A comparative study on the anisole methylation activity of lanthanum-promoted SnO_2 catalyst and its sulfate-doped analogue

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Received 24 August 2000; accepted 3 October 2000

A comparative study on the anisole methylation with methanol over lanthanum-promoted SnO_2 catalyst and its sulfate-doped analogue is presented. A maximum 2,6-xylenol selectivity of 82% was achieved at 400 °C under optimized conditions at an anisole conversion of 65% over lanthanum-promoted SnO_2 catalyst. The sulfate modification resulted in the dealkylation of anisole to phenol followed by several unselective side reactions due to the creation of strong acid sites. The activity of lanthanum-modified tin oxide catalysts in the selective formation of 2,6-xylenol is ascribed to the presence of weak Lewis acid sites and comparatively stronger basic sites.

Keywords: anisole, alkylation, 2,6-xylenol, La_2O_3 catalyst, sulfated, SnO_2 catalyst

1. Introduction

It is known that anisole can undergo an intra-molecular rearrangement reaction to *o*-cresol or intermolecular rearrangement between two molecules to methylanisole and phenol. Also, a dealkylation reaction can prevail depending upon the reaction conditions or acid–base properties of the catalyst. Bautista and co-workers found that dealkylation to phenol is predominant over $AlPO_4$–Al_2O_3 catalysts in the alkylation of anisole with methanol [1]. The selective synthesis of industrially important alkylphenols such as 2,6-dimethylphenol (2,6-xylenol) can be effected by the alkylation of phenol with methanol over different metal oxide catalysts [2–8]. Apart from the acid–base properties of the catalysts, the product selectivity is often influenced by the operating conditions and the nature of alkylating agent.

In our previous papers, we have demonstrated that modification of SnO_2 with rare earth oxides like La_2O_3, Sm_2O_3 and CeO_2 leads to the formation of weak acid sites and comparatively stronger basic sites which are suitable for the selective methylation of phenol to *o*-cresol and 2,6-xylenol [9–11]. In the present work, we have tested the activity of lanthanum-promoted SnO_2 catalyst in an attempt to explore the optimum acid–base properties of this catalyst for the selective synthesis of 2,6-xylenol from anisole in presence of methanol. The activity of this catalyst is compared with that of the sulfate-doped analogue to clearly understand the effect of acidity on the product selectivity.

2. Experimental

The lanthanum-modified SnO_2 catalyst was prepared by a co-precipitation method from the required quantities of tin(IV) chloride solution and lanthanum nitrate solution using 1 : 1 aqueous ammonia. The precipitate was washed several times with deionized water to remove anions and finally filtered and dried at 383 K. The sulfate-modified oxide was prepared as follows. The mixed hydroxide was immersed in 3 M solution of ammonium sulfate under constant stirring and finally filtered without washing and dried at 383 K for 6 h. The lanthanum nitrate and tin(IV) chloride were obtained from Indian Rare Earths, Ltd. and Ranbaxy India, Ltd., respectively.

The chemical composition of the catalysts was determined by energy dispersive X-ray analysis (Stereoscan 440, Cambridge, UK). The different oxide phases were detected by X-ray diffraction using Ni-filtered Cu Kα radiation ($\lambda = 1.5404$ Å). An Omnisorb 100 CX (supplied by COULTER Corporation, USA) unit was used for the measurement of N_2 adsorption to determine surface areas. The acid strength of sulfated oxide was measured qualitatively after the pretreatment (823 K in air) using a set of Hammett indicators. Two drops of 0.1% solution of the indicator (anthraquinone, $pK_a = -8.2$) in dry benzene were added to 0.1 g of solid suspended in 5 ml dry benzene and allowed to stand for 5 min. The color change of the indicator adsorbed on the solid surface was noted. If the color of the indicator turns to that of its acid form (colorless to yellow for anthraquinone), the acid strength of the solid is expressed as $H_0 \leqslant -8.2$.

The acidity of the catalysts was measured by n-butylamine adsorption [12]. Catalysts were kept in a desiccator saturated with n-butylamine vapor at room temperature for

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48 h. Then the weight loss of the adsorbed sample was measured by a TGA operating from 313 to 1273 K at a rate of 20 K/min. The weight losses between 423 and 573 K, 574 and 723 K, and 724 and 873 K are considered to come from weak, medium and strong acid sites, respectively.

