Ferrospinels based on Co and Ni prepared via a low temperature route as efficient catalysts for the selective synthesis of *o*-cresol and 2,6-xylenol from phenol and methanol

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Abstract

The alkylation of phenol with methanol is conducted over $Ni_{1-x}Co_xFe_2O_4$ ($x = 0$, 0.2, 0.5, 0.8 and 1.0) type systems prepared via low temperature route. Alkylation leads to predominantly *ortho* methylation of phenol, yielding *o*-cresol and 2,6-xylenol as the products. Under optimized conditions, the total *ortho* selectivity was ≥94%, regardless of the catalyst composition. Only traces of anisole is formed and hardly any other xylenol or cresol isomers are detected. Phenol conversion and the individual selectivities for *o*-cresol and 2,6-xylenol depend strongly on the catalyst composition. Selectivity for *o*-cresol was maximum for $NiFe_2O_4$ (i.e., when $x = 0$), whereas upon progressive substitution of Co^{2+} ions for Ni^{2+} ions, the 2,6-xylenol selectivity increases with a concomitant decrease in the *o*-cresol selectivity. Maximum phenol conversion and 2,6-xylenol selectivity (also total *ortho* selectivity) were observed over $CoFe_2O_4$ ($x = 1$). The activity and selectivity were shown to be strongly dependent on the surface acid–base properties of the system. The influences of surface acidity, cation distribution in the spinel lattice and various reaction parameters are discussed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: o-Cresol; 2,6-Xylenol; Selectivity

1. Introduction

The phenol alkylation in the *ortho* position has been of interest in recent years due to the increasing demand of epoxycresol novolak and poly(phenylene ether) resins in electronic industries [1,2]. The stringent specifications and demand of these chemicals necessitate the development of better catalytic systems and the process of the selective production of *o*-cresol and 2,6-xylenol. Several types of solid acid/base catalysts based on zeolites, oxides and hydrotalcite-like materials have been examined for this reaction [3–10]. However, low life time, very high reaction temperature or poor product selectivity make such systems less attractive to chemical industries. Frequently, due to coke formation catalysts deactivate with time. The commercial process for the synthesis of *o*-cresol and 2,6-xylenol is mainly based on magnesium oxide and supported vanadium–iron mixed oxide [2]. Generally, the oxide catalysts show better selectivity than zeolites and it was pointed out that Brønsted acid sites are responsible for coke formation [3].

Mixed metal oxides possessing spinel structure have been investigated in detail due to their interesting structural, electrical, magnetic and catalytic

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properties [11,12]. For a binary oxidic spinel containing divalent M cations and trivalent N cations, two extreme distributions of cations between the octahedral (Oh) and tetrahedral (Td) sites available are possible; the 'normal' $M[N_2]O_4$ and the 'inverse' $N[MN]O_4$ [13,14]; in each case the ions in the Oh sites are in square brackets. Iron-containing spinels are called ferrospinels, and in ternary spinel systems Fe^{3+} ions can be easily shifted between the Oh and Td sites by stoichiometrically varying the concentrations of other cations. Such structural feature of ferrospinel systems, compared to ordinary oxide systems, enables ferrospinels to withstand extremely reducing atmosphere [15,16], and even if reduction of Fe^{3+} to Fe^{2+} occurs, the lattice configuration remains unaltered and upon reoxidation, the original state can be regained.

Our recent works on various types of ferrospinels have revealed that those systems represented by the general formula $M_{1-x}N_xFe_2O_4$ (where M and N are transition elements such as Cr, Co, Ni and Zn and $x = 0$, 0.2, 0.5, 0.8 and 1.0) are versatile alkylating catalysts for aniline [17,18] and pyridine [19,20] for producing N-monomethyl aniline and 3-picoline, respectively. The present work is based on the investigation that the ferrite systems represented by the composition $Ni_{1-x}Co_xFe_2O_4$ ($x = 0$, 0.2, 0.5, 0.8 and 1.0) are highly selective catalysts for methylating phenol in the *ortho* position leading to *o*-cresol and 2,6-xylenol, especially when the x value is between 0.5 and 1.0. The selectivity to a particular product, viz., *o*-cresol and 2,6-xylenol, can be very well achieved by varying the Ni^{2+}/Co^{2+} ratio; only traces of O-alkylated (such as anisole) products were detected and hardly any xylenol isomers were formed throughout the experiment. A systematic catalytic evaluation study as a function of various process parameters is carried out. Cation distribution in the spinel lattice influences their acid–base properties, and hence these factors have been considered as helpful to evaluate the activity and stability of the systems.

