

Tuning the surface composition of novel metal vanadates and effect on their catalytic performance

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1. Catalyst Preparation

The preparation of bulk metal vanadate catalysts involves two steps. In the first step, the requisite quantities of appropriate metal nitrate salts were dissolved in distilled water, to which desired amount of citric acid (mole ratio of metal : citric acid = 3 : 1) was added and then the mixture was stirred at room temperature until clear solution is obtained. In the 2nd step, the required amount of NH₄VO₃ (AMV) was taken in distilled water and calculated amount of oxalic acid (OA) was added to it (mole ratio of AMV : OA = 1 : 1.5). The above solution was then heated to 60 °C on a hot plate and then kept the solution at same temperature 10 minutes under stirring. The vanadium solution turned to dark blue after the addition of oxalic acid. Afterwards, the above vanadium-oxalic acid solution was added drop wise to the metal-citric acid solution at 60 °C with constant stirring. After complete addition, the mixture was heated to 80 °C and then slowly evaporated to dryness on a hot plate. The solid thus obtained was further dried at 110 °C for 16 h in an oven. Finally, the samples were calcined in air (4 l/h) under the suitable conditions (see Table S1). Using the same procedure, five different metal vanadate catalysts were prepared. The composition of such catalysts and the atomic ratios of metal to vanadium are given in Table S1.

2. Catalyst Characterisation

ICP-OES (Optima 3000XL, Perkin-Elmer) using a microwave pressure digestion (MDS 200; CEM) with hydrofluoric acid and aquaregia at 9 bar was used to analyse the chemical composition of fresh and spent catalysts. Surface areas (BET) of the catalysts were determined on NOVA 4200e instrument by N₂-physisorption at -196 °C. The X-ray diffraction (XRD) patterns were obtained on a X-ray diffractometer STADIP (Stoe, Darmstadt, Germany) using Ni-filtered CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$). The X-ray photoelectron spectroscopic (XPS) measurements were done with a VG ESCALAB 220iXL unit using MgK_α radiation ($E = 1253.6 \text{ eV}$) at a base pressure of the UHV chamber. The C1s binding energy of 284.6 eV was used as a reference for determining the binding energies.

3. Catalytic tests

The catalytic testing was conducted in a down flow fixed bed stainless steel reactor (i.d. = 9.4 mm, length = 250 mm) in vapour phase at atmospheric pressure. In a typical experiment, 1 g of the catalyst particles (0.5-0.8 mm size) diluted with equal amount of corundum (catalyst : corundum = 1 : 1 w/w) with same size were loaded in the reactor. The catalyst was suspended between two quartz wool plugs in the middle of the reactor. Also the upper and lower portions of the catalyst bed were filled with corundum. The liquid feed of premixed MP and H₂O mixture (mole ratio of MP : H₂O = 1 : 13) was dosed using HPLC pump and was vaporized in a preheating zone. The flow rates of gases such as NH₃, air and N₂ are controlled by mass flow controllers. The molar ratio of reactant feed mixture (in general) is MP : H₂O : NH₃ : air : N₂ = 1 : 13 : 7 : 26 : 22. The reaction was carried out at in the temperature range of 320 - 460 °C; GHSV = 9500 h⁻¹ and contact time = 0.2 to 0.5 s. Two thermocouples were positioned one at the centre of the catalyst bed to indicate reaction temperature and the other one was attached to furnace through temperature indicator cum controller to monitor the temperature of the reactor. The samples were collected every hour under steady state conditions and analysed by Gas Chromatograph (GC-2014 Shimadzu, Japan) equipped with flame ionization detector (FID). The liquid samples were analysed using FFAP column, while the gases products (i.e. CO and CO₂) were analysed by GC using methaniser and GSQ column.

Table S1. Calcination conditions, V/M ratios and surface areas of various bulk metal vanadate catalysts (determined from ICP-OES; estimated from BET surface area analysis)

S. No.	Catalyst	Calcination (°C / h)	Catalyst composition V/M ratio (mole)			Surface area (m ² /g)	
			Prepared	Fresh*	Used*	Fresh	Used
1	AlVO ₄	600 / 48	1.0	1.03	1.06	36.2	33.0
2	FeVO ₄	550 / 4	1.0	0.94	1.04	10.0	9.4
3	CrVO ₄	550 / 4	1.0	1.14	1.21	16.6	12.2
4	LaVO ₄	600 / 15	1.0	1.07	1.03	6.2	5.3
5	BiVO ₄	500 / 5	1.0	0.92	1.02	1.5	2.0

The conversion, yield, selectivity and STY based on 2-methylpyrazine (MP) are defined as follows:

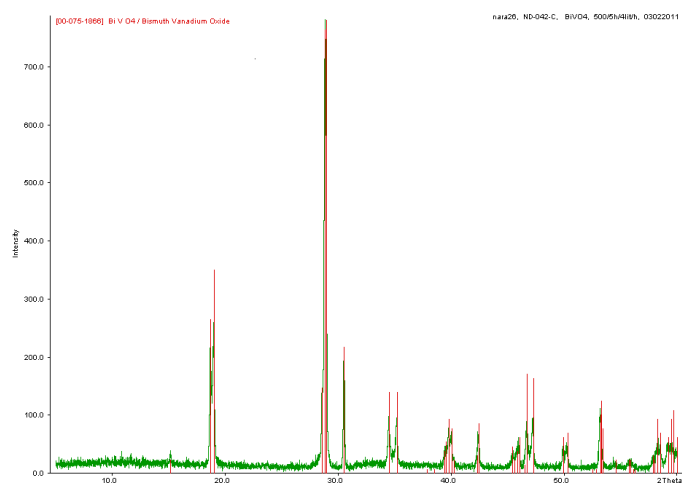
a) Conversion (%) = $n_{\text{reacted}}(\text{MP}) / n_{\text{fed}}(\text{MP}) \times 100$

b) Yield (%) = $n(\text{CP}) / n_{\text{fed}}(\text{MP}) \times 100$

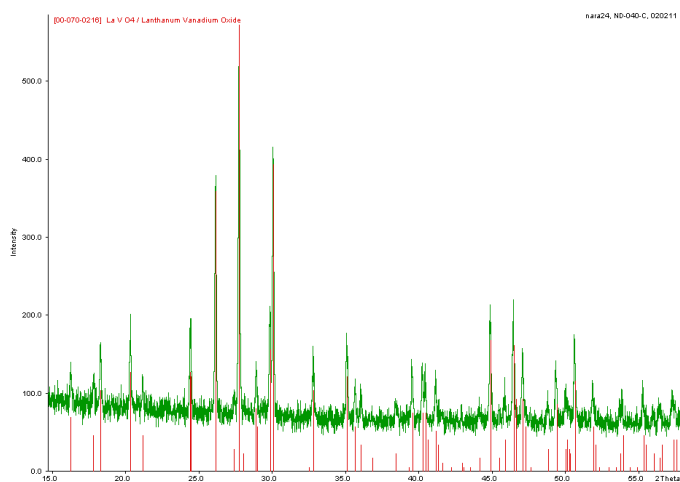
c) Selectivity (%) = $n(\text{CP}) / n_{\text{reacted}}(\text{MP}) \times 100$

d) Space time yield = $m(\text{CP in g}) / m(\text{catalyst in kg}) \times \text{h}^{-1}$

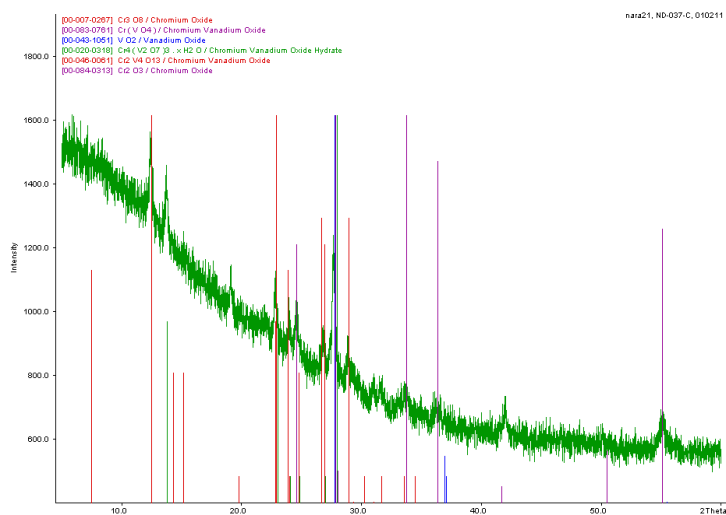
Fig. S1: Phase analysis of different metal vanadates:



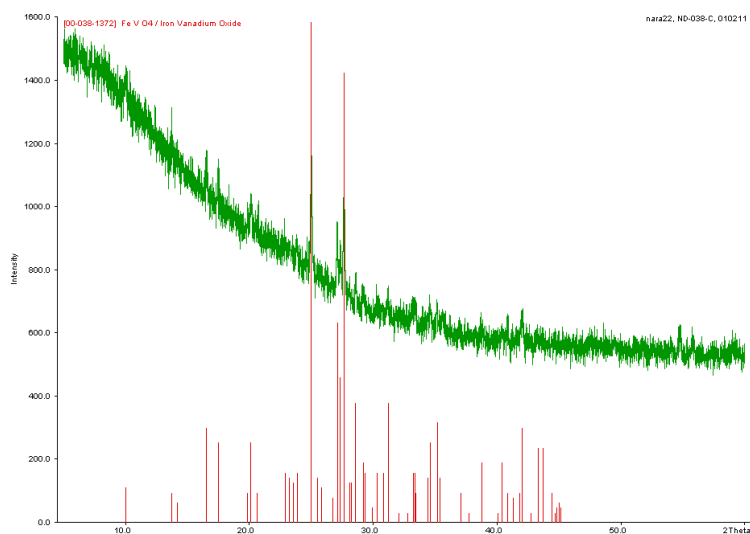
BiVO₄ sample with BiVO₄ phase [75-1866]



