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Selective oxidation and dehydrogenation of benzyl alcohol on $ABB'O_3$ (A=Ba, B=Pb, Ce, Ti and B'=Bi, Cu, Sb)-type perovskite oxides-temperature programmed reduction studies

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Abstract

Selective oxidation and dehydrogenation of benzyl alcohol have been carried out on $ABB'O_3$ (A=Ba, B=Pb, Ce, Ti and B'=Bi, Cu, Sb)-type perovskite oxides in the absence and in the presence of oxygen. Partial reduction of the catalyst is observed when the reaction is carried out in the absence of oxygen or at low partial pressures of oxygen. Reduced catalysts were characterised by XRD. Temperature-programmed reduction studies were carried out to determine the reducibility of the catalyst. Catalytic activity is found to depend on the reducibility of the catalysts. Copper-containing perovskites are highly reducible and $BaTiO_3$ and $BaCeO_3$ are the least reducible. Catalytic activity and reducibility are correlated with the metal-oxygen bonding as well as free energy of reduction of B site cations. A mechanism is proposed, which explains the ratio of benzaldehyde to toluene based on the reducibility. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Perovskite; Oxidation; Dehydrogenation; Benzyl alcohol; XRD; TPR

1. Introduction

Perovskite-type oxides have been extensively studied mainly as catalysts for complete oxidation of hydrocarbons and exhaust gases, mainly CO and NO [1–3]. Recently, there has been considerable interest in the use of perovskite and spinel-type mixed oxides for partial oxidation of hydrocarbons and oxygenated compounds [4,5]. A wide variety of catalysts such as, metal oxides and mixed metal oxides are used for the selective oxidation of various organic compounds [6–8]. Catalytic partial oxidation of alcohols is a

useful method for the preparation of aldehydes and ketones [9]. Halasz [10] has studied selective oxidation of methanol on $YBa_2Cu_3O_{7-x}$ ($x=0-1$) perovskite oxide in the presence as well as in the absence of oxygen, and observed that the catalyst undergoes reduction during the reaction. He concluded from his study that the chemical character of the constructing elements has more influence on the catalytic behaviour of perovskite than their geometrical structure. Sun and Lee [11] have studied the partial oxidation of ethanol on the same catalyst and observed high selectivity for acetaldehyde. Dissanayake et al. [12] have studied the partial oxidation of methane on Ba-Pb, Ba-Bi and Ba-Sn perovskite oxides and found that these perovskites also undergo reduction during the

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reaction. Thus, in a majority of the cases, the perovskite structure partially decomposes during the reaction. The catalytic activity of these oxides was found to be dependent on the extent of surface reduction. For many oxidation reactions, the activity of the catalyst has been successfully correlated with the reducibility of the catalyst [13–15]. Nakamura et al. [16] have reported that the ease of oxygen desorption, the diffusivity of oxygen molecules and the reducibility of perovskite oxide are closely associated with the catalytic activities for oxidation reactions, and that these properties can be varied by substitution at A or B sites. In the present work, we have studied the effect of nature of B site cation and extent of substitution at B site in $AB'B'O_3$ (A=Ba, B=Pb, Ce, Ti and B'=Bi, Cu, Sb)-type perovskite oxides on the reducibility and catalytic properties.

2. Experimental

Perovskite oxides were prepared by following the procedure reported in the literature [17–20]. The formation of single phase was ascertained by X-ray diffraction studies. Surface areas of different compositions of the oxides were determined by BET technique, using a nitrogen adsorption method. Oxygen contents of the samples were determined by iodometric titrations [21].

X-ray photoelectron spectroscopic (XPS) studies were performed in an ESCALAB Mark II spectrometer (Vacuum Generator, U.K.). The X.P spectra were recorded using Mg K_{α} radiation (1253.6 eV) and a pass energy of 25 eV. The binding energy values were determined with respect to the adventitious C1s peak, whose binding energy was assigned as 285 eV. The surface compositions were calculated according to the procedure given by Nitadori et al. [22].

