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Al-Doped FeVO$_4$ Nanoparticles for Vapour Phase Methylation of Phenol

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Al substituted FeVO$_4$ catalysts were prepared by co-precipitation method. The catalysts were characterized by X-Ray Diffraction, Brunauer-Emmett-Teller surface area analysis, Thermo gravimetric–Differential thermal analysis, scanning electron microscopy, transmission electron microscopy and X-ray photoelectron spectroscopy. The Al content increased the acidic character of the catalyst. The catalytic activity was evaluated for methylation of phenol and showed high activity and selectivity. 2% Al promoted FeVO$_4$, caused the conversion of phenol and selectivity towards 2,6-xylenol to reach 98% and 94% respectively. The catalyst has good stability, TOS studies and characterization of spent catalyst was done.

Introduction

Phenol alkylation reaction has gained importance in polymer industry. Di alkylated phenol like 2,6-xylenol is a starting material to polyphenylene ether (PPE), which is a high temperature thermoplastic.[1] Phenolic compounds are also extensively used in agrochemical and pharmaceutical industry. However high temperature reaction, deactivation and coke deposition limits the application, therefore the development of new catalyst is required to withstand the reaction condition.

Fe substituted ZrO$_2$ was prepared and the effect of Fe content as a promoter for the reaction was studied.[2] Chary et al. found the increase in 2,6- xylenol product with V$_2$O$_5$ loading up to 7.5% over zirconia support catalyst.[3] Co - Ni ferrospinel catalyst predominantly yielded ortho selective products.[4] TiO$_2$ was exploited for phenol methylation for high selectivity towards o-cresol.[5] Many other catalysts like zeolites and mixed metal oxides have been explored.[6–10] But the limitations still persists on catalyst deactivation, hence hunt for a better catalyst continues. FeVO$_4$ is exploited for its magnetic properties and electrochemical reactivity studies.[11,12] FeVO$_4$ nano-sheets exhibited gas sensing properties in detecting traces of ethanol in air and photo-catalytic degradation of methyl orange dye.[13] Pawe et al. studied the activity of industrial iron – chromium catalyst for its long term stability.[14] J. Xie et al. prepared V modified BEA zeolites[15] and Mg-bearing BEA zeolites which served as an efficient catalysts in liquid-phase selective methylation of phenol with methanol.[16]

In the present study, the catalytic effect of Iron vanadate in vapour phase methylation is explored for the first time. Al substituted FeVO$_4$ is a novel catalyst for methylation reaction.

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The catalyst is highly *ortho* selective in nature yielding > 94% 2, 6-xylenol product.

Results and Discussion

Catalyst Characterization

Figure 1 shows the XRD pattern for all the prepared samples. All the compounds crystallized in triclinic crystal system. From
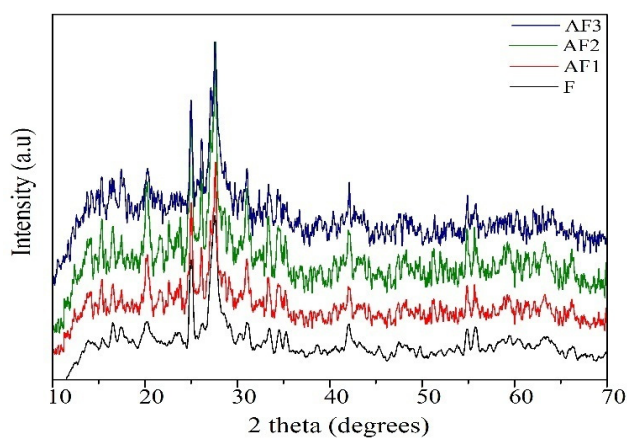

Figure 1. XRD pattern of the prepared catalysts.

Figure 2, the TEM images exhibits round shape in the size range of 50–100 nm. Figure S.1 (supplementary file) shows the SEM–EDX, which was performed for representative sample AF1. Figure S.2 (supplementary file) displays the Nitrogen sorption isotherm. It exhibits type II isotherm, which is a characteristic for non-porous and nanoparticles.[17] From Table 1, it can be concluded that pristine FeVO$_4$ has higher surface area compared to the Al doped samples.

