Vapour phase *O*-methylation of dihydroxy benzenes with methanol over cesium-loaded silica, a solid base

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Abstract

Vapour phase *O*-methylation of the dihydroxy benzenes, catechol, resorcinol and hydroquinone with methanol has been investigated in the temperature range 573–673 K over alkali-loaded fumed silica. Fumed silica (SiO_2) by itself has no *O*-methylation activity, but on impregnation with alkali metal oxides (Li, Na, K and Cs) becomes active for *O*-methylation producing mono- and dialkylated products. Activity of the catalysts and selectivity for dialkylates increase with metal loading and basicity of the metal ions (Cs > K > Na > Li). Very high conversion ($\sim$93%), at nearly 100% selectivity for *O*-methylation was obtained over Cs-loaded fumed silica in the case of resorcinol and hydroquinone. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: *O*-methylation; Dihydroxy benzenes; Methanol; Alkali-loaded silica; Basic catalysts

1. Introduction

Discovery of new environmentally clean and economical processes based on solid catalysts for the production of fine chemicals has assumed importance in recent times. Solid inorganic catalysts have advantages of being easily separable and recyclable. Besides, these catalysts result in lower corrosion and environmental problems. Many solid bases have recently been found useful in the production of fine chemicals [1–4]. A number of materials such as hydrotalcites, ETS-10 and KF/Al$_2$O$_3$ have been reported to act as heterogeneous basic catalysts [5–7].

O-methylated hydroxy benzenes are important synthetic intermediates in the production of fine chemicals and pharmaceuticals [8]. They are conventionally synthesized by methylation with dimethylsulphate [9]

or with methyl halide in the presence of sodium hydride [10]. These methylating agents are corrosive and toxic. Vapour phase methylation of aromatic hydroxy compounds with methanol over heterogeneous catalysts such as metal oxides, sulphates, phosphates and zeolites has been attempted [11–16]. Fu et al. [17–19] reported the vapour phase *O*-methylation of catechol with DMC over supported alumina. We now report the selective vapour phase *O*-methylation of the dihydroxy benzenes, catechol, resorcinol and hydroquinone with methanol over alkali-(Li, Na, K and Cs) loaded silica.

2. Experimental

Fumed silica (Cab-osil, Fluka) was used as a support for alkali metal oxides. The different alkali-loaded catalysts were prepared by an impregnation procedure using minimum amount of aqueous metal hydroxide/acetate (Li, Na, K and Cs; incipient wetness method).

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The catalysts were dried at 373 K (6 h) and calcined at 773 K (6 h) in air.

Temperature programmed desorption (TPD) of CO_2 was carried out with 0.25 g of dried sample for each experiment. The sample was activated at 673 K in a flow of He at the rate of 30 ml/min and cooled to room temperature. Ultra high pure CO_2 was passed for 1 h at room temperature at a flow rate of 25 ml/min, then flushed with He for 90 min (30 ml/min) and the temperature was raised to 723 K at the rate of 5°/min in He flow (30 ml/min). The evolved CO_2 was estimated using a TCD detector to obtain the TPD curves.

FT-IR spectra were recorded using self-supported wafers of the samples. The sample was pressured into wafers (5–6 mg/cm^2) and evacuated (10^{-5} Torr) in situ at 673 K and cooled to 298 K. After the spectrum of the sample was recorded, ultra pure CO_2 was adsorbed at 5 mm equilibrium pressure for 1 h. Then, part of the CO_2 gas was pumped out to maintain an equilibrium pressure of 0.4 mm and the spectrum was recorded. All the spectra were recorded using a Nicolet 60 SXB spectrometer with 2 cm^{-1} resolution averaging over 500 scans.

The catalytic experiments were carried out in a vertical downflow glass reactor (15 mm i.d.). All the reactions were carried out using about 2 g charge of the catalyst. The catalysts were used in the form of granules (10–22 mesh) prepared by pelletting of the powders and crushing to the desired size. The

zone (~15 cm long) above the catalyst bed packed with ceramic beads served as the feed preheater. The reactor was placed inside a temperature-controlled furnace (Geomecanique, France) with a thermocouple placed at the centre of the catalyst bed for measuring the reaction temperature. The catalyst was activated in flowing air (20 ml/min) at 773 K for 3 h prior to flushing in N_2 and adjustment of temperature for starting the experiments. The feed (mixture of dihydroxy benzene and methanol) was passed using a syringe pump (Braun, Germany) along with N_2 gas (18 ml/min). The product was cooled in a water-cooled condenser, collected in a receiver and analysed in a gas chromatograph (HP 5880A; capillary column HP1, 50 m × 0.2 mm; FID detector). Product identification was done by GC–IR, GC–MS and NMR. Carbon mass balances were carried out for many of the experiments and found to be $95 \pm 5\%$.