2. Experimental

2.1. Catalyst synthesis and characterization

Different compositions of the ferrospinel series, viz., $NiFe_2O_4$ (NF-1), $Ni_{0.8}Co_{0.2}Fe_2O_4$ (NCF-2),

$Ni_{0.5}Co_{0.5}Fe_2O_4$ (NCF-3), $Ni_{0.2}Co_{0.8}Fe_2O_4$ (NCF-4), $CoFe_2O_4$ (CF-5) were prepared by a low temperature controlled coprecipitation method reported by Date and coworkers [21], using aqueous solutions of (1) ferric nitrate 2.6 M, (2) nickel nitrate 3.4 M, (3) cobalt nitrate 3.4 M and (4) sodium hydroxide 5.3 M. The stoichiometric amounts of the premixed nitrate solutions were rapidly added to the sodium hydroxide solution. The temperature of the slurry rose to about 50 °C due to the exothermic nature of the precipitation reaction. The pH of the slurry was carefully adjusted to 10. After an aging of 8 h, the precipitate was washed free of nitrate and sodium ions. The precipitate was initially dried in air at 80 °C for 24 h. The materials were powdered and calcined at 300 °C for 36 h. Catalyst pellets of the required mesh size were then obtained by pressing under 10 t of pressure.

All the materials have been adequately characterized as reported previously [19]. The diffuse reflectance-infrared spectra (DR-IR) of the samples consists of two distinct broad peaks [19] ν_1 and ν_2, around 700 and 500 cm^{-1}, respectively. Vibration of the Td metal–oxygen group corresponds to the higher restoring force and is thus assigned to the higher frequency band (i.e., at 700 cm^{-1}), and the band at 500 cm^{-1} indicates the vibration of the Oh metal cation [22,23]. As reported by Waldren [22], the tetrahedral coordination increases the frequency of vibration, since these cations introduce a supplementary restoring force in a preferential direction along the M_{Td}–O bond. The BET surface areas of the ferrite systems were determined using an OM-NISORP 100 CX instrument; the results are presented in Table 1.

2.2. Evaluation of surface acidity and basicity

Dehydration activity of the systems can be correlated with their surface acidity. In the present case, one such experiment using cyclohexanol as the substrate has been performed. The reaction is carried out in a down-flow vapor-phase reactor. The detailed reaction procedure is given elsewhere [24]. Mole percent of cyclohexene formed has been taken as the direct measure of the acidity of the system (Table 2). The basic strength has been evaluated using adsorption studies using different electron acceptors (EAS). The basicity is correlated with the limiting amounts

Table 1
Physico-chemical characteristics of the Ni–Co ferrite systems

Composition (x)	Cation at		Concentration[a] (%)		Surface area[b] (m^2/g)
	Td site	Oh site	Ni^{2+}	Co^{2+}	
0	Fe^{3+}	$Fe^{3+}Ni^{2+}$	25.1 (25.1)	–	60.9
0.2	Fe^{3+}	$Fe^{3+}Ni_{0.8}^{2+}Co_{0.2}^{2+}$	19.9 (20.0)	4.9 (5.0)	58.3
0.5	Fe^{3+}	$Fe^{3+}Ni_{0.5}^{2+}Co_{0.5}^{2+}$	12.5 (12.5)	12.5 (12.6)	38.9
0.8	Fe^{3+}	$Fe^{3+}Ni_{0.2}^{2+}Co_{0.8}^{2+}$	5.1 (5.0)	19.9 (20.2)	35.7
1.0	Fe^{3+}	$Fe^{3+}Co^{2+}$	–	24.7 (24.8)	40.1

[a] Quantities in the parentheses indicate the theoretical value.
[b] Specific surface areas of the samples calcined at 500 °C.

of EAs adsorbed and the limiting amount values of the respective EAs employed.

2.3. Catalytic activity studies

The catalytic test was carried out on 3 g catalyst, retained by inert porcelain beads at almost the center of a vapor-phase down-flow quartz reactor (20 mm ID) (Gèomècanique, France) at atmospheric pressure. The materials were pretreated for 12 h at 500 °C under oxygen and brought down to the respective reaction temperatures using flowing dry nitrogen. The feed containing phenol and methanol was delivered using liquid syringe pump (ISCO-Model 500D). Liquid products, after condensing with a cold trap, were analyzed by a Shimadzhu GC-15A gas chromatograph using FID and a HP-ultra-capillary column. The gaseous products were analyzed using a Porapak-Q column with TCD. A blank run without any catalyst indicated negligible thermal reaction. The material balance of our experimental system was in the range of 94–95 wt.%, while the reproducibility of the experimental system was ±5%.

The phenol conversion and the product yield were expressed in mole percent. The selectivity for o-alkylation is defined as follows:

$$S_o \text{ (mol\%)} = \frac{\text{yield of } (o\text{-cresol} + 2, 6\text{-xylenol})}{\text{total conversion of phenol}} \times 100$$

whereas the individual selectivities were defined as follows:

$$S_{o\text{-cresol}} \text{ (mol\%)} = \frac{\text{yield of } o\text{-cresol}}{\text{total conversion of phenol}} \times 100$$

$$S_{2,6\text{-xylenol}} \text{ (mol\%)} = \frac{\text{yield of } 2, 6\text{-xylenol}}{\text{total conversion of phenol}} \times 100$$

3. Results and discussion

3.1. Acid–base strength distribution

Investigation of the strength and distribution of the electron donor sites on the oxide surfaces using EA having different electron affinity values is a

