Alkylation of phenol with methanol over mixed oxides of tin with some rare earth elements

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Alkylation of phenol with methanol has been carried out over Sn-La and Sn-Sm mixed oxides of varying compositions at 623 K in a vapour phase flow reactor. It is found that the product selectivity is greatly influenced by the acid-base properties of the catalysts. Ortho-cresol formation is favoured over catalysts with weak acid sites whereas formation of 2,6-xylenol occurs in the presence of stronger acid sites. The cyclohexanol decomposition reaction and titrimetric method using Hammett indicators have been employed to elucidate the acid-base properties of the catalysts.

A large number of catalysts have been used in the alkylation of phenol with methanol[1-3]. Acidic catalysts such as SiO_2-Al_2O_3 promote O-alkylation giving phenylethers while basic catalysts such as MgO or ZnO-Fe_2O_3 promote direct alkylation giving o-cresol without passing through phenyl ether intermediate[4,5]. It is evident that the selectivity of products depends on the acid-base properties of the catalysts. According to Benzouhanava et al. catalysts with strong acid sites favour O-alkylation while those with weak acid sites or strong basic sites favour C-alkylation[6]. However, Tanabe et al. have reported that acidic catalysts also give predominantly C-alkylation[7]. The nature of adsorption of phenol is very important in determining the product selectivity. The interaction of phenol with catalysts surface is affected by the acid-base properties of the catalyst.

The present paper attempts to correlate the acid-base properties of a series of Sn-La and Sn-Sm mixed oxides with the selectivity of products in the alkylation of phenol with methanol. The catalyst systems containing tin oxide and rare earth oxides are well known for their activity in oxidation reactions[8,9].

However, studies relating to their catalytic activity in industrially important reactions, which requires the combined effect of both acid and base sites have been very sparse. The acid-base properties can be tuned to the desired level by carefully adjusting the composition of mixed oxide systems.

Experimental

The Sn-Sm and Sn-La binary mixed oxides were prepared by co-precipitation method from the required quantities of stannic chloride solution and rare earth chloride solution using 1:1 aqueous ammonia as the precipitant followed by aging, washing, filtration and drying. The compositions of the mixed oxides prepared are given below.

TS82 ---SnO_2 (80%) Sm_2O_3 (20%);

TL82--- SnO_2 (80%) La_2O_3 (20%);

TS55--- SnO_2 (50%) Sm_2O_3 (50%);

TL82--- SnO_2 (50%) La_2O_3 (50%);

TS28 ---SnO_2 (20%) Sm_2O_3 (80%) and

TL28--- SnO_2 (20%) La_2O_3 (80%)

All the catalyst were sieved to a mesh size < 100 microns and calcined in air at 773 K before each experiment. The chemical composition was determined by Energy dispersive X-ray analysis (Stereoscan 440 Cambridge, UK). The different oxide phases were detected by X-ray diffraction using a Ni filtered Cu $k\alpha$ radiation (λ = 1.5404 Å). Omnisorb 100 CX (supplied by COULTER corporation, USA) unit was used for the measurement of nitrogen adsorption to determine surface areas.

In the Hammett indicator method for the determination of basicity of the samples, two drops of 0.1 % solution of the indicator (indicators used were dimethyl yellow pK_a= 3.3, methyl red pK_a= 4.8 and bromothymol blue pK_a= 7.2) in benzene were added to 0.1 g of solid suspended in benzene and allowed to stand for 5 min[10]. The basicity at various base strength of the solid was determined by titrating with 0.1 N solution of trichloroacetic acid in benzene; titration was continued until a permanent colour change was obtained.

Table 1— Physico-chemical characteristics of Sn-La and Sn-Sm mixed oxides

Catalyst	SnO_2 (%)	Ln_2O_3 (%) $Ln=Sm,La$	Surface area (m^2g^{-1})	Pore volume (cm^3g^{-1})	XRD phase	Basicity $(mmol\ g^{-1})\ pKa \geq 3.3$
TS82	76.05	23.95	102.7	0.31	SnO_2	0.18
TS55	44.27	55.73	69.0	0.44	mixed	0.10
TS28	14.34	85.66	31.6	0.69	mixed	0.12
TL82	78.11	21.89	105.7	0.28	SnO_2	0.17
TL55	45.68	54.32	55.6	0.41	mixed	0.14
TL28	17.83	82.17	26.4	0.72	mixed	0.15

Table 2—Basicity values of different catalysts activated at 773 K at different pKa

Catalyst	Basicity $(mmol^{-1}g)$		
	$pKa \geq 7.2$	$pKa \geq 4.8$	$pKa \geq 3.3$
TS82	0.064	0.139	0.178
TS55	---	---	0.102
TS28	0.038	0.076	0.127
TL82	0.076	0.203	0.165
TL55	0.051	0.114	0.139
TL28	0.038	0.063	0.152
SnO_2	---	---	0.108
La_2O_3	0.400	0.870	1.420
Sm_2O_3	0.560	0.660	0.980

The reaction was carried out in a vertical type reactor (2.2 cm internal diameter and 30 cm length) kept in a cylindrical furnace mounted vertically. The catalyst (3 g, as pellets) was loaded in the middle of the reactor and packed with glass beads. Before each experiment catalyst was activated in a current of dry air at 773 K for 6 h and then brought to the reaction temperature in the presence of nitrogen flow. The reactant feed (phenol-methanol mixture) was introduced at the top of the reactor by means of an infusion pump (SAGE, USA). The products were analysed in a gas chromatograph (GC 15-A) fitted with SE30 column ,and FID. The mass balance was noted each time and the gas products were collected using an ORSAT apparatus.