Gas phase catalytic oxidation of benzyl alcohol was carried out in a fixed bed continuous flow reactor made of pyrex glass with an i.d. of 15 mm. The temperature of the catalyst bed was measured with the help of a thermocouple placed at the centre of the catalyst bed. The alcohol was fed into the reactor by means of an infusion pump. Reactions were carried out both in the absence and in the presence of oxygen. The partial pressure of oxygen (P_{O_2}) was varied from 0–300 Torr. Various ratios of oxygen and benzyl alcohol were used

as the reactant feed along with nitrogen as the carrier gas. The partial pressure of oxygen was controlled by adjusting the flow rate of nitrogen, in order to keep the total pressure at 1 atm. Contact time (W/F ; W =weight of the catalyst, F =sum of the flow rates of benzyl alcohol, oxygen and nitrogen) was kept constant at 51 g h/mol. Products were collected in an ice cold traps after attaining steady state conditions. The products were identified by GC-MS (Shimadzu 1000 QP-EX), and quantitative analysis was carried out using Gas-Chromatography (20% carbowax on chromosorb column). After every run, the catalyst was regenerated in the air at 673 K for 4 h. Each run was carried out for 50 min.

2.1. Temperature programmed reduction (TPR) studies

The reducing gas for all the TPR experiments was a mixture of 90 vol % nitrogen and 10 vol % hydrogen. For a typical TPR experiment, 100 mg of the sample was loaded in a U tube (4 mm i.d) quartz reactor. The hydrogen uptake was monitored using gas chromatography with a thermal conductivity detector (TCD). The reducing gas was first passed through the reference arm of the TCD before entering the reactor. The reactor exit was directed through a cold trap (to remove product water) and then to the second arm of the TCD. The flow rate of the reducing gas was maintained at 32 ml/min. The temperature of the reactor was linearly increased at a rate of 20 K/min to 1173 K. The TCD output was recorded on a strip chart recorder.

3. Results and Discussion

3.1. Characterisation

X-ray diffraction analysis of $BaPb_{1-x}Bi_xO_3$ shows that this compound forms a solid solution series throughout the composition range: $0 < x < 1$. $BaPb_{1-x-y}Bi_xCu_yO_3$ forms a single perovskite phase when the copper content $y \leq 0.35$ and $x \leq 0.2$. Above this value, a mixed phase is obtained. $BaCe_{1-x}Bi_xO_3$ also forms a complete solid solution series in the whole composition range $0 < x < 1$. $BaPb_{1-x}Sb_xO_3$ forms a single phase only when antimony content

Table 1
Surface area, oxygen non-stoichiometry and crystal structure of various perovskite oxides

Catalyst	Surface area (m ² /g)	Oxygen non-stoichiometry (δ)	T* (K)	Crystal structure
BaPbO ₃	3.2	0.31	1073	Orthorhombic
BaPb _{0.6} Bi _{0.4} O ₃	3.3	0.18	1123	Orthorhombic
BaBiO ₃	3.2	0.0	1123	Monoclinic
BaPb _{0.8} Bi _{0.1} Cu _{0.1} O ₃	3.5	0.29	1123	Orthorhombic
BaPb _{0.7} Bi _{0.1} Cu _{0.2} O ₃	3.4	0.27	1123	Orthorhombic
BaPb _{0.6} Bi _{0.1} Cu _{0.3} O ₃	3.2	0.23	1123	Orthorhombic
BaPb _{0.9} Sb _{0.1} O ₃	3.5	0.29	1173	Orthorhombic
BaPb _{0.5} Sb _{0.5} O ₃	3.1	0.15	1173	Cubic
BaCe _{0.8} Bi _{0.2} O ₃	4.2	0.09	1223	Orthorhombic
BaCe _{0.2} Bi _{0.8} O ₃	3.4	0.06	1200	Monoclinic
BaTiO ₃	5.2	0.0	1173	Cubic

T*: temperature of calcination of perovskite oxides.

