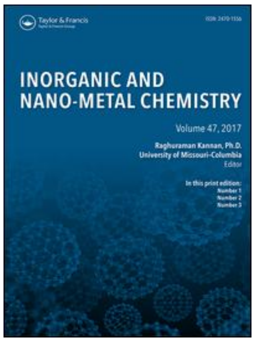

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Catalytic Activity of Vanadium Substituted Molybdophosphoric Acid Supported on Titania for the Vapor Phase Synthesis of Isophthalodinitrile

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Abstract

Different wt % of vanadium substituted molybdophosphoric acid (PMoV) loaded on titania(TiO_2) are prepared by wet impregnation method. The catalytic activity of PMoV supported titania catalyst for the vapour phase ammoxidation of m-xylene at different temperatures is reported here. The synthesized catalysts were characterized by FT-IR, XRD, N_2 adsorption-desorption, TG-DTA, TPD, TPR, SEM, EDX, and TEM. FT-IR studies confirmed that the Keggin structure of PMoV does not change even up to 460°C when loaded on TiO_2 surface. Among all the PMoV supported TiO_2 catalysts, 1.7 % PMoV/TiO_2 showed excellent activity for vapour phase ammoxidation of m-xylene with 85.4% yield of isophthalodinitrile.

Keywords:

Heteropolyacid; TiO_2; ammoxidation; m-xylene; isophthalodinitrile.

Introduction

Isophthalodinitrile (IPN) and its derivatives are important chemical intermediates for the production of various dyes, agro-chemicals, pharmaceuticals, synthetic fibre and pesticides.[1] There are several methods for the synthesis of nitriles. Among these methods, vapour phase ammoxidation process is one of the simple and economically viable method.[2,3] For vapour phase ammoxidation reaction, vanadium and molybdenum are the key components for all the catalysts.[4-12] The method of preparation and sources of vanadium/molybdenum influences the typical catalytic properties of V_2O_5 and MoO_3.[6] Ray et al reported that V_2O_5 prepared from vanadyl oxalate source exhibited much better catalytic activity as compared to V_2O_5 prepared from ammonium metavanadate.[6, 8] Hence, vanadia based catalysts of different composition from various source materials have been prepared from time to time in our group and studied for ammoxidation reaction.[6-8]

The V_2O_5-Cr_2O_3/Al_2O_3 catalyst system was investigated for ammoxidation of xylene by Ray et al[6] which showed 58% yield of IPN using feed ratio of m-xylene: ammonia: air of 1:11:14. The effect of high content of MoO_3 in Vanadium Molybdenum Phosphorus Oxide (VMPO) catalyst was studied for ammoxidation of 3-picoline exhibiting 96% yield by Roy et al.[8] Recently, Sai Prasad et al reported vanadium incorporated molybdophosphoric acid (MPAV) to prepare Mo-V-P oxide supported on Al_2O_3 for ammoxidation of m-xylene with high yield of m-tolunitrile (82%) and 22% yield of IPN using feed ratio m-xylene: NH_3: Air (1:10:40) at temperature 350-430^{o}C.[12] Scanty work is available on ammoxidation of m-xylene over heteropolyacids as catalysts. Usually molybdophosphoric acid (PMo_{12}) and vanado-molybdophosphoric acid (PMoV) catalysts are used for oxidation and ammoxidation reactions.[13-17] The order of activity of the support is Nb_2O_5>ZrO_2>Al_2O_3>SiO_2>MgO for ammoxidation reaction.[18] Though PMoV supported on TiO_2 catalyst has been reported earlier but not studied for ammoxidation of m-xylene. Here in, we report the vanadium incorporated molybdophosphoric acid (PMoV) supported on TiO_2 catalyst for the synthesis of IPN by ammoxidation of m-xylene using very low ammonia feed ratio.

In the present work, vanadium incorporated molybdophosphoric acid (PMoV) was prepared and supported on TiO_2 by wet impregnation method in order to improve and modify the catalytic properties, characterized by different techniques and evaluated for ammoxidation of m-xylene.

Experimental

Materials

Analytical reagent grade sodium molybdate, sodium metavanadate, disodium hydrogen phosphate, diethyl ether and sulphuric acid were procured from CDH India. These reagents were used without further purification in this investigation.

Preparation of catalyst

Vanadium incorporated molybdophosphoric acid; $H_4PMo_{11}VO_{40}$ (abbreviated as PMoV) was prepared according to the reported procedure.[19, 20] In brief, separately 3.05 g of sodium metavanadate was dissolved in 100 ml boiling water and 3.55 g of disodium hydrogen phosphate was dissolved in 100 ml distilled water to make a clear solution. Both the solutions were mixed together and cooled. Then the mixture was acidified with 2.5 ml conc. H_2SO_4 when the colour of the solution changed to red. To this mixture, 66.5 g sodium molybdate dissolved in 100 ml of water was added. Finally 45 ml of concentrated sulphuric acid was added slowly with continuous stirring revealing the change of coloration from dark red to light red. The PMoV was then extracted with 200 ml of diethyl ether. After separation of the oily (middle) layer as heteropolyetherate, a stream of air was passed to make it ether free. The solid that settled down was dissolved in water, concentrated to the first appearance of crystal in a desiccator over conc. H_2SO_4 and then allowed to crystallize further and dried. Then a series of PMoV supported on TiO_2 (Aldrich make heated at 500 ^oC) catalysts were prepared by wet impregnation method by varying the wt% of PMoV from 0.7 to 2.2. The required quantity of PMoV was dissolved in minimum amount of water and this solution was added to known amount of TiO_2 with constant stirring. Excess water was removed on a hot water bath, and the catalyst masses were dried in air oven at 120 ^oC for 8 h. Then the catalysts were calcined at 460 ^oC for 2 h. Finally catalysts were sized to 14-18 mesh.

