A Versatile VMPO Catalyst Prepared In Situ for Oxidative Ammonolysis of Isomeric Picolines and Xylenes

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Abstract—The V₂O₅–MoO₃–P₂O₅ (VMPO) catalyst has been prepared in situ by thermal decomposition of vanadomolybdophosphoric acid (PMoV) on TiO₂ support at 475°C. The TiO₂ supported VMPO catalysts are characterized by FT–IR, XRD, BET surface area, NH₃–TPD, and H₂–TPR. Morphology of the catalyst has been studied by TEM. The accumulated data indicate decomposition of PMoV and presence of phosphate and pyrophosphate phases of molybdenum and vanadium after calcination. TPD and TPR studies exhibit the moderate acidity and presence of V⁴⁺ in the material, respectively. The VMPO catalyst has been used for ammoxidation of six different compounds including three isomeric picolines and three isomeric xylenes to the corresponding nitriles with the yield of 90–96%.

Keywords: picoline, xylene, VMPO, oxidative ammonolysis, nitrile

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INTRODUCTION

Vapour phase ammoxidation is one of the prospective routes for production of a number of important chemicals used in industry [1, 2]. The major advantage of that method over conventional ones is combining several stages into a single process of catalytic vapour phase ammoxidation. Also the reagents involved are inexpensive air/O₂ and NH₃, and the reaction is carried out under the atmospheric pressure.

Earlier ammoxidation of 3-picoline to 3-cyanopyridine was carried out under catalysis by VZrAlON [3]. Some other catalytic systems were also used for promoting ammoxidation of various organic compounds [4–7]. The catalysts containing V_2O_5 in combination with MoO₃ and P_2O_5 were particularly efficient in ammoxidation reactions [7]. The catalytic properties of V_2O_5 depended on the methods of its preparation. According to Ray et al. [7], V₂O₅ prepared from vanadyl oxalate was more efficient than that prepared from ammonium metavanadate. In our earlier research the effect of high content of MoO₃ in V₂O₅-MoO₃-P₂O₅ (VMPO) catalyst had been studied [8]. VMPO prepared from vanadyl oxalate, ammonium heptamolybdate and orthophosphoric acid gave 96% yield of pyridine 3-carbonitrile upon ammoxidation of 3-picoline.

In the present study, TiO_2 supported VMPO catalyst was prepared from a precursor vanado-molybdophosphoric acid by a relatively uncomplicated method. The VMPO catalyst was used for ammoxidation of six different compounds including three isomeric picolines and three isomeric xylenes to corresponding nitriles. The catalytic systems of the type were characterized by different techniques in order to correlate their catalytic activity.

RESULTS AND DISCUSSION

 N_2 adsorption-desorption. The Brunauer-Emmett-Teller (BET) surface area was measured by N_2 adsorption on the surface of catalysts VMPO-10, VMPO-20, VMPO-30, VMPO-40, and TiO₂ support (Table 1). The

Table 1. BET surface area and acidity of catal	yst	S
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Catalyst	Surface area, m ² /g	Acidity, µmol/g
TiO ₂	73	63.06
VMPO-10	69	68.74
VMPO-20	62	71.80
VMPO-30	59	67.50
VMPO-40	48	64.30



Fig. 1. FT-IR spectrum of PMoV.

surface area of TiO₂ was 73 m²/g and it decreased from 69 to 48 m²/g with increase in VMPO loading from VMPO-10 to VMPO-40 which could be attributed to blocking of pores on the surface of TiO₂ by VMPO molecules [9].