Table 2
Cyclohexanol dehydration activity and limiting amounts of EAS adsorbed over different Ni–Co ferrite systems

Catalyst composition	Cyclohexene[a] (mol%)	Limiting amount of EA adsorbed ($\times 10^{-5}$ mol/m^2)	
		TCNQ	Chloranil
NF-1	12.0	2.38	1.06
NCF-2	16.7	2.02	0.97
NCF-3	24.6	1.92	0.87
NCF-4	37.2	1.91	0.71
CF-5	55.3	1.54	0.32

[a] Reaction conditions: WHSV, 1.4 h^{-1}; activation temperature, 500 °C; reaction temperature, 325 °C.
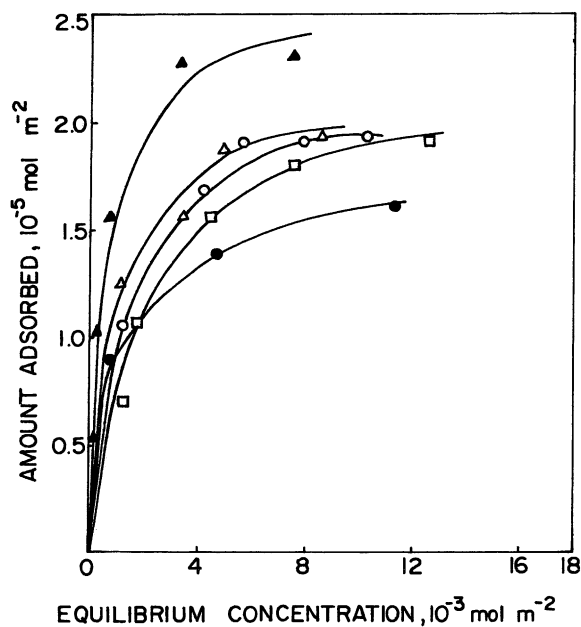
Fig. 1. Adsorption isotherms of TCNQ in acetonitrile on different Ni–Co ferrite systems calcined at 500 °C: (▲) NF-1; (△) NCF-2; (○) NCF-3; (□) NCF-4; (●) CF-5.

Fig. 2. Adsorption isotherms of chloranil in acetonitrile on different Ni–Co ferrite systems calcined at 500 °C: (▲) NF-1; (○) NCF-2; (△) NCF-3; (□) NCF-4; (●) CF-5.

well established technique [25–29]. Valuable information regarding the strength and distribution of the donor sites can be obtained by comparing the limiting concentration of the EAs adsorbed and the electron affinity values of the respective EAs used. The adsorption properties were studied with the following EAs (electron affinity values in the parenthesis): 7,7,8,8-tetracyanoquinodimethane, TCNQ (2.84 eV); 2,3,5,6-tetrachloro-1,4-benzoquinone, chloranil (2.40 eV); *p*-dinitrobenzene, PDNB (1.77 eV). The amount of EA adsorbed was determined from the difference in the concentration of EA in solution before and after adsorption, which was measured by means of a UV–Vis spectrophotometer (λ_{max} of EA in solvent: 393.5 nm for TCNQ, 288 nm for chloranil and 262 nm for PDNB).

The adsorption was found to be of a Langmuir type. The adsorption isotherms plotted for TCNQ and chloranil (Figs. 1 and 2, respectively) are used for calculating the limiting amount adsorbed; the values are presented in Table 2 (the limiting concentrations were expressed in mole per square meter; surface areas being determined using the BET
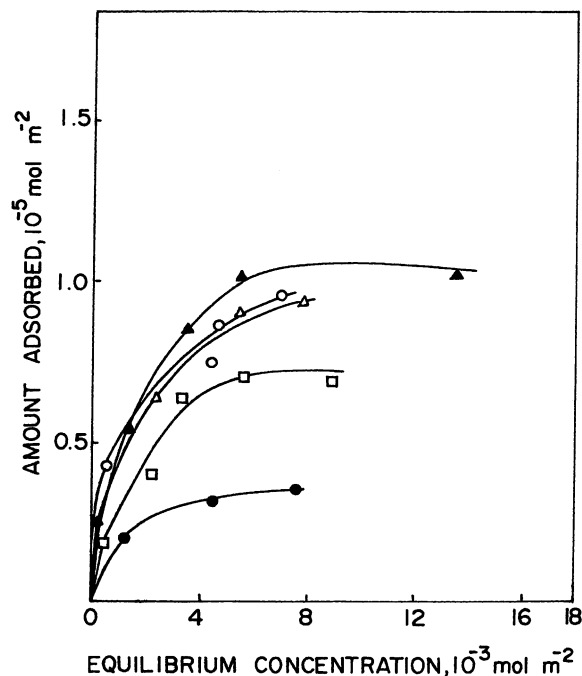
method). The adsorption of PDNB was negligible in all cases (electron affinity value 1.77 eV). The limiting amount of EA adsorbed is higher for TCNQ than for chloranil. TCNQ being a strong EA (electron affinity value 2.84 eV), its anion radicals are expected to form on weak as well as strong basic sites, whereas chloranil with intermediate electron affinity value (2.40 eV) cannot form anion radicals on weak donor sites. The negligible adsorption of PDNB for all systems indicates the absence of very strong donor sites. Therefore, the limiting amounts of TCNQ and chloranil would give an estimate of the weak or moderate basic sites. An evaluation of the results summarized in Table 2 indicates that the order of the amount of moderate basic sites is NF-1 > NCF-2 > NCF-3 > NCF-4 > CF-5, showing a decreasing trend with progressive substitution of Co^{2+} ions for Ni^{2+} ions.