Activity studies

Ammoxidation of m-xylene was carried out at atmospheric pressure in a continuous flow fixed bed pyrex glass reactor. The reactor was packed with 10 g of catalyst between two layers of porcelain beads. The upper layer of the porcelain beads served both as a preheater and a mixer for the reactants. Prior to reaction, ammonia gas was fed to the catalyst bed with a flow rate of 50 ml/min at 450 ^oC for 1 h. After bringing the reactor temperature to the required level, the molar ratio of m-xylene: ammonia: air = 1: 3: 6, was fed into preheated portion of the reactor. m-xylene was fed into the reactor through a syringe pump (Miclins). Ammonia gas and air were fed through calibrated flow meters. The reaction temperature was monitored by a thermocouple with its tip located at middle of the catalyst bed. The reactions were carried out at a temperature of 425 °C. Each experiment was of 2 h duration. The liquid product was collected in a trap kept at -5 °C. The products were analyzed by gas chromatography, using carbowax 20 M column and using thermal conductivity detector (TCD). The analysis of the non-condensable exit gas mixture was analysed using GC with TCD and it was confirmed that there were no organic species or oxides of carbon in considerable range.

Physico-chemical characterization

The FTIR spectra of the samples were recorded using Varian FTIR-800 in KBr matrix in the range of 4000-400 cm^{-1}. Powder X-ray diffraction (PXRD) pattern of the samples were taken in the range of 10 to 80^o at a rate of 1.2^o/min (Philips analytical 3710) using Cu Kα radiation. The BET surface areas of the catalysts were determined by N_2 adsorption-desorption at 77 K using Tristar 3000 surface area analyser (Micromeritics, USA). Known amounts of the samples were evacuated for 3 h at 150^oC to remove physically adsorbed water prior to surface area measurement. The acid character of the samples was studied by NH_3-TPD AutoChem-II, (Micromeritics) Chemisorptions analyser equipped with a thermal conductivity detector (TCD). About 1 g of the powdered sample contained in a quartz ‘U’ tube was degassed at 250^oC for 1 h with ultra-pure nitrogen gas. After cooling the sample to room temperature, NH_3 (20% NH_3 balanced with helium) gas was passed over the sample while it was heated at a rate of 10^oC min^{-1} and the profile was recorded. The H_2-TPR of 1.7 % PMoV/TiO_2 was carried out in an AutoChem-II, (Micromeritics) instrument. Thermo gravimetric/differential thermal analysis (TG/DTA) was performed under air with a Toledo-Metler TG/DTA/851e system at a heating rate of 5^oC min^{-1}. To examine the composition, sizes and morphologies of 1.7 % PMoV supported titania, SEM with EDX was performed at 15.0kV and at a magnification of 10^4. The images of the sample were captured by using a Hitachi S3400N. The transmission electron micrograph of PMoV supported titania was recorded by using TECNAI-G2 microscope with CCD camera.

Results and discussion

FT-IR analysis

The FTIR spectra of PMoV, 0.7% PMoV/TiO_2, 1.2%PMoV/TiO_2, 1.7% PMoV/TiO_2, 2.2% PMoV/TiO_2 are shown in Figure 1. The main characteristics bands of Keggin structure are found in the range of 500-1550 cm^{-1} related to stretching vibrations of (P-O_a), (Mo-O_d), (Mo-O_b-Mo), (Mo-O_c-Mo) bands.[21-23] The bands at 1055-1100 cm^{-1} is due to P-O. The band at 1000-900 cm^{-1} is assigned to Mo-O stretching. The 980 cm^{-1} is for V-O and 900-700 cm^{-1} may be due to Mo-O-Mo. Calcination of the catalyst does not lead to the disappearance of these bands. In fact TiO_2 shows intense and broad vibration peaks originated from Ti-O-Ti located at lower wave number 900 cm^{-1}. Vanadium substituted molybdophosphoric acid supported on titania shows two shoulders corresponding to the P-O vibration at 1068 cm^{-1} and V-O_t at 959 cm^{-1}. This confirms the presence of V^{5+} inside the Keggin unit.[24]

After impregnation of different wt % of vanadium substituted molybdophosphoric acid on the titania support, it is observed that the bands are shifted towards lower wave number region. For supported vanadium containing catalysts, practically no change is observed in the IR bands of P-O and Mo-O stretching modes. The higher wave number of the characteristic bands of the heteropoly anions is found to be broadened after supporting on titania. The IR spectra revealed that the vibration spectra of the heteropoly compounds with Keggin structure depend on the nature of metal incorporated into it. Hence from the IR spectra, it can be concluded that V-Mo-P are indeed incorporated into Keggin units. The absorption band at about 3200-3300 cm^{-1} is stretching vibration of -OH and 1600-1700 cm^{-1} bending of -OH due to molecular and protonated water respectively.