3. Results and discussion

3.1. Physicochemical properties of the samples

XRD showed that all the samples were amorphous. The surface areas (Table 1) of the samples were calculated from N_2 sorption isotherm (BET method). The surface areas decrease with metal loading and increase in basicity (molecular weight) of the metal. As part

Table 1
Physicochemical properties of the catalysts

Catalyst[a]	Metal loading as oxide (wt.%)	Surface area[b] (m^2/g)	Surface area[c] (m^2/g)	Relative basicity	
				TPD[d] (mmol CO_2/g)	FT-IR[e]
SiO_2	–	166	–	–	–
Li(1.5)SiO_2	2.25	104	161	0.062	92
Na(1.5)SiO_2	4.65	99	158	0.071	132
K(1.5)SiO_2	7.05	91	156	0.078	153
Cs(0.075)SiO_2	1.06	149	164	0.031	19
Cs(0.375)SiO_2	5.28	121	157	0.049	88
Cs(0.75)SiO_2	10.5	102	149	0.061	120
Cs(1.5)SiO_2	21.1	70	133	0.079	216
Cs(2.25)SiO_2	31.7	56	113	0.082	262

[a] The number in brackets denotes the millimole of alkali metal loaded per gram of SiO_2.

[b] Measured by N_2 adsorption (BET method).

[c] Areas calculated on the basis of SiO_2.

[d] Amount of CO_2 desorbed per gram of the sample.

[e] Relative intensity of CO_2 from FT-IR (1200–1700 cm^{-1} band after adsorption of CO_2 at 0.4 mm of equilibrium pressure) normalised to constant sample weight.

Table 2
Catalytic activity of the catalysts containing different alkali ions (conditions: temperature = 673 K, time on stream = 1 h, contact time (h) = 0.376, N_2 = 18 ml/min)

Catalyst	Catechol			Resorcinol			Hydroquinone			p-Methoxy phenol	
	Conversion	Selectivity[a] (mono)	Selectivity[b] (di)	Conversion	Selectivity[c] (mono)	Selectivity[d] (di)	Conversion	Selectivity[e] (mono)	Selectivity[f] (di)	Conversion	Selectivity[f]
Li(1.5)SiO$_2$	5.2	75.1	15.7	30.9	36.9	44.3	27.1	59.1	14.0	49.7	100
Na(1.5)SiO$_2$	10.3	71.3	22.5	45.3	33.8	52.1	44.2	47.7	31.0	63.8	100
K(1.5)SiO$_2$	17.3	63.3	31.5	65.7	22.6	64.7	49.1	45.8	41.0	75.8	100
Cs(1.5)SiO$_2$	57.2	47.0	53.0	87.4	10.7	89.3	87.9	24.8	75.2	96.4	100

[a] 2-Methoxy phenol.
[b] 1,2-Dimethoxy benzene.
[c] 3-Methoxy phenol.
[d] 1,3-Dimethoxy benzene.
[e] 4-Methoxy phenol.
[f] 1,4-Dimethoxy benzene.

of the observed decrease in area is due to an increase in the effective weight of the catalyst due to the large amount of deposited alkali oxides, surface areas were calculated on alkali free basis also (Table 1). These values are also lower than that of pure SiO_2. The decrease in surface area is attributed to the "dissolution" of the surface by the alkali during impregnation, fusion of SiO_2 particles and pore filling by the alkali oxides.

TPD of adsorbed CO_2 was carried out on the samples and the results are presented in Table 1. It was found that most of the CO_2 desorbed from the samples before 500 K with desorption peak maxima in the range 375–400 K. Though CO_2 adsorbs weakly on the catalysts and desorbs easily, the TPD data do reveal

information concerning the basicity of the samples. The amount of CO_2 desorbed increases with increase in the basicity of the metal (Li to Cs) and with increasing Cs content (Table 1). A very similar trend is also noticed in the FT-IR data on adsorbed CO_2 (Table 1). Again, the amount of CO_2 adsorbed on the catalysts as estimated by FT-IR also increase with increasing basicity of the alkali metal (Li to Cs) and with increasing Cs content.

