

## Catalysis by some metal oxides modified with phosphate ions

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Surface acidity of phosphate modified  $\text{La}_2\text{O}_3$ ,  $\text{CeO}_2$  and  $\text{SnO}_2$  has been estimated by titrimetric method using Hammett indicators. Mixed oxides of tin and lanthanum have also been prepared and subjected to phosphate modification. Surface characterization of the samples has been carried out using XRD, surface area, thermal analysis and IR spectroscopy. Phosphate content in the samples has been chemically estimated. The catalytic activity for benzylation and esterification reactions has also been investigated.

Metal oxides find wide application in the field of heterogeneous catalysis. Slight modifications of the metal oxides may result in enhanced catalytic activity and selectivity. Considerable attention has been given to anion modified metal oxides since the first serious report of superacidity came in early 1980s<sup>1,2</sup>. Numerous studies have been devoted to investigate on the sulphated metal oxides<sup>3-5</sup> but only a few reports have appeared on phosphate modified oxides<sup>6-8</sup>. The present paper deals with a comparative evaluation of the surface properties of pure and phosphate modified metal oxides of La, Ce and Sn. Mixed oxides of Sn and La were also subjected to study. The catalytic activity of these oxides was studied for test reactions such as benzylation and esterification. The data have been compared with those for the unmodified oxide.

### Materials and Methods

The rare earth oxides were prepared by the hydroxide method<sup>9</sup> from their nitrate salts [lanthanum nitrate, cerium nitrate (99.9% pure) IRE, Udyogamandal]. The precipitate was dried overnight at 120°C and then calcined for five hours at 300°C. Tin oxide was prepared from stannic chloride solution (prepared from stannous chloride by oxidation with aqua regia) by the hydroxide method. Mixed oxides were prepared by co-precipitation method<sup>10</sup> from a mixture of rare earth nitrate and stannic salt solution in required proportions. The precipitate was filtered after washing, dried overnight at 110°C and calcined at 500°C for five hours.

Phosphate modified samples were prepared by suspending the oxide samples in  $\text{H}_3\text{PO}_4$  solution or  $\text{NaH}_2\text{PO}_4$  solution as the case may be for 20 hours. It was then filtered without washing followed by drying

at 120°C overnight and calcination at 300°C for 5 hours. Phosphate modification was achieved by using  $\text{H}_3\text{PO}_4$  solutions of varying concentrations.  $\text{H}_3\text{PO}_4$  solutions, 0.1 M, 0.3 M and 0.5 M, were used for modifying  $\text{La}_2\text{O}_3$  and the systems are designated as PLa(0.1), PLa(0.3) and PLa(0.5) respectively.  $\text{CeO}_2$  modified with 0.1 M  $\text{H}_3\text{PO}_4$  is denoted as PCe(0.1).  $\text{NaH}_2\text{PO}_4/\text{H}_3\text{PO}_4$  buffer 0.1 M, at pH 4 was also used as modifier for  $\text{CeO}_2$  and  $\text{La}_2\text{O}_3$  and the systems are designated as PLa and PCe respectively. The phosphated analogues of mixed oxides were prepared by using 0.1 M  $\text{H}_3\text{PO}_4$  as modifier. The various mixed oxide systems prepared and the notations used are as follows:

Composition	Mixed oxide	Phosphated analogue
$\text{SnO}_2$ (100%)	T	PT
$\text{SnO}_2$ (80%), $\text{La}_2\text{O}_3$ (20%)	TL82	PTL82
$\text{SnO}_2$ (60%), $\text{La}_2\text{O}_3$ (40%)	TL64	PTL64
$\text{SnO}_2$ (40%), $\text{La}_2\text{O}_3$ (60%)	TL46	PTL46
$\text{SnO}_2$ (20%), $\text{La}_2\text{O}_3$ (80%)	TL28	PTL28
$\text{La}_2\text{O}_3$ (100%)	L	PL

The amount of phosphate in the modified samples was estimated chemically<sup>10</sup>. Specific surface area was measured by the BET method using low temperature nitrogen adsorption in a Gemini Micromeritics surface area analyser. XRD patterns were recorded using  $\text{CuK}\alpha$  radiation using Rigaku-Miniflux. Thermal analysis was carried out using Shimadzu TGA-50 at a heating rate of 10°C/min in nitrogen atmosphere. Surface acidity/basicity measurements were carried out by titrimetric method using Hammett indicators.

