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Vapour phase selective *O*-alkylation of phenol over alkali loaded silica

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Abstract

Vapour phase selective *O*-alkylation of phenol with methanol, ethanol, *n*-propanol and *n*-butanol has been investigated in the temperature range 573–673 K over alkali loaded (Li, Na, K and Cs) fumed silica. Fumed silica has negligible alkylation activity, but on impregnation with alkali metal oxides (Li, Na, K and Cs) becomes active for *O*-alkylation producing arylalkyl ethers. Activities of the catalysts increase with metal loading and with basicity of the metal ions (Cs > K > Na > Li). Very high conversion (∼90%) and 100% *O*-methylation selectivity was obtained over Cs loaded silica with methanol as the alkylating agent. Conversion decreases with increase in carbon chain of the alkylating agent. Catalyst deactivation rate and the reaction rates at various reaction parameters like contact time, temperature, mole ratio, were also investigated.

Keywords: *O*-Alkylation; Alkali metal loaded silica; Alkylating agent; Basicity; Deactivation rate

1. Introduction

The large *E*-factors (kg waste/kg product) [1] of most processes used at present in the fine chemicals industry makes the development of environmentally clean and economical processes based on solid catalysts are highly relevant. Solid inorganic catalysts have advantages of being easily separable and recyclable besides avoiding corrosion and environmental problems. The oxides of alkali metals are bases. Though liquid acids have replaced by solids such as zeolites in numerous reactions, the application of solid bases in fine chemicals production is not yet common. Many inorganic solid bases like alkali modified zeolites, either through ion exchange or by decomposition of alkali salts in the zeolite cages have recently been found useful in the production of fine chemicals [2–15]. The vapour phase methylation of phenol with methanol using metal oxide, sulphate, phosphate and zeolite catalysts has been extensively studied [16–27]. The products are usually mixtures of anisole (product of *O*-methylation) and cresols and xylenols (products of ring methylation), the selectivity being strongly dependent on the catalyst. Ono and co-workers [28] reported the selective *O*-methylation of phenol with dimethyl carbonate over X-zeolites. Reports on selective *O*-alkylation, however, are limited. Arylalkyl ethers are important industrial chemicals and are extensively used as a starting material for the production of dyes and agrochemical, as antioxidants for oils and grease, as stabilizers for plastics. Arylalkyl ethers could be obtained by the Williamson ether synthesis, which require the corresponding alkyl halide and a stoichiometric amount

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of sodium hydroxide or by using dimethyl sulphate, a corrosive and toxic chemical. The above methods produce waste and are environmentally unsound. The process using solid catalysts and fixed bed reactors offer many advantages such as catalyst reusability, ease of product work up and continuity of operation. We now report the vapour phase *O*-alkylation of phenol with methanol, ethanol, *n*-propanol and *n*-butanol over alkali metal (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). 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 purity CO_2 was passed for 1 h at a flow rate of 25 ml/min, then flushed with He for 90 min (30 ml/min) and the temperature 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 (Zeton Altamira AM1-200) to obtain the temperature programmed desorption curves.

FTIR spectra of adsorbed CO_2 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 mmHg equilibrium pressure for 1 h and the spectrum was recorded. Then part of the CO_2 gas was pumped out to maintain an equilibrium pressure of 0.4 mmHg and the spectrum was recorded again. 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 start of the experiments. The feed (mixture of phenol and alcohols) 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 analyzed in a gas chromatograph (HP 5880A; capillary column HP-5, 50 m × 0.2 mm; FID detector). Product identification was done by GC–IR, GC–MS and NMR.

3. Results and discussion

3.1. Physicochemical properties of the samples

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 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. The intermediate electronegativity (S_{int}) of the samples calculated [29] on the basis of Sanderson’s intermediate electronegativity decreases as expected with increasing basicity of the metal. The S_{int} values for various alkali loaded samples are given in Table 1.