For convenience the catalysts used in the present study are designated as

TL82: SnO_2 (80%)–La_2O_3 (20%),
STL82: sulfate-modified TL82.

Alkylation reactions were carried out in vapor phase in a fixed-bed down flow silica reactor. 3 g of the catalyst (as pellets 10–20 mesh) was loaded in the middle of the reactor fitted with a thermocouple for temperature measurements. The catalyst was activated in a stream of air at 723 K for 6 h and brought down to the reaction temperature under nitrogen flow. The reaction mixture (anisole and methanol) was introduced at the top of the reactor by means of an infusion pump. The products were collected in a water-cooled condenser and analyzed by a gas chromatograph fitted with a capillary column (HP-1) and flame ionization detector. Mass balance was noted each time (>95%). The identity of the products was established by the comparison of retention times of authentic samples and also by GC-MS and GC-IR.

3. Results and discussion

3.1. Catalyst characterization

A detailed study of the characterization of present catalyst systems has been already reported elsewhere [13,14]. The addition of La_2O_3 to tin oxide resulted in the broadening of XRD peaks, which indicated that the addition of a second oxide hinders the crystallization of SnO_2 by preventing the aggregation of smaller particles. TL82 showed cassiterite (SnO_2) as the prominent phase; no reflections due to a rare earth oxide phase were detected. This means that lanthanum oxide is well dispersed on the support material. The addition of sulfate anions also influenced the crystallization of SnO_2. It has been reported that the degree of crystallization of the sulfated oxide is much lower than that of the oxide without sulfate treatment [15]. Determination of acid strength of the catalysts using a set of Hammett indicators showed that sulfate treatment leads to the generation of acid sites with $H_0 \leqslant -8.2$. The important physico-chemical characteristics of different oxide catalysts employed in the present study are summarized in table 1.

3.2. Effect of anisole/methanol molar ratio

The alkylation reactions were carried out at 380 °C taking several anisole to methanol molar ratios over the TL82 catalyst to select the optimum molar ratio for elaborate study. The major product formed was 2,6-xylenol along with small quantities of phenol, methylanisole, cresol and trimethylphenol. In figure 1 the selectivities of different products and anisole conversion were plotted against molar ratios. We have selected a molar ratio of 1 : 6 for further study, as the conversion and selectivity were better.

3.3. Comparison of TL82 and STL82 at different reaction temperatures

The anisole conversion and selectivity to 2,6-xylenol as a function of temperature over TL82 and STL82 is summarized in table 2. In the case of TL82 the anisole conversion increased with increase in temperature and attained a maximum of 83% at 420 °C. Thereafter, the de-

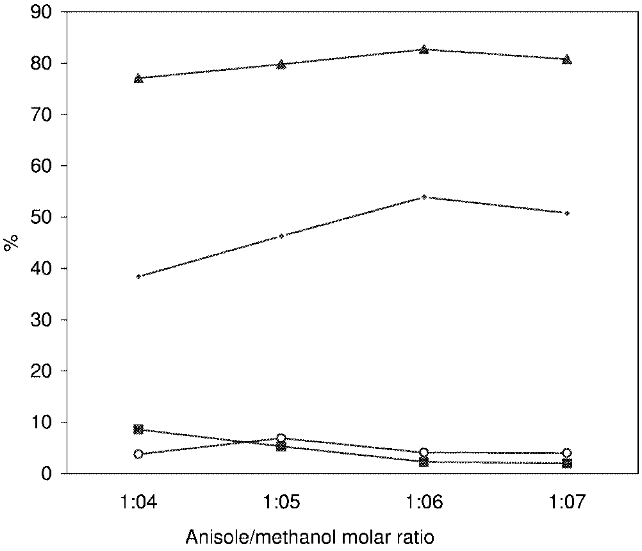

Figure 1. Effect of anisole/methanol molar ratio on the conversion of anisole with methanol. Reaction conditions: temperature 380 °C, catalyst TL82, TOS = 1 h, feed rate 4 ml/h. (♦) Conversion (%); selectivity to (■) phenol, (○) methylanisole and (▲) 2,6-xylenol.

Table 1
Physico-chemical characteristics of lanthanum-promoted SnO_2 and its sulfated analogue calcined at 823 K.