On the other hand, acidity of the system increases progressively with Co^{2+} substitution, as revealed from the cyclohexanol dehydration activity. The cy-

clohexanol dehydration (acidity) and basicity were based on weight of catalyst and mole per square meter, respectively. However, since the specific surface areas of the catalysts did not change so much with the composition, the data represented in two ways can be correlated properly. All compositions of the $Ni_{1-x}Co_xFe_2O_4$ type systems are inverse in nature. From the above results, it can be inferred that either Co^{2+} or Fe^{3+} ions are responsible for the acidity of the systems. As the composition varies, the Fe^{3+} ion concentration in the Td sites and the Oh sites remain unaltered (equally distributed) and only the Co^{2+}/Ni^{2+} ratio in the Oh sites isomorphically varies. Since the Fe^{3+} concentration is the same for all the compositions and the acidity–basicity values have been substantially influenced by Co-substitution, it is reasonable to believe that the stronger Lewis acid centers are created by Co^{2+} ions.

3.2. Alkylation of phenol

The activities and selectivities of the catalysts as a function of reaction temperature are shown in Table 3. As the temperature increased from 300 °C, the yield of both *o*-cresol and 2,6-xylenol increased apparently. Temperature did not show any marked influence on O-alkylation and anisole concentration remained less than 3% over all the catalysts, throughout the temperature range studied. As evidenced from the data presented in Table 3, the catalysts are highly liable to form only *ortho* methylated products, with total *ortho* selectivity higher than 94%. In addition to this, the reaction did not lead to any xylenol isomers under the experimental conditions. With an increase in temperature, the rate of consecutive methylation of *o*-cresol to 2,6-xylenol increased; maximum

yield of 2,6-xylenol was observed at 350 °C. With further increase in temperature, an increase in the concentrations of side products such as benzene and toluene has been noticed, with a reduction in the rate of consecutive methylation of the initially formed *o*-cresol. This leads to an increase in the selectivity of *o*-cresol and decrease in the selectivity of 2,6-xylenol, as the temperature increases from 350 to 400 °C.

Reactions with different molar ratios of phenol to methanol, viz., 2.0, 5.0, 7.0 and 10 were performed at 350 °C over CF-5. At lower methanol to phenol ratios, phenol conversion was less and a progressive increase in *o*-cresol yield was observed up to the molar ratio of 5.0. The increase in *o*-cresol concentration is associated with a concomitant rise in the 2,6-xylenol concentration. However, a maximum value of 2,6-xylenol yield was observed at a feed-mix ratio of 7.0, whereas the *o*-cresol concentration remained more or less unaffected with further increase in molar ratio from 5.0. Hence, the feed-mix ratio of 7.0 was maintained throughout the experiments. *o*-Cresol and 2,6-xylenol showed the combined selectivity higher than 94%. Increase in molar ratio enhances the ring alkylation rate, leads to the increased selectivity of alkylated phenols. The results are presented in Table 4.

The influence of feed flow rate on phenol conversion and product yield at 350 °C over CF-5 is depicted in Fig. 3. At lower contact time regions, *o*-cresol was the major product followed by 2,6-xylenol. With an increase in contact time, the 2,6-xylenol yield increased progressively followed by a corresponding decrease in the *o*-cresol yield, indicating consecutive methylation of the latter over the catalyst surface at high contact time. Traces of benzene and toluene were also detected at high contact time regions; anisole

Table 3

Effect of reaction temperature on phenol conversion, product yield and selectivities (catalyst, CF-5; WHSV, 1.27 h^{-1}; TOS, 2 h; methanol–phenol molar ratio, 7:1)

Reaction temperature (°C)	Phenol conversion	Product distribution (mol%)[a]				
		o-Cresol yield	2,6-Xylenol yield	Anisole yield	*o*-Cresol selectivity	2,6-Xylenol selectivity
300	60.0	38.7	20.3	1.1	64.5	33.8
325	85.7	38.2	42.4	2.8	44.6	49.5
350	92.3	16.9	70.2	2.9	18.3	76.1
400	85.8	34.4	41.8	0.6	40.2	48.8

[a] Other products include benzene, toluene and traces of phenolic ethers.

