Formation of anisaldehyde via hydroxymethylation of anisole over SnO_2–CeO_2 catalysts

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Hydroxymethylation of anisole has been carried out over SnO_2–CeO_2 catalysts in the temperature range 623–723 K. Methoxybenzaldehyde (anisaldehyde) and condensation products were formed along with minor quantities of methoxybenzyl alcohol, *o*-cresol, phenol and 2,6-xylenol. A maximum anisaldehyde selectivity of 64% was obtained at 623 K at an anisole conversion of 46% under optimized conditions. Catalytic activity of these systems in the formation of aldehyde is ascribed to the presence of weak acid sites and redox metal sites.

Keywords: hydroxymethylation, anisole, anisaldehyde, tin oxide, cerium oxide, catalysts

1. Introduction

Hydroxymethylation of aromatic or heteroaromatic compounds is favored in the presence of activating functional groups such as hydroxyl or alkoxy groups [1]. In most cases selectivity to hydroxymethylated products is rather low because of the formation of condensation products. Climent et al. have reported the reaction of different aldehydes with various aromatic substrates over Y-zeolites, resulting in the formation of condensation products [2]. More recently, Wu and co-workers optimized the reaction conditions to prepare benzyl alcohol via hydroxymethylation of benzene over ZSM-5 zeolite [3].

It is well known that dehydrogenation of alcohols to carbonyl compounds takes place by the intervention of acid–base pair sites through a concerted mechanism [4]. Dehydrogenation is facilitated by the presence of redox metal sites capable of undergoing a facile electron transfer process. Tin oxide is an important counterpart in many catalyst systems employed for partial oxidation reactions [5–8]. Rare earth oxides like CeO_2 can supply mobile oxygen species capable of reoxidizing reduced metal sites [9]. The present work is an attempt to utilize the partial oxidation activity of the CeO_2–SnO_2 system to affect the transformation of 2-methoxybenzyl alcohol formed by the hydroxymethylation of anisole to 2-methoxybenzaldehyde (anisaldehyde). So it will be possible to introduce an aldehyde group in the aromatic ring directly, employing the proper choice of catalysts and reaction conditions.

2. Experimental

2.1. Catalyst preparation

The binary mixed oxides of tin and cerium were prepared by a co-precipitation method from the required quantities of stannic chloride solution and cerium nitrate solution using 1 : 1 aqueous ammonia as precipitant followed by aging, washing, filtration and drying. Three different compositions were prepared, viz., SnO_2 (80%)–CeO_2 (20%), SnO_2 (50%)–CeO_2 (50%) and SnO_2 (20%)–CeO_2 (80%), and for convenience designated as TC82, TC55 and TC28, respectively. The catalysts were sieved to a mesh size $<100\ \mu$m and calcined in air for 6 h at 773 K prior to any experiment.

2.2. Catalyst characterization

Physico-chemical characterization of the catalysts has been performed by EDX, XRD, BET-SA, TG-DTA, mercury porosimetry and acidity–basicity measurements by the adsorption of n-butylamine and acetic acid, respectively. Catalysts were kept in a desiccator saturated with n-butylamine/acetic acid vapor at room temperature for 48 h. Then the weight loss of the adsorbed sample was measured by a TGA operating from 313 to 873 K at a rate of 20°/min. The weight losses between 423 and 573 K, 574 and 723 K, 724 and 873 K are considered to be weak, medium and strong acid sites, respectively [10].

2.3. Hydroxymethylation of anisole

All the reactions were carried out in a vertical type flow reactor of 2.2 cm I.D. and 30 cm length, kept in a cylindrical furnace mounted vertically. The catalyst (3 g, 10–20

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mesh size) was loaded in the middle of the reactor and packed with porcelain beads. Anhydrous formaldehyde was carried to the reaction chamber using nitrogen carrier gas at a moderate flow rate of 20 ml/h and a mixture of water (5%) and anisole were fed from a high precision pump (ISCO). Gas products were analyzed by an on-line gas chromatograph with thermal conductivity detector using a Porapack Q column. The mass balance was noted each time and liquid products were analyzed using a capillary column (HP I). Identities of the products were established by comparing the retention time of authentic samples and also by GC-MS.

