Al-MCM-41 catalysed alkylation of phenol with methanol

Krishna G. Bhattacharyya [a,*], Anup K. Talukdar [a],
Parashmani Das [a], S. Sivasanker [b]

[a] *Department of Chemistry, Gauhati University, Guwahati 781014, Assam, India*
[b] *National Chemical Laboratory, Pune 411008, Maharashtra, India*

Abstract

Mesoporous Al-MCM-41 molecular sieve materials with three different SiO_2/Al_2O_3 ratios were used as catalysts for phenol methylation with methanol as the alkylating agent. Reaction conditions such as temperature, feed flow rate, the reactant mole ratio and the catalyst SiO_2/Al_2O_3 ratio have significant influence on the distribution of products. The formation of the predominant product *o*-cresol was enhanced by lower temperature, less amount of alkylating agent in the feed and lower acidity of the catalyst with an optimum WHSV value of $1.78\,h^{-1}$. Higher acidity favoured the formation of C-alkylated products, while O-alkylation required lower acid strength of the catalyst. Formation of double alkylated products was associated with higher temperature, large contact time, excess of methanol in the feed and higher acid strength of the catalyst.
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Keywords: Al-MCM-41; Phenol methylation; *o*-Cresol; *m*-Cresol; *p*-Cresol; Anisole

1. Introduction

The use of zeolites as solid acid catalysts in various processes of refining and in production of petrochemicals and fine chemicals has grown over the last few decades because of their remarkable shape selectivity, durability and reusability [1,2]. However, the small size of their cages and pore apertures has become a drawback in the treatment of heavy feeds or in the diffusion of large reactant and product molecules. Extensive efforts to synthesise mesoporous materials with regular, well-defined channel systems were rewarded when the Mobil Research and Development Corporation (USA) announced the synthesis of a family of mesoporous molecular sieves, M41S, in 1992. One of the members of this family, MCM-41, has attracted considerable interest due to its periodic framework of regular mesopores, large surface area and good thermal stability [3–5]. The acidity of MCM-41 was low, comparable to that of zeolites due to the disordered wall structure [5–8]. Incorporation of Al-atoms into the MCM-41 structure has been known to impart acidity with Bronsted acid sites corresponding to framework Al-atoms and both framework and non-framework Al-atoms contributing to Lewis acid sites [9]. Al-MCM-41 has already been proposed as an alkylation catalyst [10] in replacement of the environmentally hazardous Friedel-Craft catalysts $AlCl_3$, HF, H_2SO_4, etc. [11]. The combination of large pores and mild acidity in Al-MCM-41 has been exploited to carry out Friedel-Craft alkylation and acylation successfully [12–20]. The activity of MCM-41 in the transformation of small molecules is generally similar to that of amorphous silica-alumina as expected from

* Corresponding author. Tel.: +91-361-571529;
fax: +91-361-570133.
E-mail address: krishna111@sancharnet.in (K.G. Bhattacharyya).

their comparable acidities. However, MCM-41 gives much better results for the transformation of bulky molecules, e.g. cracking and hydrocracking of gas oil [1].

Medinavaltierra et al. [21] developed MCM-41/γ-Al$_2$O$_3$ catalysts that contained mainly Lewis acid sites and reported successful para-selective alkylation of toluene with isopropanol. The heteropolyacid (HPA)-supported MCM-41 was found to be more active than the bulk HPA and H$_2$SO$_4$ in liquid phase alkylation of 4-*tert*-butylphenol with isobutene and styrene, which require strong acid sites [19,22–24]. In the alkylation of benzene with tetradecene, heteropolyacid (i.e. H$_3$PW$_{12}$O$_{40}$)-loaded MCM-41 afforded higher benzene conversion and mono-alkylate selectivity than silica-alumina and H-MCM-41 [25,26]. Fe-containing MCM-41 materials were found to be highly active and 100% selective for benzylation of benzene with benzyl chloride [11]. Shape selective alkylation of 2,4-di-*tert*-butylphenol with cinnamyl alcohol and tertiary butylation of anthracene, naphthalene and phenanthrene has also been reported over MCM-41 [12,14,19]. In the transformation of *m*-xylene over MCM-41, the unidirectional mesopore system of the materials had a significant effect on the selectivity of products, but such shape selectivity was not observed in toluene alkylation with methanol [1].