3.2. Activities of the catalysts

The catalytic activities of different alkali-loaded silica samples are presented in Table 2 and Fig. 1a. Pure
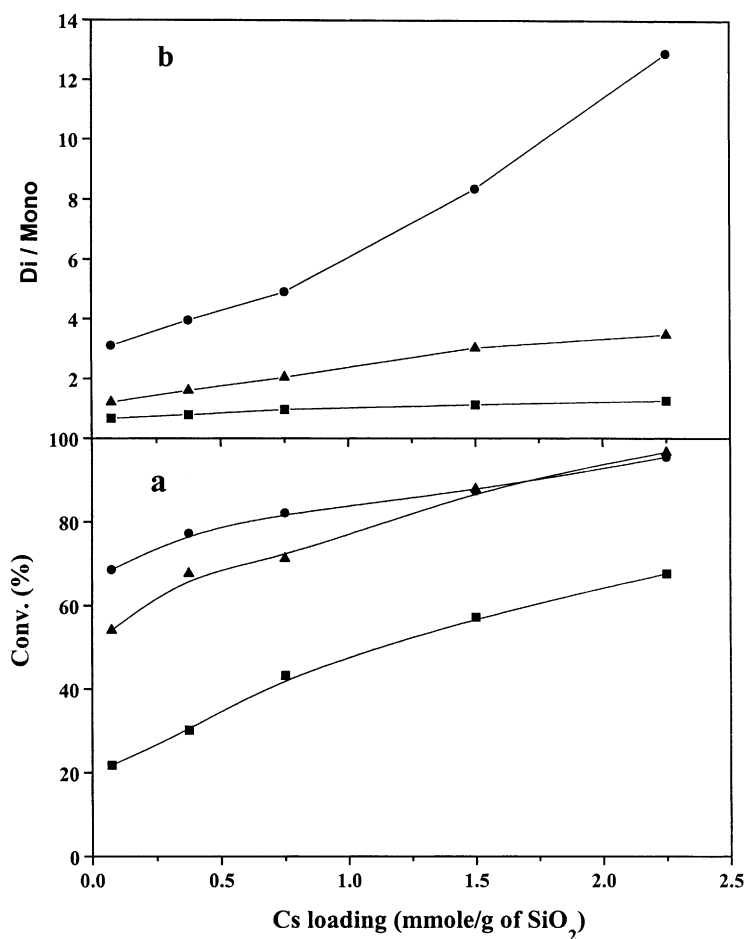

Fig. 1. Influence of Cs content of catalyst on conversion of dihydroxy benzenes and dimethoxy benzene/monomethoxy phenol ratios: (a) conversion; (b) dimethoxy/monomethoxy product (di/mono) ratios (conditions: temperature = 673 K, time on stream (TOS) = 1 h, contact time = 0.376 h, N_2 = 18 ml/min, substrate/methanol (mol) = 1/5). (■) Catechol; (●) resorcinol; (▲) hydroquinone.

SiO_2 has little O-methylation activity; alkali-(Li, Na, K and Cs) loaded silica is catalytically active. For a given molar loading (1.5 mmol/g) of the alkali ions, activity and O-methylation selectivity of the catalysts (in the case of all the three substrates) is in the order, $Cs(1.5)SiO_2 > K(1.5)SiO_2 > Na(1.5)SiO_2 > Li(1.5)SiO_2$. The data reported in Table 2 and Fig. 1 were obtained at 673 K and, hence, the conversions are rather high over many catalysts. Experiments carried out at 573 K (lower conversions, 10–30%) also

confirmed the above ordering of the catalysts. Fig. 1a reveals that the activity of the catalysts also increases with increasing Cs content (basicity).

The influence of duration of run on the conversion of dihydroxy benzenes and distribution of products is presented in Fig. 2. The catalyst investigated was $Cs(1.5)SiO_2$. It is observed that the catalyst deactivates with duration of run in the case of all substrates. Interestingly, it is noticed that the monomethoxy product formation decreases with time more than the dimethoxy isomer. Studies on other alkali-loaded catalysts reveal (data not reported) that the catalysts deactivate to different extent depending on the alkali metal and the substrate. The average deactivation rates calculated over a 3 h period for different alkali-loaded catalysts for the three dihydroxy benzenes and p-methoxy phenol are presented in Fig. 3. The average deactivation rate is defined as the difference in conversion between first and third hour divided by the average conversion during this period.
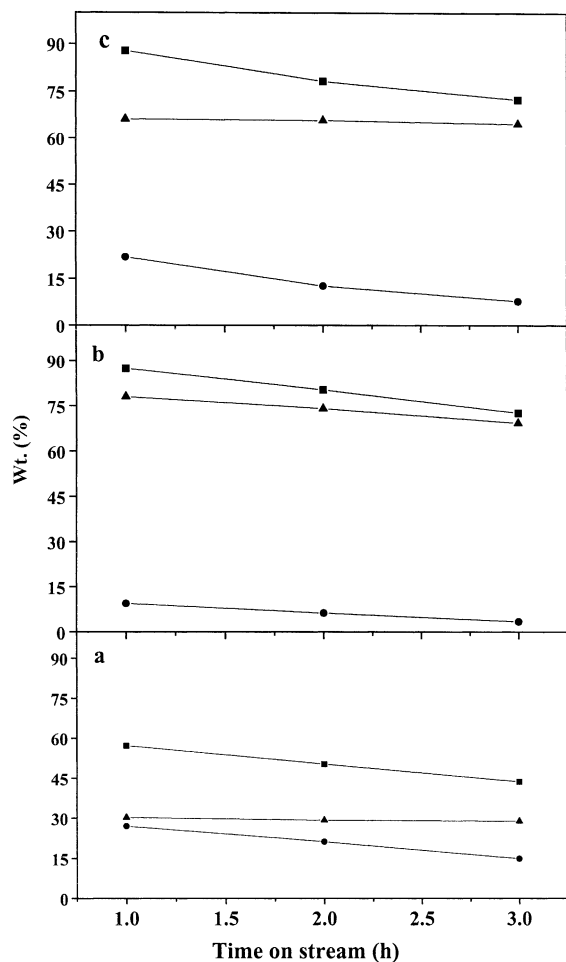