$x \leq 0.5$. The crystal structure is not altered by the replacement of Pb or Bi by Cu in BaPb_{1-x-y}Bi_xCu_yO₃ and Pb by Ce in BaPb_{1-x}Bi_xO₃. The oxygen non-stoichiometry, surface area values and crystal structures of various perovskite oxides prepared are given in Table 1. The surface compositions determined from XPS studies for various compounds are BaPbO₃: Ba (1.00), Pb (1.77), O (8.06); BaBiO₃: Ba (1.00), Bi (1.83), O (13.52); BaPb_{0.6}Bi_{0.1}Cu_{0.3}O₃: Ba (1.00), Pb (1.19), Bi (0.60), Cu (0.12), O (6.01).

3.2. Catalytic Studies

The major products obtained in the partial oxidation of benzyl alcohol on all the perovskite oxides in the absence of oxygen are benzaldehyde and toluene. However, when the reaction is carried out in the presence of oxygen, small amounts of benzoic acid and benzyl benzoate are also obtained. In the absence of oxygen, hydrogen and water were also observed in the product stream. In the presence of oxygen in the reactant feed, however, no hydrogen was detected in the product stream. This is due to the complete oxidation of hydrogen in the presence of oxygen. This shows that, partial oxidation of benzyl alcohol proceeds through a dehydrogenation step. A similar dehydrogenation step has been proposed for the partial oxidation of methanol by Halasz [10].



Fig. 1 shows the effect of time on stream on con-

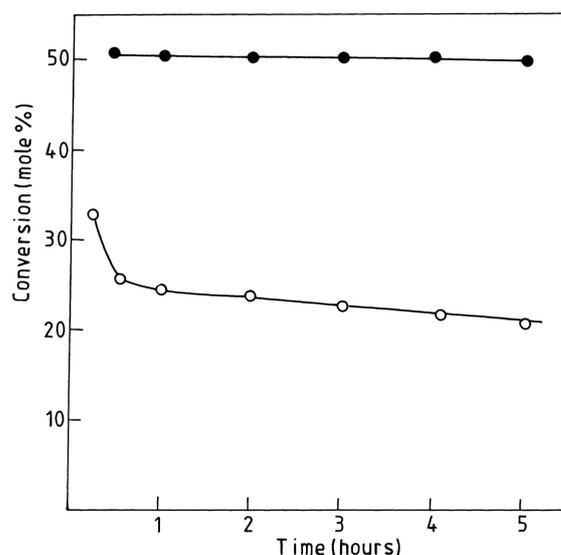


Fig. 1. Mole % conversion as a function of time in benzyl alcohol oxidation on BaPb_{0.6}Bi_{0.4}O₃ (● in the presence of oxygen, P_{O₂} = 132 Torr, Δ in the absence of oxygen) Reaction temperature: 623 K, W/F: 51 g h/mol.

version, when the reaction was carried out in the presence as well as in the absence of oxygen on BaPb_{0.6}Bi_{0.4}O₃. It can be seen from the figure that the activity of the catalyst in the absence of oxygen is lower than that in the presence of gas phase oxygen. Further, the catalyst is found to undergo a slight deactivation with time in the absence of oxygen. But when the reaction is carried out in the presence of oxygen, almost no deactivation is observed for 5 h.