XRD analysis

The X-ray diffraction profiles of different wt% of PMoV supported with titania are presented in Figure 2. Strong peaks of anatase phase TiO_2 is detected in all the XRD spectra. Only small intense peak from the supported Keggin ions are observed in the spectra[25]. Whereas 2.2% PMoV/TiO_2 contains small intense peak indicating the presence of rutile phase that leads to loss of surface area as confirmed by BET surface area analysis.[26]

N_2 adsorption-desorption

Nitrogen adsorption-desorption isotherms of TiO_2, 0.7% PMoV/TiO_2, 1.2% PMoV/TiO_2, 1.7%PMoV/TiO_2, and 2.2% PMoV/TiO_2 are summarized in Table 1. The specific surface area of TiO_2 is 44.05 m^2/g and it decreases with an increase in loading of PMoV. The surface area is observed to decrease from 41.46 m^2/g to 31.06 m^2/g with increase in PMoV loading from 0.7 wt% to 2.2 wt%. This may be due to the fact that PMoV molecules block the pores on the titania surface[27].

TG-DTA analysis

The TGA-DTA profile of 0.7 % PMoV/TiO_2, 1.2 % PMoV/TiO_2, 1.7 % PMoV/TiO_2, 2.2 % PMoV/TiO_2 catalysts are presented in Figure 3. There are two distinct stages of weight loss in the catalyst. All the TGA profile showed weight loss between 50-160^oC corresponding to desorption of physically adsorbed water i.e., elimination of water of crystallization which binds the Keggin unit in the primary structure forming water bridges [28, 29]. From the TGA curve, it is worthwhile to mention that the catalyst is stable up to 590 ^oC may be due to the presence of titania. The peak intensity appears to be proportional to the content of titania. The endothermic peak between 500-590^oC of DTA curve indicates the removal of residual sulphate and phosphate from titania.

NH_3 -TPD

The total acidity of PMoV supported catalysts were evaluated by NH_3-TPD measurements. The quantity of acidity present in different wt% of PMoV supported on TiO_2 are given in Table 1. The TPD profiles of 1.2% PMoV/TiO_2 (a), 1.7% PMoV/TiO_2 (b), 2.2% PMoV/TiO_2 (c) are shown in Figure 4. There are three temperature zones associated with the acid strength (weak, medium and strong) which can be distinguished according to literature.[30, 31] Titania supported heteropoly acids calcined at 450 ^oC showed a broad desorption peak at 140-280^oC. The low temperature desorption peak at about 100^oC corresponds to weak acid sites while the high temperature broad desorption peak that appear at 400-500 ^oC could be due to strong interaction of ammonia with well dispersed 1.7%PMoV on titania. The strong acid site present in 1.7 wt% of PMoV/TiO_2 catalyst is shown in Figure 4(c).

TPR

The H_2 -TPR spectrum of 1.7 % PMoV/TiO_2 sample is shown in Figure 5. The sample revealed a single broad reduction peak at 600^oC indicating that the reduction of free metal oxides is formed by the partial decomposition of Keggin ion during temperature programmed reduction. The broad reduction peak ascribed to the reduction of segregated vanadium oxide species. The substitution of molybdenum by V atom in the Keggin ion does not have a pronounced effect of destabilization of the Keggin unit. This is an interesting observation that V can change its oxidation state from V^{+5} to V^{+4} without destabilising the Keggin ion.[25]

SEM analysis

The SEM image of TiO_2 and 1.7 % PMoV/TiO_2 are shown in Figure 6(A) and (B). The Figure 6(A) suggests that the mesoporous titania heated at 600 ^oC have well-ordered tiny particle. After impregnation with 1.7% PMoV over titania support, the surface morphology of the catalyst 6(B) has changed. It showed agglomerated irregular shaped crystalline structure indicating the reduction of tetragonal symmetry due to the incorporation and dispersion of Keggin unit over the surface of the support. No significant morphological changes in the SEM micrograph occurred for the deactivated sample 6(C). Hence the material is highly stable for ammoxidation reaction.

EDX spectra

EDX investigation was performed on fresh and used 1.7 % PMoV/TiO_2 sample to get information regarding surface composition of the active components as shown in figure 7 (A) and (B). The spectra of the catalyst suggest the presence of various elements like Ti, Mo, V, P and O in appropriate proportion. Hence, EDX analysis confirms the incorporation of heteropoly compounds on the surface of titania.

TEM analysis

The TEM images at magnification of (a) 50 nm of 1.7 % PMoV/TiO_2 is shown in Figure 8. From the image, it is clear that the material exhibits spherical morphology with average particle size 175-185 nm. The Keggin Units are well dispersed over the surface of the support material.

Catalytic activity

Very few studies were carried out on ammoxidation of m-xylene using vanadium substituted heteropoly acid as catalyst. Lee et al reported vanadia/titania xerogel catalyst for ammoxidation of m-xylene which gave 70% yield of IPN.[32] But the inherent disadvantages of the reaction were high NH_3 ratio, low yield and decreased catalytic activity. Cavani[33] reported that the substitution of one or more molybdenum atoms by V in the primary structure of molybdophosphoric acid leads to the enhancement of the oxidation potential of heteropoly acid

(HPA) due to the vanadium reducibility. So, vanadium may act as a structural promoter in the catalyst precursor facilitating the formation of the active Mo-O-V surface species.[34, 35] Due to the structural flexibility and redox capability of vanadium, it may facilitate the direct participation of V in the activation of gas phase oxygen, ammonia and m-xylene on the active sites of the catalyst. Another important aspect of the titania support is that it is capable of releasing oxygen from the surface due to mobility of lattice oxygen and to form oxygen vacancies at relatively mild conditions.[31] We have carried out ammoxidation of m-xylene over a series of PMoV supported TiO_2 catalysts. Among them 1.7 % PMoV/TiO_2 catalyst gave 88.6 % conversion. As water is one of the by-products, its presence enhances the stability of the catalyst because it can favour the surface reconstruction of heteropolyacids supported on titania during the reaction.[33]