Table 4
Effect of methanol to phenol molar ratio on phenol conversion and selectivities of *o*-cresol and 2,6-xylenol over CF-5 (reaction temperature, 350 °C; WHSV, 1.27 h^{-1}; TOS, 2 h)

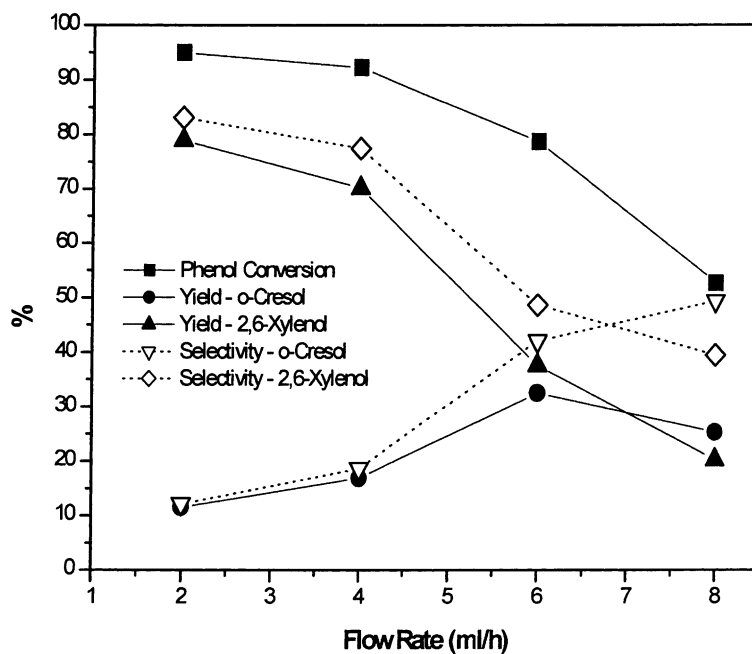|	Molar ratio (MeOH/PhOH)			
	2	5	7	10
Product distribution (wt.%)				
Non-aromatics	Nil	Nil	0.4	0.7
Benzene	0.1	0.1	0.1	Nil
Toluene	0.3	0.4	0.2	0.1
Anisole	1.9	3.0	2.7	2.3
Unreacted phenol	51.4	18.2	7.7	8.0
o-Cresol	11.2	17.4	16.9	16.8
2,6-Xylenol	30.7	60.8	70.2	69.7
Other alkylphenols	2.5	0.1	0.8	1.3
Others	1.9	Nil	0.8	1.2
Phenol conversion	48.6	81.8	92.3	92.0
Selectivity				
o-Cresol	23.0	21.3	18.3	18.3
2,6-Xylenol	63.1	74.4	76.1	75.8
Total *ortho* selectivity	86.2	95.7	94.4	94.0

Fig. 3. Effect of contact time on phenol conversion and product yield over CF-5. Reaction temperature, 350 °C; catalyst amount, 3 g; feed molar ratio (methanol to phenol), 7.0; TOS, 2 h.
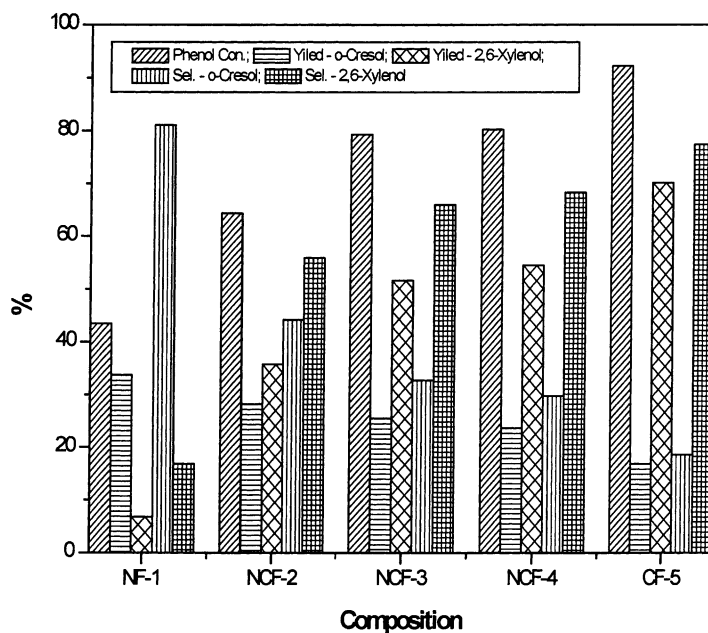
Fig. 4. Product distribution and selectivity pattern of phenol alkylation using methanol over different Co–Ni ferrite systems. Reaction temperature, 350 °C; feed molar ratio (methanol to phenol), 7.0; WHSV, 1.27 h^{-1}; TOS, 2 h.

concentration virtually remained unaffected with space velocity variations.

Catalytic activity as a function of composition is shown in Fig. 4. Co–Ni concentration is a decisive factor influencing the performance of the systems. Maximum yield for 2,6-xylenol was observed for CF-5, i.e., the system possessing the highest Co/Ni ratio ($x = 1$). As x decreases (i.e., progressive substitution of Co^{2+} by Ni^{2+} ions), the rate of consecutive alkylation reduces and, hence the o-cresol yield increases, with a substantial reduction in the total phenol conversion. In other words, NF-1 gave o-cresol as the major product, and upon progressive replacement of Ni^{2+} with Co^{2+} ions, the system facilitates consecutive methylation of the initially formed o-cresol to 2,6-xylenol, along with an enhancement in total phenol conversion.