Fig. 2. Effect of time on stream on conversion of dihydroxy benzenes and product distribution over $Cs(1.5)SiO_2$: (a) catechol; (b) resorcinol; (c) hydroquinone (conditions: contact time = 0.376 h, temperature = 673 K, substrate/methanol (mol) = 1/5, N_2 = 18 ml/min). (■) Conversion; (●) monomethoxy phenol; (▲) dimethoxy benzene.
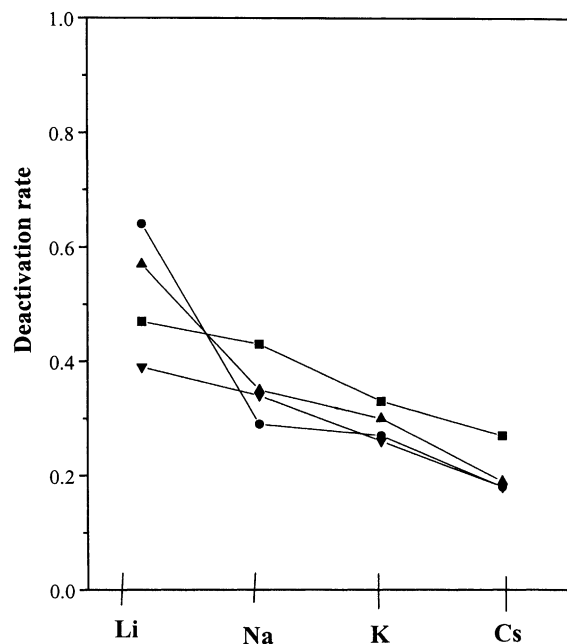

Fig. 3. Influence of substrate on catalyst deactivation rate (conditions: temperature = 673 K, contact time = 0.376 h, N_2 = 18 ml/min, substrate/methanol (mol) = 1/5; catalysts contain 1.5 mmol alkali metal/g of SiO_2; deactivation rate = $2(C_1 - C_3)/(C_1 + C_3)$, where C_1 and C_3 are conversions at 1 and 3 h, respectively). (■) Catechol; (●) resorcinol; (▲) hydroquinone; (▼) p-methoxy phenol.

Catechol deactivates the catalyst much more than the other compounds and deactivation decreases with increasing basicity. The greater deactivation observed for catechol may be due to its stronger adsorption on the catalyst through the two adjacent –OH groups. Decrease in deactivation with basicity may also be related to the mode of adsorption of the compound. Over a less basic catalyst, the molecule may adsorb by interaction of its π-electron system, while on a more basic catalyst, it may adsorb by the –OH group as shown in Scheme 1. *p*-Methoxy phenol causes the least deactivation of the catalysts.
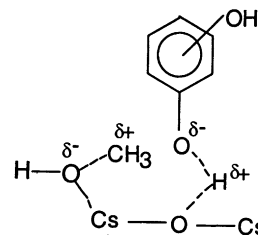
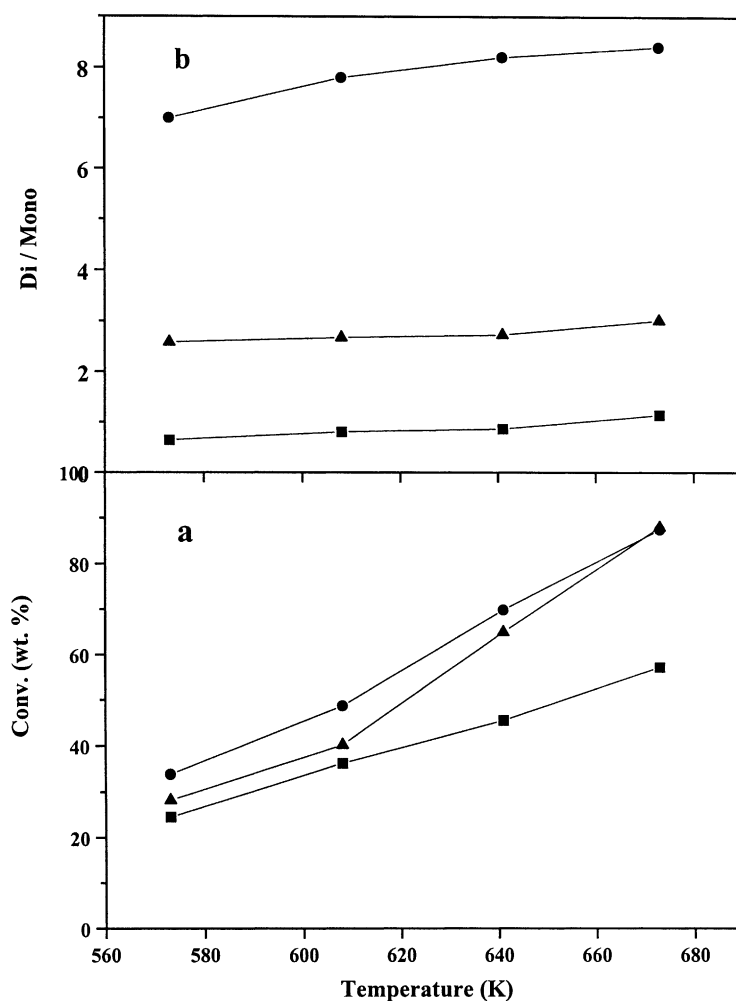Scheme 1. Probable mode of adsorption of the reactants.