Temperature programmed desorption 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

Table 1
Physicochemical properties of the catalysts

Catalyst[a]	Metal loading as oxide (wt.%)	S_{int}	Surface area[b] (m^2/g)	Surface area[c] (m^2/g)	Relative basicity	
					TPD[d] (mmol CO_2/g)	FTIR[e]
SiO_2	–	–	166	–	–	–
Li(1.5)SiO_2	2.25	3.98	104	164	0.062	102
Na(1.5)SiO_2	4.65	3.96	99	161	0.071	140
K(1.5)SiO_2	7.05	3.92	91	156	0.078	180
Cs(0.075)SiO_2	1.43	4.22	149	164	0.031	24
Cs(0.375)SiO_2	5.28	4.18	121	156	0.049	96
Cs(0.75)SiO_2	10.5	4.09	102	149	0.061	168
Cs(1.5)SiO_2	21.1	3.91	70	133	0.079	229
Cs(2.25)SiO_2	31.7	3.69	56	116	0.082	281

[a] The number in brackets denotes the mmoles 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 FTIR (1200–1750 cm^{-1} band; after adsorption of CO_2 at 5 mm of equilibrium pressure of Hg) normalised to constant sample weight.

CO_2 desorbed increases with basicity of the metal (Li to Cs) and with Cs content (Table 1). A similar trend is also noticed in the FTIR data on adsorbed CO_2 (Table 1). Again, the amount of CO_2 adsorbed on the catalysts as estimated by FTIR also increases with basicity of the alkali metal (Li to Cs) and Cs content.

3.2. *Activities of the catalysts*

Catalytic activities of different alkali loaded silica samples are presented in Table 2. Pure SiO_2 has little *O*-alkylation activity, but alkali loaded silica is catalytically active. For a given molar loading (1.5 mmol/g) of the alkali ions, *O*-alkylation activity of the catalysts (in case of all alkylations) is in the order Cs(1.5)SiO_2 > K(1.5)SiO_2 > Na(1.5)SiO_2 > Li(1.5)SiO_2. Table 2 also reveals that the activity of the catalysts also increases with increasing Cs content (basicity). Assuming the absence of boundary, inter- and intraparticle diffusion effects, phenol conversion (X_p) can be fitted in the first-order rate equation

$$\ln\left[\frac{1}{1-X_p}\right] = k\left(\frac{W}{F}\right) \quad (1)$$

where W is the weight of the catalyst, and F the feed rate in mol/s.

Table 2
Activities of the catalysts in *O*-alkylation of phenol

Catalyst[a]	Methylation		Ethylation		*n*-Propylation		*n*-Butylation	
	Conversion	Selectivity	Conversion	Selectivity	Conversion	Selectivity	Conversion	Selectivity
SiO_2	3.4	6.9	2.2	3.3	1.7	2.2	–	–
Li(1.5)SiO_2	1.2	100	–	–	–	–	–	–
Na(1.5)SiO_2	12.3	100	9.9	100	2.6	100	2.0	100
K(1.5)SiO_2	30.1	100	13.3	100	8.7	100	4.5	100
Cs(0.075)SiO_2	33.2	100	20.2	100	15.1	100	14.7	100
Cs(0.375)SiO_2	59.8	100	41.6	100	38.3	100	30.5	100
Cs(0.75)SiO_2	69.7	100	51.2	100	42.8	100	37.7	100
Cs(1.5)SiO_2	91.4	100	61.5	100	44.9	100	39.2	100
Cs(2.25)SiO_2	92.8	100	63.0	100	49.1	100	41.4	100

[a] The number in brackets denotes the mmol of alkali metal loaded per gram of SiO_2 (conditions: temperature = 673 K, contact time = 0.38 h, time on stream = 1 h, alcohol/phenol = 5 mol, N_2 = 18 ml/min).

Runs were performed at four feed rates in the range 1.5–6.5 × 10^{-5} mol/s and at reaction temperatures in the range 573–673 K. The $\ln[1/(1-X_p)]$ versus W/F plots according to Eq. (1) are almost linear and passing through the origin, indicating a good fit of the data to Eq. (1). Calculations were used only to compare the rates of the reactions over the different catalysts and were not aimed at finding the detailed rate equations.

The slope of the straight lines yielded the values of the initial reaction rate constant, k, in mol/(g s). The values obtained at various temperatures for different catalysts, after 1 h are presented in Table 3.