3. Results and discussion

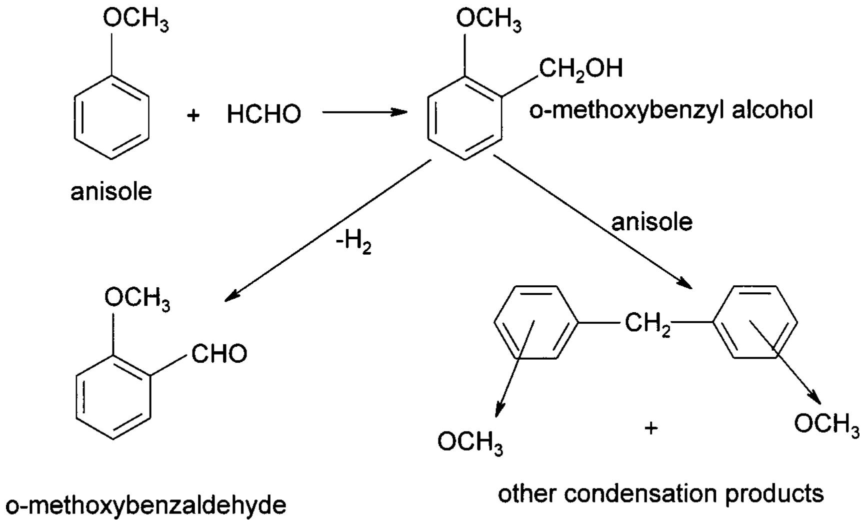
3.1. Physico-chemical characteristics

The important physico-chemical characteristics of the catalysts are presented in table 1. Energy dispersive X-ray analysis was used to determine the chemical composition of all the mixed oxides prepared. The broadening of XRD peaks after the addition of CeO_2 to tin oxide indicates that the addition of a second oxide hinders the crystallization of SnO_2 by preventing the aggregation of smaller particles. TC82 showed cassiterite as the prominent phase; no reflections due to rare earth oxide phase were detected. This means that rare earth oxide is well dispersed on the support material. The specific area of these samples was higher compared to other systems. TC55 and TC28 showed the co-existence of both SnO_2 and rare earth oxide phases. The BET surface areas determined by N_2 adsorption were in the order TC82 $>$ TC55 $>$ TC28. The higher surface area of the TC82 sample may be due to the presence of a small amount of rare earth oxide component, which prevent the agglomeration 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 decreasing surface area of other systems. The pore volume of the catalysts increased in the order TC82 $<$ TC55 $<$ TC28. The catalyst TC82 was found to contain only few number of pores with radius $>$30 Å. Other systems contained a larger number of pores with radius $>$30 Å. So a notable variation in the pore volume and pore volume distribution was observed as the composition of the catalyst was varied. The distribution of acidic and basic sites as determined by the adsorption of n-butylamine and acetic acid is given in table 1. It can be seen that the strength and distribution of acidic and basic sites vary as the composition of the catalyst is changed. Basicity of mixed oxides varies in the order TC82 $>$ TC28 $>$ TC55. A detailed account of the physico-chemical characterization of rare-earth-modified tin oxide catalysts is reported elsewhere [11].

Table 1
Physico-chemical characteristics of SnO_2–CeO_2 catalysts.

Catalyst	SnO_2[a] (wt%)	CeO_2 (wt%)	Surface area (m^2/g)	Pore volume (ml/g)	Acidity[b] (mmol/g) W	M	S	Basicity[b] (mmol/g) W	M	S
TC82	79.2	20.8	104.9	0.30	0.12	0.06	–	0.08	0.14	0.41
TC55	47.8	52.2	57.0	0.41	0.05	0.14	0.11	0.06	0.16	0.28
TC28	23.6	76.4	28.2	0.69	0.07	0.07	–	0.07	0.19	0.33
SnO_2	100	–	36.1	0.45	0.23	0.01	–	0.03	0.09	0.19
CeO_2	–	100	31.9	0.41	0.05	0.03	–	0.05	0.29	0.22

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



Scheme 1.