Fig. 4. Effect of temperature on conversion of dihydroxy benzenes and dimethoxy benzenes/monomethoxy phenol ratios over Cs(1.5)SiO$_2$: (a) conversion; (b) dimethoxy/monomethoxy product (di/mono) ratios (conditions: TOS = 1 h, contact time = 0.376 h, N$_2$ = 18 ml/min, substrate/methanol (mol) = 1/5). (■) Catechol; (●) resorcinol; (▲) hydroquinone.

3.3. Reactivities of the dihydroxy benzenes

If we examine the relative activities of the three dihydroxy compounds, catechol, resorcinol and hydroquinone, we find that their reactivity increases in the order, catechol < hydroquinone < resorcinol. The reason for this reactivity trend is the difference in the acidities of the three compounds and ease of formation of the likely surface intermediate (Scheme 1) on the catalyst.

The reactivity trend exactly matches the acidity of the three dihydroxy compounds (catechol < hydroquinone < resorcinol) and electron density trends at the o-, m- and p-positions of phenol. The $+M$ effect of the –OH group tends to cause a lower electron density at the m-position in the case of resorcinol and favours the formation of [HO–C_6H_4–$O^{\delta-}$] adsorbed species (Scheme 1). On the other hand, in the case of catechol and hydroquinone, the higher electron densities at the o- and p-positions will destabilize
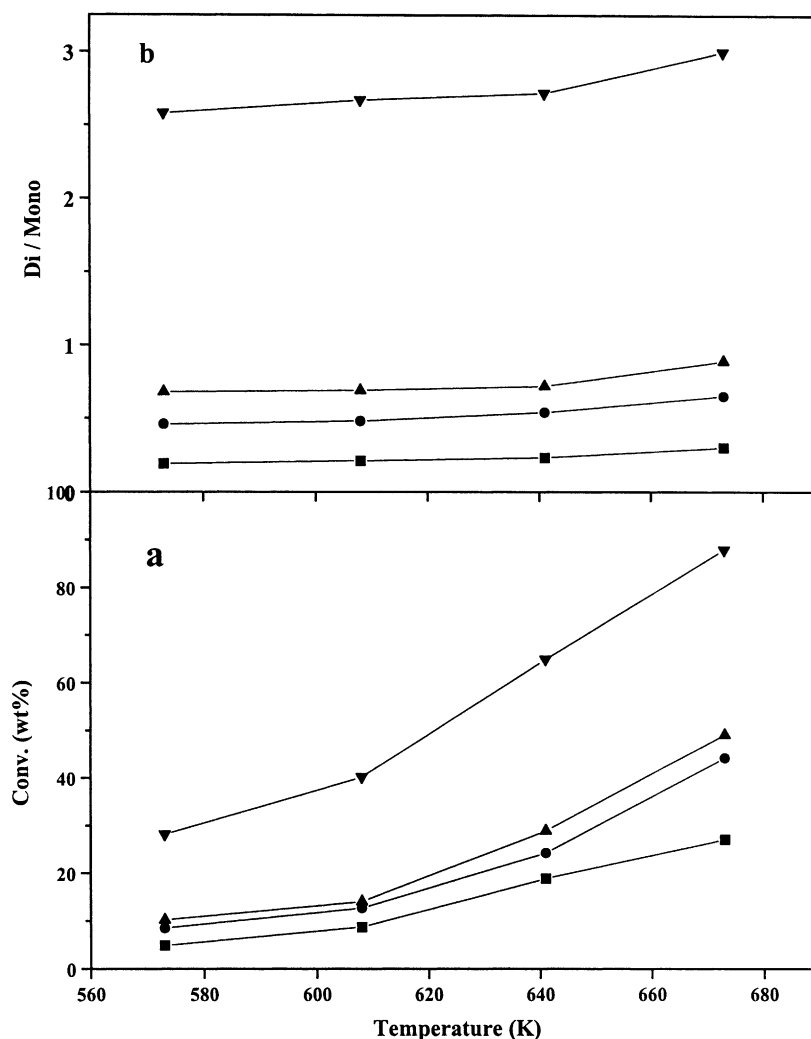