Time on stream studies under the experimental conditions of WHSV of 1.27 h^{-1}, reaction temperature of 350 °C and a methanol to phenol molar ratio of 7 were carried out over a period of 10 h (Fig. 5). Among the systems, CF-5 exhibited excellent stability; both NCF-4 and NCF-3 showed slight deactivation, whereas both NCF-2 and NF-1 deactivated rapidly.
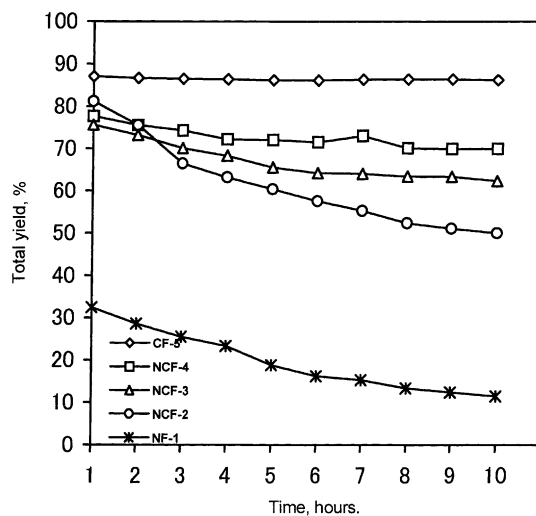

Fig. 5. Stability of different Co–Ni systems for *ortho* alkylation of phenol. Total yield (o-cresol + 2, 6-xylenol) is plotted against time in hours. Reaction temperature, 350 °C; feed molar ratio (methanol to phenol), 7.0; WHSV, 1.27 h^{-1}.

4. Catalytic pathway

From the detailed investigation of phenol methylation using methanol as the alkylating agent, we have seen that substitution of Co^{2+} ions for Ni^{2+} ions enhances consecutive *ortho* methylation of phenol by methanol, leading to progressively higher selectivity of 2,6-xylenol. The catalytic effectiveness to a greater extent is determined by the cation distribution in the ferrospinel lattice. Both acidic and basic characters vary with composition and therefore the variation of acid–base properties with composition is an important factor in explaining the catalytic effectiveness of the present systems. We have noticed an increase in 2,6-xylenol concentration with increase in contact time. However, the increase in 2,6-xylenol concentration occurring at the expense of *o*-cresol as shown in Fig. 3 indicates the consecutive methylation of *o*-cresol over the catalyst surface at high contact times. In all cases anisole concentration was negligible and did not show any marked variation with space velocity changes. Hence, the bimolecular mechanism as suggested by Pierantozzi and Nordquist [30], in which anisole served as its own alkylating agent cannot be considered in the present case. If anisole is acting as an intermediate, the rearrangement step would be significantly influenced by space velocity changes and one can expect more anisole at high space velocities. In order to confirm this argument, we have passed anisole alone over the catalysts, where neither phenol nor any alkylated phenols could be detected. Additionally, when a feed mixture of *o*-cresol and methanol was passed over these catalysts enormous amount of 2,6-xylenol (more than 78% over CF-5) was detected (Table 5).

Surface acid–base property of the catalyst is a very strong influencing factor. All the ferrospinel systems are highly selective to *ortho* alkylation. As reported by Tanabe and Nishizaki [31], the Brønsted acid sites

Table 5
Methylation of *o*-cresol using methanol over CF-5 (reaction temperature, 350 °C; methanol–*o*-cresol molar ratio, 3; WHSV, $1.3 \, h^{-1}$)

Product distribution	wt.%
Non-aromatics	0.1
Benzene	0.1
Toluene	0.1
Anisole	1.2
Phenol	2.5
Unreacted *o*-cresol	17.2
2,6-Xylenol	78.0
Methyl anisole	0.3
Other alkyl phenols	0.2
Others	0.3
o-Cresol conversion	82.8
2,6-Xylenol selectivity	94.3

strongly interact with the aromatic ring. Such interactions make the phenol molecule orient parallel to the catalyst surface (Fig. 6) and therefore the *o*- and *p*-positions of the ring will become equally accessible for the incoming group leading to poor selectivity for *ortho* alkylation. However, using the Co–Ni ferrospinel catalysts, under the optimized conditions, the total *ortho* selectivity was above 94%. Additionally, the exit composition was free from any xylenol or cresol isomers. These observations strongly reject the possibility of a parallel orientation of the phenol molecule over the catalyst surface. High *ortho* selectivity can be explained by assuming vertical orientation of adsorbed phenol on the Lewis sites, as postulated for γ-alumina surface by Klemm et al. [32]. The mechanism is shown in Fig. 7, according to which the phenolate ion is adsorbed on the Lewis acid site and the hydrogen ion is bound to the basic site. This proton site activates methanol to produce a carbonium ion, which reacts with the aromatic ring of the adjacently adsorbed phenolate species at the *ortho* position.
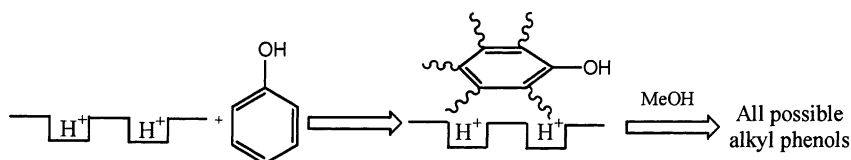