Table 3
Rate constant values in phenol methylation

Catalyst	Rate constant, k ($\times 10^{-3}$ mol/(g s))			
	573 K	608 K	640 K	673 K
Li(1.5)SiO_2	–	–	0.01	0.01
Na(1.5)SiO_2	0.01	0.08	0.07	0.09
K(1.5)SiO_2	0.05	0.11	0.19	0.26
Cs(0.075)SiO_2	0.01	0.05	0.08	0.19
Cs(0.375)SiO_2	0.02	0.17	0.31	0.65
Cs(0.75)SiO_2	0.13	0.27	0.45	0.86
Cs(1.5)SiO_2	0.22	0.44	0.75	1.77
Cs(2.25)SiO_2	0.28	0.49	0.79	1.86

The number in brackets denotes the mmol of alkali metal loaded per gram of SiO_2 (conditions: contact time = 0.38 h, time on stream = 1 h, alcohol/phenol = 5 mol, N_2 = 18 ml/min).

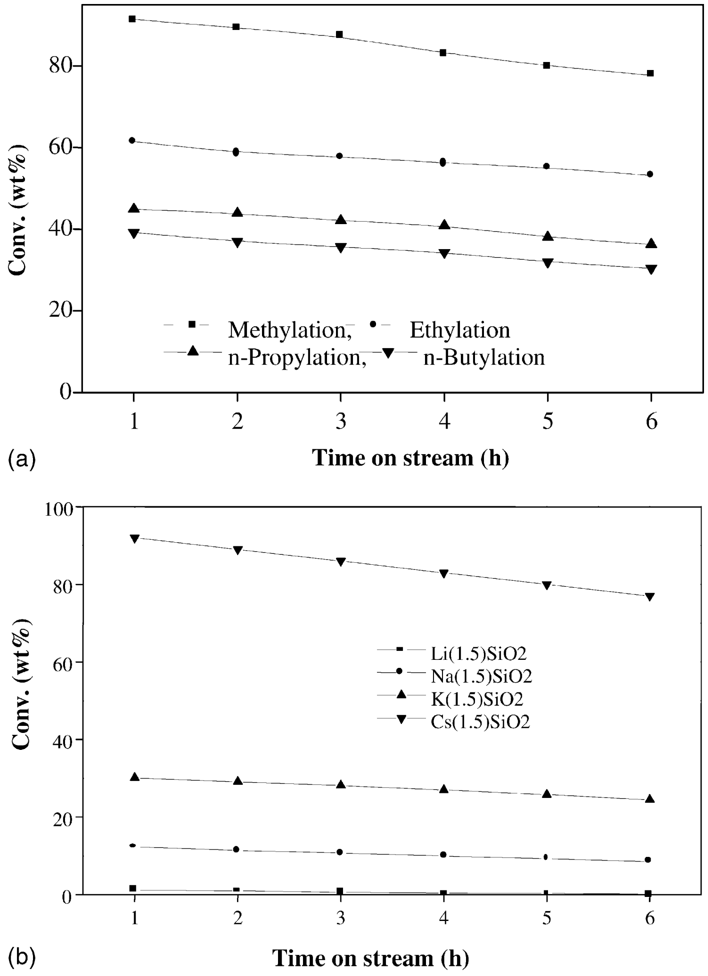

Fig. 1. Influence of duration of run on conversion: (a) over Cs(1.5)SiO_2; (b) methylation over different catalysts (conditions: temperature = 673 K, contact time = 0.38 h, alcohol/phenol = 5 mol, N_2 = 18 ml/min).

3.3. Reactivities of the alcohols

The relative activities of the alcohols are in the order *n*-butanol < *n*-propanol < ethanol < methanol. The reason for this reactivity trend may be due to differences in their adsorption characteristics. The acidity order of the alcohols is *n*-butanol < *n*-propanol < ethanol < methanol. It is possible that the higher acidity of methanol causes it to adsorb strongly on the basic surface enhancing its activity. The mechanism

