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Vapour phase O-methylation of 2-naphthol over the solid bases alkali-loaded silica and Cs-loaded MCM-41

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O-alkylation of 2-naphthol has been investigated in the vapour phase over alkali-loaded fumed silica and Cs-MCM-41. Both SiO_2 and MCM-41 had low C-alkylation activities and no O-alkylation activity. The introduction of alkali ions considerably increases 2-naphthol conversion with 2-methoxynaphthalene being the major product. The activity of the catalysts increases with alkali loading and the basicity of the metal ($Cs > K > Na > Li$). Very high conversion ($\sim$99%) of 2-naphthol and selectivity ($>$95%) for 2-methoxynaphthalene are obtained over Cs-loaded fumed silica and MCM-41. A small amount of 1-methyl-2-hydroxynaphthalene is also formed over the Li-, Na- and K-loaded silica.

Keywords: O-alkylation, 2-naphthol, alkali-metal-loaded silica, MCM-41

1. Introduction

The production of fine chemicals through environmentally clean and economical processes is an area of growing importance. Many of the processes used at present in the fine chemicals industries are either non-catalytic or based on homogeneous catalysts, which are difficult to recover and reuse. Solid inorganic catalysts, on the other hand, are easily separable and recyclable. Besides, these catalysts are often benign and environmentally friendly. Heterogeneous catalysis over solid bases is another growing area of research [1]. Many solid bases have recently been found useful in the production of fine chemicals [2–4]. Alkali and alkaline earth metal oxides, rare earth oxides, supported alkali metals (ions) and clay minerals act as heterogeneous basic catalysts.

2-methoxynaphthalene is an important intermediate in the production of naproxen, a widely used non-steroidal anti-inflammatory agent. Conventionally, it is produced by the methylation of 2-naphthol with dimethylsulphate and alkali or with a methyl halide and sodium hydroxide in tetrahydrofuran. The above methylating agents are corrosive and toxic. Moreover, these conventional processes are atom inefficient and generate waste. For example, if one were to alkylate 2-naphthol stoichiometrically with dimethylsulphate and neutralize the H_2SO_4 with sodium carbonate, the atom efficiency (AE) [5] would be just 0.62. On the other hand, the direct methylation with methanol will have an AE of 0.88; the only unwanted product is water. Besides methanol is far cheaper and easier to handle than methyl sulphate.

Conventionally, methylation reactions are carried out in the liquid phase in batch reactors with attendant economic penalties due to their non-continuous nature. Processes using solid catalysts and fixed-bed reactors offer many advantages such as catalyst reusability, ease of product work up and continuity of the operation. Fixed-bed vapour phase methylation of phenol using methanol and dimethylcarbonate has been reported [6–16] over basic zeolites. To the best of our knowledge public reports on the vapour phase methylation of 2-naphthol are not available. We now report the vapour phase methylation of 2-naphthol with high selectivities and conversion over alkali-loaded silica and Cs-loaded MCM-41.

2. Experimental

Fumed silica (Cab-O-Sil, Fluka, surface area 166 m^2/g) was used as a support for the alkali metal oxides. The different alkali-loaded catalysts were prepared by an impregnation procedure using minimum amount of aqueous metal hydroxides/acetate (Li, Na, K and Cs) solutions (incipient wetness method). The catalysts were dried at 373 K (6 h) and calcined at 773 K (6 h) in air. MCM-41 samples were prepared hydrothermally using a gel with the following molar composition in terms of oxides [17]:

$$SiO_2 : 0.27(CTMA)_2O : 0.13(TMA)_2O : 60H_2O.$$

Sodium silicate (28.48% SiO_2, 9.03% Na_2O, 62.5% H_2O), cetyltrimethylammonium bromide (99%, Aldrich), tetramethylammonium hydroxide (TMAOH, 25% aqueous solution, Aldrich) and fumed silica (Cab-O-Sil, 99%, Fluka) were used in the synthesis.

Samples of Cs-loaded MCM-41 were prepared by stirring 3 g of MCM-41 in a solution containing the appropriate amount of cesium acetate in 15 g methanol for 3 h at 60 °C.

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The solvent was removed quickly under vacuum in a rotary evaporator and the materials were subsequently calcined at 500 °C for 5 h in air.

The catalytic experiments were carried out in a vertical downflow glass reactor (15 mm i.d.). All the reactions were carried out using 2 g charge of the catalyst. The catalysts were used in the form of granules (10–22 mesh) prepared by pelleting 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 center 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 2-naphthol and methanol) was passed using a syringe pump (Braun, Germany) along with N_2 gas (45 ml/min). A high mole ratio of 1 : 10 (naphthol : methanol) was used in the studies due to the poor solubility of naphthol in methanol. The product was cooled in a water-cooled (ice-cold) condenser, collected in a receiver and analyzed in a gas chromatograph (HP 5880A; capillary column HP, 50 m × 0.2 mm; FID detector). Product identification was done by GC-IR and GC-MS.