Fig. 5. Effect of temperature on conversion of hydroquinone and dimethoxy benzene/monomethoxy phenol ratios: (a) conversion; (b) dimethoxy/monomethoxy product (di/mono) ratios (conditions: TOS = 1 h, contact time = 0.376 h, substrate/methanol (mol) = 1/5, N_2 = 18 ml/min). (■) Li(1.5)SiO_2; (●) Na(1.5)SiO_2; (▲) K(1.5)SiO_2; (▼) Cs(1.5)SiO_2.

the above transition state. Besides, steric effects may also be responsible for the lower reactivity of catechol.

Selectivity for O-methylation (sum of mono and dimethoxy products) also increases in the same order as above. A decrease in the formation of monomethoxy products is noticed with increasing basicity in the case of all the three substrates due to the increase in dimethoxy products formation (Table 2). This is due to faster conversion of the monomethoxy phenols compared to the dihydroxy compounds with increasing catalyst basicity. Studies on the methylation of p-methoxy phenol (pMP) reveal this to be true. The conversion of pMP to the dimethoxy product is 1.8 and 1.4 times faster than the conversion of hydroquinone (HQ) over Li(1.5)SiO$_2$ and Na(1.5)SiO$_2$ catalysts, respectively (at 673 K, Table 2). However, over Cs(1.5)SiO$_2$, pMP is only marginally more reactive (1.1 times) than HQ at 673 K.

Examining the dimethoxy/monomethoxy product (di/mono) ratios of the three substrates over different Cs–SiO$_2$ catalysts (Fig. 1b), one finds that the increase with basicity is small for catechol and HQ, while it is large for resorcinol. When di/mono ratios
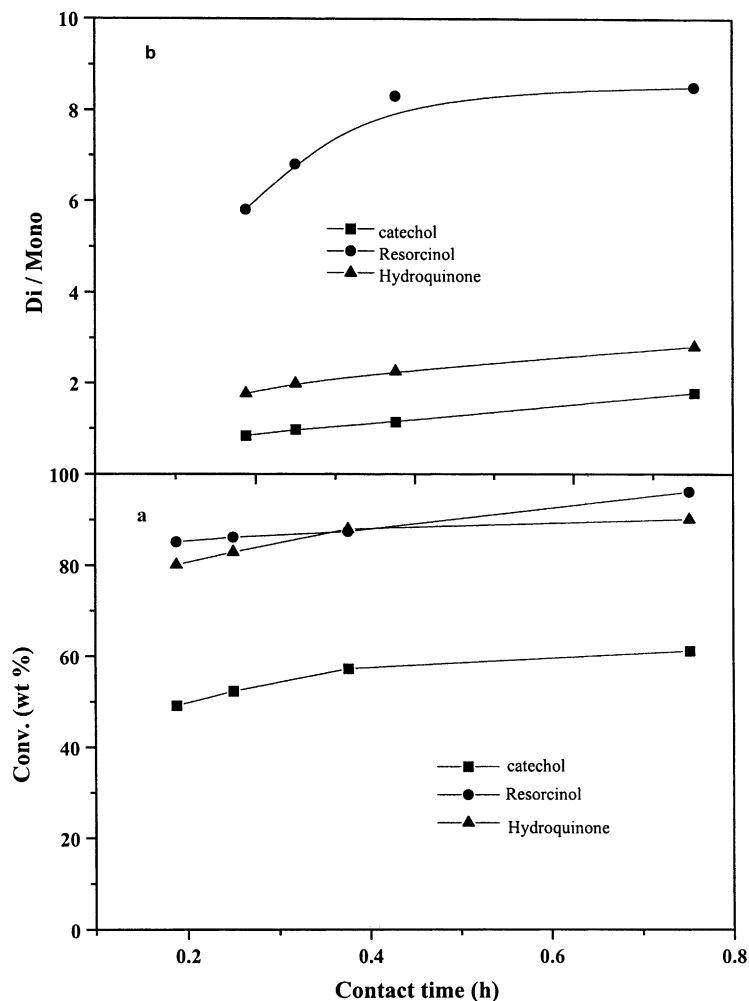