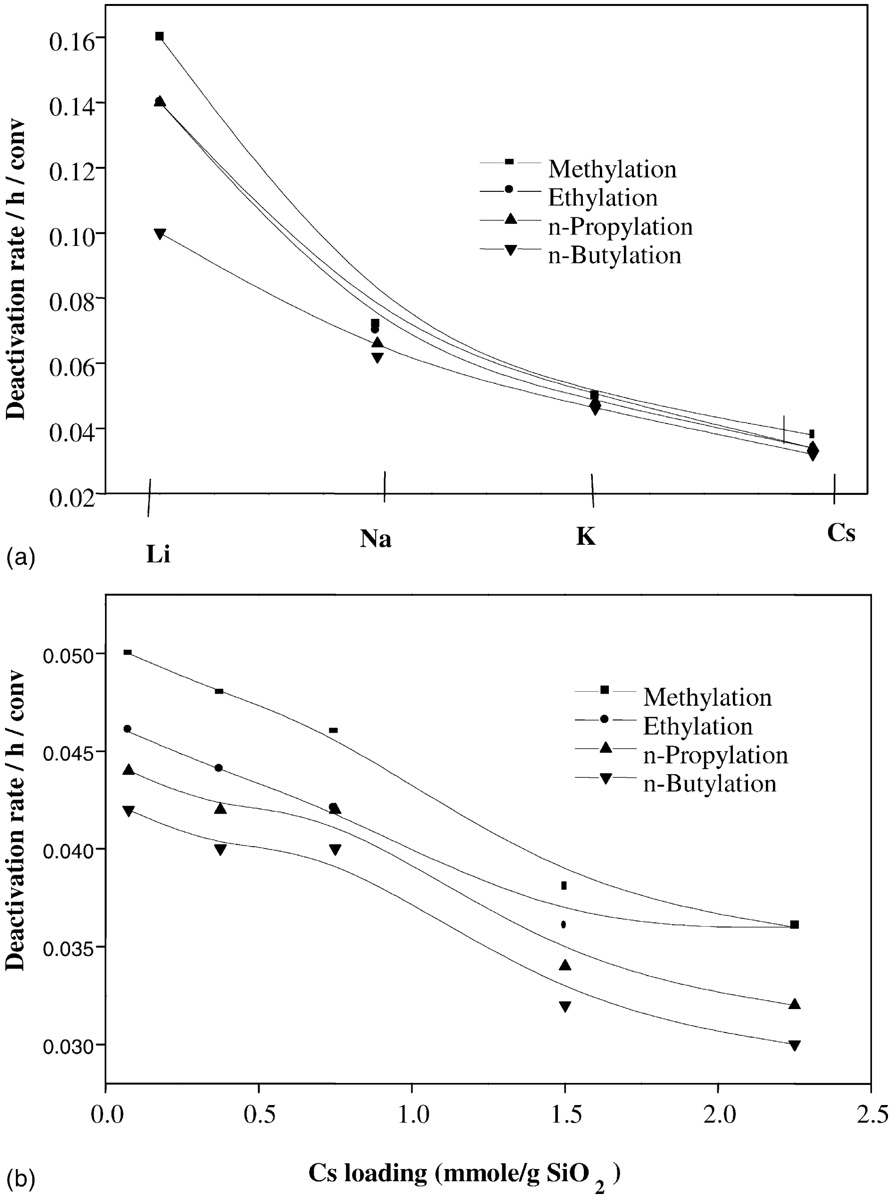

Fig. 2. Influence of substrate on catalyst deactivation rate: (a) over different alkali loaded catalysts; (b) over various Cs loaded catalysts (deactivation rate, $h = 2(C_1 - C_6)/5(C_1 + C_6)$, where C_1 and C_6 are conversions at 1 and 6 h, respectively) (conditions: temperature = 673 K, contact time = 0.38 h, alcohol/phenol = 5 mol, N_2 = 18 ml/min).

of the reaction probably involves the formation of a phenolate species aided by the basic O^{2-} sites on the surface of alkali loaded silica.

3.4. Influence of time on stream

The influence of duration of run over Cs(1.5)SiO_2 on the conversion of phenol with alcohols is presented in Fig. 1a. The influence of time on stream on the conversion of phenol with methanol over different alkali (Li, Na, K and Cs) loaded catalysts is presented in Fig. 1b. It is observed that the catalyst deactivates with time on stream in the case of all the alcohols. Deactivation arises from coke deposition on the catalysts and it was confirmed by ESR spectroscopy, X-ray photoelectronspectroscopy and the amount of coke