Preliminary experiments showed that no ammoxidation reaction takes place in vapour phase in the absence of any catalyst. This reaction was then carried out using different wt% of vanadium substituted molybdo phosphoric acid supported titania (Figure 9). From figure 9, it is evident that from lower to higher wt% (0.7 -1.7) PMoV/TiO_2, both the conversion and yield increases. At higher wt% (2.2%) of PMoV supported on TiO_2, the conversion and yield decreases. This may be due to the first observation that the nitrile yield is found to be dependent on PMoV loading. Secondly, it is strongly dependent on acid strength. High acid strength of 1.7 wt% PMoV supported materials resulting in high yield of IPN is due to enhancement of adsorption capacity of ammonia. The high value of IPN yield obtained on 1.7% PMoV/TiO_2 might be due to the manifestation of reduction of V^{+5} to V^{+4} when it is present in the Keggin frame work. Apparently at temperature above 425°C the oxygen coordinated to the active site of the catalyst can be easily exchanged and can participate in partial oxidation reactions.

As shown in Scheme 1, a pathway is proposed for this reaction. The key step in this proposed mechanism involves the formation of a carbanion intermediate from m-xylene by abstraction of a proton by hetero polyanion(HVPOM) ion. The subsequent steps involve the oxidation followed by rearrangement of the carbanion intermediate. Then after interaction with NH_3 with the intermediate, it is converted to IPN. In this Scheme 1, only one $-CH_3$ group has been shown to be converted to –CN group and same type of mechanism holds good for the other $-CH_3$ group.

Effect of temperature

The promotional effect of temperature of reaction has been investigated at six different temperatures (350, 375, 400, 425 and 450 °C) keeping the other parameters fixed (Figure10). It is observed that the conversion (42.9 % to 88.6%) and yield (41.6% to 85.4%) increases with increasing temperature from 350 to 425 °C. After that, a decrease in the conversion of m-xylene and yield of IPN is observed.

Reusability of the catalyst

Reusability is one of the important aspects of heterogeneous catalyst, which provides useful information about the recycling capacity during the catalytic cycles. The catalyst with 1.7% loading was used for recycling experiments. In order to regenerate the catalyst after completion of reaction, air is passed over the catalyst at $450^{o}C$ for 3 h. The regenerated catalyst was used for further run in the ammoxidation of m-xylene. As shown in Figure 11, the yield decreased to 78 % in the regenerated catalyst after 20 cycles. The activity loss observed with the regenerated catalyst may be due to reduced vanadium species as well as carbonaceous surface deposition on the catalyst during reaction.[11]

Conclusions

The vanadium substituted molybdophosphoric acid (PMoV) supported on TiO_2 exhibited excellent catalytic activity for ammoxidation of m-xylene using very low feed ratio of ammonia. Among all the catalysts, the one with 1.7 wt% PMoV/TiO_2 showed the highest conversion (88.6 %) and yield (85.4 %) of isophthalodinitrile. The high activity and selectivity of the catalyst might be due to synergistic effect of high acid sites, presence of anatase phase of TiO_2 and well dispersion of the PMoV over the support. FTIR, XRD and EDX showed the incorporation of vanadium in the Keggin unit of PMoV. The yield of IPN is found to be dependent on PMoV loading. The reusability test exhibits a good recycling capacity of the PMoV supported on TiO_2.

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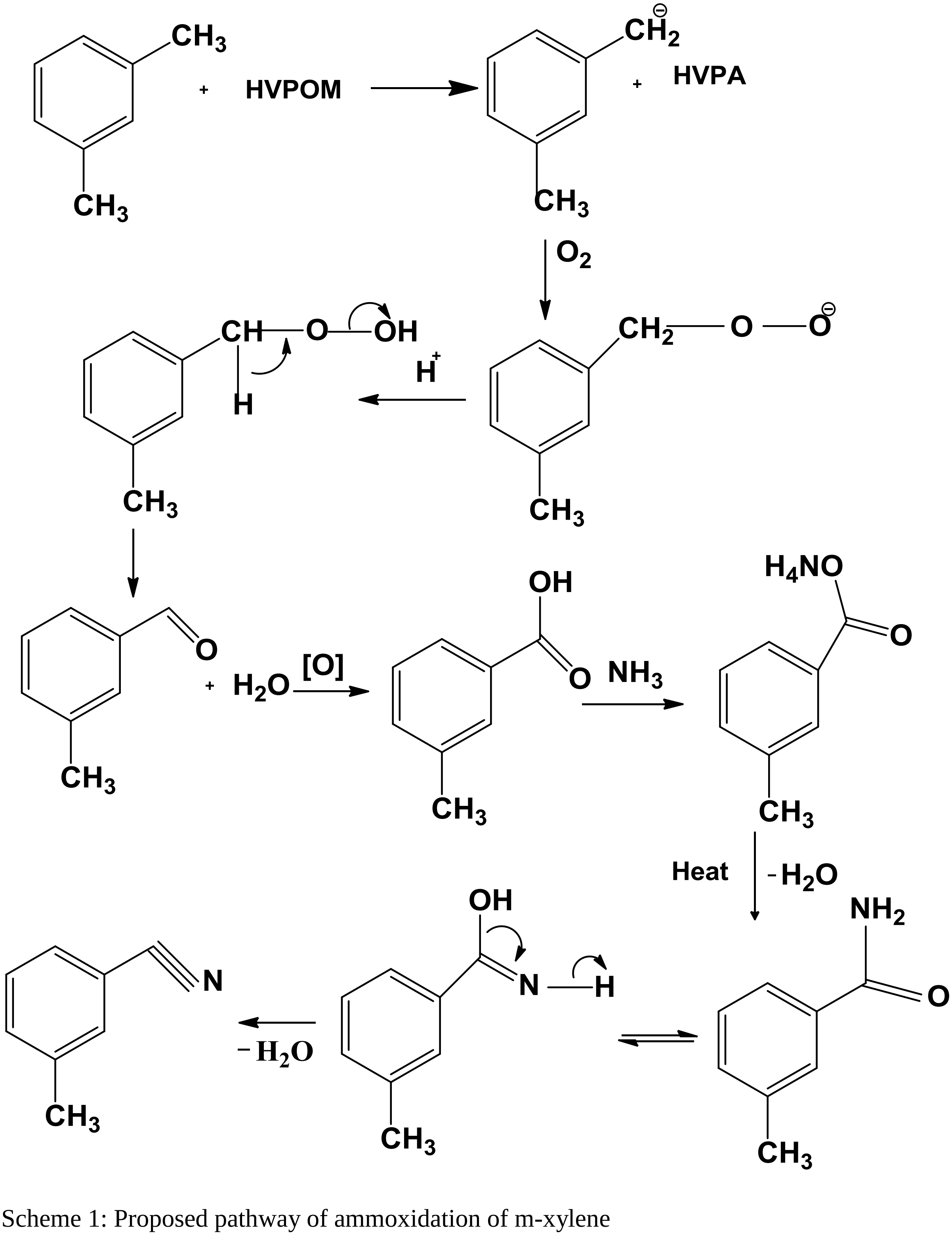
Table 1: BET surface area and NH_3-TPD of different wt% of PMoV/TiO_2 catalysts