3. Results and discussion

The catalytic activities of silica samples loaded with different alkali metals and MCM-41 with different amounts of Cs in the O-methylation of 2-naphthol at 673 K are presented in table 1 along with the surface areas of the samples. The surface areas of the samples decrease with increasing metal loading and basicity of the loaded metal. The decrease is attributed to the "dissolution" of the surface by the alkali during impregnation. SiO_2 and MCM-41 have low activities, both of them producing mainly the C-alkylated product. No 2-methoxynaphthalene was detected over these catalysts. The introduction of alkali ions increases dramatically the activity and O-alkylation selectivity of the catalysts. Conversion and selectivity (for O-methylation) increase with metal loading and basicity of the alkali metal (Cs > K > Na > Li, table 1). As Cs/SiO_2 was found to be the most active catalyst, more experiments were carried out at different Cs loadings (figure 1). A general trend of increasing activity with increasing Cs loading is noticed. The influences of duration of run (time on stream, TOS) on conversion and product distribution in the case of $Cs(1.5)SiO_2$ are presented in figure 2. It is seen that the catalyst deactivates with time, a conversion loss of ~20% occurring in about 3 h (~100% at 1 h and 87.3%

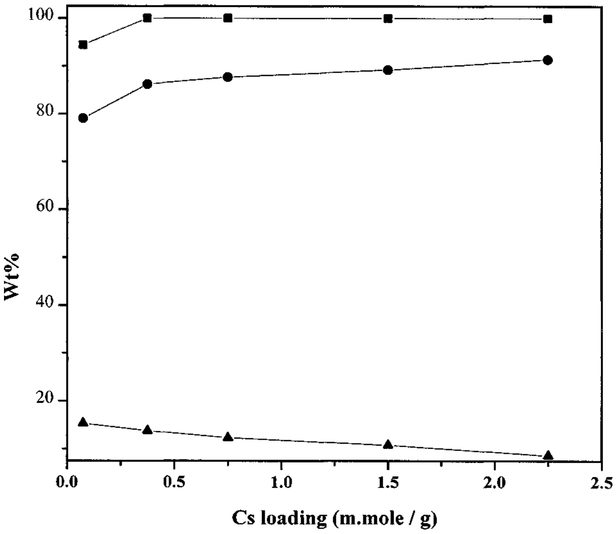


Figure 1. Influence of Cs loading on conversion and product yields: (■) conversion, (●) 2-methoxynaphthalene and (▲) 1-methyl-2-methoxynaphthalene. Conditions: time on stream 1 h, temperature 673 K, 2-naphthol/MeOH (mol) = 0.1, WHSV 2.28 h^{-1}, N_2 45 ml/min.

Table 1
Activities of alkali-loaded catalysts in the alkylation of 2-naphthol with methanol.[a]

Catalyst[b]	Surf. area[c] (m^2/g)	Conv. (wt%)	Yield of products (wt%)			
			2-methoxy-naphthalene	1-methyl-2-methoxynaphthalene	1-methyl-2-hydroxynaphthalene	Others
SiO_2	166	9.2	–	–	6.7	2.5
$Li(1.5)SiO_2$	104	45.2	23.9	8.5	12.8	–
$Li(2.25)SiO_2$	98	50.1	27.3	9.2	13.6	–
$Na(1.5)SiO_2$	99	53.0	38.6	9.2	5.2	–
$Na(2.25)SiO_2$	89	61.0	43.3	10.2	7.5	–
$K(1.5)SiO_2$	91	57.1	41.7	9.9	5.5	–
$K(2.25)SiO_2$	82	68.0	51.0	11.2	5.8	–
$Cs(1.5)SiO_2$	70	100	89.1	10.9	–	–
MCM-41	1055	4.7	–	–	3.8	0.9
Cs(0.075)MCM-41	837	88.3	70.9	13	4.4	–
Cs(0.15)MCM-41	771	95.7	87.8	8.9	–	–
Cs(0.225)MCM-41	675	98.9	95.7	3.2	–	–

[a] Conditions: temperature 673 K, time on stream 1 h, 2-naphthol/MeOH (mol) = 1 : 10, WHSV 2.28 h^{-1}, N_2 45 ml/min.

[b] The number in parentheses denotes the mmol of alkali metal loaded on 1 g of SiO_2 and MCM-41.

