

Epoxidation of styrene by TBHP to styrene oxide using barium oxide as a highly active/selective and reusable solid catalyst

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Styrene can be oxidised by TBHP to styrene oxide with high selectivity/yield using barium oxide (with or without gallium oxide support) as a simple, inexpensive and reusable solid catalyst; compared to the other alkaline and rare earth metal oxides, barium oxide showed a much better performance in the styrene epoxidation.

Styrene oxide (which is an important organic intermediate in the synthesis of fine chemicals and pharmaceuticals) is conventionally produced by epoxidation of styrene using stoichiometric amounts of peracid as an oxidizing agent.¹ However, peracids are very expensive, corrosive, hazardous to handle, non-selective for the epoxide formation and also lead to formation of undesirable products, creating voluminous waste. In order to overcome these limitations, a number of studies have reported on the epoxidation of styrene over easily separable solid catalysts, containing Ti,²⁻⁷ Fe or V⁴ or nanosize-gold,⁸ using safer oxidizing agent, such as TBHP (tertiary butylhydroperoxide)^{2,8} or H₂O₂.³⁻⁷ With H₂O₂ as an oxidizing agent, although the styrene conversion was high, the selectivity for styrene oxide was very poor. Recently Choudhary and coworkers⁹ used bohemite or alumina as a catalyst for the selective epoxidation of styrene by anhydrous H₂O₂ with a continuous removal of the reaction water. It is, therefore, interesting to know whether other simple metal oxides, such as alkaline and rare earth oxides have activity in the selective epoxidation of styrene. The present work was undertaken for this purpose. In this communication, we report, for the first time, the use of a simple, inexpensive and reusable metal oxide, such as BaO, for the selective epoxidation of styrene by TBHP with a very good selectivity/yield for styrene oxide. However, the other alkaline earth oxides and also rare earth oxides show a much lower performance in the epoxidation.

The styrene epoxidation by anhydrous TBHP over commercial BaO and other alkaline and rare earth metal oxides and supported BaO [prepared by impregnating barium nitrate (2 mmol g⁻¹(support)) on different supports (*viz.* SiO₂, Ga₂O₃, Al₂O₃, In₂O₃ and Si-MCM-41) by incipient wetness technique, drying and calcining at 500 °C for 4 h] was carried out under reflux, using a reaction mixture containing 10 mmol styrene, 15 mmol TBHP and 0.1 g of catalyst, by procedures described earlier.⁸ Results of the epoxidation over the different catalysts are presented in Tables 1 and 2.

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Table 1 Performance of different alkaline and rare earth metal oxides for the epoxidation of styrene to styrene oxide by anhydrous TBHP (SO = styrene oxide, PA = phenylacetaldehyde, Bzh = benzaldehyde, OP = other products)

Catalyst	Conversion (%)		Selectivity (%)				SO Yield (%)	TOF ^b
	Styrene	TBHP	SO	PA	Bzh	OP ^a		
Nil	7.5	16.5	11.0	7.7	1.7	81.7	0.8	—
MgO	15.9	28.0	19.8	7.0	4.9	68.2	3.2	1.1
CaO	0.9	45.3	—	—	—	100	≅0.0	0.0
SrO	15.2	24.2	60.2	8.0	0.0	31.8	9.2	3.1
BaO	40.7	32.1	78.7	8.9	1.1	11.2	32.0	10.7
BaO ^c	33.1	26.0	78.5	9.0	1.0	11.5	26.0	10.8
La ₂ O ₃	3.2	19.5	69.0	4.7	0.0	26.3	2.2	0.7
CeO ₂	28.7	52.4	38.9	6.0	4.2	50.7	11.2	3.7
Nd ₂ O ₃	20.0	23.2	62.8	8.0	1.1	28.0	12.6	4.2
Sm ₂ O ₃	9.8	14.2	48.6	5.2	0.0	46.1	4.8	1.6
Eu ₂ O ₃	9.8	12.1	50.2	5.3	0.0	44.4	4.9	1.6
Gd ₂ O ₃	15.7	16.0	60.0	10.8	0.0	29.0	9.4	3.1
Tb ₂ O ₃	9.8	10.5	48.3	8.2	0.0	43.5	4.7	1.5
Er ₂ O ₃	7.4	13.0	60.0	3.6	0.5	35.8	4.4	1.5
Yb ₂ O ₃	10.9	21.7	4.1	2.9	0.0	88.3	0.4	0.1

^a Benzoic acid and phenylacetic acid. ^b Defined as mmols of styrene oxide formed per gram of catalyst per hour. ^c For its 5th reuse (amount of catalyst used was 0.08 g).

The results in Table 1 reveal the following important information:

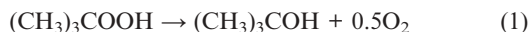
(1) Among the alkaline earth metal oxides, the BaO catalyst showed the best performance, *i.e.* the highest styrene oxide selectivity (79%) and yield (32%) in the epoxidation.