The liquid phase benzylation of toluene was carried out by adding 0.1 g of the catalyst to 10 ml toluene and 1 ml benzyl chloride in an R.B flask. The mixture was refluxed with stirring for 1 hour. The esterification was carried out by stirring 0.5 ml acetic acid and 10 ml butanol in presence of 0.3 g of the catalyst in an RB flask at 98°C for five hours. The products were analysed using a Chemito 8610 Gas chromatograph.

### Results and Discussion

The concentration of phosphate ions obtained by the chemical analysis is given in Table 1. Surface concentration of phosphate ions per unit surface area was also calculated. The amount of phosphate ions was found to increase with an increase in the concentration of the  $H_3PO_4$  solution used. The surface concentration of phosphate ions obtained in certain samples was higher than the values reported in the case of anatase<sup>6-8</sup>. The phosphate content of  $La_2O_3$  samples decreased when  $NaH_2PO_4$  was used as the modifier while an appreciable variation could not be observed for  $CeO_2$ . The phosphate uptake by  $CeO_2$  was quite low when compared to  $La_2O_3$ . The phosphate content was quite low for  $SnO_2$  also. In the case of mixed oxides, the phosphate content gradually increased with increase in the amount of La incorporated.

In spite of the high phosphate concentration, XRD analysis confirmed the localisation of phosphate ions mainly on the oxide surface without detectable amounts of a three dimensional phosphate phase. Phosphate ions can be considered to be finely dispersed on the oxide surface. The intensity of XRD peaks was found to decrease upon phosphate modification as a result of the retardation of crystallisation. Such lower degree of crystallinity of modified oxides as compared to pure oxides is already reported<sup>1-5</sup>. In mixed oxide systems the intensity of diffraction peak corresponding to  $SnO_2$  decreased as the % of  $La_2O_3$  increased and new peaks corresponding to crystalline  $La_2O_3$  started appearing. No compound formation was observed in these mixed oxide systems calcined at 500°C. Peak intensity of the mixed oxide systems was also reduced due to phosphate modification.

The specific surface area of modified samples was found to be higher than that of the corresponding unmodified samples, which can also be attributed to the delayed crystallisation<sup>3</sup>. The phosphate groups being well dispersed on the surface prevents the oxide

Table 1 — Phosphate content of various samples

Catalyst	% of phosphorus	Phosphate ions/nm <sup>2</sup>
PLa(0.1)	2.81	7.26
PLa(0.3)	4.02	11.209
PLa(0.5)	4.95	14.78
PLa	2.13	6.24
PCe(0.1)	0.39	3.62
PCe	0.42	3.80
PT	0.25	0.52
PTL82	2.86	4.70
PTL64	3.44	5.66
PTL46	3.50	6.48
PTL28	3.90	7.89

particles from coming closer during calcination. It was also observed that the surface area of the phosphated samples decreased with increase in surface phosphate concentration obtained using higher concentrations of  $H_3PO_4$  solution. In the case of mixed oxides, incorporation of  $La_2O_3$  was found to result in an increase in the surface area value. But as more and more of  $La_2O_3$  was introduced, the surface area was found to decrease probably due to agglomeration. Thus TL82 showed the maximum and TL28 the minimum surface area. The same trend was also observed for the phosphated analogues.

The thermal stability of modified oxides was tested by thermogravimetric analysis. The TG curve of  $La(OH)_3$  shows an initial weight loss at 100-200°C due to the removal of adsorbed water. This is followed by formation of hexagonal  $LaOOH$  intermediate (250-350°C) which is finally converted into  $La_2O_3$  (350-420°C)<sup>11,12</sup>. The final weight loss (450-800°C) corresponds to the decomposition of the surface carbonate layer that is formed by the interaction of basic lanthanum hydroxide with the atmospheric  $CO_2$ <sup>13</sup>. In the case of  $Ce(OH)_2$  an initial weight loss due to loss of adsorbed water was observed. During the temperature range of 250-450°C, water formed by the combination of adjacent OH groups was eliminated leading to the formation of  $CeO_2$ .