Sl No	Catalyst	Surface area (m^2/g)	Acidity (µmole/g)
1	TiO_2	44.05	-
2	0.7 % PMoV/TiO_2	41.46	624.6
3	1.2 % PMoV/TiO_2	41.22	718.7
4	1.7 % PMoV/TiO_2	31.69	805.3
5	2.2 % PMoV/TiO_2	31.06	742.3



Scheme 1: Proposed pathway of ammoxidation of m-xylene

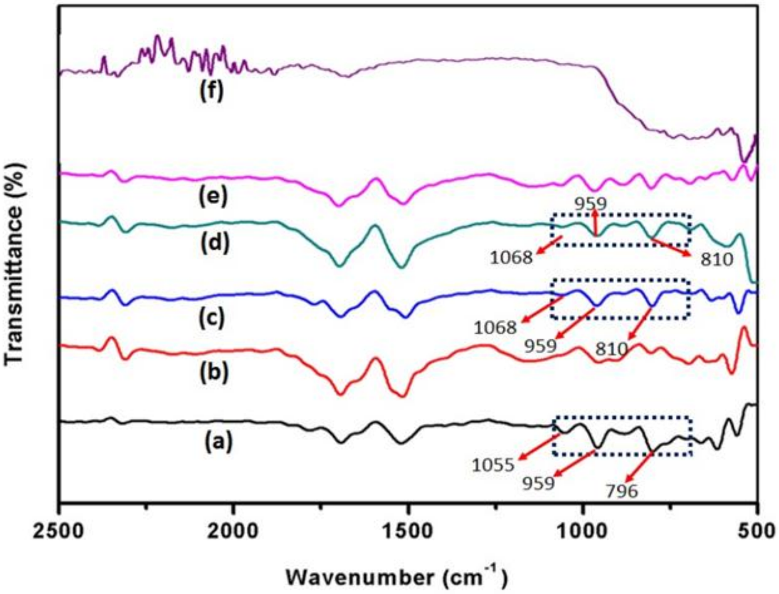


Figure 1: FT-IR Spectra of (a) PMoV (b) 0.7% PMoV/TiO$_2$ (c) 1.2% PMoV/TiO$_2$ (d) 1.7% PMoV/TiO$_2$ (e) 2.2% PMoV/TiO$_2$ and (f) TiO$_2$