Fig. 6. Effect of contact time on conversion of dihydroxy benzenes and dimethoxy benzene/monomethoxy phenol ratios over Cs(1.5)SiO$_2$: (a) conversion; (b) dimethoxy/monomethoxy product (di/mono) ratios (conditions: TOS = 1 h, temperature = 673 K, N$_2$ = 18 ml/min, substrate/methanol (mol) = 1/5).

are plotted vs. conversion (not shown), it is noticed that in the case of HQ and catechol, the increase is slow (both falling on a nearly common curve), while it is very rapid for resorcinol. This suggests a much greater reactivity of *m*-methoxy phenol than the *o*- and *p*-methoxy isomers. The greater reactivity of the monomethoxy phenols than the dihydroxy compounds is probably due to differences in the mesomeric effects of the –OCH$_3$ and –OH groups.

3.4. Effect of temperature

The reactivities of the three substrates at different temperatures (573–673 K) are presented in Fig. 4a.

Conversion increases with temperature for all the substrates. Both mono and di *O*-methylated products increase with temperature. For catechol, the increase is less compared to resorcinol and hydroquinone. The influence of temperature in the methylation of HQ over different alkali-loaded catalysts is presented in Fig. 5a and b. Though activity (as expected) increases from Li to Cs, the activity of the Cs catalyst is much larger than those of the other catalysts. Small amounts of the dehydroxylated products, phenol and anisole were also formed over Li(1.5)SiO$_2$, Na(1.5)SiO$_2$ and K(1.5)SiO$_2$ at higher temperatures. The di/mono ratios observed at different temperatures for the three substrates and the different catalysts are presented in
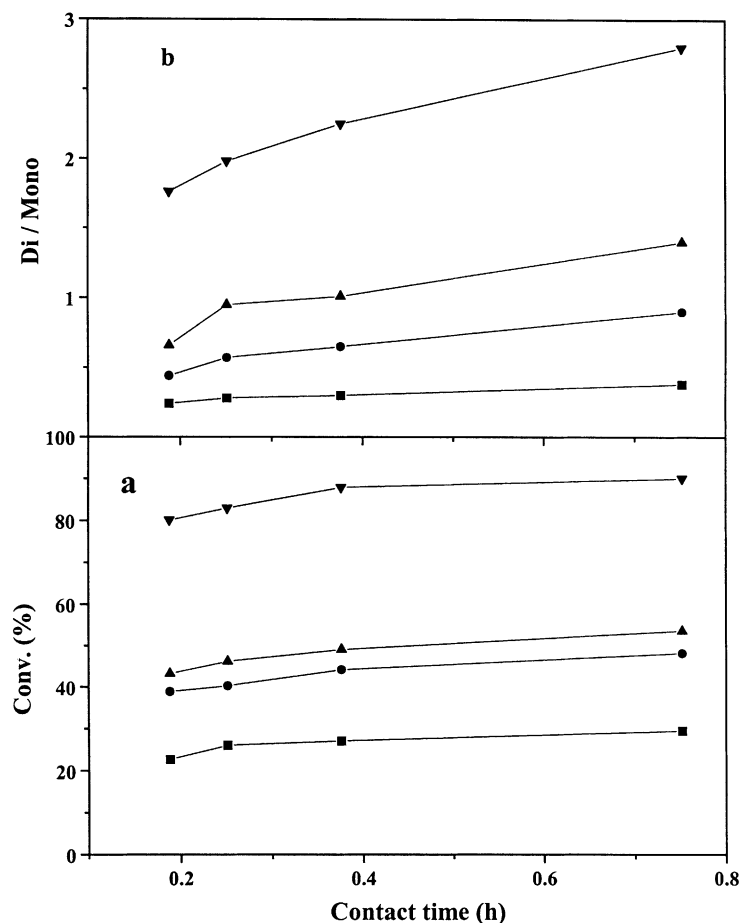

Fig. 7. Effect of contact time on conversion of hydroquinone and dimethoxy benzene/monomethoxy phenol ratios: (a) conversion; (b) dimethoxy/monomethoxy product (di/mono) ratios (conditions: TOS = 1 h, temperature = 673 K, substrate/methanol (mol) = 1/5, N$_2$ = 18 ml/min). (■) Li(1.5)SiO$_2$; (●) Na(1.5)SiO$_2$; (▲) K(1.5)SiO$_2$; (▼) Cs(1.5)SiO$_2$.

Figs. 4b and 5b. It is noticed that the di/mono ratios also increase with temperature suggesting more rapid conversions of the monomethyl product at higher temperatures. The di/mono ratios are much larger for resorcinol than the other two substrates (Fig. 4b). Similarly, the ratios are much larger over the Cs catalyst than over the other three catalysts (Fig. 5b).