Figure 2. TEM image of sample F and AF3.

Table 1. Surface area, conversion and acidity details of prepared catalysts.

Catalyst	BET surface area(m2/g)	Conversion (%)[a]	Acidity (mmol/g)			Total acidity (mmol/g)
			Weak	moderate	strong	
F	35	57	0.014	0.014	0.025	0.053
AF1	25	98	0.020	0.051	-	0.071
AF2	18	83	0.029	-	0.035	0.064
AF3	15	59	0.20	-	0.033	0.053

[a] at Ph: MeOH mole ratio 1: 12

Evaluation of catalyst acidity

From Figure 3 it can be seen for sample F (pristine $FeVO_4$), a combination band at 1492 cm^{-1} has a contribution from Lewis
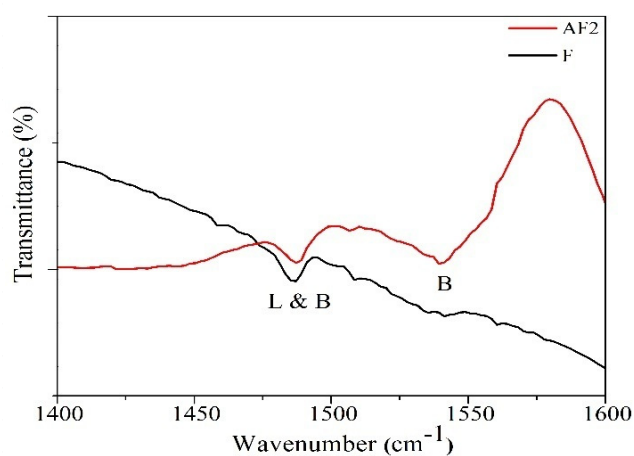

Figure 3. In situ -Pyridine IR spectra of sample F and AF1.

and Bronsted acid sites as seen. When Al is doped in $FeVO_4$, it results in the generation of Bronsted acid sites. Thus the weak band around 1540 cm^{-1} is observed.[20] From the TPD profile (Figure 4) it can be observed that with Al doping, there is
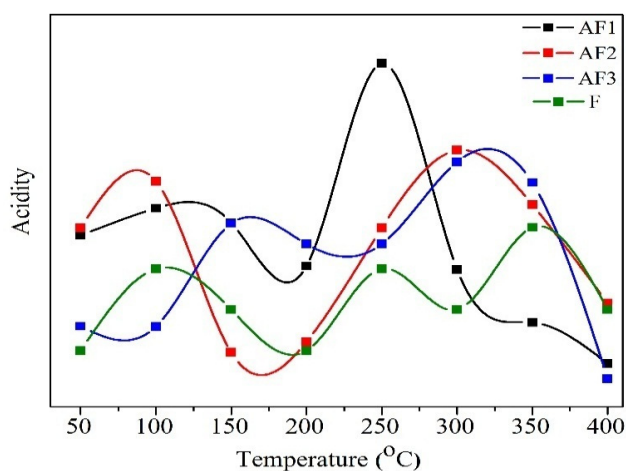

Figure 4. NH_3 –TPD profile of catalysts showing distribution of weak, moderate and strong acid sites.