The phenol–methanol reaction produces specialty organic chemicals such as cresols, xylenols and anisole, which have wide-ranging uses in solvents, resins, germicides, antifoulants, antioxidants and other industrial products. In the present work, the reaction was studied over Al-MCM-41 under different sets of conditions.

2. Experimental

2.1. Synthesis of Al-MCM-41

Al-MCM-41 with three different SiO$_2$/Al$_2$O$_3$ ratios was synthesised following the modified synthesis procedure of Chen et al. [8]. A typical synthesis procedure was as follows: 15 g of hexadecyltrimethylammonium chloride (C$_{16}$TMACl, 29 wt.% solution, Fluka) was added to 15 g of NH$_4$OH (29 wt.% solution, Qualigens, India) to bypass the exchange procedure for preparing the hexadecyltrimethylammonium

hydroxide solution. 0.3617 g of sodium aluminate was dissolved in the above solution of hexadecyltrimethylammonium hydroxide. The resulting solution was combined with 4.6 g of tetramethylammonium hydroxide pentahydrate (TMAOH·5H$_2$O, Fluka), 30 g of tetramethylammonium silicate solution (assay > 99.99% in water, Fluka) and 7.5 g of fumed SiO$_2$ (Sigma) under stirring. The composition of the final gel mixture in mole ratio was: 1.00 Al$_2$O$_3$:76.02 SiO$_2$:2.39 (C$_{16}$TMA)$_2$O:5.76 (TMA)$_2$O:1230.75 H$_2$O. The pH of the gel was 11.6. The reaction mixture was transferred into a teflon-lined autoclave and was statically heated at 343, 363, 383 K and finally at 423 K for 80 h. The resulting solid products were recovered by centrifugation, washed with deionised water and dried in air at room temperature. For the removal of the organic species occluded in the pores of MCM-41, the synthesised samples were calcined in air by raising the temperature at 2–3° min^{-1} to 813 K and then keeping at this temperature for 8 h. The Na-MCM-41 was refluxed with 1M NH$_4$NO$_3$ solution at 353–363 K repeatedly to obtain NH$_4$-MCM-41, which was further calcined to obtain H-MCM-41. Al-MCM-41 samples with different SiO$_2$/Al$_2$O$_3$ ratios were prepared by modifying the molar composition of the gel during synthesis as: Al$_2$O$_3$:uSiO$_2$:1.25 Na$_2$O:x(C$_{16}$TMA)$_2$O:y(TMA)$_2$O:z(NH$_4$)$_2$O:2xHCl:w H$_2$O, where $25.58 \leq u \leq 204.62$, $1.02 \leq x \leq 36.83$, $3.07 \leq y \leq 30.69$, $0 \leq z \leq 36.83$ and $326.63 \leq w \leq 5402.05$, respectively. The synthesis was confirmed by XRD measurements.

2.2. Reaction study

The reactions were carried out in a fixed bed down-flow glass reactor (length 40 cm, i.d. 15 mm). The catalyst (10–22 mesh) was pre-activated by heating at 743 K for 4 h. The feed was prepared by dissolving the required amount of phenol in the required amount of methanol and was fed from the top with a syringe pump (SAGE 352, USA) to the reactor kept at the desired temperature. The flow rate of dry nitrogen through the reactor was maintained at 10 ml min^{-1}.

The products of the reactions were collected at intervals of 1, 1.5 and 2 h by circulating chilled water and were analysed with GC, GC-MASS and GC-IR. The products were quantified using a GC (HP-5880A, HP-5 column, 50 m × 0.32 mm × 1.05 μm).