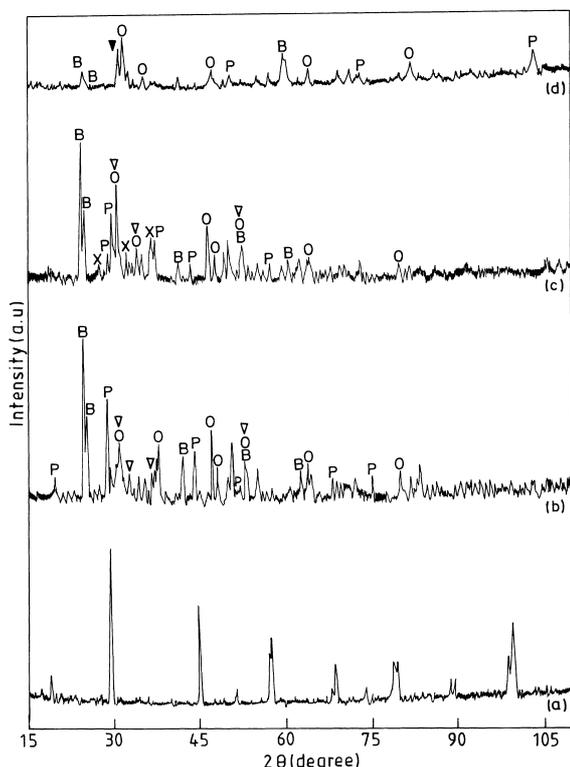


Fig. 2. XRD pattern of various perovskite oxides after benzyl alcohol oxidation in absence of oxygen. Reaction temperature: 673 K, W/F : 51 g h/mol, P_{O_2} : 0 Torr (a) $BaPb_{0.6}Bi_{0.4}O_3$ (before reaction), (b) $BaPb_{0.6}Bi_{0.4}O_3$, (c) $BaPb_{0.8}Bi_{0.1}Cu_{0.1}O_3$, (d) $BaPb_{0.9}Sb_{0.1}O_3$. (p: parent phase, o PbO_x , ∇ Bi_2O_3 , x Cu_2O , Sb_2O_3 , B: $BaCO_3$).

XRD analysis after reaction ($P_{O_2} = 0$ Torr) shows that catalyst undergoes partial reduction due to the removal of lattice oxygen (Fig. 2). Haber [23] pointed out that the removed oxygen ion can be replenished in two ways: gaseous oxygen adsorbed on the vacancy sites and the bulk lattice oxygen diffusing to the surface and entering the oxygen vacancy sites. When the rate of diffusion of lattice oxygen is higher than the rate of adsorption of oxygen from gas phase, the catalysts undergo bulk reduction, as observed when the reaction is carried out in the absence or at low partial pressures of oxygen. When the partial pressure of oxygen in the reactant feed is high, lattice oxygen consumed during the reaction can be replenished by gaseous oxygen, so that the oxidation may proceed continuously. Hence, when the reaction is carried out in the presence of

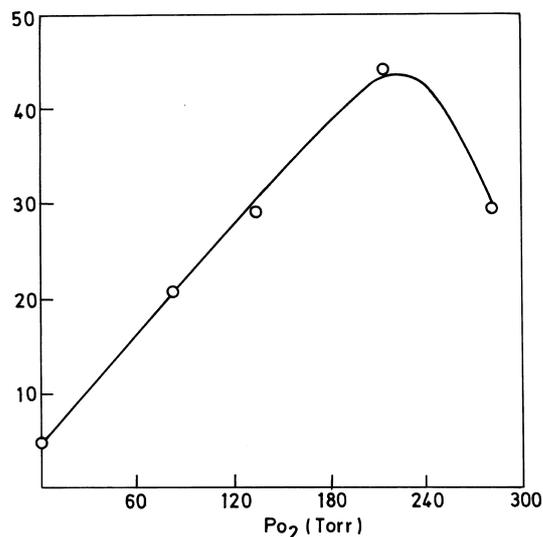


Fig. 3. Effect of partial pressure of oxygen on conversion in benzyl alcohol oxidation on $BaPb_{0.6}Bi_{0.4}O_3$. (Reaction temperature: 623 K, W/F : 51 g h/mole).

oxygen, the activity is found to be high and the catalyst does not undergo deactivation.

Fig. 3 shows the effect of partial pressure of oxygen on activity when the reaction is carried out on $BaPb_{0.6}Bi_{0.4}O_3$. It is observed that the activity increases with the increase in P_{O_2} and passes through a maximum at 216 Torr. Further increase in the P_{O_2} decreases the conversion. This is explained on the basis of Langmuir–Hinshelwood-type mechanism. According to this type of mechanism, dehydrogenation of alcohol occurs between benzyl alcohol and oxygen adsorbed on the catalyst surface. As the P_{O_2} increases, the amount of oxygen adsorbed on the surface increases, resulting in high conversion. However, at high P_{O_2} (>216 Torr) the catalyst surface may be saturated with more of adsorbed oxygen species, which prevents the adsorption of benzyl alcohol, thereby decreasing the conversion. All the catalysts under investigation showed a similar trend; the optimum P_{O_2} for maximum conversion seems to depend on the nature and concentration of B site metal ions. When the reaction is carried out in the absence of oxygen, lattice oxygen is involved in the reaction, whereas, when the reaction is carried out in the presence of oxygen, both lattice and adsorbed oxygen are involved. Margolis proposed that during oxidation, oxygen covers the whole solid