Results and discussion

The physico-chemical characteristics of the catalysts are summarised in Table 1. X-ray diffraction patterns of Sn-La binary mixed oxides of varying compositions show that the intensity of diffraction peaks decreases after the addition of La_2O_3 to SnO_2 system. So the addition of a second oxide hinders the crystallization of SnO_2 by preventing the aggregation

of the smaller particles. TL82 sample showed cassitterite as the prominent phase, no reflections due to La_2O_3 phase were detected. This means that rare earth oxide is well dispersed on the SnO_2 support material. The values of specific surface area of these samples are higher compared to those of the other systems. TS55, TL55, TS28 and TL28 show the co-existence of both SnO_2 and rare earth oxide phases. The BET surface areas determined by N_2 adsorption follow the order TS82 > TS55 > TS28 and TL82 > TL55 > TL28. The higher surface area values of TS82 and TL82 may be due to the small amount of rare earth oxide, which prevents the aggregation of SnO_2 particles. As more and more rare earth oxide is added to SnO_2, agglomeration takes place and this may be the reason for the lower surface area of the other samples. It can be seen that basicity of the catalysts is in the order TS82 > TS28 > TS55 and TL82 > TL28 > TL55 at an activation temperature of 773 K. The basicity values at various pK_a values using different Hammett indicators are given in Table 2.

Conversion and selectivity of the products in the alkylation of phenol with methanol over Sn-La and Sn-Sm binary mixed oxides of varying composition are shown in Table 3. It can be seen that all the catalysts afford very little O-alkylated products and hence the C-alkylation takes place predominantly over these catalyst systems. The selectivity of o-cresol and 2,6-xylenol, which are the main products, varies with the catalyst composition. Maximum selectivity is observed for 2,6-xylenol in the case of TS55 and TL55 catalysts. Moreover, some amount of trimethylphenols is also formed over these catalysts. In the case of TS82 and TL82 o-cresol is the main product, whereas TS28 and TL82 afford o-cresol and 2,6-xylenol in nearly equal amounts. The conversion of phenol over these two catalysts is less, which is due to the lower surface area of these samples.

Table 3—Alkylation of phenol with methanol over mixed oxides of tin with lanthanum and samarium

Product distribution (wt %)	Catalysts					
	TS82	TS55	TS28	TL82	TL55	TL28
Anisole	0.15	0.31	0.18	0.15	0.30	0.17
Phenol	23.86	23.21	40.00	24.69	24.39	43.82
o-cresol	45.61	22.74	29.96	43.25	26.97	26.75
2,6-Xylenol	27.64	41.79	27.26	29.14	41.84	26.57
Others	0.04	2.90	1.17	0.32	nil	1.11
Conversion (%)	76.14	76.79	60.00	75.31	75.61	56.18
Sel. C-alkylation	99.81	99.60	99.70	99.80	99.60	99.67
Sel. o-cresol	59.90	29.61	49.93	57.42	35.66	47.61
Sel. 2,6-xylenol	36.30	54.42	45.43	38.69	55.33	47.29

"Reaction conditions: catalyst weight = 3 g; reaction temp. = 623 K; molar ratio (phenol:methanol) = 1:6; feed rate = 4 ml/h; time on stream = 1 h; calcination temp. = 773 K.
bTrimethylphenol.

Table 4—Decomposition of cyclohexanol over different catalysts

Catalyst	Conversion (%)	Sel. Cyclohexene (%)	Sel.Cyclohexanone (%)
TS82	48.16	25.86	74.14
TS55	58.12	46.40	53.60
TS28	45.80	42.80	57.20
TL82	45.03	22.75	77.24
TL55	54.75	40.72	59.78
TL28	47.47	36.02	63.98

Reaction conditions: reaction temp. = 623 K, feed rate = 4 ml/h, catalyst weight = 2.7 g.

We tried to correlate the acid-base properties of the catalysts with dehydration and dehydrogenation activity employing cyclohexanol decomposition as a test reaction[11]. The selectivity of cyclohexene is found to be in the order TL55 > TL28 > TL82 and TS55 > TS28 > TS82 (Table 4). So TS55 and TL55 systems are more acidic compared to other systems, while TS28 and TL28 are least acidic. Now the product selectivity can be easily correlated with the acid-base properties of the catalysts. The higher selectivity of secondary alkylated product 2,6-xylenol in the case of TS55 and TL55 must be due to their higher acidity. Moreover, a considerable amount of trimethylphenol also is formed over these two catalysts. Over less acidic systems TS82 and TL82, o-cresol is the main product.

In the decomposition of cyclohexanol, dehydrogenation was the main reaction. However, we found that in the decomposition of isopropanol and isobutanol selectivity of dehydration products is high. Only weak acid sites are required for the dehydration of isopropanol, and isobutanol whereas stronger acid sites are needed for the dehydration of cyclohexanol.

Qualitatively it can be concluded that most of the acid sites present on these catalysts are weak in strength. From the titration methods it is found that comparatively strong basic sites are also present on these systems. These observations are supported by the observations of Benzouhanava et al. that weak acid sites or strong basic sites favour C-alkylation[6]. The formation o-cresol and 2,6-xylenol can be attributed to the nature of adsorption of phenol over the catalyst surface.

From the above discussion it is clear that product selectivity in the alkylation of phenol with methanol depends mainly on the acid-base properties of the catalysts. As the catalyst acidity increases, 2,6-xylenol and trimethylphenol selectivity increases. Hence, weaker acid sites are required for the formation of o-cresol whereas the formation of 2,6-xylenol demands the presence of stronger acid sites.

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