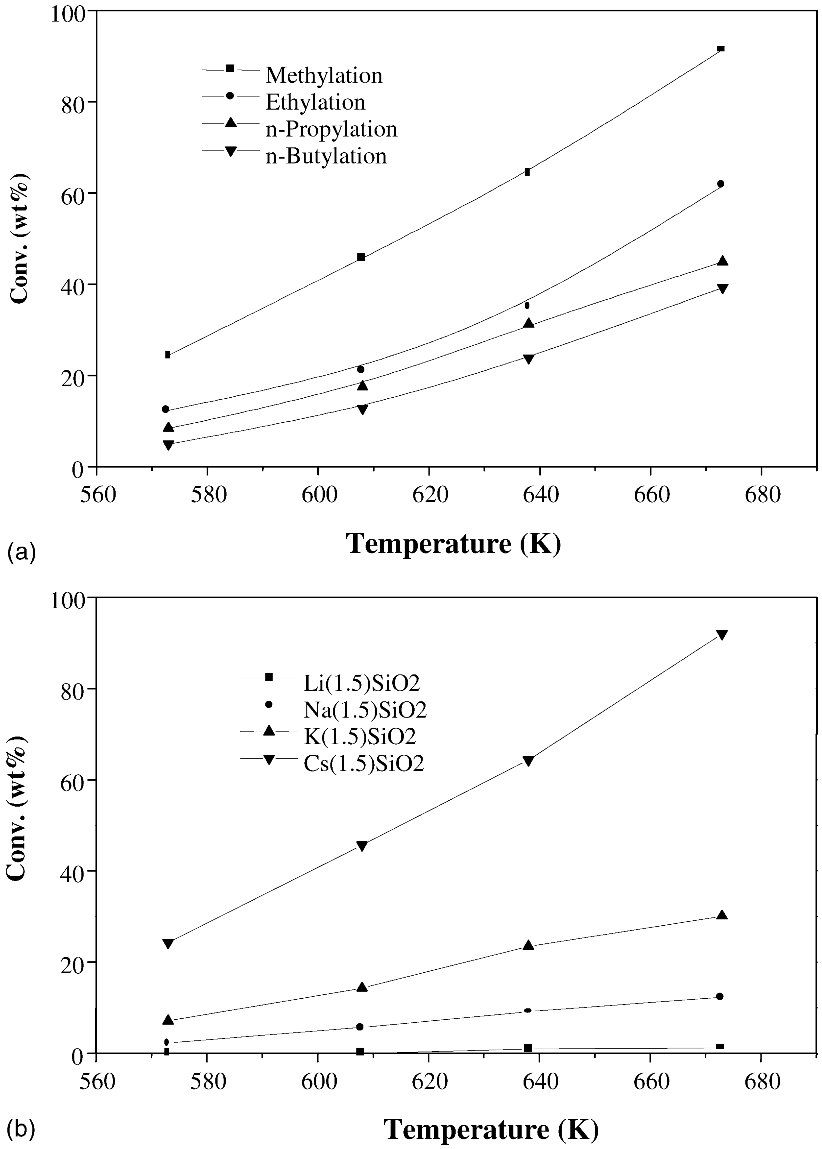

Fig. 3. Effect of temperature on conversion: (a) Over Cs(1.5)SiO_2; (b) methylation over different catalysts (conditions: time on stream = 1 h, contact time = 0.38 h, alcohol/phenol = 5 mol, N_2 = 18 ml/min).

was estimated by chemical analysis [30]. At higher temperatures, the deactivation of the catalysts is more due to rapid coke formation and catalysts deactivate to different extents depending on the alkali metal and alkylating agents. A parameter called the average deactivation rate is used to compare the different catalysts and alcohols. The average deactivation rate is defined as the average activity loss per hour during the experimental period divided by the average conversion during this period. The parameter defines the activity loss per unit conversion in unit time and is therefore useful for comparing different catalysts with different intrinsic activities. The deactivation rate for different alkali (Li, Na, K and Cs) loaded catalysts are plotted in Fig. 2a. The deactivation rate for different Cs loaded catalysts are plotted in Fig. 2b. Methanol deactivates the catalyst much more than the other alkylating agents and deactivation decreases with increasing basicity of