3. Results and discussion

The selectivity for the *o*-isomer in comparison to the total selectivity of the *p*- and the *m*-isomers was more than 70% in all the reactions. The selectivity for the double alkylated products (DAP) (2,6-xylenol and 2,4-xylenol) was comparatively low. The major side product in all the reactions was anisole, which was the result of facile O-alkylation. The C_1–C_5 hydrocarbons that might have resulted from methanol transformation [1,27] are not taken into account here. The total selectivity of the C-alkylated products compared to that of the O-alkylated products was high. The selectivities for both 2,6-xylenol and 2,4-xylenol were found to be identical. The so-called "tunnel shape selectivity" [1] proposed in the case of MCM-41, was not observed in the present reaction.

3.1. Effect of temperature

The effect of reaction temperature on the selectivities of the principal products is shown in Fig. 1. The general trend for the alkylation reaction is that the conversion increases with increase in temperature and attains a steady state at high temperatures [28–30]. In this reaction also, the overall conversion of phenol increased from 11.7% at 573 K to 44.2% at 698 K when a steady state was nearly attained. The selectivity of *o*-cresol decreased from 43.7 to 27.6% in the same temperature range, while the corresponding decrease in the selectivity of the mixture of *p*- and

Fig. 1. Effect of reaction temperature on total conversion and selectivity of products (SiO_2/Al_2O_3 ratio 30, WHSV $1.78\,h^{-1}$, reaction time 2 h, catalyst load 2 g and phenol–methanol mole ratio of 1:4).

m-cresols was from 17.2 to 7.9%. A similar decreasing trend in the selectivity of anisole from 27.1 to 17.3% was observed. The selectivities of 2,6-xylenol and 2,4-xylenol on the other hand increased from 1.9 to 11.0% and 2.5 to 8.8%, respectively, in the same temperature range. The ratio of the selectivities of total cresols to anisole (TCr/An) in this temperature range showed that the formation of C-alkylated products was much more than that of the O-alkylated products and with an increase in temperature, both types of products decreased resulting in a gradual reduction in the ratio. Although all the three isomers, *o*-, *m*- and *p*-cresol, recorded a decrease with rise in reaction temperature, the ratio of the selectivities of *o*-cresol to that of *p*- and *m*-cresols taken together [oCr/($p+m$)Cr] exhibited an increase from 2.54 (573 K) to 3.49 (698 K) indicating that the formation of *o*-cresol remained the favoured reaction path even at high temperature compared to its isomerisation into the *m*- or the *p*-isomer.

3.2. Effect of WHSV

With an increase in the WHSV of methanol from 0.89 to $3.56\,h^{-1}$, the conversion of phenol declined from 30.9 to 10.7% with the same negative influence in the selectivities of DAPs from 7.0 to 1.7% for 2,6-xylenol and from 6.6 to 1.8% for 2,4-xylenol, respectively. The selectivity of anisole, however, increased from 22.4 to 34.2% in this WHSV range. Interestingly, highest selectivities were found for cresols with WHSV $1.78\,h^{-1}$. Higher values of the ratio of the selectivities of total cresols to anisole (2.15) and the selectivity of *o*-cresol (43.0%) have established that intermediate WHSV ($1.78\,h^{-1}$) was suitable for the production of *o*-cresol. The formation of the double-alkylated products was favoured by low WHSV or a large contact time between the catalyst and the feed whereas formation of *o*-cresol required an optimum contact time, which was neither very small nor very large. The formation of the *p*- and *m*-cresols followed the same trend as *o*-cresol indicating that these products resulted from isomerisation of the *o*-isomer. These trends are illustrated in Fig. 2.