enhancement of the acidic sites. From Table 1, of sample AF1 the moderate acidic sites were enhanced, while as the Al content increased it added strong acidic character to the catalyst. The total acidity is responsible for the activity however, enhanced selectivity of catalyst AF1 can be explained considering the TPD profile. Catalyst F showed weak TPD profile, while AF1 showed a distinct peak in temperature range of 200–300 °C, classified as moderate acidity region. However AF2 and AF3 showed peaks in the temperature range of 300–400 °C which is
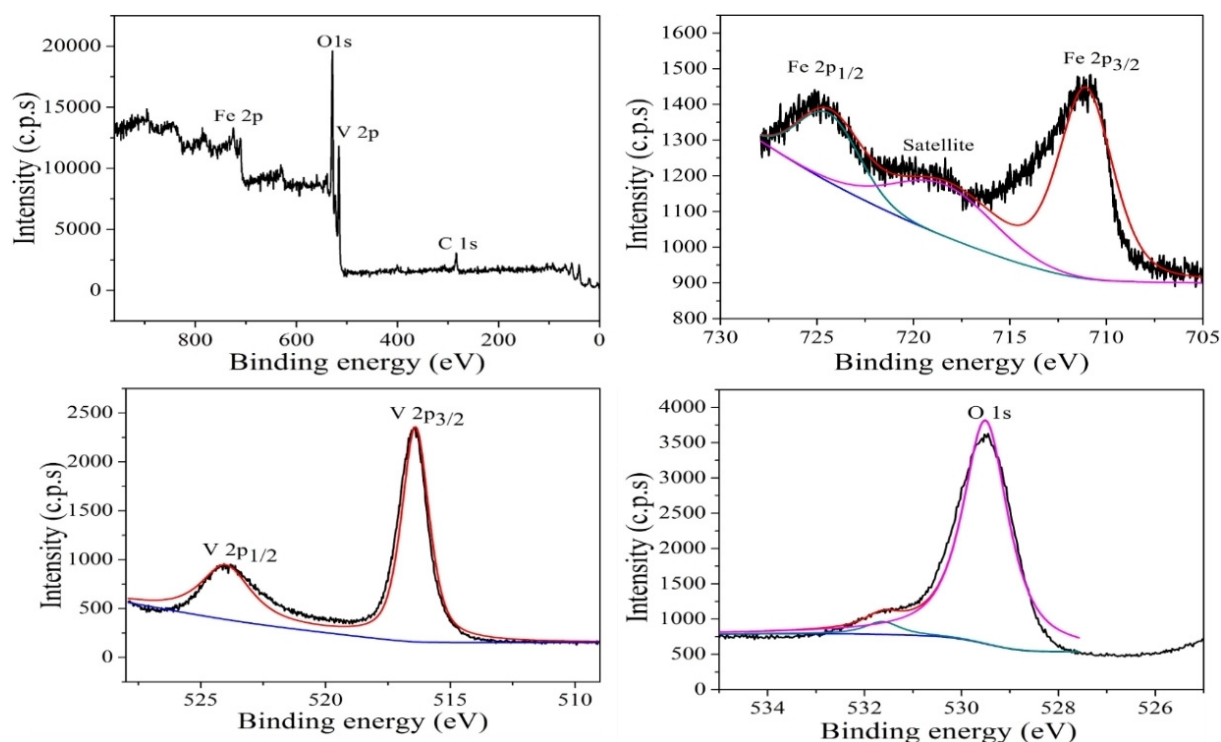
Figure 5. XPS spectra of FeVO$_4$.

associated to strong acidity region. Sample AF1 exhibits a big desorption peak at 250 °C, which indicates the presence of good amount of moderate acid sites. Whereas, the strong acidic sites are observed in ascending manner for F, AF2 and AF3, accept AF1 which showed moderate acidity.

Spectral studies

XPS is a very powerful tool to determine the chemical states of the catalyst. Figure 5 shows the XPS spectra of FeVO$_4$. The peaks observed at 724 and 711 eV corresponds to Fe 2p$_{1/2}$ and Fe 2p$_{3/2}$ respectively. The satellite peak at 718 eV confirmed that Fe exists in $+3$ oxidation state.[19] The Peaks in Figure 5 at 516 and 524 eV represent the V 2p$_{3/2}$ and V 2p$_{1/2}$ respectively, the characteristic peak of vanadium in $+5$ oxidation state. In Figure 5 the main peak at 529.5 eV corresponds to the O 1s lattice oxygen while the small hump at 531.6 eV represents the defect oxygen.[18] Therefore our studies confirm the existence of the elements in required valence state.