Table 2

Catalytic performance data for benzyl alcohol oxidation on different oxides. [Reaction temperature=637 K, W/F=51 g h/mol]

Catalyst	In the absence of oxygen			In the presence of oxygen ($P_{O_2}=132$ Torr)					
	Conversion (mole%)	Selectivity (mole%)		Conversion (mole%)	Selectivity (mole%)				T_{max} (K)
		Benz- aldehyde	Toluene		Benz- aldehyde	Toluene	Benzoic acid	Benzyl benzoate	
BaPdO ₃	25.8	63.2	36.8	51.1	75.2	24.8	—	—	913
BaPb _{0.6} Bi _{0.4} O ₃	28.8	76.6	23.4	62.1	82.6	17.4	—	—	873
BaBiO ₃	40.1	87.1	12.9	82.6	95.3	1.7	—	3.0	803
BaPb _{0.8} Bi _{0.1} Cu _{0.1} O ₃	41.9	94.3	5.7	72.1	79.1	10.9	1.4	8.2	848
BaPb _{0.7} Bi _{0.1} Cu _{0.2} O ₃	46.9	94.0	6.0	88.7	68.8	12.1	4.2	14.9	797
BaPb _{0.6} Bi _{0.1} Cu _{0.3} O ₃	49.3	96.6	3.4	92.6	62.8	16.0	5.1	15.1	698
BaPb _{0.9} Sb _{0.1} O ₃	34.7	84.1	15.9	61.2	78.7	4.7	5.4	10.8	823
BaPb _{0.5} Sb _{0.5} O ₃	42.0	92.8	7.2	61.2	79.0	4.1	5.6	11.3	773

surface. From the catalytic point of view, it is difficult to distinguish between surface oxygen and oxide ions coming from the lattice [24].

The catalytic activities of different catalysts are summarised in Table 2. It is seen that Cu-containing perovskites are more active than any other catalysts. Conversion of benzyl alcohol increases with decrease in T_{max} , measured from TPR studies. For CO oxidation on cuprates, it was reported that the catalytic activity depends on the extent of reduction. Catalytic studies carried out on barium cuprates showed that their activities for selective oxidation of methanol differ significantly, with Ba₂Cu₃O₅ being more active than YBa₂Cu₃O₇. This was attributed to the high reducibility of the former catalysts [25]. Similar results were reported by Dissanayake et al. for oxidative coupling of methane on Ba–Pb, Ba–Bi and Ba–Sn

perovskite oxides. They found that the catalytic activity of Ba–Pb and Ba–Bi was higher when compared to that of Ba–Sn perovskite oxide. XRD analysis confirmed that BaPbO₃ and BaBiO₃ undergo extensive transformation following exposure to the reaction mixture, whereas, BaSnO₃ retains its perovskite structure [12]. It can be seen that the percentage conversion of benzyl alcohol on BaTiO₃ and BaCeO₃ is the lowest (Table 3), when compared to other perovskite oxides. XRD studies carried out before and after the reaction have revealed that, unlike other catalysts, BaTiO₃ and BaCeO₃ do not undergo bulk reduction. These results show that the catalytic activity of these perovskite oxides for partial oxidation of benzyl alcohol depends on their reducibility.

