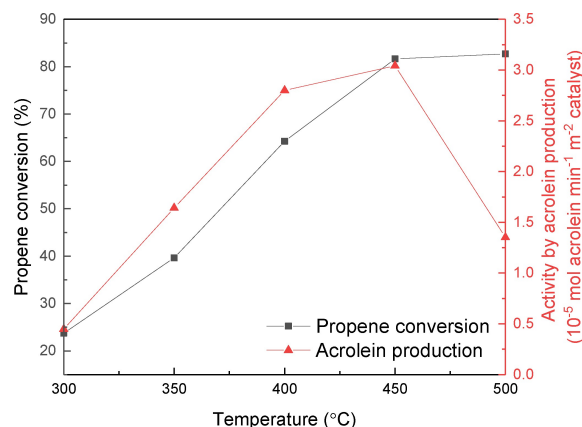


Figure 6. Propene conversion and activity of acrolein production the

temperature of 379 °C. As shown in Figure 6, a similar acrolein production rate of 3.0×10^{-5} mol acrolein $\text{min}^{-1} \text{m}^{-2}$ catalyst was achieved at 400–450 °C under conventional heating. By comparing the acrolein production rate in the conventional and microwave-assisted processes, it could be assumed that the catalyst performance is largely related to the temperature of the catalyst bed. Although the catalyst bed temperature appeared lower under microwave irradiation than with conventional heating, the temperature measured using an IR camera is the average temperature of the whole catalyst bed and localised hotspots are likely to be at higher temperatures.

Several byproducts have been identified in the selective oxidation of propene to acrolein over bismuth molybdate catalysts, including acetaldehyde, acetone, acrylic acid, acetic acid, ethene, butadiene, benzene, CO, and CO₂ as well as trace amounts of crotonaldehyde and methyl vinyl ketone. Bui et al. carried out an investigation into the mechanisms of product formation and identified that acrolein, acetaldehyde, acetone, acetic acid and CO_x were primary products which could be further converted to the secondary products acrylic acid, ethene, butadiene and benzene.^[17]

In this study we have observed similar products to Bui et al., although at high conversion acrolein and CO_x accounted for 93–95% of the products formed, which meant quantification of minor byproducts was difficult. However, it was noticeable that under microwave heating at low conversions ($\leq 25\%$) the major byproducts were C₂ and C₃ oxygenates with very little CO_x, in contrast to previous studies using conventional heating. This suggests that heating the catalyst surface, but not the gas stream can be advantageous for selective oxidation reactions if gas phase oxygen does not participate in non-selective oxidation and secondary reactions are limited, shifting the product distributions observed.

Conclusions

Microwave assisted catalysis can have several advantages of conventional heating. When designing catalysts for use in microwave-assisted catalysis both the catalyst performance and the dielectric properties need to be considered. Although several bismuth molybdate phases have been found to be active for selective oxidation, many of these could not be heated in the microwave electric field and so were not active under microwave heating.

Partial substitution of molybdenum with vanadium can increase the ability of the catalyst to convert the microwave energy into heat and enhances the propene conversion and the acrolein production rate. The investigation of bismuth molybdate vanadate with different Mo:V ratios found that tetrahedral phase $\text{Bi}_{1-x/3}\text{V}_{1-x}\text{Mo}_x\text{O}_4$ with $x=0.6$ gave the best acrolein reaction rates. This was attributed to the reduced particle size and the increase in the dielectric loss tangent as vanadium was incorporated, resulting in high temperatures being reached at a microwave power of 15 W. However, the input power of the microwave can also affect the performance. At high power (> 15 W), the steady state catalyst bed temperature and perform-

ance dropped which was attributed to the catalyst sintering or a solid-state phase transition at the extremely high temperatures reached due to the observed thermal runaway.

The understanding of how the dielectric properties influence the catalyst performance from this study will enable the design of improved catalysts for use under microwave heating in the future. The development of new catalysts will help develop the field of microwave-assisted catalysis, allowing processes to utilise the energy advantages that the selective heating using microwave field provides.