Fig. 6. Parallel orientation of the aromatic ring of the phenol molecule on the catalyst surface containing Brønsted acid sites.
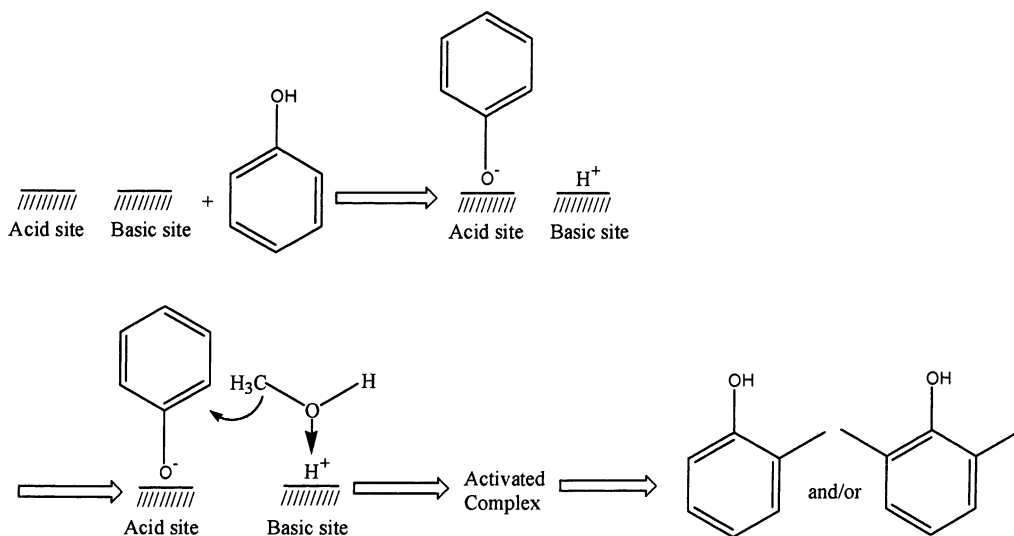
Fig. 7. Reaction mechanism of phenol alkylation using methanol—role of Lewis acid–base centers.

In the present case, the catalytic activity follows the order: CF-5 > NCF-4 > NCF-3 ≅ NCF-2 > NF-1. From the adsorption study of EAs and their dehydration activity, it is clear that substitution of Co^{2+} for Ni^{2+} creates an increase in acidity with a concomitant decrease in the amount of basic sites. In ferrites, the Fe^{3+}–O distance is larger when Fe^{3+} is in Oh symmetry than in the Td symmetry. This suggests that the Fe^{3+} ions in the Oh symmetry will be more acidic than in the Td symmetry. Recent works based on advanced surface analysis techniques such as low-energy ion scattering (LEIS), a technique used for identifying the surface atomic layer of solid surfaces [16], have revealed that the outermost atomic layer of spinels contains mainly Oh cations, and hence the Oh cations play a dominating role in determining the catalytic properties. We have observed that both acidity and catalytic activity increase during Co-substitution. The 2,6-xylenol/o-cresol ratio is decreased by Ni^{2+} substitution for Co^{2+} in the Oh sites, which is the lowest when Ni^{2+} is completely substituted for Co^{2+}. As explained before, Ni^{2+} substitution reduces acidity of the system, which tends to suppress the secondary alkylation activity. This conclusion is in agreement with that reported by Namba et al. [10], who have proposed that stronger acid sites are required for secondary alkylation reaction to yield 2,6-xylenol, whereas only weaker acid sites are needed for the formation of primary alkylated product o-cresol. We believe that a controlled interplay of strength as well as the number of acidic sites determine the product selectivity and catalytic activity.

5. Conclusions

1. $Ni_{1-x}Co_xFe_2O_4$ (x = 0, 0.2, 0.5, 0.8 and 1.0) type systems were studied for alkylation of phenol using methanol as the alkylating agent. All the systems are found to be highly selective for *ortho* methylated products, with the total *ortho* selectivity $\geq 94\%$, under the optimized reaction conditions. Systems possessing low x values predominantly gave o-cresol, whereas an increase in the x value leads to increase in the rate of consecutive methylation of the initially formed o-cresol, leading to higher selectivity for 2,6-xylenol.
2. Catalytic activity and product selectivity depend largely on the Co^{2+}/Ni^{2+} ratio in the spinel matrix. A large Co^{2+}/Ni^{2+} ratio leads to better phenol conversion and very high 2,6-xylenol selectivity.
3. The activity and selectivity were shown to be strongly dependent on the surface acid–base properties of the system. It was observed that substitution of Co^{2+} for Ni^{2+} ions increases the acidity of

the system. Phenol conversion increases together with 2,6-xylenol selectivity upon substitution of Co^{2+} for Ni^{2+} ions.