Benzoic acid and benzyl benzoate are formed only when the reaction is carried out in the presence of

Table 3

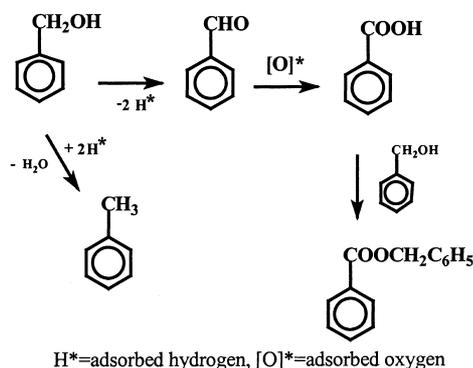
Comparison of M–O bonding energy and molar free energy of reduction (ΔG^0) of pure oxides which occupy B sites in the perovskite structure with the T_{max} and catalytic activity of the perovskite oxides. (Reaction conditions: temperature, 673 K; W/F, 51 g h/mol)

M–O	Bonding energy ^a (kJ/mol)	ΔG^0 ^b (kJ/mol)	Perovskite	T_{max} (K)	Conversion (mole %)	rate ^c (mole/h/m ²)
Cu–O	96.6	–108.9	BaPb _{0.6} Bi _{0.1} Cu _{0.3} O ₃	698	49.3	0.30
Sb–O	106.3	–85.3	BaPb _{0.5} Sb _{0.5} O ₃	773	42.0	0.26
Bi–O	108.6	–50.4	BaBiO ₃	803	40.1	0.24
Pb–O	119.7	–25.0	BaPbO ₃	913	25.8	0.15
Ti–O	277	+212	BaTiO ₃	>1000	14.3	0.05
Ce–O	293.2	+225	BaCeO ₃	>1000	10.6	0.04

^a M–O bonding energy was calculated according to the procedure given by Shimizu [30].

^b ΔG^0 : Free energy of reduction was calculated for the reaction: metal oxide + H₂ → metal + H₂O [31].

^c Normalized rate per unit surface area.



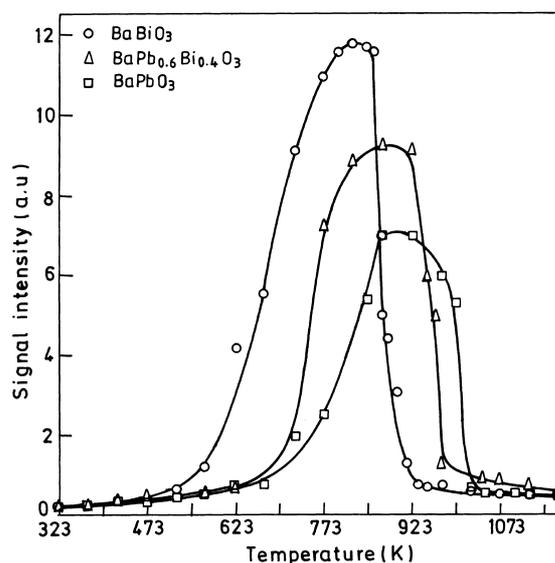
Scheme 1.

oxygen (Table 2). This shows that adsorbed oxygen is responsible for the formation of benzoic acid and benzyl benzoate. Benzyl benzoate may be formed by the condensation of benzoic acid with benzyl alcohol. A similar mechanism has been reported by Dube et al. on spinel type oxides [5]. The possible presence of more labile oxygen species on the surface of $\text{BaPb}_{1-x-y}\text{Bi}_x\text{Cu}_y\text{O}_3$ and $\text{BaPb}_{1-x}\text{Sb}_x\text{O}_3$ may account for their high selectivity for benzoic acid and benzyl benzoate. The overall reaction scheme can be represented as follows (Scheme 1):

According to this mechanism, benzaldehyde is formed by the dehydrogenation of benzyl alcohol. The adsorbed hydrogen species formed by the dehydrogenation can take up lattice oxygen, leading to the reduction of the catalysts, or it can interact with benzyl alcohol to give toluene. This implies that the ratio of benzaldehyde to toluene is dependent on the reducibility of the catalysts.