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

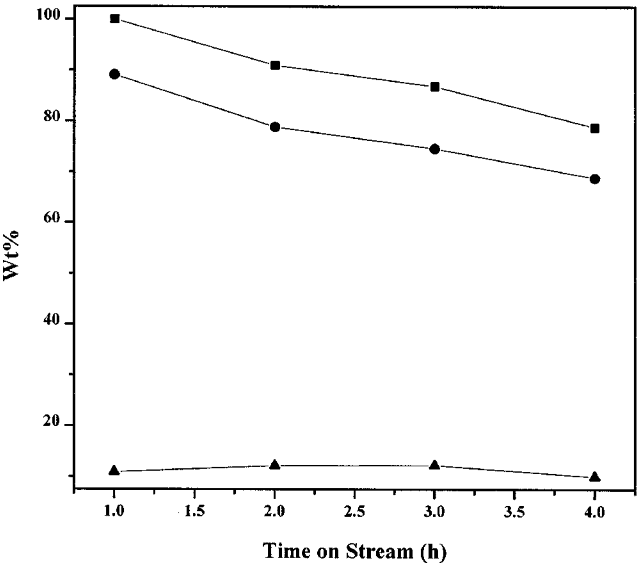


Figure 2. Influence of time on stream on conversion and product yields on Cs(1.5)SiO_2: (■) conversion, (●) 2-methoxynaphthalene and (▲) 1-methyl-2-methoxynaphthalene. Conditions: temperature 673 K, 2-naphthol/MeOH (mol) = 0.1, WHSV 2.28 h^{-1}, N_2 45 ml/min.

at 4 h). The yield of 2-methoxynaphthalene also decreases from 89.1 to 68.8% during the above period (figure 2). The yield of the C-alkylated product is nearly constant, being about 10.9% at 1 h and 10.0% at 4 h, suggesting a preferential deactivation of the O-alkylation activity. The data reported in the other figures and table 1 were collected at a TOS of 1 h.

The influences of temperature and space velocity (WHSV) on the reaction are presented in figures 3 and 4. Fumed silica and MCM-41 possess negligible activity under the reaction conditions (table 1). The different products formed over the catalysts are shown in scheme 1. The yields of the C-methylated products, 1-methyl-2-hydroxynaphthalene (II) and 1-methyl-2-methoxynaphthalene (III) decrease with increasing basicity of the alkali ion (Li > Na > K > Cs, table 1). Though the yield of II decreases rapidly and is not at all present in the product from Cs/SiO_2 (table 1), the yield of III decreases only marginally and is formed even over the Cs catalyst. Usually C-alkylation is believed to be catalyzed by acidic sites. The formation of this compound (III) even over the most basic catalyst (Cs/SiO_2) is a result of the 1-position being highly activated by the substituent in the 2-position. 1-methyl-2-methoxynaphthalene (III) can be formed from 1-methyl-2-hydroxynaphthalene (II) or from 2-methoxynaphthalene (I). The absence of II in the products from Cs catalysts suggests that III is probably formed mainly from I over Cs catalysts. This is supported by WHSV studies over Cs(1.5)SiO_2 (figure 4) which reveal an increase in III with increasing contact time, due to further reaction of compound I. Concomitantly, the yield of I decreases with contact time. In the case of the other alkali-loaded catalysts, 1-methyl-2-hydroxynaphthalene (II) is present in substantial amounts due to C-alkylation of 2-naphthol over these catalysts.

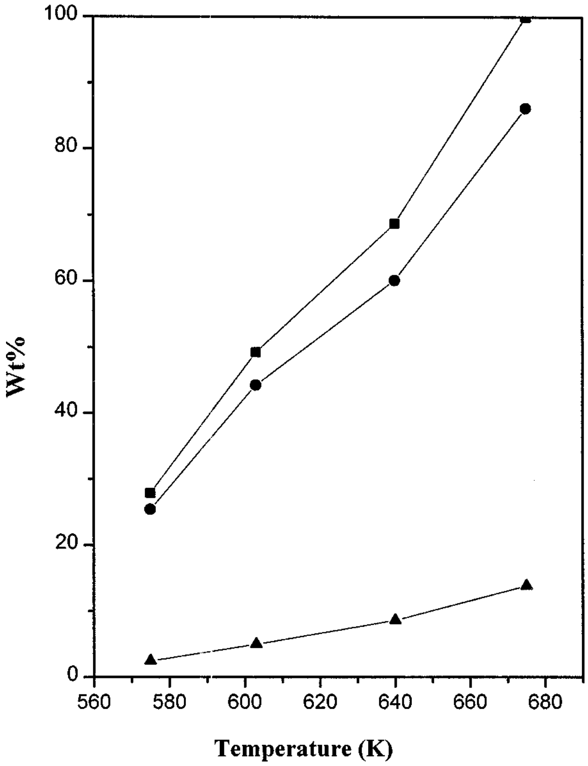


Figure 3. Influence of temperature on conversion and product yields on Cs(1.5)SiO_2: (■) conversion, (●) 2-methoxynaphthalene and (▲) 1-methyl-2-methoxynaphthalene. Conditions: time on stream 1 h, 2-naphthol/MeOH (mol) = 0.1, WHSV 2.28 h^{-1}, N_2 45 ml/min.