4. Fe^{3+} ions in the Oh coordination will be more acidic than in the Td coordination due to the longer Fe^{3+}–O bond distance in the former case. In addition to this, the substitution of Co^{2+} for Ni^{2+} creates still more acidic centers, as revealed from the adsorption and dehydration studies. Therefore, it is believed that the Oh cations play a dominating role in determining catalytic properties. In conclusion, stronger acid sites are required for secondary alkylation to yield 2,6-xylenol, whereas only weaker acid sites are needed for the formation of primary alkylation to yield *o*-cresol.

References

[1] H. Feige, in: B. Elvers, S. Hawkins, G. Schultz (Eds.), Ulmann's Encyclopedia of Industrial Chemistry, Vol. A19, 5th Edition, VCH, Weinheim, 1999, p. 313.

[2] R. Dowbenko, in: J.I. Kroschwit, M. Houl-Grant (Eds.), Kirk–Othmer Encyclopedia of Chemical Technology, Vol. 2, 4th Edition, 1999, p. 106.

[3] E. Santhacesaria, D. Grasso, D. Galosa, S. Carra, Appl. Catal. 64 (1990) 83.

[4] F. Nozaki, I. Kimura, Bull. Chem. Soc. Jpn. 50 (1977) 614.

[5] K. Li, I. Wang, K. Chang, Ind. Eng. Chem. Res. 32 (1993) 1007.

[6] M.C. Samolada, E. Grgoriadou, Z. Kiparissides, I.A. Vasalos, J. Catal. 152 (1995) 52.

[7] C. Bezouhanova, M.A.Al. Zahari, Appl. Catal. 83 (1992) 45.

[8] S. Sato, K. Koisumi, F. Nozaki, Appl. Catal. A 133 (1995) L7.

[9] S. Velu, C.S. Swamy, Appl. Catal. A 162 (1997) 81.

[10] S. Namba, T. Yoshima, Ttba, N. Hara, Stud. Surf. Sci. Catal. 5 (1980) 105.

[11] H.K. Harold, C.K. Mayfair, Adv. Catal. 33 (1985) 159.

[12] R.R. Rajaram, A. Sermon, J. Chem. Soc., Faraday Trans. I 81 (1985) 2577.

[13] F.C. Romeijn, Phil. Res. Rep. 8 (1953) 304.

[14] T.F.W. Barth, E. Posnjak, Z. Kristallogr. 82 (1932) 325.

[15] C.S. Narasimhan, C.S. Swamy, Appl. Catal. 2 (1982) 315.

[16] J.P. Jacobs, A. Maltha, J.R.H. Reintjes, T. Drimal, V. Ponec, H.H. Brongersma, J. Catal. 147 (1994) 294.

[17] K. Sreekumar, T.M. Jyothi, M.B. Talawar, B.P. Kiran, B.S. Rao, S. Sugunan, J. Mol. Catal. A 152 (2000) 225.

[18] K. Sreekumar, T. Raja, B.P. Kiran, S. Sugunan, B.S. Rao, Appl. Catal. A 182 (1999) 327.

[19] K. Sreekumar, T. Mathew, R. Rajgopal, R. Vetrivel, B.S. Rao, Catal. Lett. 65 (2000) 99–105.

[20] K. Sreekumar, T. Mathew, B.M. Devassy, R. Rajgopal, R. Vetrivel, B.S. Rao, Appl. Catal. A 205 (2001) 11.

[21] P.S. Anilkumar, J.J. Schotri, S.E. Kulkarni, C.E. Deshpande, S.K. Date, Mater. Lett. 27 (1996) 293.

[22] R.D. Waldren, Phys. Rev. 99 (1955) 1727.

[23] W.B. White, B.A. DeAngelies, Spectrochim. Acta A 23 (1967) 985.

[24] W.S. Chin, M.D. Lee, Appl. Catal. A 83 (1992) 201.

[25] K. Isumi, K. Meguro, J. Adhes. Sci. Technol. 4 (1990) 393.

[26] S. Sugunan, G.D. Rani, J. Mater. Sci. Lett. 10 (1991) 887.

[27] H.P. Leftin, M.C. Hobson, Adv. Catal. 14 (1963) 163.

[28] A. Teinin, Adv. Catal. 15 (1964) 256.

[29] R.P. Porter, W.K. Hill, J. Catal. 5 (1996) 366.

[30] R. Pierantozzi, A.F. Nordquist, Appl. Catal. 263 (1986) 21.

[31] K. Tanabe, T. Nishizaki, in: F.C. Tompkins (Ed.), Proceedings of the Sixth International Congress on Catalysis, The Chemical Society, London, 1977.

[32] L.H. Klemm, C.E. Klopfenstein, J. Shabtai, J. Org. Chem. 35 (1970) 1069.