Catalyst	SnO_2[a] (%)	La_2O_3[a] (%)	Sulfate[a] (%)	Surface area (m^2/g)	Pore volume (m^3/g)	Acidity (mmol/g) W	M	S
TL82	89.11	10.79	–	108.8	0.28	0.12	0.05	–
STL82	–	–	5.81	193.7	0.25	0.06	0.57	0.93
SnO_2	100	–	–	36.1	0.45	0.23	0.01	–

[a] From EDX analysis.
[b] W, M and S stand for weak, medium and strong acidic sites.

Table 2
Alkylation of anisole with methanol – effect of temperature on the product distribution over TL82 (a) and STL82 (b).[a]

	350 °C		380 °C		400 °C		420 °C	
	a	b	a	b	a	b	a	b
Product selectivity (%)								
Phenol	0.4	12.9	2.2	17.9	3.9	20.1	5.5	18.8
Methylanisole	22.6	18.2	4.1	2.2	–	–	–	–
Cresol	3.6	6.7	6.7	9.9	5.7	8.8	6.6	4.4
2,6-xylenol	63.9	50.5	81.6	47.1	82.5	43.2	75.7	44.2
TMP	4.1	10.8	5.3	18.9	7.8	25.4	12.1	29.2
Conversion (%)	43.2	48.4	56.8	62.1	65.2	69.4	83.6	65.8

[a] Reaction conditions: temperature 350–420 °C, anisole/methanol molar ratio 1 : 6, TOS = 1 h, feed rate 4 ml/h.

Table 3
Self-reaction of methylanisole over TL82 catalyst.[a]

Reaction temperature (°C)	Conversion (%)	2,6-xylenol selectivity (%)
350	43.6	95.4
380	49.3	92.2
400	56.3	89.1
420	62.5	84.5

[a] Reaction conditions: temperature 350–420 °C, TOS = 1 h, feed rate 4 ml/h.

composition of methanol was appreciable. Maximum 2,6-xylenol selectivity was attained at 380 °C and at higher temperature, it decreased due to the formation of more and more trimethylphenol, phenol and cresol. The selectivity to methylanisole decreased with increase in temperature and it was not detected above 380 °C. The large amount of phenol formed in the case of the sulfated oxide catalyst supports the fact that stronger acid sites facilitate dealkylation of anisole. Bautista and co-workers observed that dealkylation to phenol is predominant over $AlPO_4$–Al_2O_3 catalysts in the methylation of anisole [1]. The dealkylated product phenol also can undergo further reactions to afford cresols, xylenols and polymethylated phenols. In short, the various reaction pathways possible for the acid catalyst such as decomposition of anisole to phenol and ring alkylation to cresol, methylanisole, xylenols and polymethylated products resulted in the poor selectivity during the methylation of anisole. The higher selectivity of 2,6-xylenol over tin–lanthanum mixed oxides is ascribed to the existence of weak acid sites and comparatively stronger basic sites.

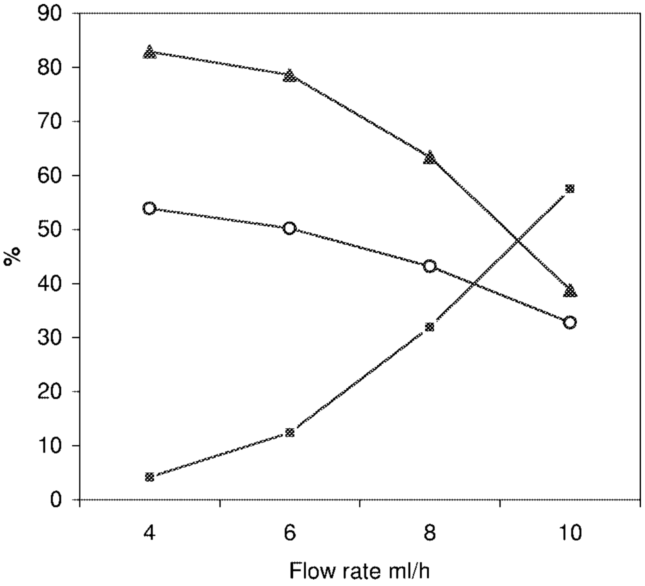

Figure 2. Effect of feed rate on the conversion of anisole with methanol. Reaction conditions: temperature 380 °C, catalyst TL82, TOS = 1 h, anisole/methanol molar ratio 1 : 6. (○) Conversion; selectivity to (■) methylanisole and (▲) 2,6-xylenol.