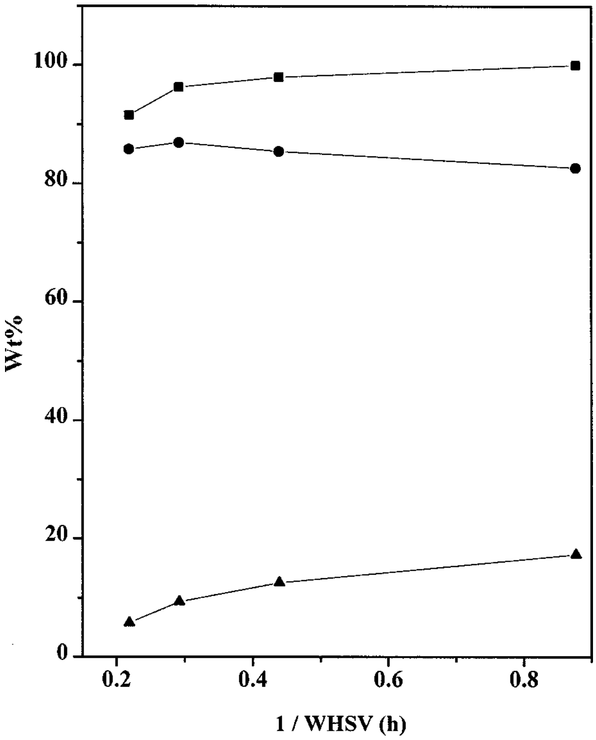
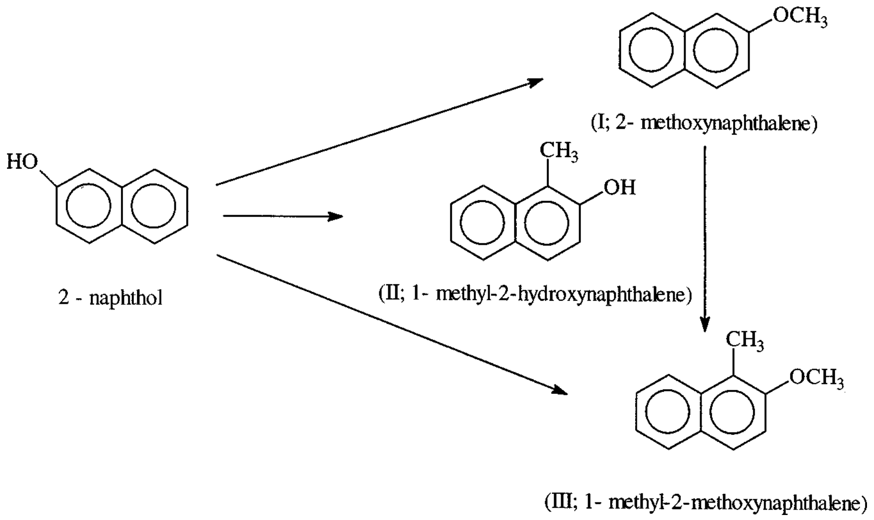


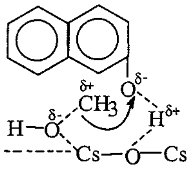
Figure 4. Influence of contact time on conversion and product yields on Cs(1.5)SiO_2: (■) conversion, (●) 2-methoxynaphthalene and (▲) 1-methyl-2-methoxynaphthalene. Conditions: time on stream 1 h, temperature 673 K, 2-naphthol/MeOH (mol) = 0.1, N_2 45 ml/min.



Scheme 1. Products of methylation of 2-hydroxynaphthalene (2-naphthol).

The influence of temperature on activity and product yields is presented in figure 3. Along with increasing conversion, C-alkylation activity also increases, as seen from the yields of compound III (1-methyl-2-methoxynaphthalene). Again as already noted, an increase in contact time favors C-alkylation (figure 4).

The mechanism of the reaction probably involves the formation of a transient 2-naphtholate species on the basic O^{2-} site on the surface of alkali-metal-loaded silica and Cs-loaded MCM-41 and its reaction with $(CH_3)^{\delta+}(OH)^{\delta-}$ species adsorbed on the adjacent alkali ions, as shown below. When the activation of the phenolic groups is relatively small (as in the case of the less basic catalysts), C-alkylation of the ring can also occur producing 1-methyl-2-hydroxynaphthalene,



4. Conclusion

The studies reveal that Cs supported SiO_2 and MCM-41 are good catalysts for the O-alkylation of 2-naphthol in the vapour phase. Nearly 95% yield of 2-methoxynaphthalene is obtained. The small amount of 1-methyl-2-methoxynaphthalene formed over Cs catalysts is a result of the further alkylation of 2-methoxynaphthalene.

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