Raman studies of peroxide formation, decomposition, and reduction on Ba/MgO

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Ba/MgO is an active catalyst for the oxidative coupling of methane to form ethane and ethylene. It has been proposed that activation of methane occurs via reaction with peroxide species present at the surface of the catalyst. In the present work, Raman spectroscopy has been used to investigate the formation, decomposition, and reduction of BaO_2 on 4 mol% Ba/MgO. The presence of BaO_2 is evidenced by the presence of a band at 842 cm^{-1}. The peroxide forms above 300°C but is stable to decomposition at temperatures up to 500°C. Reduction of BaO_2 to BaO proceeds via $Ba(OH)_2$. $BaCO_3$ forms when either BaO or BaO_2 is exposed to CO_2. Once formed, $BaCO_3$ is stable to decomposition in He or O_2 at temperatures up to 500°C. Only $BaCO_3$ is observed when a mixture of CH_4 and O_2 is passed over the catalyst at 500°C.

Keywords: Raman spectroscopy; barium peroxide

1. Introduction

Group IA or IIA ions supported on basic metal oxides (e.g., Li/MgO, Ba/MgO, Sr/La_2O_3) have been demonstrated to exhibit reasonably high activity and selectivity for the oxidative coupling of methane to ethane and ethylene [1–4]. While it has been shown that oxygen ions present at the surface of these catalysts are responsible for the activation of methane to form CH_3 radicals, which then recombine largely in the gas phase to form C_2H_6, identification of the specific oxygen anions involved in this process remains a subject of on-going investigation. In the case of Li/MgO, ESR studies have revealed the presence of Li^+O^- centers, and theoretical calculations have suggested that such centers could readily activate methane to CH_3 radicals and OH^- anions [1]. However, there is some question whether the concentration of Li^+O^- centers is sufficient to serve as the primary sites for catalysis. Investigations conducted with Ba/MgO have provided convincing evidence for the role of peroxide anions in the oxidative coupling of methane. XPS studies carried out in combination with activity measurements have shown a strong correlation between activity of Ba/MgO and the surface concentration of O_2^{2-} anions [4]. The presence of peroxide anions has recently been confirmed by in situ Raman spectroscopy on Ba/MgO [5]. A band at 842 cm^{-1}, characteristic of BaO_2, was observed at temperatures up to 800°C. In the presence of CH_4 and O_2 at temperatures above 700°C the peroxide signal disappeared and a strong carbonate band appeared at 1050 cm^{-1}. In other work [6], it has been demonstrated that noncatalytic oxidative coupling of methane will occur over BaO_2 at temperatures as low as 400°C.

This paper reports the results of Raman observations of a 4 mol% Ba/MgO catalyst at temperatures up to 500°C. The purpose of the investigation was to study the formation, stability, and reactivity of active oxygen species on the catalyst as a function of gas composition at temperatures near the onset of oxidative coupling. Of particular interest was to establish the temperature range in which BaO_2 could be formed and the stability of BaO_2 to thermal decomposition and to reduction by H_2 and CH_4. The interactions of BaO and BaO_2 with CO_2 were also examined, as were their interactions of the catalyst with a CH_4/O_2 mixture.

2. Experimental

A 4 mol% Ba/MgO catalyst was prepared by adding $Ba(NO_3)_2$ (Aldrich, 99.98%) to a slurry of MgO (Mallinckrodt, USP) in deionized water. After stirring at room temperature for 24 h, the water was evaporated by heating the slurry over a hot plate for 4 h. The wet powder was dried in a vacuum oven at 25°C for 1 h and then calcined in air for 4 h at 500°C. The BET surface area of the calcined catalyst is 34.2 m^2/g. The gases used are helium (99.999%, Matheson), hydrogen (99.99%, Amerigas), methane (99.97%, Matheson), carbon dioxide in helium (4.07%, Matheson), and O_2 (99.997%, Alphagaz).

