Evidence for weak base site participation in the vapour phase methylation of catechol over solid base catalysts

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The vapour phase alkylation of catechol over supported caesium catalysts gives good selectivity to guaiacol formation, and TPD studies indicate that this result can be correlated with the presence of weak basic sites on the catalyst.
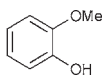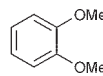
Vapour phase alkylation of catechol is commercially important for the production of oxy-alkylated products, namely guaiacol and veratrole. These are synthetic intermediates used in the production of flavourings, fragrances and pharmaceuticals.[1] Studies on phenol alkylation have shown that product selectivity depends on the acid–base property of the catalyst surface.[2] The addition of metal ions to alumina is known to generate new active sites which are basic in nature.[3] Available literature on the vapour phase alkylation of catechol over solid base catalysts, though limited, suggests that the basic sites are primarily responsible for the formation of C-/O-alkylated products.[4,5] This is further supported by the report that CO_2 adsorption over the basic sites leads to catalyst deactivation.[6,7] However, there is no evidence to suggest that the weak sites over the base catalysts are primarily important for the formation of mono oxy-methylated products, in particular guaiacol. Here, for the first time, such a correlation is proposed, i.e. that a correlation exists between the weak base sites on a catalyst surface and selectivity to guaiacol.
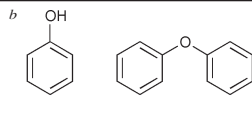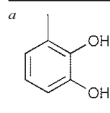
The supported caesium catalysts were prepared by impregnating Al_2O_3, SiO_2 and TiO_2, all of commercial origin, with an appropriate amount of an aqueous solution of caesium hydroxide (10% Cs by mass). The resulting solids were dried and calcined in air at 673 K for 4 h. Temperature programmed desorption (TPD) was performed using CO_2 gas at a heating rate of 10 K min^{-1} in the temperature range 373–973 K.

The vapour phase alkylation of catechol with methanol was carried out in a vertical flow-type reactor at 623 K at atmospheric pressure (ca. 650 mm Hg). Before the start of the experiment, the catalyst (ca. 2 g) was activated in the reactor at 673 K for 1 h in nitrogen and then the solid was cooled to the reaction temperature. A pre-mixed catechol–methanol (1:3 w/w ratio) mixture was fed from the top of the reactor at a fixed rate of 5.1 ml min^{-1} (methanol-free catechol flow rate 0.95 mol h^{-1}) by means of a Sage syringe pump. After 1 h the liquid products were analysed by GC (FID) using a DB-1 capillary column. The reaction products were further confirmed by GC–MS (VG-11-250 data system) and ^{13}C NMR (Brucker AC-400) spectroscopy.

The reaction data for the vapour phase alkylation of catechol over unsupported and supported catalysts are shown in Table 1. The acidic oxides (Al_2O_3, SiO_2 and TiO_2) do not show much guaiacol formation. However, the basic oxide MgO shows a selectivity of 65% for guaiacol. This suggests that the basic sites on the catalyst surface are involved in the formation of guaiacol. It is interesting to note that caesium oxide alone shows a low activity and selectivity towards guaiacol formation. However, impregnation of caesium on to the acidic oxides (Al_2O_3, SiO_2 and TiO_2), increased the selectivity for guaiacol significantly. Both alumina and caesium-modified alumina show the highest reaction activity as compared to the other unsupported and supported oxides. This suggests that the stronger and larger number of acidic sites on the catalyst surface promotes more ring alkylation than side (O-) alkylation. In the case of both alumina and caesium-modified alumina a significant amount of polyalkylated products is also formed. The formation of phenol, and to a lesser extent diphenyl ether, indicates that both dehydration and ring alkylation are the two competitive

Table 1 Reaction data on unsupported and supported cesium catalysts

Catalyst	Activity mol h^{-1} g^{-1}	Selectivity (%)			
		Guaiacol	Veratrole	C-alkylated products[a]	Others[b]
TiO_2	0.718	10	2	36	42
Al_2O_3	2.341	18	3	73	6
SiO_2	0.133	20	43	33	4
MgO	0.106	65	15	15	5
Cs_2O	0.053	16	17	6	57
10 wt% Cs_2O/TiO_2	0.426	37	12	10	41
10 wt% Cs_2O/Al_2O_3	1.409	58	1	28	13
10 wt% Cs_2O/SiO_2	0.505	75	16	4	5

[a] / [b] structures

reactions operating over the acidic sites. This is supported by the fact that both TiO_2 and $Cs–TiO_2$ show a significant amount of dehydrated products as compared with Al_2O_3 and $Cs–Al_2O_3$ catalysts.

The distribution of basic sites over unpromoted and promoted catalysts are shown in Fig. 1 and 2. The TPD profiles of CO_2 over Al_2O_3 and MgO (Fig. 1) show that although Al_2O_3 is more acidic than MgO it also has a larger number of strong basic sites (885 K) with respect to MgO (912 K). The stronger basic sites on MgO at 912 K indicate that, apart from O^{2-} basic sites of MgO, the adjacent Mg^{2+} sites may also participate in CO_2 adsorption.[8] On the other hand, MgO has a greater number of weaker basic sites (559 K) than Al_2O_3. The fact that more guaiacol is formed on MgO than Al_2O_3 indicates that weaker basic sites may be primarily involved for the higher selectivity of guaiacol. Fig. 2 clearly demonstrates this finding. Here it is seen that addition of caesium to acidic supports transforms stronger base sites into weak sites, thus enhancing the selectivity for guaiacol. The higher selectivity for guaiacol at weaker basic sites over $Cs–SiO_2$ (75%) as compared with $Cs–Al_2O_3$ (58%) further supports the assumption that the formation of guaiacol is related to the strength and the number of the weak basic sites. However, in the case of $Cs–TiO_2$, the lower selectivity for guaiacol (37%) may suggest the possibility of an interaction between the promoter and titania, leading to compound formation.

In conclusion, it is evident from the foregoing results that the transformation of stronger basic sites to weaker ones upon addition of Cs_2O results in higher selectivity for guaiacol. Further work is in progress to explain the characteristic aspects of the title reaction in detail.

Fig. 1 CO_2 TPD profiles of MgO and Al_2O_3.
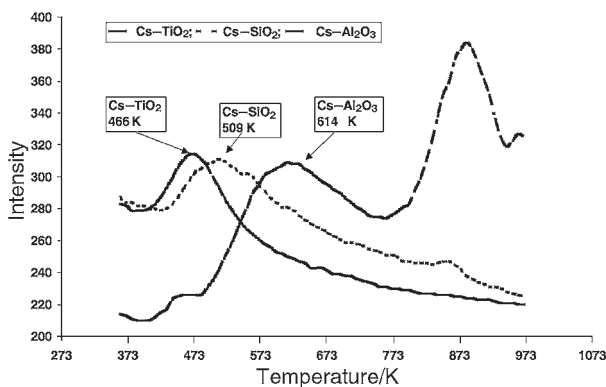
Fig. 2 CO_2 TPD profiles of Cs on TiO_2, SiO_2 and Al_2O_3.

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