3.3. Effect of mole ratio of the feed

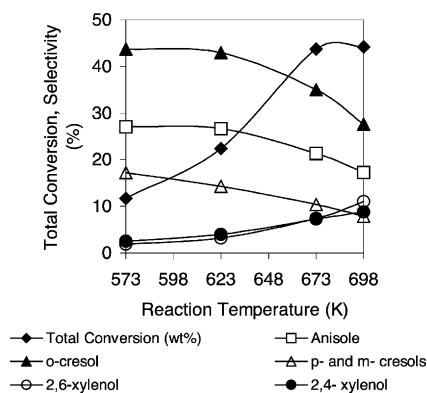The feed consisting of phenol and methanol was used in three different mole ratios of 1:4, 1:10 and
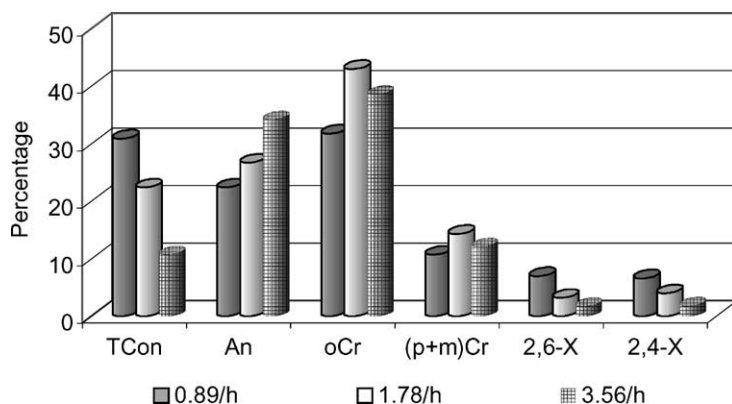
Fig. 2. Influence of feed flow rate (WHSV) on overall conversion and product distribution (reaction temperature 623 K, phenol–methanol mole ratio 1:4, catalyst load 2 g, SiO_2/Al_2O_3 ratio 30, reaction time 2 h).

1:15. An increase in the molar ratio of methanol: phenol resulted in an increase in the conversion of phenol from 22.4 to 37.5%. An increase in the amount of methanol in the feed had negative influence on the selectivities of anisole (decreased from 26.7 to 10.4%), o-cresol (from 43.0 to 26.7%) and the mixture of p- and m-cresol (from 14.3 to 7.5%). The isomerisation of o-cresol decreased with an increase in the amount of methanol (4–15 mol for each mole of phenol) in the reaction mixture resulting in an increase in the ratio of the selectivity of o-cresol to that of p- and m-cresols [oCr/($p + m$)Cr] from 3.0 to 3.6. A steady increase in TCr/An values from 2.15 to 3.30, and in selectivities of 2,6-xylenol (3.2–7.9%) and 2,4-xylenol (4.0–7.3%) indicated that the formation of C-alkylated products including the double-alkylated products was dependent upon the availability of excess methylating agent.

3.4. Effect of SiO_2/Al_2O_3 ratio

Two different samples of Al-MCM-41 with SiO_2/Al_2O_3 ratios of 30 (catalyst A), and 76 (catalyst B) were used in the methylation reaction. The total conversion of phenol improved from 22.4 to 81.2% corresponding to an increase in the ratio of SiO_2/Al_2O_3 in the catalyst. Under identical conditions, the selectivities of anisole, o-cresol and the mixture of p- and m-cresols decreased, while those of the double-alkylated products were much enhanced (Fig. 3). It has been reported [9] that with an increase

in aluminum content of Al-MCM-41, the number of surface acid sites increases but the acid strength decreases. Anisole formation requires sites with lower acid strength compared to those necessary for cresol formation [26] and it is expected that anisole formation would decline with an increase in the SiO_2/Al_2O_3 ratio. In the present work, anisole selectivity actually came down by a factor of 3 (26.7–8.6%) upon increasing the SiO_2/Al_2O_3 ratio from 30 to 76. Thus, strong acidity favoured C-alkylation, while lower acidity led to O-alkylation resulting in a much higher selectivity for o-cresol at a lower SiO_2/Al_2O_3 ratio compared to the combined selectivity of the m- and p-isomers.