3.3. TPR Studies

In order to rationalise the differences in the observed catalytic activity of various catalysts, temperature-programmed reduction studies were carried out. Fig. 4 shows the TPR profiles of the series $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ for different x values. It can be seen that the reducibility of the catalyst increases with increase in the Bi content. Reduction of BaBiO_3 takes place at a considerably lower temperature compared to the cases for the other two catalysts in the same series. It can be seen that, though the reduction of BaPbO_3 and $\text{BaPb}_{0.6}\text{Bi}_{0.4}\text{O}_3$ starts at the same temperature, the reduction of the latter is complete at a lower tempera-

Fig. 4. TPR profiles of $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$.

ture. The temperature of maximum uptake of hydrogen (T_{max}) increases in the order $\text{BaBiO}_3 < \text{BaPb}_{0.6}\text{Bi}_{0.4}\text{O}_3 < \text{BaPbO}_3$, showing that the reducibility of the catalysts increases in the reverse order. It can be seen from Table 2 that the catalytic activity increases with the decrease in T_{max} . This shows that reducibility of the catalyst plays an important role in determining the catalytic activity of the catalyst. It has been reported that the reduction of Bi_2O_3 is more favourable than that of PbO in a reducing atmosphere [26]. Hence, the increase in the reducibility of $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ with increase in x can be attributed to the presence of more reducible bismuth ions. Therefore, it is presumed that the reducibility of these perovskites depends on the nature and concentration of B site metal ions.

Fig. 5 shows the TPR profiles of various catalysts in the series $\text{BaPb}_{1-x-y}\text{Bi}_x\text{Cu}_y\text{O}_3$ with varying values of y , keeping the value of x constant. All the catalysts show a broad TPR profile in the range 473–1000 K, showing that reduction takes place in a single stage. Halasz et al. observed only a single peak for the reduction of mixed oxides $\text{YBa}_2\text{Cu}_3\text{O}_5$, $\text{Ti}_2\text{CaBa}_2\text{Cu}_2\text{O}_{14}$ and $\text{YBa}_2\text{Cu}_3\text{O}_7$ [26]. These results show that, though the reducibility of the component oxides present is different, within the perovskite structure all the individual oxides interact in a synergistic way, result-

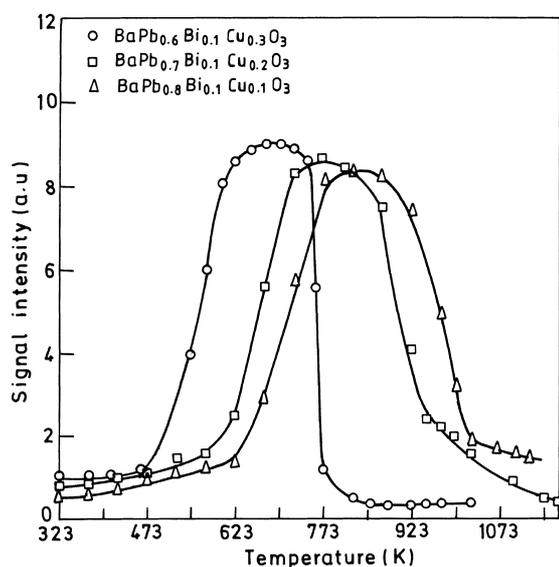


Fig. 5. TPR profiles of $\text{BaPb}_{1-x-y}\text{Bi}_x\text{Cu}_y\text{O}_3$.

ing in the reduction of the whole perovskite structure in a single stage. It has been reported that CuO undergoes reduction in two different stages [27]: first, CuO to Cu_2O and then to metallic copper. However, in the perovskite structure only a single reduction step is observed. Further, the presence of highly reducible copper ions in the perovskite structure brings down the reduction temperature drastically. A similar synergistic effect of CuO on the reduction of NiO has been reported by Robertson et al. [28]. These data suggest that the presence of reducible cations in the perovskite structure increases the reducibility of the perovskite. It can be seen that the T_{max} of the catalyst decreases with increase in copper content of the catalyst.