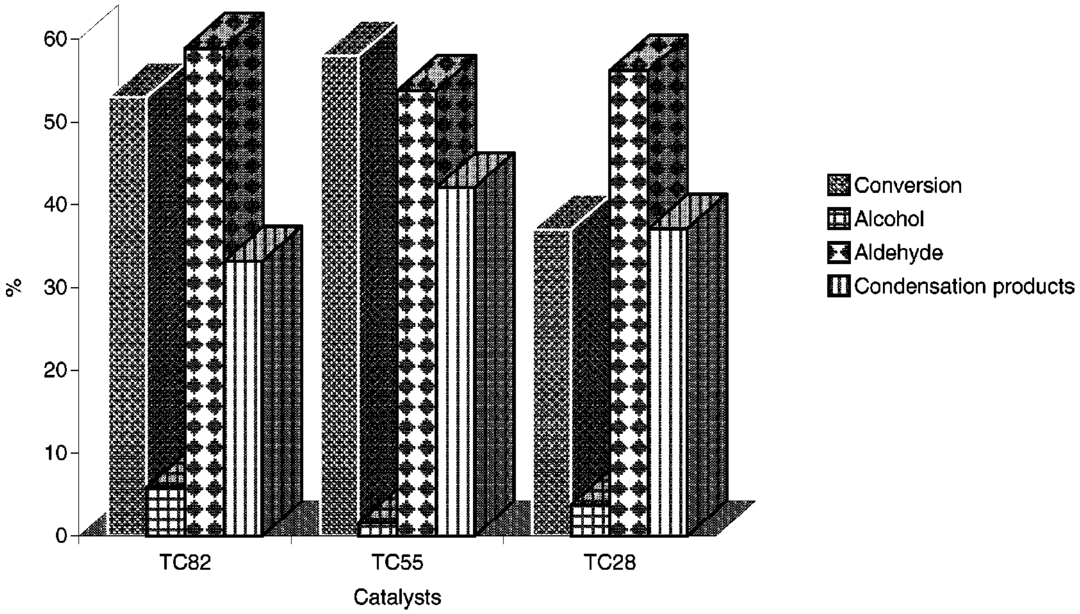


Figure 1. Hydroxymethylation of anisole over different catalysts. Anisole/formaldehyde mol ratio = 1 : 2, reaction temperature 623 K, TOS = 1 h, pressure 1 atm, WHSV = 1 h^{-1}.

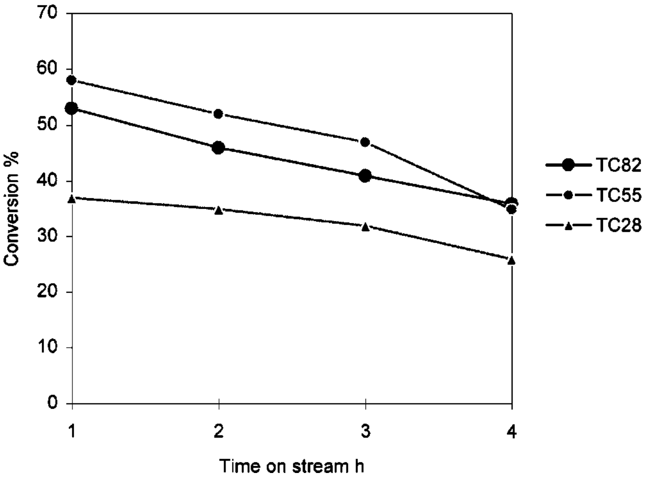


Figure 2. Stability of the catalysts with time on stream. Anisole/formaldehyde mol ratio = 1 : 2, reaction temperature 623 K, pressure 1 atm, WHSV = 1 h^{-1}. (●) TC82, (•) TC55 and (▲) TC28.