3.5. Deactivation of the catalysts

The deactivation of the catalyst Al-MCM-41 with three different SiO_2/Al_2O_3 ratios of 30, 50 and 76 for the phenol alkylation reaction was studied by carrying out the reaction continuously for 11 h (Fig. 4(a) and (b)). The deactivation of acid catalysts may be caused by coke formation, selective adsorption of undesirable agents present in the feed and sintering in which the catalyst framework gets collapsed. The principal cause of deactivation has mostly been the buildup of a layer of pseudographitic carbon referred to as coke or carbonaceous residues [27,31]. The carbonaceous residues block the pore system and cover the reaction sites leading to deactivation. On acid zeolites, methanol gets converted into hydrocarbons following
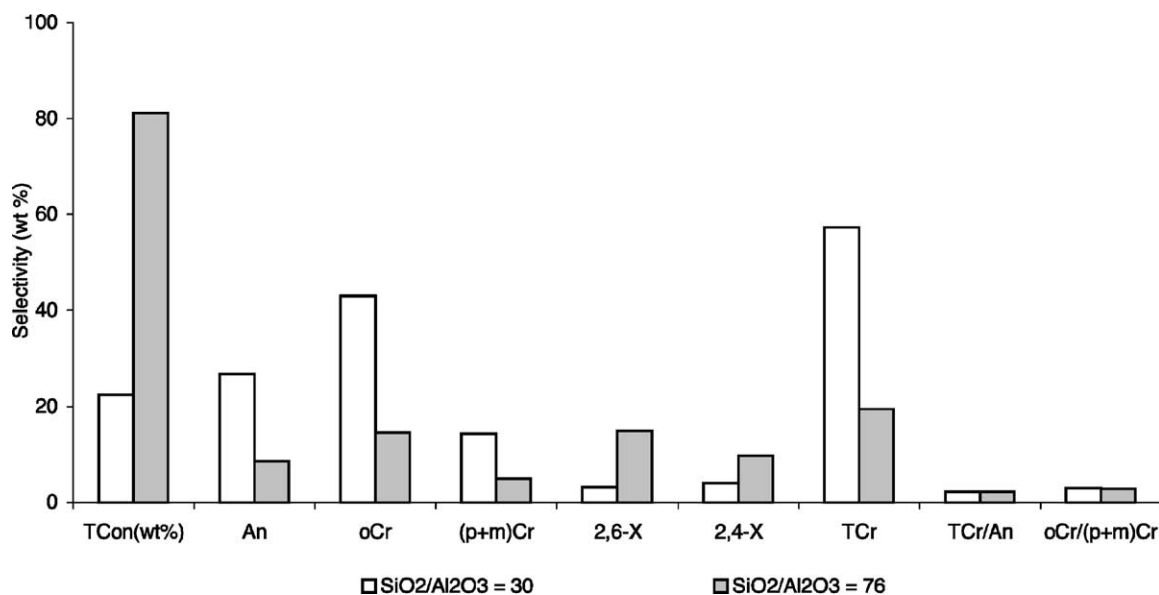
Fig. 3. Total conversion and product selectivities at two SiO_2/Al_2O_3 ratios of 30 and 76 (reaction temperature 623 K, WHSV 1.78 h^{-1}, catalyst load 2 g, phenol:methanol mole ratio 1:4, reaction time 2 h, TCon: total conversion, An: anisole, oCr: o-cresol ($p + m$), Cr: p- and m-cresols, 2,6-X: 2,6-xylenol, 2.4-X: 2,4-xylenol, TCr: total cresols).
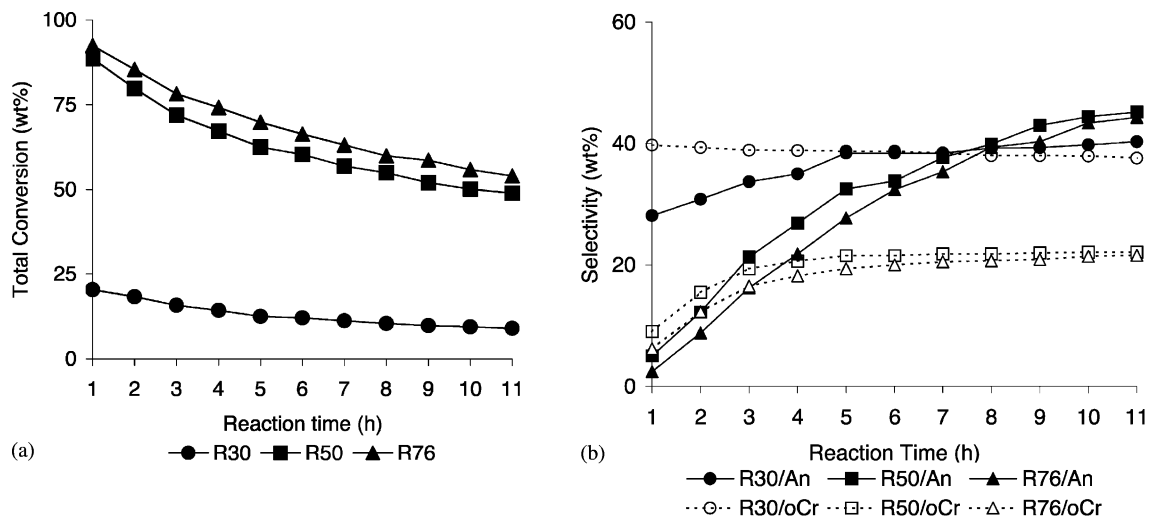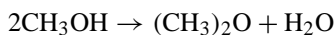