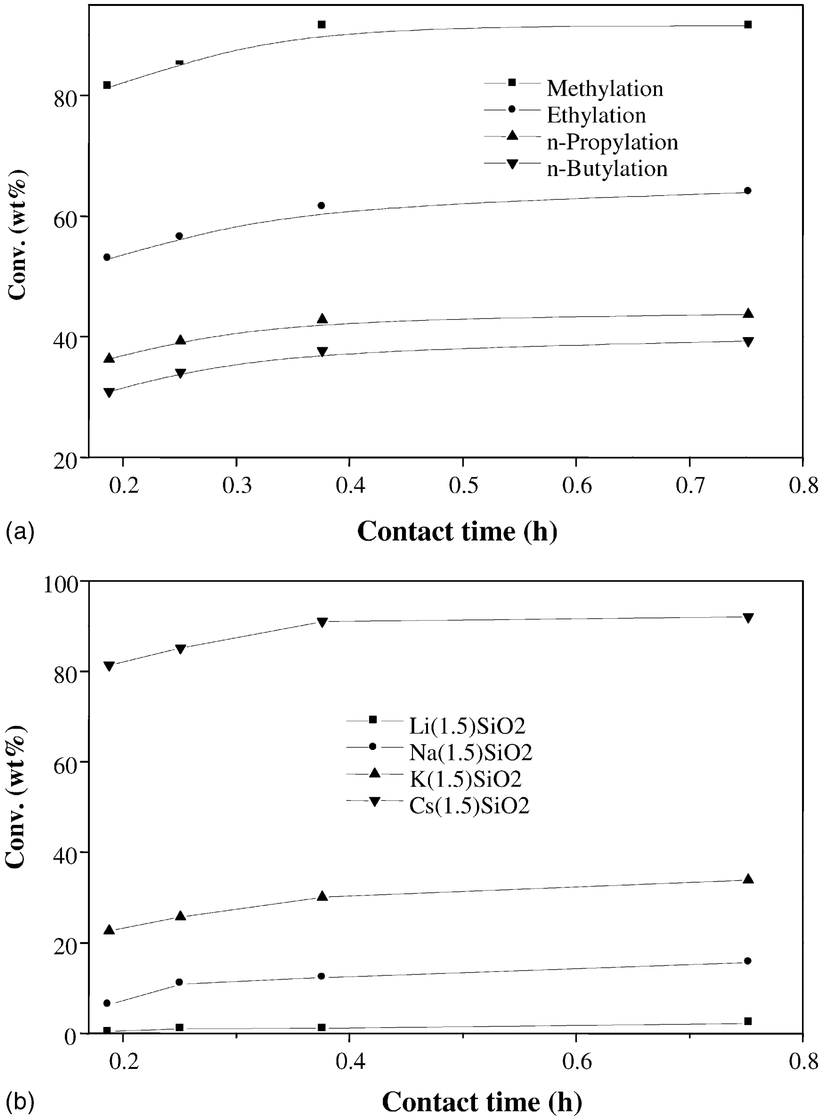

Fig. 4. Effect of contact time on conversion: (a) over Cs(1.5)SiO_2; (b) methylation over different catalysts (conditions: time on stream = 1 h, temperature = 673 K, alcohol/phenol = 5 mol, N_2 = 18 ml/min).

the catalysts. The greater deactivation of the catalyst by methanol may be due to its stronger adsorption compared to other alcohols. The decrease in deactivation rate with basicity may be related to the mode of adsorption of the phenol. Over the more acidic catalysts, phenol molecule may adsorb by interaction of its π-electron cloud, while on a more basic catalyst, it may adsorb by the –OH group. One would expect greater deactivation when the molecule is adsorbed flat on the surface as ring condensation reactions that lead to coke are more likely in this adsorption mode.