3.5. Effect of contact time

Conversion increases with increase in contact time (studied from 0.188 to 0.752 h at 673 K) for all the substrates (Fig. 6a). Though the reactivities of resorcinol and HQ are similar, the reactivity of catechol is much lower. Conversions of all the three compounds increase with increase in contact time. Examining the influence of contact time on di/mono ratio (Fig. 6b), we observe that the ratio is larger and increases more rapidly with contact time for resorcinol than for the other two. The influence of contact time on conversion of HQ and di/mono ratios over the different alkali-loaded catalysts is presented in Fig. 7a and b, respectively. As already reported, the Cs catalyst is much more active than the other three catalysts at all the contact times investigated. Similarly, the di/mono ratio also increases more rapidly over the Cs catalysts than over the others. Though both Figs. 6 and 7 reveal an increase in conversion with contact time, the increase is more rapid at lower contact times (<0.36 h) than at higher contact times. The influence of contact time on the distribution of mono and dialkylated products for the three substrates over Cs(1.5)SiO$_2$ is presented in Fig. 8. At the conditions of the study, the yield of the dialkylated product is more than the monoalkylated product due to high conversions in the case of resorcinol and HQ. A crossover of the curves for the di and mono substituted products is seen for catechol. However, in all the cases, concentration maxima for the intermediate monoalkylated product (expected for consecutive reactions) is not observed. This is mainly due to the second methylation step being faster than the first one ($k_2 > k_1$ in the sequence of reactions shown below) and the maximum being reached at lower contact times (lower conversions) than those used in this study.
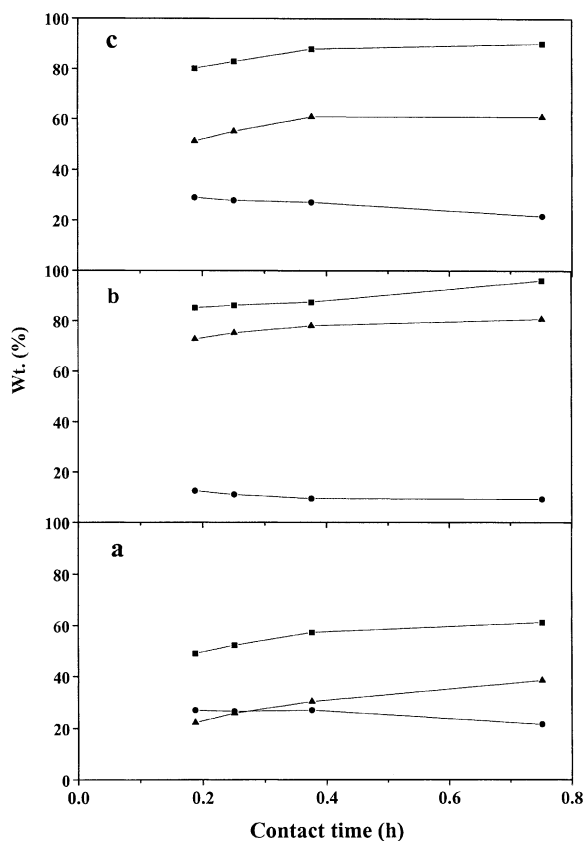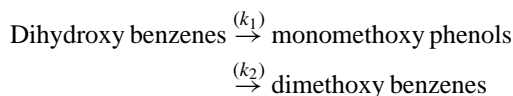
Dihydroxy benzenes $\overset{(k_1)}{\rightarrow}$ monomethoxy phenols

$\overset{(k_2)}{\rightarrow}$ dimethoxy benzenes

Fig. 8. Effect of contact time on conversion and product distribution over Cs(1.5)SiO$_2$: (a) catechol; (b) resorcinol; (c) hydroquinone (conditions: TOS = 1 h, temperature = 673 K, substrate/methanol (mol) = 1/5, N$_2$ = 18 ml/min). (■) Conversion; (●) monomethoxy phenol; (▲) dimethoxy benzene.

4. Conclusions

This study reveals that alkali supported SiO$_2$ samples are good catalysts for the *O*-methylation of catechol, resorcinol and hydroquinone in the vapour phase. The most active and selective catalyst is Cs–SiO$_2$ with about 1.5 mmol of Cs/g of catalyst. Resorcinol is more reactive than the other two dihydroxy benzenes. The trend in reactivities of the dihydroxy benzenes can be explained if a [HO–C$_6$H$_4$–O$^{\delta-}$]-adsorbed intermediate is postulated to be formed on the catalyst surface. The intermediate monomethylated compounds are more reactive than the parent dihydroxy compounds, more so in the case of resorcinol. Catalyst

deactivation is more for catechol than for resorcinol and hydroquinone and decreases with increasing basicity of the catalyst.

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