Samples for Raman spectroscopy were prepared by pressing a pellet of the air-calcined powder (10 000 psi). The pellet was placed in a quartz Raman cell [7] and reduced in H_2 at 500°C for 18 h, after which it was oxidized in O_2 at 500°C for 24 h. Spectra were acquired using a double monochromator operated as a spectrophotometer. A single-notch holographic filter (Kaiser Optical HNF-1164) was used to eliminate Rayleigh scattering, and the signal was detected by a photodiode array (Princeton Instruments EIRY-1024). The Raman spectra were recorded with a spectral resolution of 1.8 cm^{-1}. The 488.0 nm line of an argon ion laser was used and the laser power at the sample was set to 50 mW. Decomposition of the sample due to laser heating was not observed, so the samples were not rotated.

3. Results and discussion

Prior to oxidation, the catalyst was reduced at 500°C for 18 h in 1 atm of flowing H_2, and then cooled to 25°C. The sample was then heated in 1 atm of flowing O_2. With the exception of a weak band at 1056 cm^{-1} due to surface carbonate species, no Raman bands were observed below 300°C. Fig. 1 shows that after calcination for 13 h at 300°C a band appears at 842 cm^{-1}. Raising the oxidation temperature to 400°C increases the intensity of this band significantly. Increasing the temperature to 500°C does not change the band intensity further. The position of the band at 842 cm^{-1} is characteristic of O–O stretching vibrations in peroxide anions, and both the band shape and position are identical to those reported previously by Lunsford et al. [5]. Assignment of this band to BaO_2 is strongly supported by the similarity of the band shape and position to those for bulk BaO_2 (see spectrum d in fig. 1) [8].

The decomposition of BaO_2 was examined at 500°C. Spectra a and b in fig. 2 show that after 24 h at this temperature only partial decomposition had occurred. This is not surprising since thermochemical calculations for the reaction $BaO_2 \rightleftharpoons BaO + \frac{1}{2}O_2$ indicate that at 500°C the partial pressure of O_2 must be below 0.35 Torr for decomposition to occur. The free energy of formation of BaO_2 given in ref. [9] was used for these calculations.

The reduction of BaO_2 was carried out in a 1 atm flow (10 cm^3/min) of H_2. Significant reduction did not occur below 400°C. As shown in fig. 2, reduction of BaO_2 occurs slowly over a 40 min period. When the temperature is raised to 500°C the reduction of BaO_2 is complete in 10 min. The disappearance of the band at 842 cm^{-1} is accompanied by the appearance of a broad band at 3550 cm^{-1} and a much weaker one at 3730 cm^{-1} (see fig. 3). The first of these bands is characteristic of OH groups in bulk $Ba(OH)_2$ [10,11] and the second is characteristic of OH vibrations in $Mg(OH)_2$ [12]. With increasing time at 500°C the intensity of both hydroxyl