FT-IR. The main characteristics bands of PMoV (Fig. 1) [10-12] were observed in the region of 500-1550 cm⁻¹. FT-IR spectra of calcined VMPO-10, VMPO-20, VMPO-30, and VMPO-40 catalysts and TiO₂ (Fig. 2) exhibited a shift and broadening of the bands. Absence of main characteristics bands in the supported samples indicated decomposition of Keggin structure over the support. The band at 960 cm⁻¹ were attributed to V⁴⁺=O of vanadium pyrophosphate supported by XRD. The band at 989 cm⁻¹ corresponded to Mo=O chain. The bands at 1212-1220 and 1356-1370 cm-1 were assigned to symmetric and asymmetric stretching vibrations of the phosphate groups. This result indicated decomposition of Keggin ion of vanado-molybdophosphoric acid over TiO₂ after calcination. The broad and weak band at 800–489 cm⁻¹ could be attributed to Ti–O–Ti.

XRD analysis. The X-ray diffractograms of the catalysts (Fig. 3) $[2\theta = 23.33^\circ, 27.26^\circ, 27.32^\circ, 27.34^\circ (JCP-DS-832388)]$ demonstrated the presence of $(VO)_2P_2O_7$ along with MoOPO₄ phases [12, 13]. A very small peak at $2\theta = 41.18^\circ$ (JCPDS-821031) indicated presence of the active Mo(PO₃)₃ phase which was supported by the peaks at $2\theta = 45.89^\circ$ and 49.30° . Probably the low concentration of phosphorus oxides in the catalyst was responsible for formation of the intermediate phosphate. Typically, phosphorus oxide enhanced stability of a cat-



Fig. 2. FT-IR spectra of (*1*) VMPO-10, (*2*) VMPO-20, (*3*) VMPO-30, (*4*) VMPO-40, and (*5*) TiO₂.

alyst. So, activity of the material increased appreciably due to the presence of vanadium and molybdenum pyrophosphate and phosphate, respectively. Probably slight shifting occurred in each spectrum due to enhancement of different wt % of VMPO loading on TiO_2 (the anatase form).

TGA analysis. The TGA profiles (Fig. 4) demonstrated weight loss in the range of room temperature to 450°C indicating two distinct stages. In the first stage between room temperature and 155°C loss of adsorbed water (i.e. <5%) took place. The second stage at above 155°C indicated the weight loss of water of crystallisation that bound the Keggin unit closely in the secondary



Fig. 3. XRD pattern of (*1*) VMPO-10, (2) VMPO-20, (3) VMPO-30, (4) VMPO-40, and (5) TiO₂; (*I*) Anatase, (*II*) Mo(PO₃), (*III*) MoOPO₄, and (*IV*) (VO₂)P₂O₇.

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Fig. 4. TGA profiles of (a) VMPO-10, (b) VMPO-20, (c) VMPO-30, (d) VMPO-40.

structure of heteropoly acid (water bridges). The weight loss between 155 and 455°C indicated that PMoV was hydrated with 28 molecules of water [14–18].

 NH_3 -TPD analysis. Pure TiO₂ demonstrated three desorption peaks (Fig. 5) at 106, 332, and 604°C associated with weak, medium and strong acidity, accordingly [19–21]. The catalyst acidity increased with simultaneous increase in strong acid sites. Upon further increase of acidity (VMPO-30 and VMPO-40), it decreased from strong acid site to moderate acid sites over it (Table 1).

 H_2 -TPR analysis. In VMPO-10 and VMPO-20 (Fig. 6) two reduction peaks at 460 and 770°C correspond to reduction of V⁵⁺ to V⁴⁺ species [22]. One broad peak recorded for VMPO-30 and VMPO-40 indicated the presence of V⁺⁴ in the active phase of (VO)₂P₂O₇ which was confirmed by XRD.

TEM. The TEM images of VMPO-30 demonstrated the spherical morphology with average particle size 170–180 nm.

ESR spectra. At room temperature ESR spectrum of VMPO-30 consisted of a peak of 35 G width centered at 336.823 mT. The broad isotopic signal with g = 1.9037 indicated presence of V⁴⁺ ions characterized by unpaired 3d electrons of s = 1/2 with nuclear spin I = 7/2.