The phosphate modified samples in both the cases show a gradual weight loss due to the slow removal of adsorbed and structural water. There is no prominent weight loss indicating the thermal stability of the phosphate-modified samples. Enhanced thermal stability of phosphated anatase has been previously reported<sup>6</sup>. The presence of phosphate ions in the modified samples was further confirmed by IR spectra, which showed a broad peak around 980-1080

$\text{cm}^{-1}$ , which can be assigned to the P-O stretching mode of phosphate anion<sup>14</sup>.

The results of the acidity/basicity measurements by Hammett indicator method are given in Tables 2-5. Phosphate modified  $\text{La}_2\text{O}_3$  samples were found to be acidic except in the case where  $\text{NaH}_2\text{PO}_4$  buffer was used as the modifier. Modified catalyst still remained basic but the basicity was lower than that of pure  $\text{La}_2\text{O}_3$ . The concentration of  $\text{H}_3\text{PO}_4$  solution seemed to have a negligible effect on the acidity. In spite of the increase in the phosphate content, acidity remained more or less the same.

Unmodified  $\text{CeO}_2$  was slightly acidic with acidic

sites of  $H_0 \leq 7.2$ . But phosphate modification resulted in the development of acid sites of  $H_0$  between 4.8 and 7.2. Thus the acidity and acid strength was found to increase upon phosphatation. In the case of ceria not much difference was found in the acidity generated by  $\text{H}_3\text{PO}_4$  and  $\text{NaH}_2\text{PO}_4$  modifiers. Even though ceria is more acidic than  $\text{La}_2\text{O}_3$ , the phosphated samples exhibited reverse trend with phosphated  $\text{La}_2\text{O}_3$  being more acidic. This may be due to the higher phosphate content or due to the difference in the mode of adsorption. The acidic sites in  $\text{SnO}_2$  are present at  $H_0$  4.8 and 7.2 and basic sites at  $H_0$  3.3. Thus  $\text{SnO}_2$  is found to possess weakly basic and

Table 2—Acidity/basicity of  $\text{La}_2\text{O}_3$  and phosphate modified  $\text{La}_2\text{O}_3$  activated at various temperatures

Sample	Temp (°C)	Basicity(mmol/g)			Acidity(mmol/g)		
		$H_0 \geq 3.3$	$H_0 \geq 4.8$	$H_0 \geq 7.2$	$H_0 \leq 3.3$	$H_0 \leq 4.8$	$H_0 \leq 7.2$
$\text{La}_2\text{O}_3$	300	1.23	0.25	0.23			
	500	1.10	0.22	0.21			
	700	1.01	0.20	0.19			
$\text{PO}_4^{3-}/\text{La}_2\text{O}_3$ (0.1M $\text{H}_3\text{PO}_4$ )	300				0.32	0.32	0.37
	500				0.22	0.27	0.35
	700				0.12	0.25	0.30
$\text{PO}_4^{3-}/\text{La}_2\text{O}_3$ (0.3M $\text{NaH}_2\text{PO}_4$ )	300				0.31	0.32	0.55
	500				0.23	0.25	0.36
	700				0.16	0.21	0.25
$\text{PO}_4^{3-}/\text{La}_2\text{O}_3$ (0.5M $\text{H}_3\text{PO}_4$ )	300				0.27	0.38	0.55
	500				0.23	0.25	0.38
	700				0.18	0.23	0.27
$\text{PO}_4^{3-}/\text{La}_2\text{O}_3$ (0.1M $\text{NaH}_2\text{PO}_4/0.1\text{M}$ $\text{H}_3\text{PO}_4$ )	300	1.04	0.15	0.13			
	500	0.88	0.14	0.11			
	700	0.31	0.13	0.05			

Table 3—Acidity/basicity of  $\text{CeO}_2$  and phosphate modified  $\text{CeO}_2$  activated at various temperatures