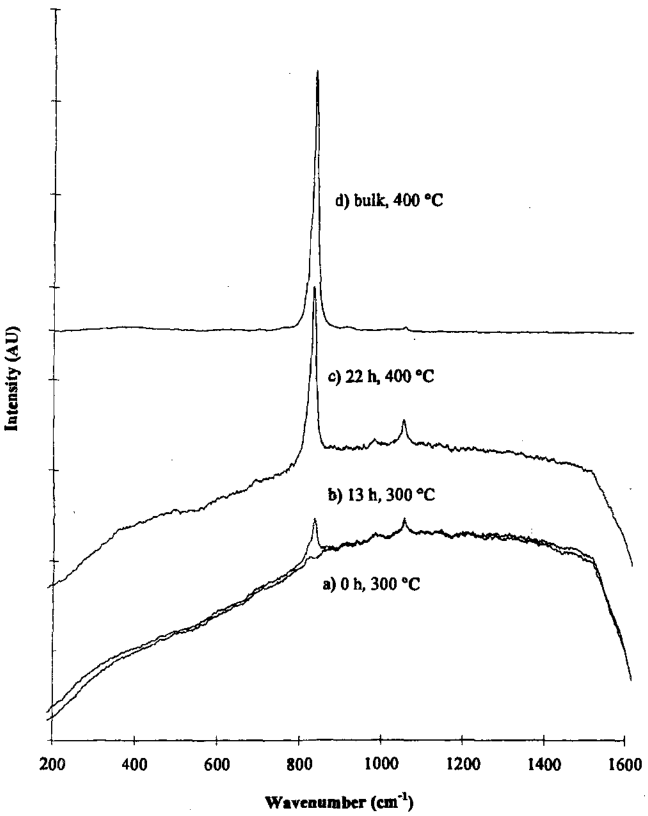

Fig. 1. Raman spectra of 4 mol% Ba/MgO taken after exposure to 1 atm O_2 at (a) 300°C for 0 h, (b) 300°C for 13 h, (c) 400°C for 22 h, and (d) the spectrum of bulk BaO_2 at 400°C.

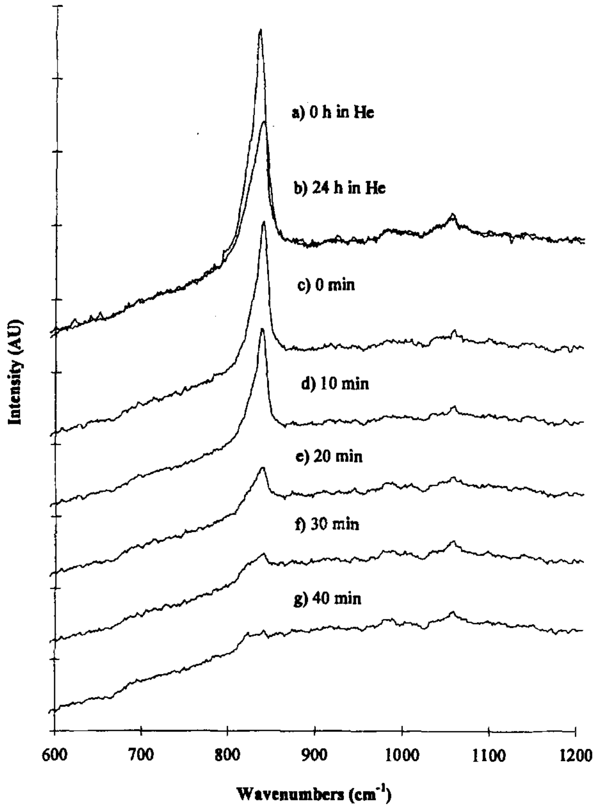

Fig. 2. Raman spectra of 4 mol% Ba/MgO taken after oxidation in 1 atm O_2 at 400°C for 18 h and then heating in 1 atm He at 500°C for (a) 0 h and (b) 24 h and after reduction in H_2 at 400°C for (c) 0 min, (d) 10 min, (e) 20 min, (f) 30 min, and (g) 40 min.