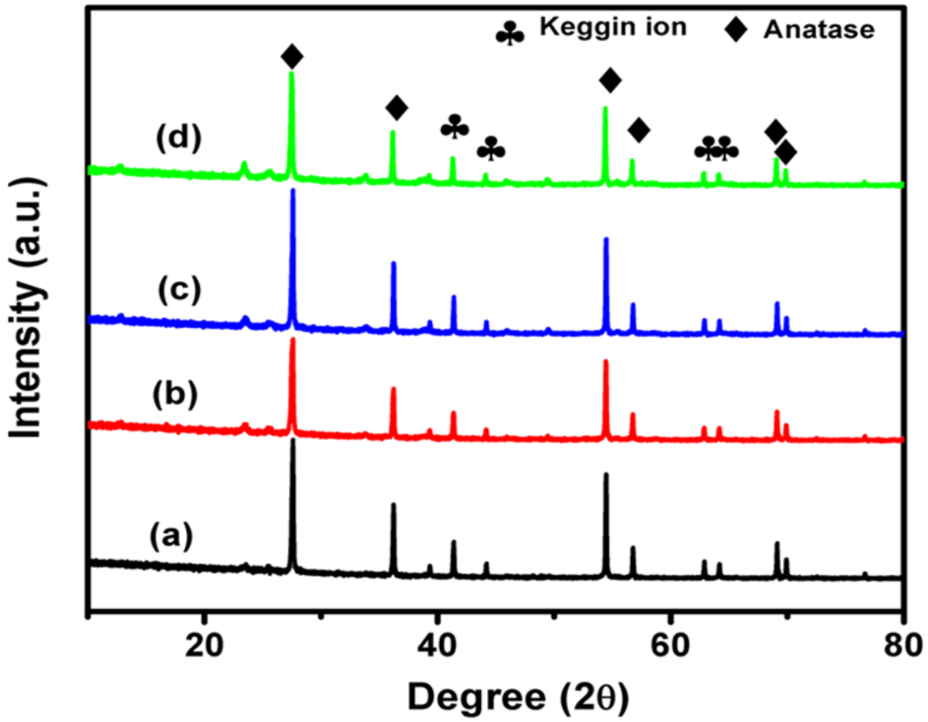


Figure 2: High angle XRD of (a) 0.7% PMoV/TiO_2 (b) 1.2% PMoV/TiO_2 (c) 1.7% PMoV/TiO_2 and (d) 2.2% PMoV/TiO_2

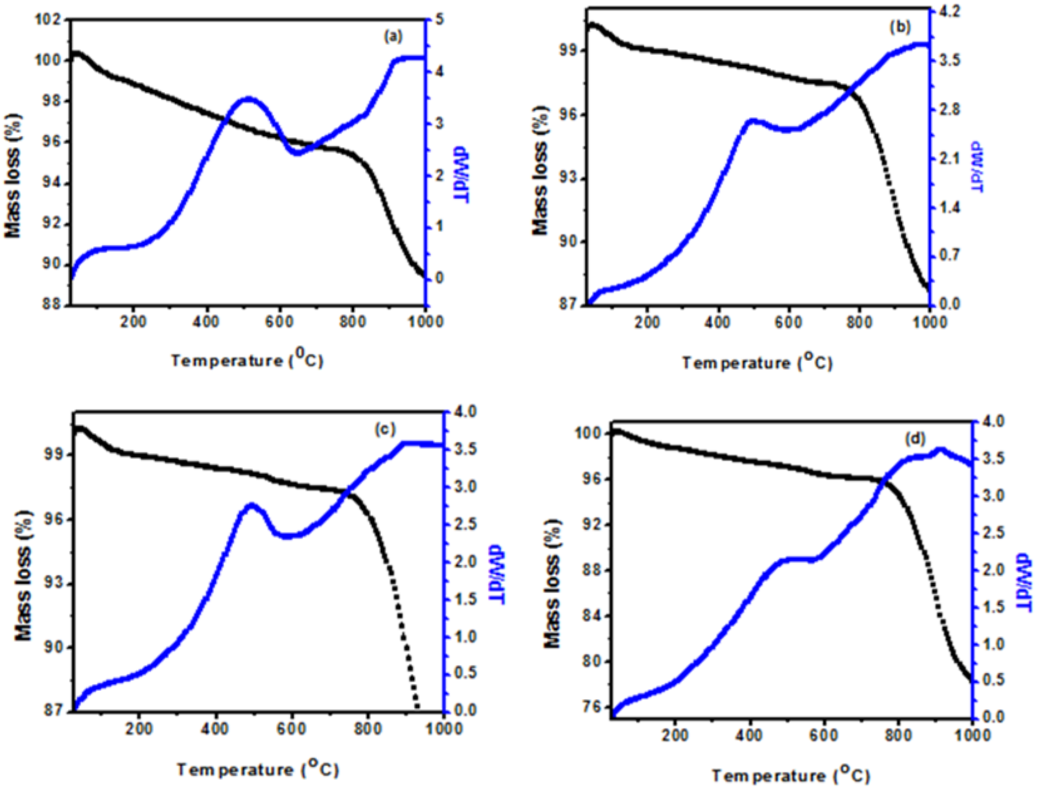


Figure 3: TG-DTA spectra of (a) 0.7% PMoV/TiO_2 (b) 1.2% PMoV/TiO_2 (c) l 1.7% PMoV/TiO_2 and (d) 2.2% PMoV/TiO_2.

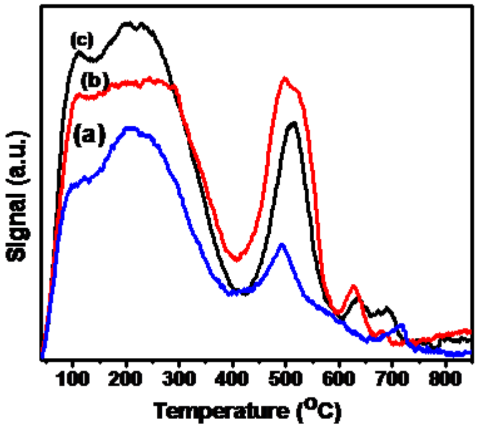


Figure 4: NH_3-TPD of (a) 1.2%PMoV/TiO_2, (b) 1.7% PMoV/TiO_2 and(c) 2.2% PMoV/TiO_2

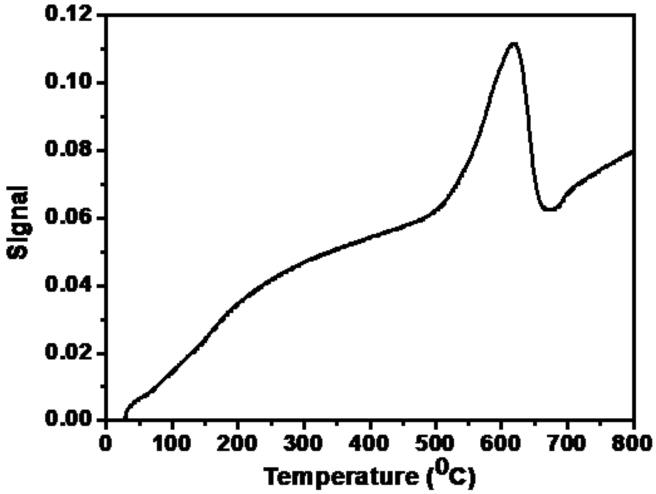


Figure 5: TPR spectra of 1.7 % PMoV/TiO_2.