Sample	Temp (°C)	Basicity(mmol/g)			Acidity (mmol/g)		
		$H_0 \geq 3.3$	$H_0 \geq 4.8$	$H_0 \geq 7.2$	$H_0 \leq 3.3$	$H_0 \leq 4.8$	$H_0 \leq 7.2$
$\text{CeO}_2$	300	0.08	0.05				0.13
	500	0.05	0.03				0.20
	700	0.03	0.02				0.03
$\text{PO}_4^{3-}/\text{CeO}_2$ (0.1M $\text{H}_3\text{PO}_4$ )	300	0.05				0.08	0.28
	500	0.03				0.05	0.25
	700	0.01				0.04	0.05
$\text{PO}_4^{3-}/\text{CeO}_2$ (0.1MN $\text{aH}_2\text{PO}_4$ )	300	0.06				0.05	0.23
	500	0.12				0.03	0.08
	700	0.01				0.02	0.04

Table 4—Acid strength distribution of  $\text{SnO}_2$  and  $\text{PO}_4^{3-}/\text{SnO}_2$  at various temperatures

Catalyst	Temp (°C)	Basicity			Acidity		
		$H_0 \geq 3.3$	$H_0 \geq 4.8$	$H_0 \geq 7.2$	$H_0 \leq 3.3$	$H_0 \leq 4.8$	$H_0 \leq 7.2$
T	300	0.05	-	-	-	0.21	0.26
T	500	0.10	-	-	-	0.08	0.09
T	600	-	-	-	0.030	0.13	0.29
PT	300	-	-	-	0.16	0.51	0.53
PT	500	-	-	-	0.32	0.37	0.55
PT	600	-	-	-	0.21	0.34	0.63

Table 5 — Acidity/basicity of Sn-La mixed oxides and its phosphated analogues activated at 600 °C

Sample	Basicity (mmol/g)			Acidity (mmol/g)		
	$H_0 \geq 3.3$	$H_0 \geq 4.8$	$H_0 \geq 7.2$	$H_0 \leq 3.3$	$H_0 \leq 4.8$	$H_0 \leq 7.2$
T				0.03	0.13	0.29
TL82	0.42	0.11	0.08			
TL64	0.32	0.04	0.03			
TL46	0.26	0.05	0.02			
TL28	0.25	0.03	0.03			
La	1.01	0.20	0.19			
PT				0.21	0.34	0.63
PTL82				0.44	0.52	0.55
PTL64				0.53	0.53	0.58
PTL46				0.39	0.37	0.21
PTL28				0.24	0.32	0.34
PLa(0.1)				0.12	0.25	0.30

acidic sites. Incorporation of basic  $\text{La}_2\text{O}_3$  to  $\text{SnO}_2$  decreases the acidity and the mixed oxides were found to be basic. The phosphated analogues were, however, acidic and followed the same trend as that of pure oxides.

The increase in acidity upon phosphation can be assigned to the electron withdrawing effect of the phosphate group, which makes the metal center more electron deficient. Generally,  $\text{H}_3\text{PO}_4$  modified samples were found to have a greater acid strength and acidity than  $\text{NaH}_2\text{PO}_4$  modified ones.

Flaig Bauman *et al*<sup>15</sup> have proposed a mechanism in which adsorption occurs by an exchange process between surface hydroxyl groups and  $\text{H}_2\text{PO}_4^-$  ions in solution,  $\text{H}_3\text{PO}_4$  being dissociated only to the first degree at  $\text{pH} < 7$ . The following structure (I) is postulated. When  $\text{NaH}_2\text{PO}_4$  is used as the modifier, one of the OH groups is replaced by ONa.