Fig. 4. (a) Deactivation of the catalysts with respect to total conversion (R30, R50 and R76 are, respectively, Al-MCM-41 with SiO_2/Al_2O_3 ratios of 30, 50 and 76. The reaction temperature was 623 K, WHSV 1.78 h^{-1}, phenol:methanol molar ratio 1:4, catalyst load 2 g). (b) Deactivation of the catalysts with respect to anisole and o-cresol selectivity (R30, R50 and R76 are, respectively, MCM-41 with SiO_2/Al_2O_3 ratios of 30, 50 and 76. An: anisole, oCr: o-cresol, reaction temperature 623 K, WHSV 1.78 h^{-1}, phenol:methanol molar ratio 1:4, catalyst load 2 g).

the sequential reactions [27]:

$$2CH_3OH \rightarrow (CH_3)_2O + H_2O$$

$$(CH_3)_2O \rightarrow R–CH = CH_2 \quad (R = H, CH_3, \text{etc.})$$

$$\text{Olefins} \rightarrow \text{isoalkanes} + \text{aromatics}$$

In the phenol alkylation reaction, the catalyst Al-MCM-41 underwent deactivation very rapidly and the conversion of phenol came down by 56, 45 and 42%, respectively, for the catalysts with the SiO_2/Al_2O_3 ratio of 30, 50 and 76 in 11 h of continuous run (Fig. 4(a)). The selectivities of anisole and *o*-cresol were enhanced with time on stream (Fig. 4(b)), while that of the double-alkylated products showed decreasing trends. It has been reported [26,30] that the selectivity of zeolites for coke formation is much more dependent on pore size than on pore volume, and large pore zeolites deactivate rapidly, whereas medium-pore zeolites inhibit coke formation and deactivate slowly in hydrocarbon reactions, the rate of coke formation being 50–1000 times higher on the large pore zeolites than those with small or intermediate pores. The lower tendency for coke formation in narrow-pore acid catalysts (like ZSM-5) was explained by the "shape-selective coke formation" concept, where only monoaromatic hydrocarbons could enter into the pores. The polycyclic aromatics, responsible for coke formation, could build up in large pore acid catalysts. Thus, in the alkylation of phenol with methanol over mesoporous Al-MCM-41, where both monoalkylphenols and polyalkylphenols were generated, intermolecular cyclisation and polycondensation of the polyalkylphenols may lead to fused-ring aromatic coke precursors. The aromatics produced by cracking of methanol may also lead to coke formation and to catalyst deactivation.