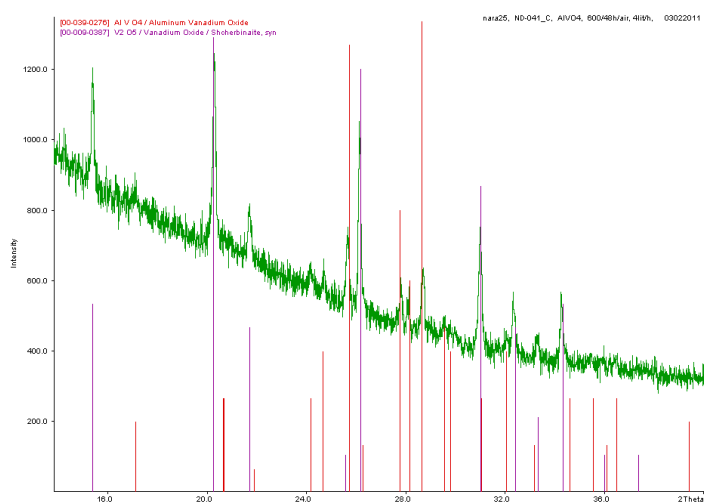
LaVO₄ sample with LaVO₄ phase [70-0216]



CrVO₄ sample with the following phases: Cr₃O₈ [07-0267]; CrVO₄ [83-0761]; VO₂ [73-1051]; Cr₄(V₂O₇)₃ · x H₂O [20-0318]; Cr₂V₄O₁₃ [46-0061]; Cr₂O₃ [84-0313].



FeVO₄ sample with a FeVO₄ phase [38-1372].



AlVO₄ sample with AlVO₄ phase [39-0276] and V₂O₅ [09-0378].

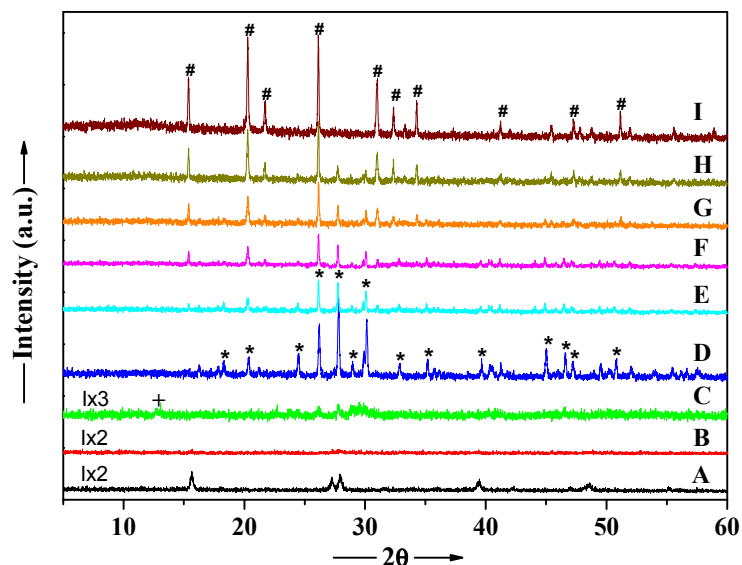


Fig. S2. X-ray diffraction patterns of various $\text{La}_a\text{V}_b\text{O}_x$ catalysts with varying La/V mole ratio (A = pure La_2O_3 ; B = $\text{La}_{0.9}\text{V}_{0.1}\text{O}_x$; C = $\text{La}_{0.7}\text{V}_{0.3}\text{O}_x$; D = $\text{La}_{0.5}\text{V}_{0.5}\text{O}_x$; E = $\text{La}_{0.3}\text{V}_{0.7}\text{O}_x$; F = $\text{La}_{0.15}\text{V}_{0.85}\text{O}_x$; G = $\text{La}_{0.1}\text{V}_{0.9}\text{O}_x$; H = $\text{La}_{0.05}\text{V}_{0.95}\text{O}_x$; I = pure V_2O_5) (* = LaVO_4 ; # = V_2O_5 ; + = $\text{La}_{0.33}\text{V}_2\text{O}_5$; Ix2 and Ix3 = peak intensity multiplied by 2 and 3 times, respectively).