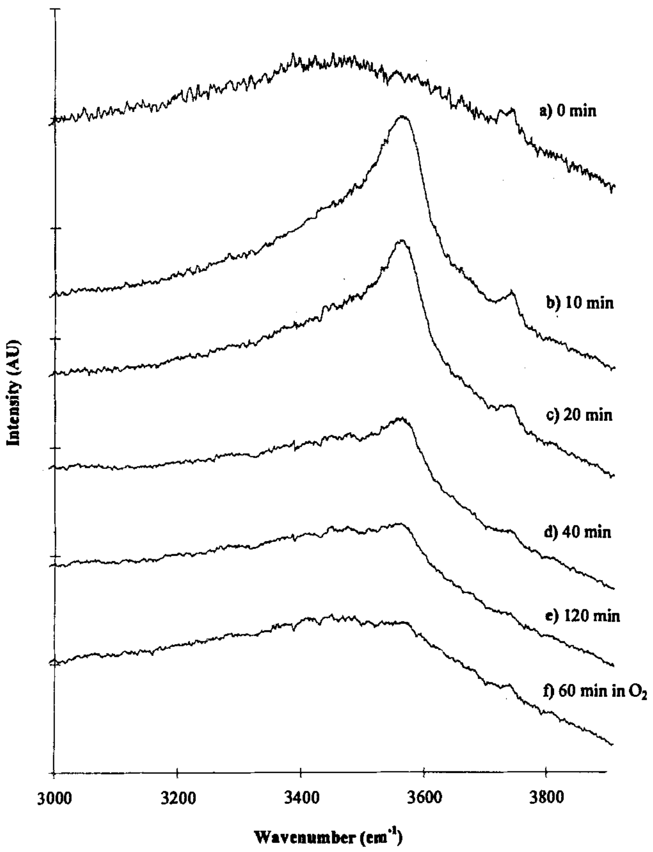

Fig. 3. Raman spectra of 4 mol% Ba/MgO taken after oxidation in 1 atm O_2 at 400°C for 18 h and then reduction in 1 atm H_2 at 500°C for (a) 0 min, (b) 10 min, (c) 20 min, (d) 40 min, (e) 120 min, and (f) after subsequent oxidation in 1 atm O_2 at 500°C for 60 min.

peaks declines. The temporal evolution of the bands for BaO_2 and $Ba(OH)_2$ suggests that at 500°C, BaO_2 is rapidly reduced to $Ba(OH)_2$ via the process $BaO_2 + H_2 \rightleftharpoons Ba(OH)_2$, and that $Ba(OH)_2$ subsequently undergoes slow dehydration to form BaO via the process $Ba(OH)_2 \rightleftharpoons BaO + H_2O$. Thermochemical calculations support this interpretation, since the partial pressure of H_2O need be only less than 928 ppm at 500°C for the dehydration of $Ba(OH)_2$ to become thermodynamically favorable [9]. Since the impurity level in the He is < 10 ppm, decomposition of $Ba(OH)_2$ should occur. Following the dehydration of $Ba(OH)_2$ to BaO, the initial concentration of BaO_2 could be restored by oxidizing the sample in 1 atm O_2 at 500°C.

No significant peroxide reduction was evident when the catalyst was exposed to 20 cm^3/min CH_4 at temperatures below 400°C. At 400°C, coke formed on the pellet and there was a corresponding decrease in overall Raman signal intensity. The peroxide peak intensity decreased relative to the background, but bands characteristic of carbonate did not appear. After exposing the catalyst to O_2 at 500°C, the coke disappeared and the overall intensity of the Raman signal returned to its original level; however, the peroxide peak intensity was smaller than that seen originally and carbonate peaks appeared at 695 and 1056 cm^{-1}. When the catalyst was exposed to CH_4 at 500°C, no coke formation was observed, but the peroxide disappeared and the carbonate bands appeared, as shown in spectra a and b of fig. 4. While not shown, the reduction of BaO_2 by CH_4 was accompanied by a rise in the intensity of the hydroxyl band at 3474 cm^{-1}, characteristic of $Ba(OH)_2$.

Spectra c–g in fig. 4 show the effects of exposing the catalyst to a 9 : 1 CH_4 : O_2 mixture flowing at 100 cm^3/min at 500°C. The band at 842 cm^{-1} for BaO_2 disappears within about 8 min and bands at 695 and 1056 cm^{-1} for $BaCO_3$ appear. The carbonate could not be decomposed at 500°C, even after extensive oxidation, nor could the band at 842 cm^{-1} be restored even after oxidation in 1 atm of O_2 at 500°C for 24 h.