Table 2 Performance of different supported BaO catalysts for the epoxidation of styrene by anhydrous or aqueous TBHP

Catalyst	Conversion (%)		Selectivity (%)				SO Yield (%)	TOF ^a
	Styrene	TBHP	SO	PA	Bzh	OP		
Epoxidation using anhydrous TBHP								
BaO/SiO ₂	25.0	29.0	18.0	0.2	0.6	79.2	4.5	4.9
BaO/In ₂ O ₃	23.6	28.6	36.2	3.8	2.0	58.0	8.5	9.2
BaO/Ga ₂ O ₃	49.3	45.3	58.0	1.2	6.0	34.9	28.6	30.9
BaO/Ga ₂ O ₃ ^b	42.2	38.9	58.3	1.1	55.8	34.8	24.6	31.8
BaO/Al ₂ O ₃	25.5	40.2	30.0	8.7	1.3	60.0	7.7	8.3
BaO/Si-MCM-41	27.4	45.6	30.0	5.6	4.4	60.0	8.2	8.9
Epoxidation using aqueous TBHP								
BaO/In ₂ O ₃	31.0	38.3	40.2	6.8	0.3	52.7	12.5	13.5
BaO/Ga ₂ O ₃	40.1	58.6	56.1	0.6	2.3	41.1	22.5	24.3
BaO/Al ₂ O ₃	20.4	32.4	41.0	6.5	2.5	50.0	8.4	9.1
BaO/Si-MCM-41	30.8	48.0	36.2	3.1	2.7	58.0	11.1	12.0

^a Defined as mmols of styrene oxide formed per gram of BaO deposited on the support per hour. ^b For its 4th reuse (amount of catalyst used was 0.085 g).

(2) The CaO showed the lowest performance (high conversion of TBHP but <1% conversion of styrene). The observed high conversion of TBHP is due to its decomposition over the catalyst (with the evolution of oxygen) according to the reaction:



This catalyst in fact inhibits the styrene oxidation; even in the absence of any catalyst, the styrene conversion is much higher than that obtained in the presence of the CaO catalyst.

(3) The SrO catalyst also showed a good styrene oxide selectivity (60.2%) but at a low conversion of styrene (15.2%).

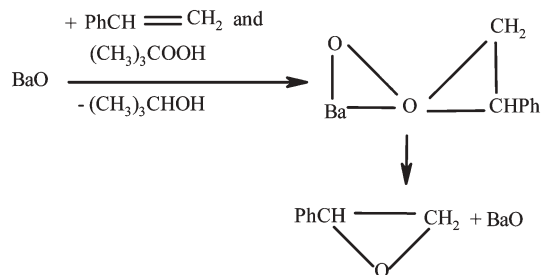
(4) Among the rare earth metal oxides, the CeO₂, Nd₂O₃ and Gd₂O₃ catalysts showed a good performance in the epoxidation of styrene. When comparing the styrene oxide yield, the three catalysts showed a somewhat comparable performance. However, they differed in their styrene conversion activity and epoxide selectivity; the CeO₂ catalyst was more active but less selective for the epoxidation. Also, the Nd₂O₃ and Gd₂O₃ showed higher styrene oxide selectivity (62.8 and 60%, respectively) but at a low styrene conversion (20 and 15.7%, respectively).

(5) The Er₂O₃ and La₂O₃ also showed high epoxide selectivity (60 and 69%, respectively) but at a very low conversion of styrene (7.4 and 3.2%, respectively). The Yb₂O₃ showed very poor epoxide selectivity and also low styrene conversion activity. The other rare earth oxides Tb₂O₃, Sm₂O₃ and Eu₂O₃ catalysts showed good epoxide selectivity (about 50%) but low styrene conversion activity (<10% conversion).

The alkaline and rare earth metal oxides showed the following order for their performance in the epoxidation (the value in brackets shows the styrene oxide yield): BaO (32%) >> Nd₂O₃ (12.6%) > CeO₂ (11.2%) > Gd₂O₃ (9.4%) > Eu₂O₃, Sm₂O₃, Tb₂O₃ and Er₂O₃ (4.4–4.9%) > MgO (3.2%) > La₂O₃ (2.2%) > without catalyst (0.8%) > Yb₂O₃ (0.4%) > CaO (0.0%).

Among the supported BaO catalysts (Table 2), the BaO/Ga₂O₃ showed the best performance (28.6% styrene oxide yield). It may be noted that both the conversion and selectivity/yield were more when anhydrous TBHP was used instead of aqueous TBHP. However, in case of the other supported BaO catalysts, the selectivity/yield was better for aqueous TBHP. Among the different supports used for the supported BaO catalyst, Ga₂O₃ was found to be the best one, probably because of its redox properties. The TOF for the BaO/Ga₂O₃ catalyst was much higher [30.9 mmol g⁻¹(BaO) h⁻¹] than that observed for the BaO (without support) catalyst [10.7 mmol g⁻¹(BaO) h⁻¹]. This is expected most probably because of the finely dispersed BaO on the support.

Both the Ga₂O₃-supported and unsupported BaO catalysts showed excellent reusability in the epoxidation (Tables 1 and 2). It is also interesting to note that the TOF of the BaO (without support) catalyst (which is an inexpensive metal oxide) is quite comparable to that [11–12 mmol g⁻¹(cat.) h⁻¹] of the very expensive supported nanosize-gold,⁸ Ti/SiO₂³ and Ti-HMS¹⁰ catalysts, reported earlier for the styrene epoxidation by TBHP.



Scheme 1

The very high activity of BaO, as compared to other alkaline and rare earth metal oxides, may be attributed to the relatively easier formation of barium peroxide species by the reaction of barium oxide with TBHP, and its further reaction with styrene (Scheme 1). Further work is necessary to understand/confirm the reaction mechanism.

The epoxidation would be a totally green process if the oxidant TBHP is replaced by H₂O₂ (which after consumption leaves water as a side product) or, more preferably, by molecular oxygen. Unfortunately, barium oxide is a highly basic metal oxide and hence has high H₂O₂ decomposition activity. It showed almost no epoxidation activity when molecular oxygen was used as an oxidizing agent.

In summary, unsupported or Ga₂O₃-supported BaO is a highly active and environmentally friendly (easily separable, reusable and non-toxic) and also inexpensive catalyst for the difficult to accomplish epoxidation of terminal alkenes, such as styrene, with high conversion and selectivity/yield.

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