The formation of *o*-cresol and the isomerisation of *o*-cresol to *p*- and *m*-cresols showed two distinctive trends with time on stream. For the catalyst with SiO_2/Al_2O_3 ratio of 30, *o*-cresol selectivity was high, decreasing slowly with time from 39.7 to 37.6%; the isomerisation to the *p*- and *m*-isomers also showed a decrease from 14.5 to 10.7% within the 11 h period. The ratio of the selectivity of *o*-cresol to the selectivities of *p*- and *m*-cresols showed an increase (2.74–3.51) for this catalyst with SiO_2/Al_2O_3 ratio of

30. On the other hand, the other two catalysts with SiO_2/Al_2O_3 ratios of 50 and 76 showed an increase in *o*-cresol selectivity from 9.0 to 22.1% and 6.2 to 21.6%, respectively, during the 11-h run. The selectivity for *p*- and *m*-cresols also increased simultaneously, while the ratio of the selectivity of *o*-cresol to that of *p*- and *m*-cresols decreased with time on stream for both the catalysts (4.09–3.11 for SiO_2/Al_2O_3 ratio of 50 and 4.43–3.27 for SiO_2/Al_2O_3 ratio of 76). The ratio of the selectivity of total cresols to that of anisole showed a decreasing trend for all the three catalysts indicating that O-alkylation gradually took over from C-alkylation with time on stream. This is in good agreement with the observation [26] that lower acid strength favoured anisole formation. C-alkylation was the dominant process initially for both catalyst 2 (SiO_2/Al_2O_3 50) and catalyst 3 (SiO_2/Al_2O_3 76), which have higher acid strength compared to catalyst 1 (SiO_2/Al_2O_3 30). This is reflected in the values of the ratio of the selectivities for total cresol and anisole (TCr/An). While this ratio decreased gradually with time for all the three catalysts, the decrease was much more rapid for the catalysts 2 and 3 than for the catalyst 1, which had a lower acid strength. The formation of unexpected or unknown products, which was likely to be more pronounced with catalyst 3 due to its higher acid strength, might have suppressed the formation of cresols. The catalyst 1 had a higher rate of deactivation compared to the other two catalysts. The distribution of products in the deactivation study indicated that the extent of coking was probably not sufficient to narrow down the channel dimensions. The deactivation must have occurred through active site coverage rather than through pore blockage. Tsai and Wang [32] observed a similar deactivation trend during cumene disproportionation over large pore zeolite beta. The declining selectivities of the double-alkylated products with time were likely to be due to lowering of acidity of the catalysts.
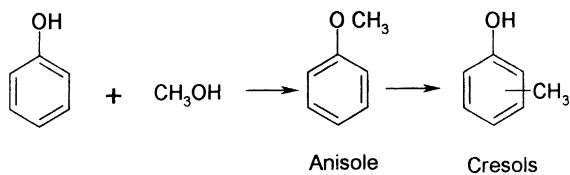
4. Conclusions