Catalytic activity. Study of ammoxidation of 2-, 3-, and 4-picoline as well as o-, m- and p-xylene was carried out using VMPO-10, VMPO-20, VMPO-30, and VMPO-40 catalysts (Figs. 7, 8). With increased PMoV loading, conversion of initials and yield of products increased from VMPO-10 to VMPO-30 and then marginally decreased with VMPO-40, indicating that nitrile yield was dependent on VMPO loading. The VMPO-30 catalyst demonstrated the most efficient catalytic activity. The low catalytic functionality of VMPO-10 and VMPO-20 was attributed to low availability of active phases. The higher yield of nitrile on VMPO-30 catalyst could be due to the presence of V4+ [23]. The important feature of the TiO₂ support was its interaction with the active phases of phosphates and pyrophosphates of vanadium and molybdenum (oxygen release) [24].



Fig. 5. NH₃–TPD profiles of (*1*) TiO₂, (*2*) VMPO-10, (*3*) VMPO-20, (*4*) VMPO-30, and (*5*) VMPO-40.

It is evident that pyrophosphates of vanadium and phosphates of molybdenum found in the calcined VMPO catalysts influenced on ammoxidation. The small concentration of phosphorus oxides in the catalysts was the source of phosphates and pyrophosphate phases, and also the minimum amount of vanadium was essential for the increase of the catalytic activity in the course of ammoxidation. Hence, the highest activity of the catalyst VMPO-30 was due to presence of the phosphate and pyrophosphate phases of Mo and V [25].

The VMPO-30 demonstrated the superior and effective interactions between the support and its active phases which was in accord with XRD results.



Fig. 7. Ammoxidation of isomeric picolines on VMPO-10–VMPO-40 (conv—conversion, pic—picoline, cp cyanopyridine).



Fig. 6. H₂-TPR profiles of (*1*) VMPO-10, (*2*) VMPO-20, (*3*) VMPO-30, and (*4*) VMPO-40.

Ammonia acted as a proton acceptor for the intermediate compounds of the process, provided nitrogen atoms in formation of amide, nitrile and also acted as a regulator of the rate and degree of oxidation reaction of organic materials. Conversion of feed materials decreased as ammonia concentration was increased. Generally ammonia reduces the overall rate of oxidation of hydrocarbons and their oxygen derivatives [26].

Effect of temperature. The effect of reaction temperature on the ammoxidation of isomeric 2-, 3-, and 4-picoline and *o*-, *m*-, and *p*-xylene was studied with VMPO-30 catalyst. With the reaction temperature increase from 375 to 425°C, both conversion of feed ma-



Fig. 8. Ammoxidation of isomeric xylenes on VMPO-10–VMPO-40.

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Fig. 9. Experimental set up for catalytic ammoxidation reaction. (MFC) mass flow controller; (TE) temperature element; (wc) water condenser; (GLS) gas liquid separator, (GC) gas chromatograph.

terials and yield of the corresponding nitriles increased. At temperature >425°C conversion and yield decreased.

Conversion of picolines and xylenes could be listed in the order of 4-picoline > 2-picoline > 3-picoline and p-xylene > o-xylene > m-xylene at 425°C on VMPO-30 catalyst.

XRD of the used catalyst. XRD study of the used VMPO-30 catalyst after 25 cycles of the process revealed presence of the following phases: Anatase (TiO₂), Rutile (TiO₂) and Vanadium Molybdenum Oxide (V₂MoO₈). The anatase phase was converted to rutile phase, and different phosphates and pyrophosphates of molybdenum and vanadium were also converted to vanadium molybdenum oxide phases. Hence, decrease in the conversion of the feed material could be due to the absence of different phosphates and pyrophosphates of molybdenum and vanadium.