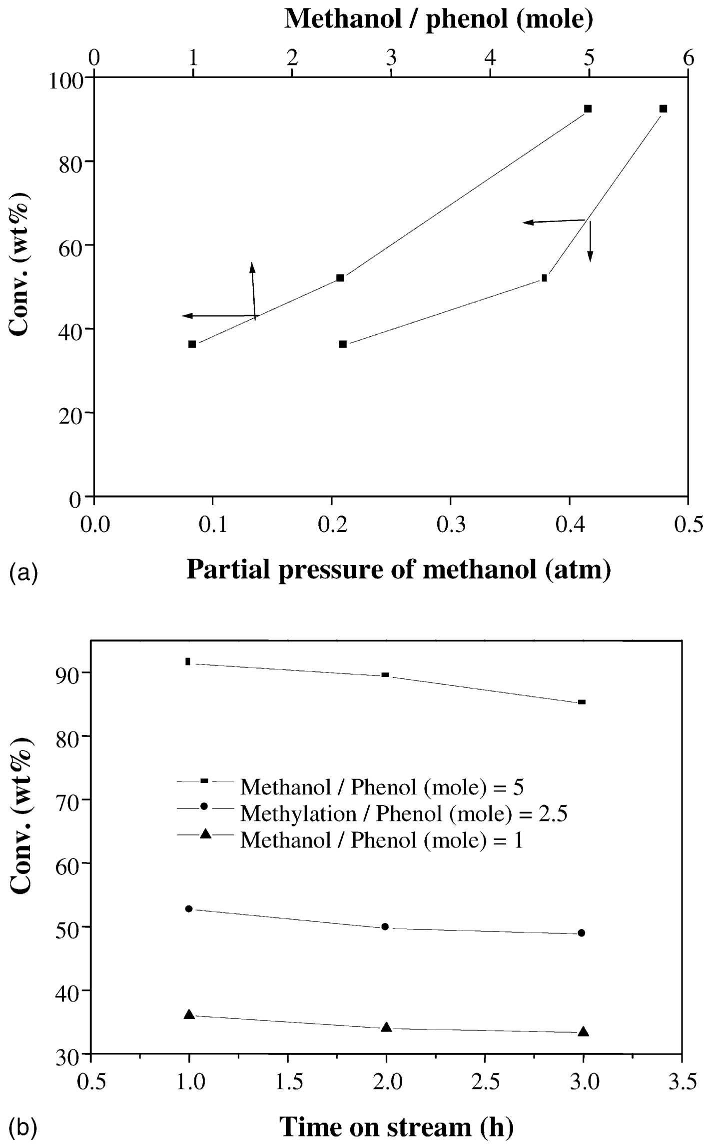

Fig. 5. (a) Effect of feed mole ratios on conversion over Cs(1.5)SiO_2 (temperature = 673 K, time on stream = 1 h, contact time = 0.38 h, N_2 = 18 ml/min). (b) Effect of time on stream on conversion for different mole ratios over Cs(1.5)SiO_2 (temperature = 673 K, contact time = 0.38 h, N_2 = 18 ml/min).

3.5. *Effect of temperature*

Conversions obtained with different alkylating agents at different temperatures (573–673 K) over Cs(1.5)SiO_2 are presented in Fig. 3a. Conversion is found to increase with temperature in all the cases. The influence of temperature on methylation over different alkali loaded silica samples is presented in Fig. 3b. Though the activity increases from Li to Cs, the activity of the Cs catalyst is much larger than the other catalysts (Fig. 3b). Studying the influence of time on stream over Cs(1.5)SiO_2 at different temperatures it is revealed the catalyst deactivates faster at higher temperatures. The activity loss per hour calculated from the above data are 1, 0.9, 0.8 and 0.8, respectively, at 613, 598, 583 and 573 K.

3.6. *Effect of contact time*

Conversion increases with increase in contact time (studied from 0.19 to 0.75 h at 673 K) for all the alcohols (Fig. 4a) over Cs(1.5)SiO_2. At all contact times, conversion is higher for methylation followed by ethylation, *n*-propylation and *n*-butylation. For all the alkylations, conversion increases rapidly with contact time initially ($<$0.36 h) and then levels off. The influence of contact time on methylation over different catalysts is presented in Fig. 4b. For methylation, the conversion increases with contact time for all the catalysts but the Cs loaded catalyst is more reactive than other alkali loaded catalysts (Fig. 4b). Studying the influence of time on stream on activity of Cs(1.5)SiO_2 at different contact times it is revealed that the deactivation rates appear to be nearly similar at the different contact times.

3.7. *Influence of mole ratio of reactants in methylation of phenol*

The conversion of phenol decreases as the methanol to phenol mole ratio decreases. The conversion decreases to almost one third as the methanol to phenol mole ratio decreases from 5 to 1. The influence of MeOH partial pressure in the feed (including N_2) on conversion is presented in Fig. 5a. The corresponding MeOH/phenol (mole) ratios are also presented in the figure. At higher methanol to phenol mole ratio, the catalyst deactivation is more compared to deactivation at lower mole ratios (Fig. 5b). The deactivation per hour is 3.6, 2.3 and 1.9%, respectively, at mole ratios of 5, 2.5 and 1.

4. Conclusions

The study reveals that alkali supported SiO_2 samples are good catalysts for the alkylation of phenol with methanol, ethanol, *n*-propanol and *n*-butanol in the vapour phase. The most active catalyst is Cs-SiO_2. Methanol is more active compare to other three alcohols in the *O*-alkylation of phenol. At lower temperature deactivation is less and decreases with increasing basicity of the catalyst. Deactivation is less when the methanol to phenol mole ratio is less and so for other three alcohols. Deactivation rate (calculated on the basis of unit conversion) decreases with the increase in basicity of the catalyst.

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