Catalytic Activity

The products of phenol methylation reaction were *ortho* selective consisting of o-cresol and 2,6-xylenol. The influence of reaction temperature on phenol methylation was studied and Figure 6 shows the obtained results. Reactions were carried out at 250, 300, 350 and 400 °C under atmospheric pressure over the prepared catalysts. A constant increase in the phenol conversion was seen till 350 °C, while it remained constant at
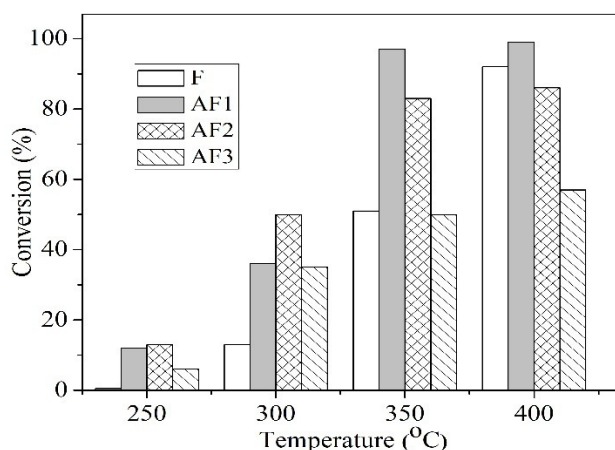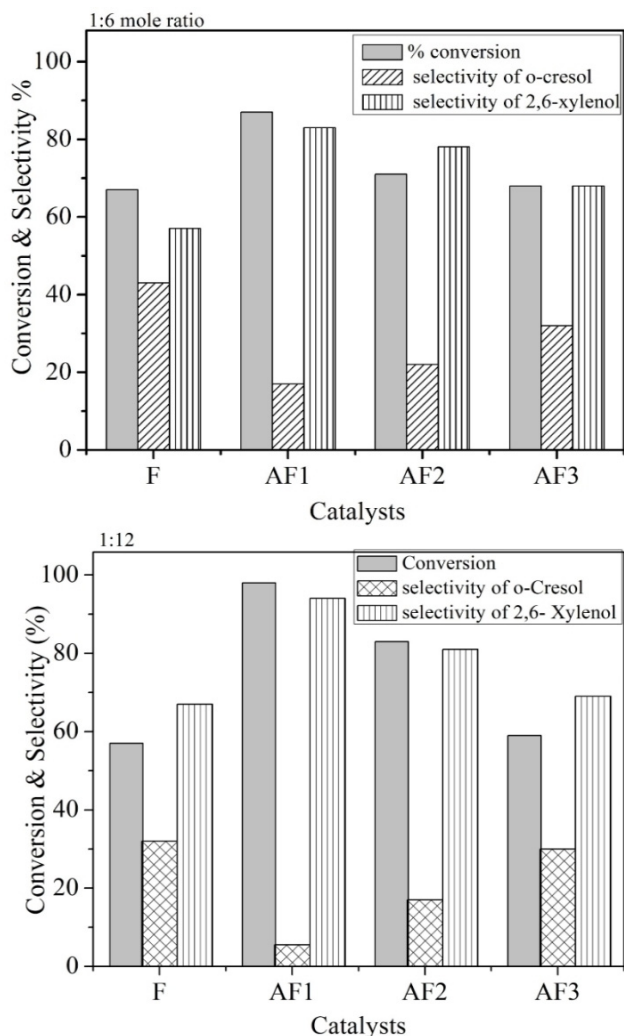