Conversion of phenol–methanol mixture selectively to *o*-cresol is an established reaction carried over various oxide catalysts. The present study shows that Al-MCM-41 can similarly bring about high selectivity for *o*-cresol formation. The methylation of phenol
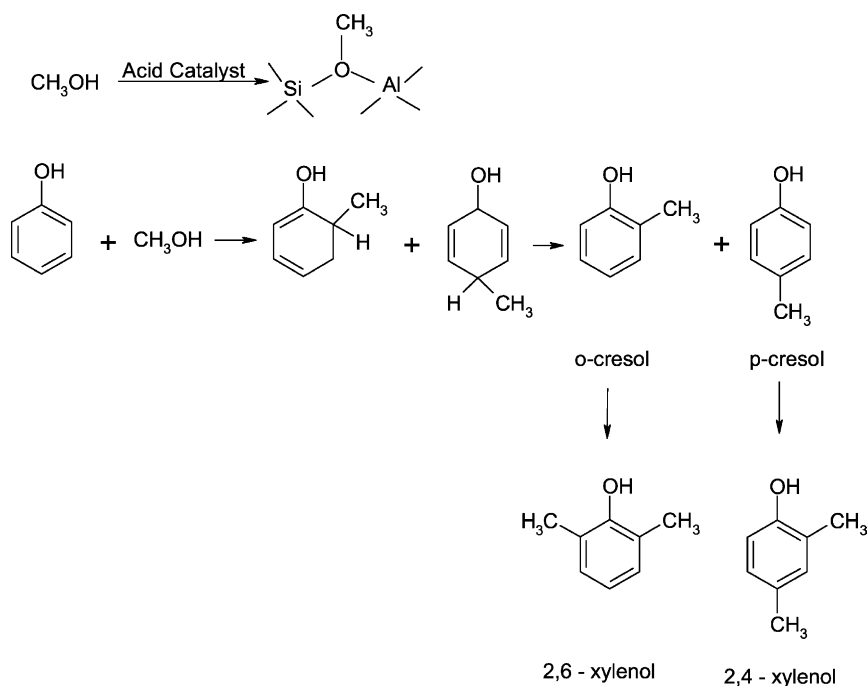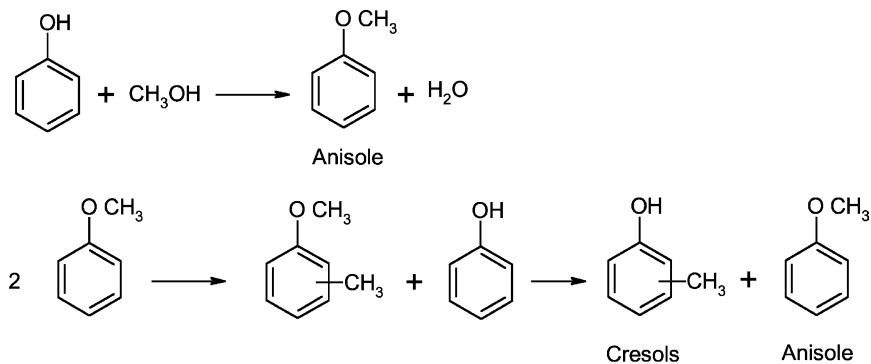
Scheme 1.

is likely to proceed via the following mechanism:

This may follow either of the two schemes (Schemes 1 and 2). The OH and OCH$_3$ groups being *o*-, *p*-directing, there should be very little production of *m*-cresol, while the *o*- and *p*-cresols should have equal yield. In the present case, however, the selectivity for *o*-cresol was much more than the *p*-cresol (and *m*-cresol), indicating that Scheme 1 alone cannot explain the product selectivity pattern. If Scheme 2 is followed, the ratio of total cresols selectivity to anisole selectivity should be equal to 1, which is not the case in the present work. On the other hand, if Scheme 1 is followed in exclusion of Scheme 2, there

Scheme 2.

should be very little anisole in the products. Presence of substantial amounts of anisole in the products and a value of nearly 2.0 for the cresols to anisole ratio, indicate that both the schemes are operating simultaneously with Scheme 1 being the predominant one.

Al-MCM-41 appears to be a promising catalyst for the methylation of phenol. Lower temperature, less amount of methanol in the feed and lower acid strength favoured the formation of *o*-cresol with $1.78\,h^{-1}$ as the most suitable WHSV. Total cresols/anisole ratio showed that the lower acid strength led to O-alkylation, while C-alkylation required higher acidity of the catalyst. The selectivities for the double-alkylated products, which were enhanced by higher temperature, higher availability of alkyl cations in the feed and higher acidity; were comparatively low. Even if the catalyst with lower SiO_2/Al_2O_3 ratio (catalyst 1) deactivated fast compared to the catalysts with higher SiO_2/Al_2O_3 ratio (catalyst 3) and possessed lower conversion, it offered higher activity towards the formation of cresols and anisole with less amount of undesired products. Thus, the present catalyst Al-MCM-41 may be launched as a potential candidate for the production of substituted phenols.

Acknowledgements

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