Room-temperature exposure of the catalyst to 4 mol% CO_2 in He, following oxidation at 500°C, resulted in the formation of carbonate species, but no significant loss in the intensity of the peroxide band at 842 cm^{-1}. Raising the temperature to 500°C resulted in a modest increase in the intensity of the carbonate bands at 695 and 1056 cm^{-1}, as well as a slight decrease in the intensity of the peroxide band. The down scale shift in

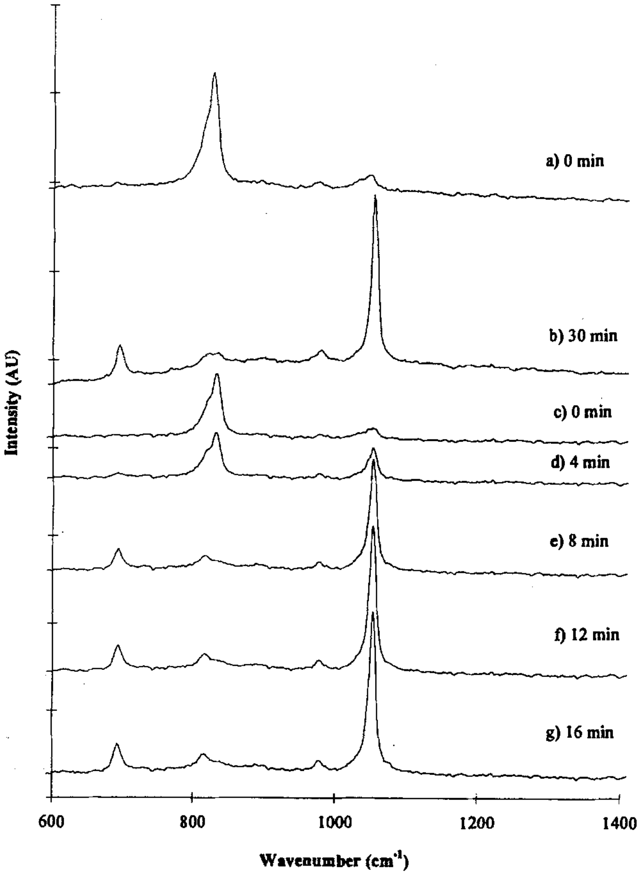

Fig. 4. Raman spectra of 4 mol% Ba/MgO taken after oxidation in 1 atm O_2 at 400°C for 18 h and then reduction in 1 atm of CH_4 at 400°C for (a) 0 min and (b) 30 min and after exposure to a 9 : 1 CH_4 : O_2 mixture at 500°C for (c) 0 min, (d) 4 min, (e) 8 min, and (f) 12 min, (g) 16 min.