Figure 6. Catalytic activity profile over a temperature range. Feed ratio (phenol: methanol) $= 1:12$ and N$_2$ flow rate $= 600$ ml/h.
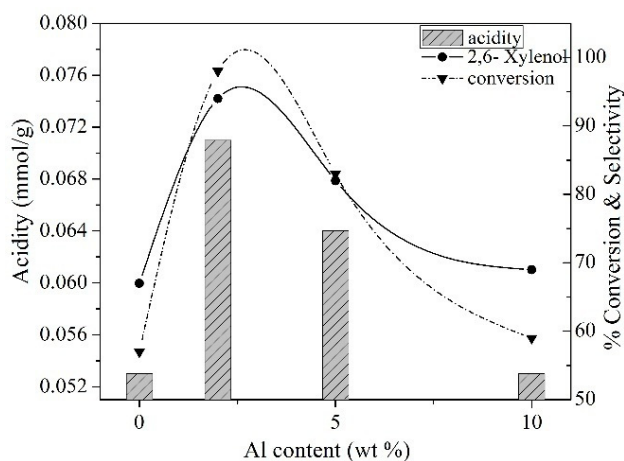
400 °C. However, at higher temperatures (> 350 °C) the selectivity of xylenol decreased (supplementary file Figure S.3). Figure 7 displays effect of feed mole ratio on the reaction. The conversion of phenol and selectivity of 2,6- xylenol increases with decrease in mole ratio of the reactants over all the catalysts. This increase in conversion with decrease in mole ratio is consistent with the literature.[2] The overall selectivity of 2,6-xylenol increases from 84% to 98% with decrease in mole ratio from 0.16 to 0.08 over the catalyst AF1. Pawe et al. reported 99% conversion of phenol with 85% selectivity towards 2,6-xylenol.[14] However in this study a conversion of
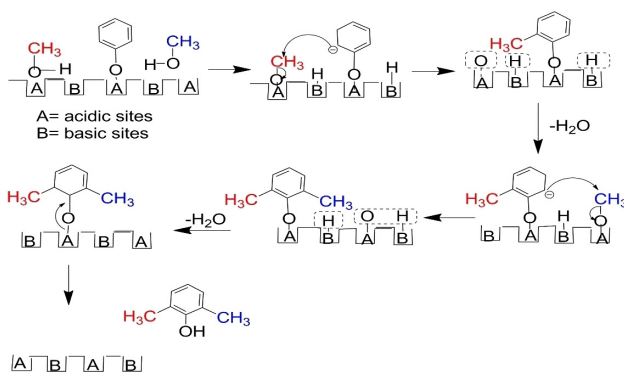
Figure 8. Effect of surface acidity on phenol conversion and selectivity of 2,6-xylenol.

Scheme 1. Proposed reaction mechanism to 2,6xylenol product.

Figure 7. Effect of mole ratio of the feed on conversion of phenol and selectivity of 2,6-xylenol at 350 °C, feed flow 2 mL/h, N_2 flow rate = 600 ml/h.

98% was achieved (which is nearly 99%) with 94% selective towards 2,6-xylenol product. Therefore, it may be claimed that AF1 to be a selective catalyst over the reported one.

From Figure 8, it can be known that the percent conversion is directly proportional to the acidic sites, while the selectivity towards 2,6- xylenol is related to medium acidic sites. From Table 1 the trend for total acidity: AF1 > AF2 > AF3 = F which explains the conversion. This effect is interpreted from the point of view that 2% Al served as a promoter, resulting in rise in moderate acidic sites, while the consequent decrease in activity with higher Al content could be due to stronger acid sites. AF1 showed highest conversion because of increased number of moderate acid strength sites. Therefore, higher conversion of phenol was due to increased acidic sites, while a higher selectivity for 2,6- xylenol moderate and strong acidic sites. The transformation of phenol to 2,6-xylenol mechanism is displayed in Scheme 1. The phenol molecule adsorbs vertically on the catalyst surface as a phenolate moiety. It prefers vertical adsorption due to the moderate acidic sites of the catalyst

whereas presence of strong acid sites could lead horizontal adsorption due to strong interactions with the π – electrons of the benzene ring. The methanol molecule undergoes O—H scission thereby gets adsorbed on the catalyst as a methoxy species. The ortho position of the phenolate ion becomes electron rich and acquires the methyl moiety from the methoxy species. In second step, the second ortho site gets alkylated, and the 2,6- xylenol product desorbs from the surface.