EXPERIMENTAL

Preparation of the catalyst. Vanado-molybdophosphoric acid; $H_4PMo_{11}VO_{40}$ (abbreviated as PMoV) was prepared according to the reported procedure [27]. In brief, 3.05 g of sodium metavanadate was dissolved in 100 mL of boiling water, and 3.55 g of disodium hydrogen phosphate was dissolved in 100 mL of distilled water separately. Both solutions were mixed together and cooled down. Then the mixture was acidified with 5 mL of concentrated H_2SO_4 till the colour of the solution changed to cherry red. To this mixture, 66.5 g of sodium molybdate dissolved in 100 mL of water were added. Finally, 45 mL of concentrated sulphuric acid were added slowly with continuous stirring accompanied by change in colour from cherry red to light red. The PMoV was then extracted with 200 mL of diethyl ether. After separation of the oily (middle) layer, stream of the air was passed to make it ether free. The solid that settled down was dissolved in water, concentrated to the first appearance of crystals in a desiccator over concentrated H₂SO₄, then allowed to crystallize further and dried. Then a series of PMoV supported on TiO₂ (Aldrich make heated at 500°C for 3 h) catalysts were prepared in situ by varying the wt % of PMoV from 10 to 40%. The required quantity of PMoV was dissolved in minimum amount of water and the solution was added to the known amount of TiO₂ with constant stirring. Excess water was removed on a hot water bath, and the catalyst masses were dried in an air oven at 120°C for 8 h. Then the catalysts were calcined at 500°C for 2 h. Finally, catalysts were sized to 14-18 mesh. The catalysts were referred to as VMPO-10, VMPO-20, VMPO-30, and VMPO-40 corresponding to 10, 20, 30, and 40% PMoV respectively.

Physico-chemical characterization. FT-IR (KBr) spectra were recorded on a Varian FTIR-800 spectrophotometer. X-Ray diffraction spectra were measured in the range of 10° to 70° at a rate of 1.5 deg/min (Philips analytical 3710) using CuK_{α} radiation. The Brunauer–Emmett-Teller surface areas were measured by N2 adsorption on the surface of the prepared catalyst at -196°C using a Tristar 3000 surface area analyser (Micromeritics, USA). The known amount of a catalyst sample was evacuated for 3 h at 150°C to remove the physically adsorbed water. The acid character of the catalysts was studied by temperature programmed desorption (TPD) of NH₃ in a Chemisorb 2720 (Micromeritics, USA). About 1 g of the powdered sample contained in a quartz tube was heated at 250°C for 3 h upon Ar flow. After cooling the sample to room temperature, NH_3 (0.4%) NH₃ balanced in He) gas was passed over the sample to clean the surface of the catalyst. Then analysis of the sample was carried out upon helium flow with heating rate 10°C/min and heated up to 900°C. The temperature programmed reduction with H₂ of the prepared catalyst was carried out in an AutoChem-II (Micromeritics, USA) instrument. TGA was used to measure the weight loss of the synthesized catalyst in the air atmosphere with a STA449 F3 Jupiter Thermo Gravimetric Analyser system at the rate of 5 deg/min. Transmission electron micrograph (TEM) images of catalysts were taken by using a TECNAI-G2 microscope with charge coupled camera.

Activity studies. Ammoxidation of three isomeric picolines and three isomeric xylenes was studied in a fixed bed continuous flow glass reactor (Fig. 9) under atmospheric pressure. The reactor was packed with 10 g of catalyst between two layers of porcelain beads. The upper layer of the porcelain beads served dual purpose as a pre-heater and mixer for the reactant. Before the reaction, ammonia gas was fed to catalyst bed at the rate of 50 mL/min at 450°C for 1 h. Then molar ratio of feed: ammonia: air (1:3:6) was introduced into the reactor. The system temperature was measured by a thermocouple. The reactions were performed in the temperature range of 375-450°C for 2 h. The liquid product was trapped at 0°C. The products were analysed by gas chromatography (GC), using carbowax 20 M column with a thermal conductivity detector (TCD).

CONCLUSIONS

 TiO_2 Supported VMPO prepared by thermal decomposition of PMoV has been found to be a versatile catalyst. VMPO-30 Demonstrated the highest catalytic activity for ammoxidation of three isomeric picolines and three isomeric xylenes which could be due to the presence of different well dispersed phases of vanadium pyrophosphates and molybdenum phosphates.

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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