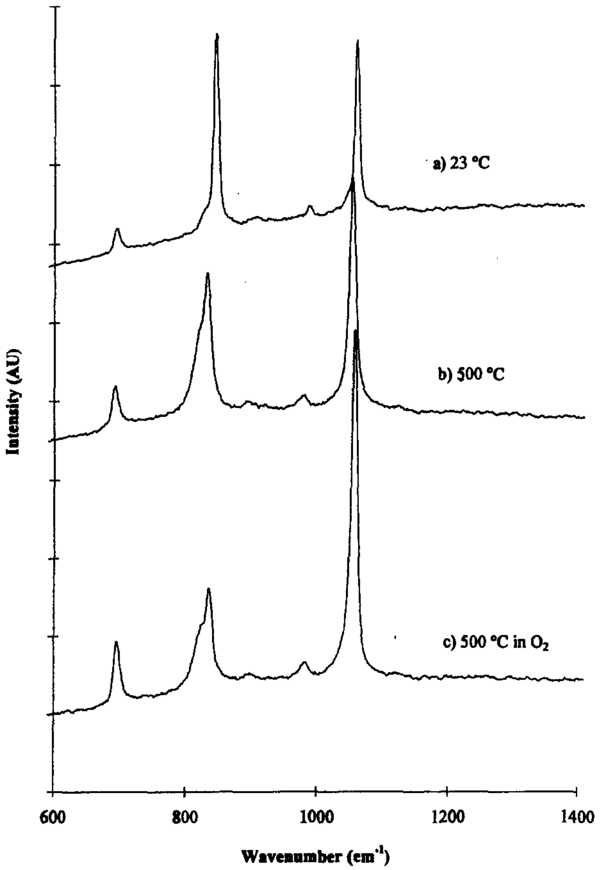

Fig. 5. Raman spectra of 4 mol% Ba/MgO taken after oxidation in 1 atm O_2 at 400°C for 18 h and subsequent exposure to 4 mol% CO_2 at (a) 23°C and (b) 500°C and after oxidation in 1 atm O_2 at 500°C.

the frequency of the Raman band and its broadening with increasing temperature are due to lattice expansion at elevated temperature [13]. Carbonate bands of similar intensity to those seen in fig. 5 were formed upon exposure of Ba/MgO, reduced in H_2, to CO_2. In this case, the peroxide band was absent from the spectrum. Oxidation of either the preoxidized or prereduced catalyst at 500°C in 1 atm of O_2 following exposure to CO_2 did not remove the carbonate features form the spectrum nor did it result in formation of peroxide anions.

The stability of $BaCO_3$ in the experiments conducted with CH_4, CH_4/O_2, or CO_2 is consistent with the thermodynamics for the reactions $BaCO_3 + \frac{1}{2}O_2 \rightleftharpoons BaO_2 + CO_2$ and $BaCO_3 \rightleftharpoons BaO + CO_2$ [9]. For the first of these reactions the CO_2 partial pressure would have to be below 7.47×10^{-6} Torr at 500°C and 1 atm of O_2 for the conversion of $BaCO_3$ to BaO_2 to be favorable, and for the second reaction the partial pressure of CO_2 would have to be below 1.28×10^{-7} Torr for $BaCO_3$ to decompose to BaO. Even at 800°C, a temperature at which the catalyst exhibits high activity [1–4], partial pressures of CO_2 less than 1.64 Torr would be required to decompose $BaCO_3$. The absence of any evidence for $MgCO_3$ at 500°C is consistent with the thermodynamic stability of that compound. At 400°C, the highest temperature for which thermodynamics data are available [9], $MgCO_3$ will decompose to MgO at CO_2 partial pressures of less than $2.45 \times 10^{+4}$ Torr [9].

The above discussion suggests that under the reaction conditions used typically for the oxidative coupling of methane (CH_4/O_2 ratios of 2–5 at temperatures of 700–850°C, and the CO_2 selectivities in the range of 20–50%), Ba will be present predominantly as bulk $BaCO_3$. The presence of peroxide anions on the surface of the carbonate is very likely, since ex situ XPS characterization of 4% Ba/MgO following exposure to a $CH_4 : O_2$ mixture for 1 h at 800°C and subsequent cooling to room temperature indicates that roughly 20% of the surface species are O_2^{2-} anions and 40% are CO_3^- anions [4]. The absence of a visible Raman peak for peroxide anions under reaction conditions (see also ref. [5]), suggests that at temperatures in excess of 500°C, the surface concentration of these species is very small.

4. Conclusions

The formation of BaO_2 from BaO supported on MgO occurs above 300°C. Once formed, BaO_2 is stable to thermal decomposition up to 500°C. The reduction of BaO_2 to BaO occurs readily above 400°C and proceeds via $Ba(OH)_2$ as an intermediate. $BaCO_3$ is formed at room temperature and above upon reaction of BaO or BaO_2 with CO_2 introduced into the gas phase or formed via the oxidation of CH_4. Once formed, $BaCO_3$ cannot be decomposed at temperatures up to 500°C. Only $BaCO_3$ is observed when the catalyst is exposed to a mixture of CH_4 and O_2 at 500°C.

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