In the case of $\text{BaPb}_{1-x}\text{Sb}_x\text{O}_3$, the antimony rich catalysts were found to be more reducible, with T_{max} decreasing with increase in Sb content. The extent of reduction was also found to be increased with the increase in Sb content. However, in the case of the series $\text{BaCe}_{1-x}\text{Bi}_x\text{O}_3$, the reducibility decreases when the cerium content increases. $\text{BaCe}_{0.2}\text{Bi}_{0.8}\text{O}_3$ shows a well defined peak with T_{max} (797 K), while $\text{BaCe}_{0.8}\text{Bi}_{0.2}\text{O}_3$ shows a broad TPR profile without having a well defined T_{max} . It was observed that the conversion of benzyl alcohol on $\text{BaCe}_{0.8}\text{Bi}_{0.2}\text{O}_3$ was only 14.5%, whereas, it was 35.6% on $\text{BaCe}_{0.2}\text{Bi}_{0.8}\text{O}_3$ under the same reaction conditions, in accordance with the high

reducibility of the latter system. Yao et al. have shown that, in the case of low surface area ceria, the major peak of reduction occurs at 1000 K. Below 1273 K, ceria can be reduced by hydrogen only to Ce_2O_3 [29]. Therefore, the more difficult reducibility of $\text{BaCe}_{0.8}\text{Bi}_{0.2}\text{O}_3$ can be attributed to the presence of less reducible cerium ions in large amounts. When BaTiO_3 was subjected to TPR, no peak was observed till 1173 K. XRD analysis after TPR studies showed that, it did not undergo reduction. Hence, the low activity of BaTiO_3 can be attributed to its low reducibility.

These studies show that the reducibility of the perovskite oxides depends on the nature as well as the concentration of metal ions occupying B sites. Table 3 correlates the metal–oxygen (M–O) bonding energy calculated for the oxides and molar free energy of reduction (ΔG^0) for various oxides with T_{max} and catalytic activity. As the M–O bonding energy decreases, T_{max} decreases, showing that reducibility of the oxides increases due to the easy removal of lattice oxide ions. This is reflected in the molar free energy of the reduction of corresponding metal ions ($\text{M}^{n+} \rightarrow \text{M}^0$). The reducibility increases in the order: $\text{BaTiO}_3 \cong (\text{BaCeO}_3 < \text{BaPbO}_3 < \text{BaBiO}_3 \cong \text{BaPb}_{0.5}\text{Sb}_{0.5}\text{O}_3 < \text{BaPb}_{0.6}\text{Bi}_{0.1}\text{Cu}_{0.3}\text{O}_3$. This illustrates that the presence of highly reducible cations in the perovskite structure increases the reducibility, a similar trend to that of pure oxides is also observed for perovskite oxides. Similar results have also been reported for LaMO_3 ($\text{M} = \text{Co}, \text{Ni}, \text{Fe}$) perovskite oxides by Nitadori et al. [21]. They observed that the reducibility follows the order: $\text{LaCoO}_3 > \text{LaNiO}_3 > \text{LaFeO}_3$ and reflects the nature of B site cations. It is seen that the benzaldehyde to toluene ratio increases with decreasing T_{max} or M–O bonding energy (Table 2). According to the mechanism shown in Scheme 1, as the M–O binding energy decreases, the probability of adsorbed hydrogen species taking up lattice oxide ions increases, leading to the reduction of the catalyst, instead of interacting with benzyl alcohol to produce toluene. This results in high selectivity of benzaldehyde on more reducible catalyst. Therefore, one can conclude that the chemical behaviour of the components of perovskite-type mixed oxides controls their catalytic properties as well as the reduction properties. There is a linear relationship between M–O bond energy and T_{max} or ΔG^0 as well as between T_{max} and catalytic activity, thus establishing the importance of ease of

reducibility of these systems to the observed catalytic activity.

4. Conclusions

The perovskite phases are found to undergo reduction during the reaction. The extent of reduction depends on the partial pressure of oxygen in the reactant feed. From the TPR studies, one finds that the reducibility of the perovskite oxides depend on the nature of B site cations and extent of substitution at B sites. Reducibility of the perovskite has been correlated with the metal–oxygen bond energy of the metal ion. The catalytic activity increases with decrease in the metal–oxygen bond energy or with higher reducibility. A high ratio of benzaldehyde to toluene is obtained on more reducible catalysts.

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