Table 4
Self-reaction of anisole over TL82.[a]

Reaction temperature (°C)	Conversion (%)	Selectivity (%)		
		Phenol	*o*-cresol	2,6-xylenol
350	12.2	76.4	22.2	–
380	18.4	80.1	16.5	2.2
400	22.6	78.2	13.6	3.4

[a] Reaction conditions: temperature 350–400 °C, TOS = 1 h, feed rate 4 ml/h.

3.4. Self-reaction of methylanisole and reaction pathway

The reaction of methylanisole alone over TL82 was performed at different temperatures and the results are presented in table 3. As the temperature was increased the conversion of methylanisole to xylenol also increased. To understand the reaction pathway in more detail the effect of feed rate on the product selectivity in the reaction of anisole and methanol was studied and the results are depicted in figure 2. The flow rate of the feed was changed from 4 to 10 ml/h. It can be seen that the selectivity to methylanisole increases with increase in feed rate with a concomitant decrease in the selectivity of 2,6-xylenol. This suggests that the methylanisole is the possible intermediate in the formation of 2,6-xylenol over SnO_2–La_2O_3 catalysts. The isomerisation of methylanisole to 2,6-xylenol further supports this reaction pathway. When anisole alone was passed over the catalyst under similar conditions phenol and *o*-cresol were detected as major products but the conversion was low (table 4).

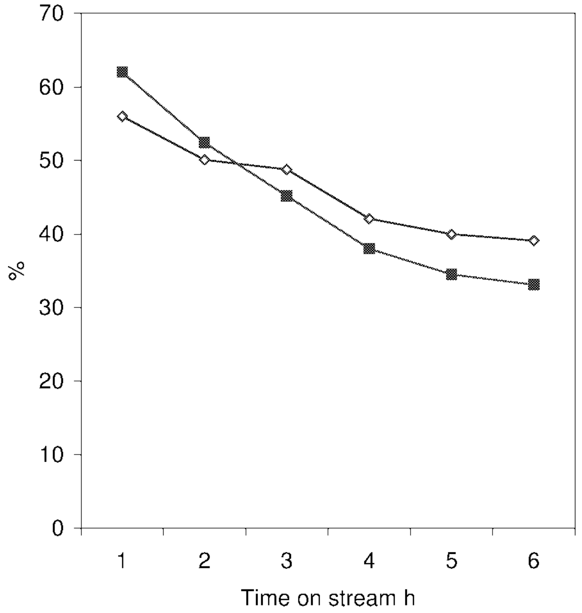

Figure 3. Effect of time on stream on the conversion of anisole with methanol over TL82 and STL82 catalysts. Reaction conditions: temperature 380 °C, feed rate 4 ml/h, anisole/methanol molar ratio 1 : 6. (◇) TL82 and (■) STL82.

3.5. Catalyst stability

Conversion of anisole as a function of time was investigated over TL82 and its sulfated analogue STL82 and results are depicted in figure 3. An initial deactivation was observed over both the catalysts. Similar deactivation was reported on metallic oxide during the alkylation of phenolic compounds. The acidic catalyst, STL82 showed high initial activity and deactivated rapidly with time compared to the non-sulfated analogue.

4. Conclusions

Lanthanum-modified tin oxide catalysts are found to be active in the selective transformation of anisole to 2,6-xylenol using methanol as the alkylating agent. A maximum 2,6-xylenol selectivity of 82% was observed at an anisole conversion of 65% at 400 °C under optimized conditions. Also at higher anisole conversions the selectivity to 2,6-xylenol was high. The same reaction over acidic, sulfated oxide resulted in the non-selective formation of xylenol. A large amount of the dealkylation product phenol was observed in the case of sulfated oxide, whereas the formation of phenol was negligible over its non-sulfated analogue. The secondary reactions are suppressed over lanthanum-modified SnO_2 due to the unavailability of strong acid sites. The presence of strong acid sites leads to the dealkylation of anisole to phenol followed by several side reactions. It is proposed that 2,6-xylenol is formed by the isomerization of methylanisole. The activity of lanthanum-modified tin oxide catalysts in the selective formation of 2,6-xylenol is ascribed to the presence of weak Lewis acid sites and comparatively stronger basic sites.

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