3.2. Catalytic activity

Reaction of anisole and formaldehyde at 623 K resulted in the formation of methoxybenzaldehyde and different condensation products along with small amounts of methoxybenzyl alcohol (scheme 1). The hydroxymethylation of anisole over different catalysts containing a varying amount of cerium oxide is shown in figure 1. Maximum selectivity of aldehyde achieved was 59% over the TC82 catalyst at an anisole conversion of 53%, whereas in the case of TC55 a large amount of condensation products were formed which is ascribed to its higher acidity. During the preliminary screening of the catalysts we found that single oxides were not active in bringing about the reaction. The initial conversions of anisole over SnO_2 and CeO_2 were found to be 19 and 16%, respectively. The catalytic activity was tested for a period of 4 h and it is found that all the catalysts deactivate with time on stream (figure 2). Catalyst deactivation must be due to the formation of high molecular weight compounds as a result of condensation reactions, which poisons the active sites. It is also expected that the oxidation state of redox metal sites changes during the dehydrogenation of alcohol to aldehyde.

Table 2
Effect of anisole/formaldehyde molar ratio on the product selectivity.[a]

Molar ratio	Anisole conversion (%)	Product selectivity (%)		
		Methoxy benzyl alcohol	Methoxy benzaldehyde	Condensation products
1 : 3	56	2.6	59.1	36.1
1 : 2	53	5.9	58.9	33.2
1 : 1	52	1.8	52.3	41.2
2 : 1	57	0.7	45.3	48.9

[a] Reaction conditions: reaction temperature 623 K, TOS = 1 h, pressure 1 atm, WHSV = 1 h^{-1}, catalyst TC82.

The effect of anisole/formaldehyde molar ratio on the product selectivity is presented in table 2. Anisole conversion was not much influenced by the change in molar ratio. An increase in anisole/formaldehyde ratio was accompanied by a decrease in the selectivity of aldehyde, evidently as a result of the competing condensation reaction between anisole and formaldehyde which is favored at higher anisole concentration.

As the reaction temperature was increased from 623 to 723 K the selectivity of methoxybenzaldehyde dropped from 59 to 29%, with a concomitant increase in the selectivity of condensation products (figure 3). At higher temperatures many products were formed including small amounts of phenol, *o*-cresol, methylanisole and 2,6-xylenol. Phenol

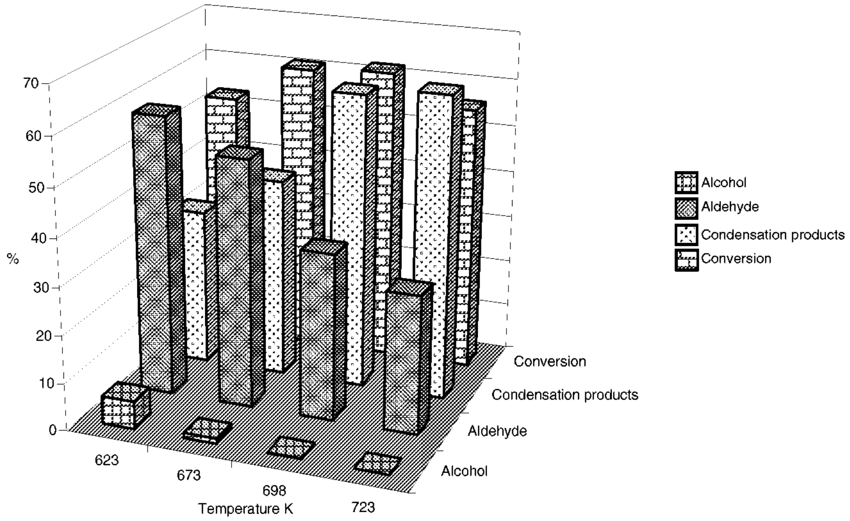


Figure 3. Effect of temperature on anisole conversion and product selectivity. Anisole/formaldehyde mol ratio = 1 : 2, catalyst TC82, TOS = 1 h, pressure 1 atm, WHSV = 1 h^{-1}.