Experimental Section

Catalyst Synthesis

A group of bismuth-based Bi–M–O oxides, where M is V, Mo or a combination of V and Mo, were prepared using a sol-gel method (see ESI for full details).^[18] The appropriate amounts of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, NH_4VO_3 and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ and citric acid were dissolved in water and stirred at 60 °C for 24 h to remove the solvent. The resultant gel was dried overnight, then calcined in static air at 500 °C for 2 h with a ramp rate of 2 °C min^{-1} .

A second group of bismuth-based Bi–M–O oxides, where M is V, Mo, Fe or Ti were prepared using a hydrothermal method (see ESI for full details).^[19]

The appropriate amounts of metal precursors ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, Na_3VO_4 , $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$) were dissolved in 5 mL of HNO_3 (4 M). NaOH (2 M) was added dropwise into the solution until the target pH value was reached and stirred for 2 h. The suspension was transferred into a 100 mL Teflon-lined stainless-steel autoclave to 70% of the total volume and heated at 160 °C for 24 h at autogenous pressure and then cooled to room temperature. The resulting solids were separated by filtration and dried at 110 °C overnight. Full details are given in the ESI.

Catalyst Characterisation

The physical properties of the catalysts were characterised using a combination of X-ray diffraction and nitrogen physisorption. Full details are given in the ESI.^[20,21]

Dielectric properties were analysed using TM_{010} modes of a cyl- ϵ resonant microwave cavity.^[21] f_0 and Q_0 were measured with an empty quartz tube, and f_s and Q_s were recorded with the samples inserted into the tube. The real part and imaginary part of the complex permittivity were calculated using the cavity perturbation theory described in the ESI.

Evaluation of Catalytic Performance

The catalytic performance of the prepared catalysts was evaluated for the selective oxidation of propene to acrolein at atmospheric pressure in a laboratory fixed bed reactor using either conventional or microwave dielectric heating.

0.2 g of catalyst was placed in a quartz reactor tube (7 mm internal diameter) held between plugs of quartz wool. Propene, nitrogen and oxygen were introduced using mass flow controllers (Bronkhorst) to give a total flow rate of 50 ml min^{-1} (propene:O₂:He = 5:10:85). The outlet lines were heated to 140 °C to prevent condensation of the products. Products were analysed using online gas chromatography (See ESI for details).

For conventional heating experiments the reactor was placed in a tubular furnace (ϵ -elements) and the temperature was monitored using a thermocouple at the centre of the catalyst bed.

For experiments carried out using microwave dielectric heating a TM_{010} single-mode microwave cavity was used. The reactor tube was located in the middle of the cavity. 2.5 GHz microwave radiation with a power of 0–30 W irradiated the catalyst bed through a hole in the side of the cavity perpendicular to the catalyst bed. On the opposite side of the cavity, an infrared camera was mounted to detect the temperature of the catalyst bed when steady state was achieved.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are openly available in Cardiff University Research Portal at <http://doi.org/10.17035/d.2024.0316223812>.

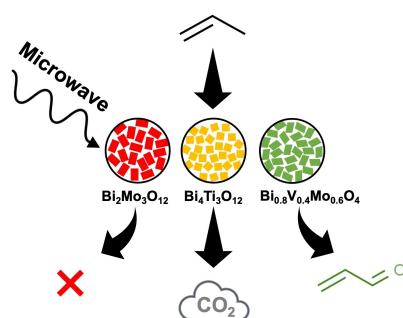
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RESEARCH ARTICLE

The selective oxidation of propene to acrolein was investigated under microwave heating using bismuth molybdate vanadate catalysts. The dielectric properties of the catalyst are crucial to enable it to be heated in the microwave electric field. High loss tangents lead to high temperatures and combustion (yellow catalyst), while low loss tangents mean catalysts cannot be heated to the reaction temperature (red catalyst). Partially substituting molybdenum with vanadium enabled the dielectric properties to be tuned to maximise the acrolein yield (green catalyst).



*J. Sun, J. S. Hayward, M. Barter, D. R. Slocombe, J. K. Bartley**

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Designing Heterogeneous Catalysts for Microwave Assisted Selective Oxygenation