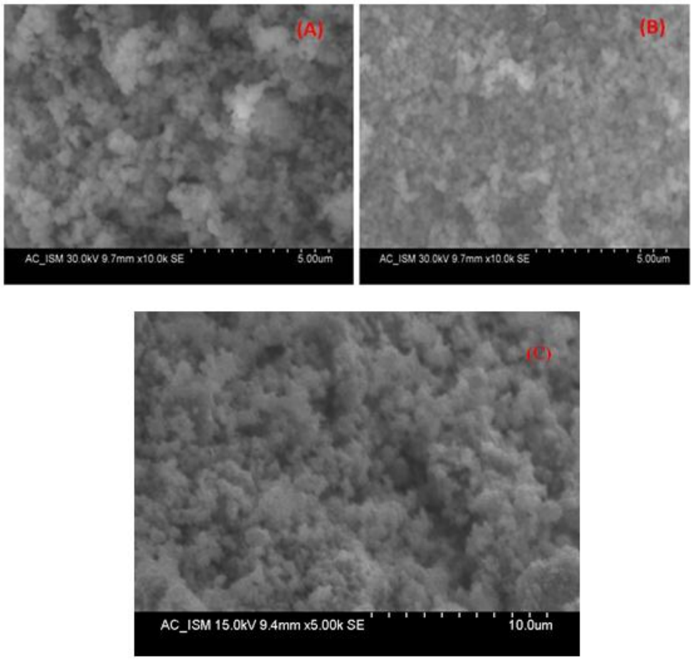


Figure 6: SEM image of (A) pure mesoporous TiO_2calcined at 600°C, (B) 1.7 % PMoV/TiO_2 and (C) Deactivated sample of 1.7 % PMoV/TiO_2.

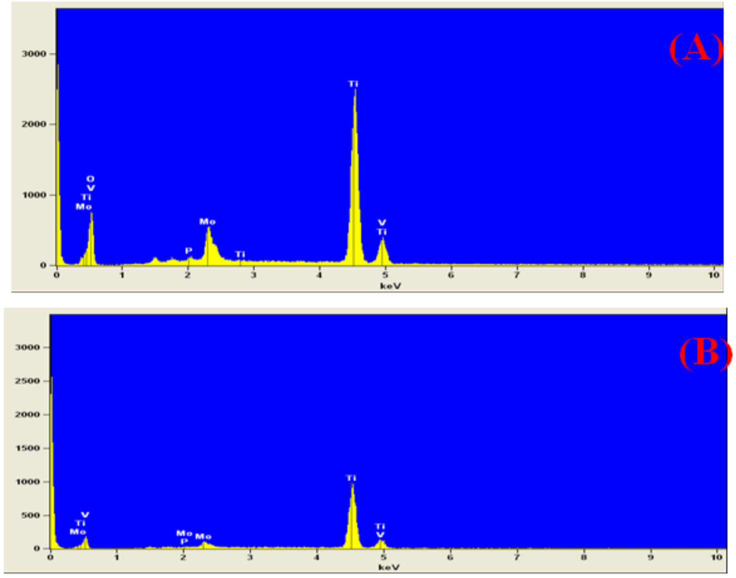


Figure 7: EDX spectra of (A) activated 1.7 % PMoV/TiO_2 sample and (B) deactivated 1.7 % PMoV/TiO_2 sample.

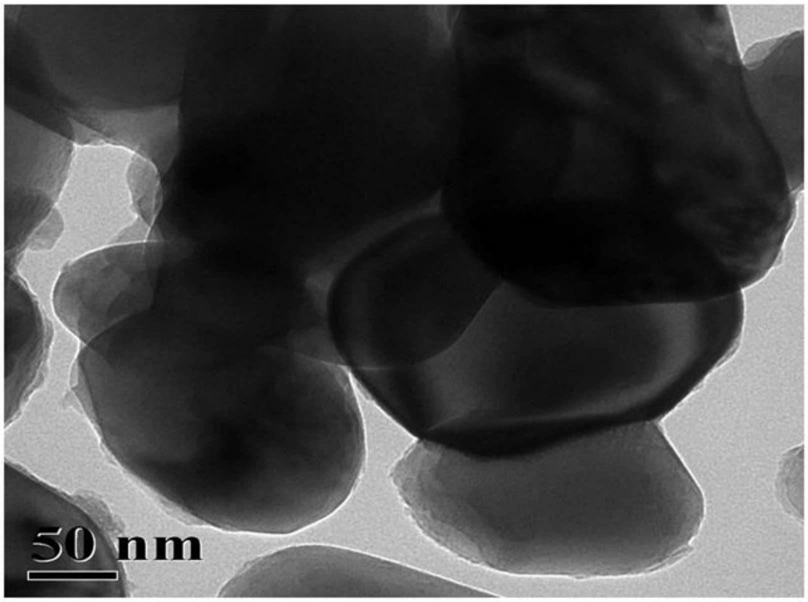


Figure 8: TEM image of 50 nm of 1.7 % PMoV/TiO_2 sample.