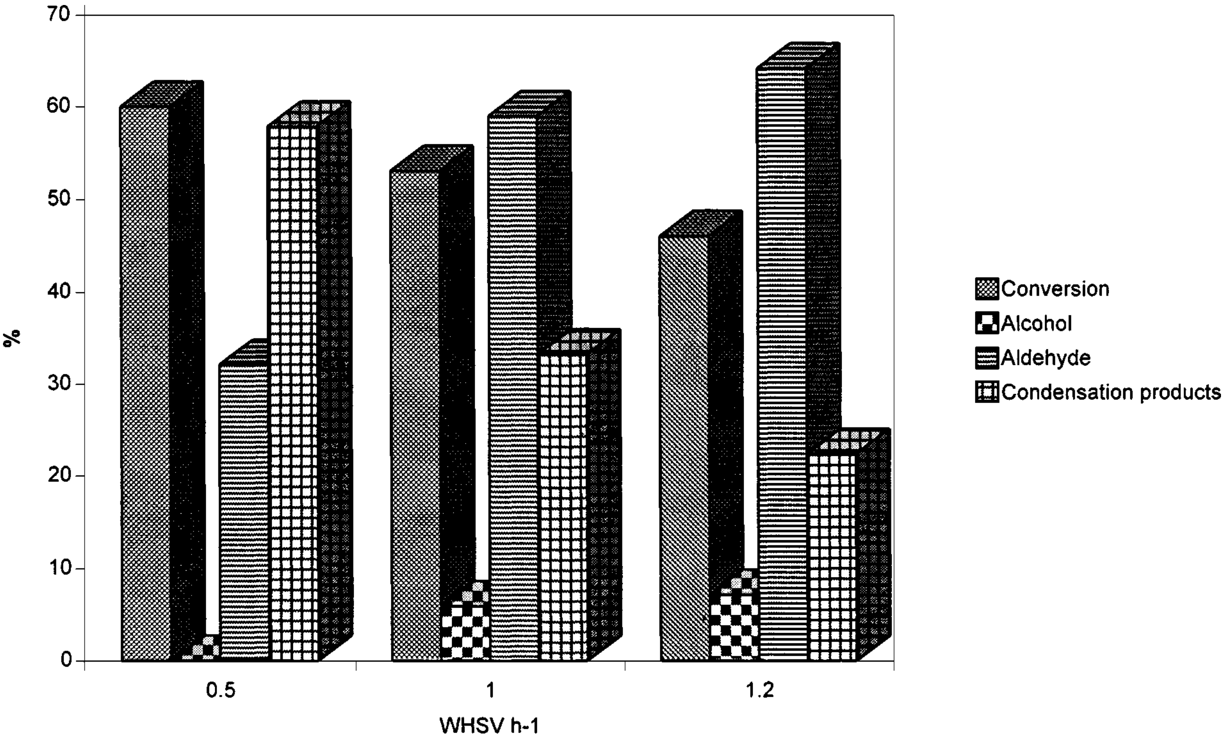


Figure 4. Effect of WHSV on anisole conversion and product selectivity. Anisole/formaldehyde mol ratio = 1 : 2, reaction temperature 623 K, TOS = 1 h, pressure 1 atm, catalyst TC82.

is formed by the dealkylation of anisole at higher temperatures. *o*-cresol, methylanisole and 2,6-xylenol must be formed by the reductive hydroxymethylation of anisole and phenol. Moreover, at higher temperature the self-reaction of formaldehyde resulted in the reduction of anisole conversion.

The effect of WHSV on the product selectivity is shown in figure 4. The selectivity of aldehyde was improved by increasing the flow rate of the feed (WHSV = 1.2 h^{-1}). A sharp increase in the selectivity of methoxybenzaldehyde from 32 to 64% was obtained upon changing the WHSV from 0.5 to 1.2 h^{-1}, with a concomitant decrease in the selectivity of condensation products.

4. Conclusions

Hydroxymethylation of anisole over SnO_2–CeO_2 catalysts resulted in the formation of methoxybenzaldehyde (anisaldehyde) by the subsequent dehydrogenation of the methoxybenzyl alcohol. The catalytic activity of these systems in the formation of aldehyde is ascribed to the presence of weak acid sites and redox metal sites. Stronger acid sites lead to the formation of condensation products. Similar catalyst systems with enhanced stability can be developed to affect the formation of aldehydes.

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