In $\text{La}_{0.7}\text{V}_{0.3}\text{O}_x$ catalyst, very weak reflections correspond to LaVO_4 are observed. The reflection at $2\theta = 12.47^\circ$ appeared in $\text{La}_{0.3}\text{V}_{0.7}\text{O}_x$ sample belongs to crystalline $\text{La}_{0.33}\text{V}_2\text{O}_5$ phase whereas other reflections observed are due to LaVO_4 phase. With increasing vanadium content the intensity of LaVO_4 reflections decreased and the peaks related to V_2O_5 has started to appear from $\text{La}_{0.3}\text{V}_{0.7}\text{O}_x$ catalyst onwards. In other words, the intensity of V_2O_5 reflections increase continuously with increase of vanadium content, as expected.

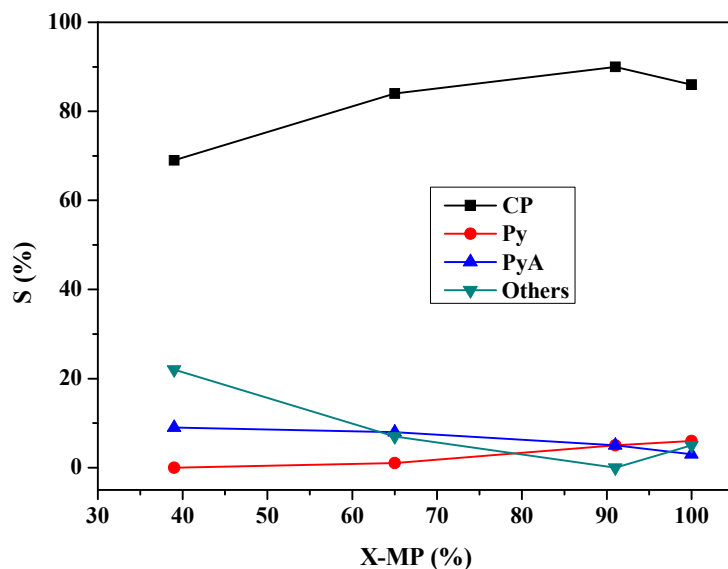


Fig. S3. Variation of selectivity of products as a function of conversion of MP over the best $\text{La}_{0.1}\text{V}_{0.9}\text{O}_x$ catalyst (S=selectivity; X-MP=conversion of 2-methylpyrazine; CP=2-cyanopyrazine; Py=pyrazine; PyA=pyrazinamide; Others=CO, CO_2 and unknown products)

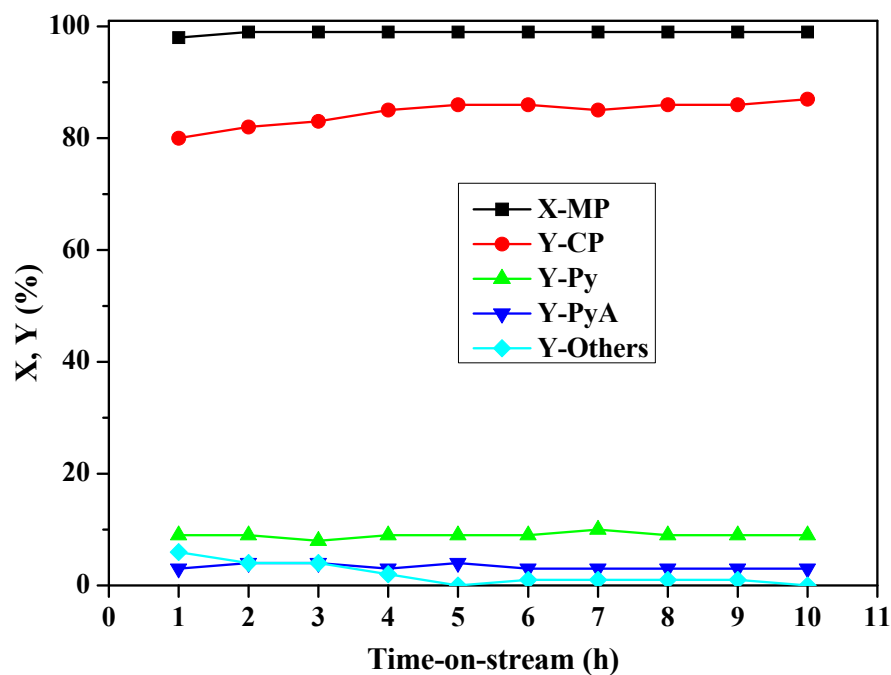


Fig. S4: Long-term stability of the $\text{La}_{0.1}\text{V}_{0.9}\text{O}_x$ catalyst ($T=420\text{ }^\circ\text{C}$; X-MP=conversion of 2-methylpyrazine; Y-CP=yield of 2-cyanopyrazine; Y-PyA=yield of pyrazinamide; Y-Py=yield of pyrazine; Y-Others=yields of CO, CO_2 and unknown products)