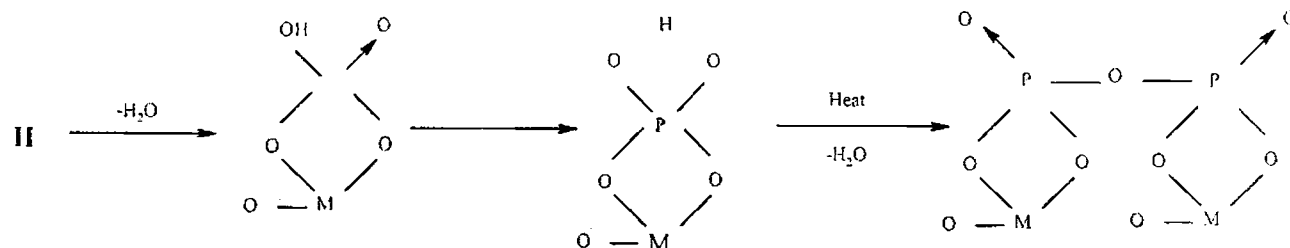
The second mechanism involves the dissociative adsorption of  $\text{H}_3\text{PO}_4$  leading to the blockage of Lewis acid sites and the proposed structure is denoted as II. On heating, dehydroxylation occurs leading to



bridged structures as given in Scheme 1. In this case Bronsted acidity is generated. When  $\text{NaH}_2\text{PO}_4$  is used the  $\text{H}^+$  of the P-OH groups are converted into P-ONa which will reduce the Bronsted acidity. This explains the lowering of acidity in this case.

The catalytic activity was tested for benzylation and esterification reactions and the results are given in Table 6. Lewis acid sites are believed to be more active towards benzylation reaction than Bronsted sites, whereas esterification in liquid phase is considered to be mainly catalysed by Bronsted acid sites.

The modified  $\text{La}_2\text{O}_3$  and  $\text{SnO}_2$  samples showed a lesser activity towards benzylation reaction compared



Scheme 1

Table 6—Data on the catalytic activity towards benzylation and esterification

Catalyst	Surface area (m <sup>2</sup> /g)	Benzylation reaction		Esterification reaction	
		Conversion %	Rate constant (10 <sup>-7</sup> s <sup>-1</sup> m <sup>-2</sup> )	Conversion %	Rate constant (10 <sup>-7</sup> s <sup>-1</sup> m <sup>-2</sup> )
La <sub>2</sub> O <sub>3</sub>	44.92	16.78	11.36	31.66	4.69
PLa(0.1)	75.64	14.08	5.61	70.78	9.10
PLa	66.27	18.74	8.60	-	-
CeO <sub>2</sub>	34.80	57.15	1.59	67.98	17.62
PCe(0.1)	40.92	68.65	1.61	59.59	9.8
PCe	41.46	79.24	2.04	-	-
T	40.01	88.82	15.19	12.30	1.82
PT	93.08	51.00	2.13	70.68	7.32
TL82	82.01	72.17	4.33	65.84	7.28
PTL82	117.94	74.38	3.21	59.52	4.26
TL64	63.99	92.58	11.29	69.77	10.40
PTL64	104.95	84.76	4.98	36.50	2.40
TL46	61.86	85.15	5.16	87.40	18.60
PTL46	104.87	56.39	3.72	46.35	3.30
TL28	59.87	84.90	8.77	83.99	17.00
PTL28	95.95	88.32	6.21	73.51	7.69

to pure oxides irrespective of the higher acidity and surface area values whereas the reverse trend was observed for esterification. This leads to the assumption that the phosphate modification in these cases occurs by the blockage of Lewis sites thereby leaving them inaccessible for the reactant molecules during benzylation reaction. The Bronsted sites created during the process, catalyse the esterification reaction. This trend was completely reversed for CeO<sub>2</sub>. In the case of CeO<sub>2</sub>, Lewis acid sites can be assumed to be more active resulting in a better activity towards benzylation reaction.

In the case of mixed oxides, TL64 was found to be the most active towards benzylation. This is consistent with the fact that maximum acidity was observed for the same. The modified oxides were less active towards benzylation suggesting that the Lewis acid sites are weaker compared to pure oxides. However the esterification results also showed the same trend with the modified oxides.

To conclude phosphation generally leads to an increase in surface area and a decrease in crystallinity and the samples are thermally stable. Phosphation can occur through adsorption atco-ordinatively unsaturated Lewis acid sites and exchange of OH groups by H<sub>2</sub>PO<sub>4</sub><sup>-</sup> ions. The catalytic activity and surface acid-base properties mainly depend on the amount of phosphate adsorbed and also the nature of adsorption.

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