Time on stream

Phenol conversion was found to increase with increase in reaction time and it reached 98% conversion after 3 h as seen in Figure 9, thereafter, it remains constant up to 6 h and subsequently starts decreasing to 80% after 10 h. Initially, the selectivity towards xylenol increased for the first few hours (maximum of 94% after 3 h), but gradual decrease to 82% was seen after 10 h. This drop in selectivity is ascribed to the rise in formation of o-cresol by-product. The time on stream results reveal that deactivation of catalyst could be due to blockage of active acid sites by carbon deposition.
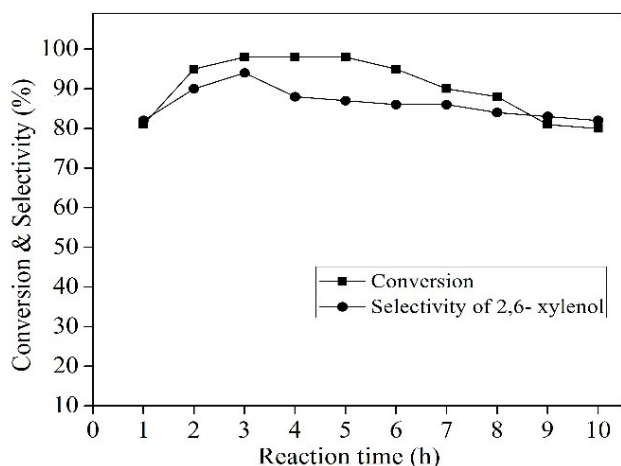
Figure 9. Influence of time on stream on phenol conversion and selectivity of 2,6- xylenol at 350 °C, 1:12 (phenol to methanol) mole ratio feed, feed flow 2 mL/h, N_2 flow rate $=$ 600 ml/h.

Studies on the spent catalysts

The spent catalyst shows activity for phenol methylation with slight drop in conversion from 98% to 80% after 10 h. This indicates that the catalyst has undergone some changes during the course of reaction. The cause for deactivation was investigated by XRD and TG-DTA and was compared with the fresh sample. The XRD pattern of the spent catalysts indicates noise of the amorphous carbon deposition (supplementary file Figure S.4). The TG-DTA profile in Figure 10 shows an exothermic weight loss due to deposited coke. The deposited carbon
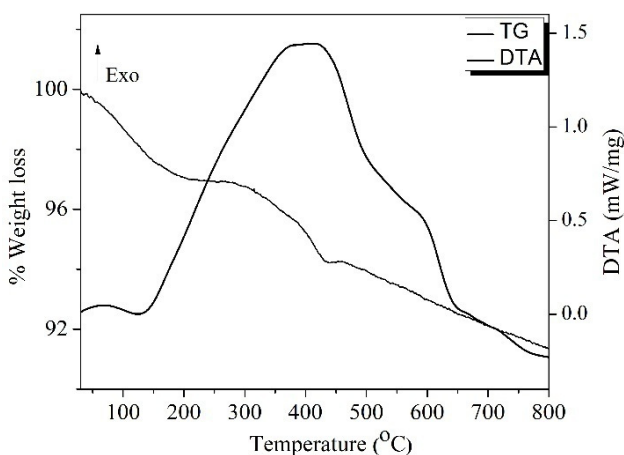
Figure 10. TG-DTA profile of the spent catalyst AF1.

undergoes oxidation from 350 to 650 °C. It is seen that the amorphous carbon oxidizes in the range 300 to 500 °C, while graphitic carbon requires a higher temperature at 600 °C with agreement with literature.[21] The shoulder peak in DTA in the region of 550 °C – 600 °C refers to a small amount of graphic

carbon. These results suggest subsequent blocking of catalyst making its active surface inaccessible for reaction and decline in the catalytic activity.

Conclusions

Al substituted $FeVO_4$ nanoparticles were prepared by simple co-precipitation method and were tested for vapour phase phenol methylation. The Al doping substantially enhanced the activity and selectivity of $FeVO_4$ nanoparticles by imparting acidity. 2% Al doped $FeVO_4$ exhibited excellent combination and imparted high activity and selectivity so as to achieve highest 98% conversion and 94% selectivity towards 2,6-xylenol product over the catalyst.

The appropriate surface acidity of the catalyst was highly responsible for the activity and selectivity. Feed composition and reaction temperature had an influence on phenol conversion. The performance of the catalyst was quite stable up to 10 h. The spent catalyst was examined and it revealed coke formation which may lead to deactivation.

Supporting Information Summary

The content has SEM-EDX data, details of Nitrogen sorption studies, phenol conversion profiles, XRD pattern of the spent catalyst and all the required details of the experimental section.

Conflict of Interest

The authors declare no conflict of interest.

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