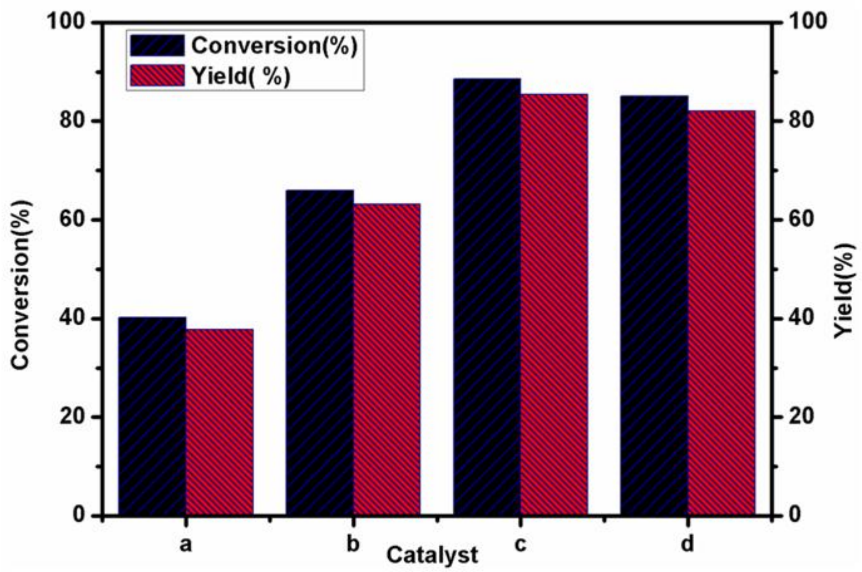


Figure 9: Ammoxidation of m-xylene over (a) 0.7% PMoV/TiO_2, (b) 1.2% PMoV/TiO_2, (c) 1.7% PMoV/TiO_2 and (d) 2.2% PMoV/TiO_2.

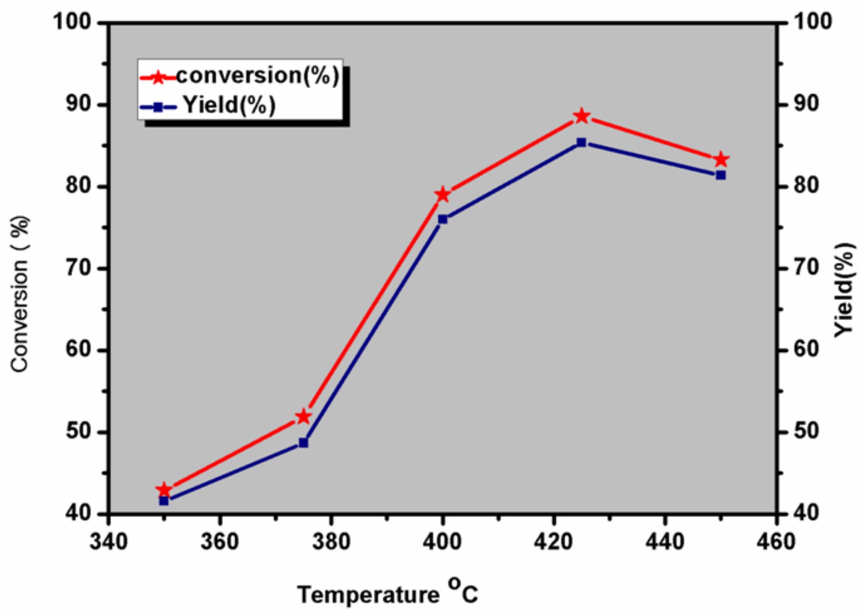


Figure 10: Effect of temperature on the conversion and yield over 1.7% PMoV/TiO_2 catalyst.

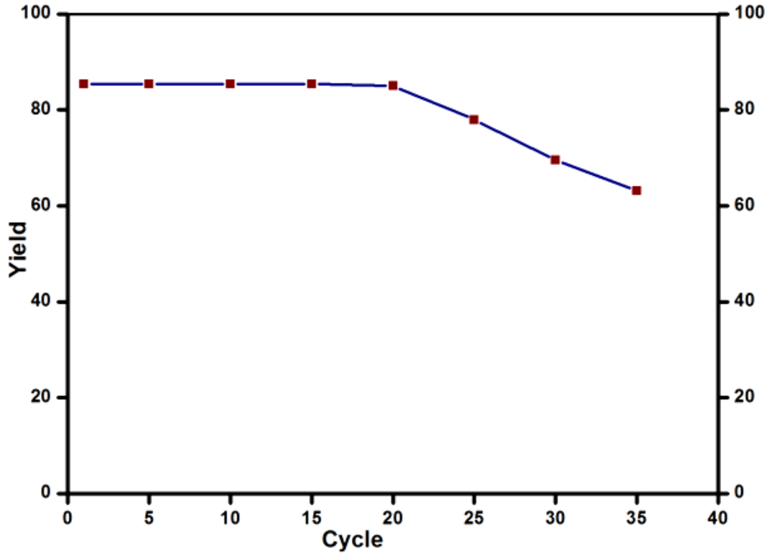


Figure 11: Effect of yield of isophthalonitrile with respect to number of cycle over 1.7 wt% PMoV/TiO_2 catalyst