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

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Tuning the surface composition of metal vanadates using different cations leads to the development of a new class of highly effective catalysts tested in the ammoxidation of 2-methylpyrazine. Especially, an enrichment of V in the near-surface region is beneficial for improved selectivity. With this approach, a knowledge based optimisation of the catalysts was possible for the first time, which indeed led to highly efficient novel LaVO_x catalysts with a high yield of 2-cyanopyrazine ($\geq 85\%$) and extremely high space-time-yields (ca. $525 \text{ g}_{\text{CP}}^{-1} \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1}$).

It is widely accepted that the surface properties usually determine the performance of heterogeneous catalysts.¹ Thus it is reasonable to optimize the performance of catalysts by a systematic variation of the surface properties (e.g. composition) of the materials. With this approach, we extended our efforts to develop novel metal vanadate catalysts for the ammoxidation of 2-methylpyrazine. Ammoxidation has been emerging as a clean and environmentally benign process for the production of various industrially important nitriles.² In particular, ammoxidation of 2-methylpyrazine (MP) to 2-cyanopyrazine (CP) is of special commercial interest because CP is an intermediate to produce pyrazinamide (PyA), an effective anti-tubercular drug.³ To date, a variety of catalysts, e.g. V–Sb–Mn–O,⁴ V–Ti–O,⁵ heteropolyacids⁶ and FePO_4 ,⁷ have been examined. However, most of these catalysts showed some drawbacks, for instance poor thermal stability (e.g. heteropolyacids), low molar yields and much lower space-time-yields of CP. Therefore, there is a need to look for a new class of catalysts with an intention to develop efficient systems with good long-term stability. For the first time, we have examined bulk metal vanadates which are known as catalysts for the oxidative dehydrogenation of alkanes [e.g. ref. 8] and oxidation of MeOH,⁹ but they were never applied for the ammoxidation of MP. Herein, we report a very attractive catalytic system for the direct synthesis of CP from MP by gas phase ammoxidation. The goal of this study is also to develop highly active and selective catalysts with a special emphasis on tuning the surface composition to enhance the molar and space-time-yields of CP.

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All metal vanadate (MV) catalysts were prepared by the same simple citric acid decomposition method.¹⁰ The V/Me atomic ratios (Me = Al, Fe, Cr, La, Bi) are kept constant at 1. In addition, LaVO_x solids were synthesized with a wide range of the La/V ratio from 1:0 to 0:1. More details on the preparation and characterization of catalysts are described in ESI.† Catalytic tests were performed in a fixed bed stainless steel reactor. The products were determined off-line by GC; formulas for calculation of conversion and yields are given in ESI.†

Calcination conditions, V/Me ratios and surface areas of various bulk MVs are given in Table S1, ESI.† BET surface areas are found to depend on the nature of the metal present and are varied in the range from 1.5 to $36 \text{ m}^2 \text{ g}^{-1}$ (Table S1, ESI†). However, the spent samples exhibit a marginal decrease in surface areas compared to their corresponding fresh catalysts. The phase composition of various MVs is presented in Table 1. It is clear that syntheses lead to phase mixtures in some cases, e.g. the AlVO_4 catalyst shows a mixture of V_2O_5 and AlVO_4 , where the majority of reflections correspond to V_2O_5 . In a similar way CrVO_4 also exhibits different vanadate phases containing Cr- and V-oxides. On the other hand, FeVO_4 , LaVO_4 and BiVO_4 display pure metal vanadate phases that correspond to triclinic FeVO_4 , monoclinic LaVO_4 and the monoclinic scheelite structure of BiVO_4 , respectively.

From the XRD results, it can be understood that the formation of a pure crystalline phase clearly depends on the kind of the metal used.

The LaVO_4 solid was selected for further variation of the V/Me ratio due to its superior catalytic performance as described below. Therefore, different LaVO_x solids with varying La/V ratios were prepared and initially analysed by XRD.

Table 1 Phase composition of the different metal vanadate samples. In brackets, the number of the Powder Diffraction Files is noted. Diffractograms are presented in Fig. S1 (ESI†)

Sample	Phase composition
AlVO_4	AlVO_4 [39–0276]; V_2O_5 [09–0378]
FeVO_4	FeVO_4 [38–1372]
CrVO_4	Cr_3O_8 [07–0267]; CrVO_4 [83–0761]; VO_2 [73–1051]; $\text{Cr}_4(\text{V}_2\text{O}_7)_3 \times \text{H}_2\text{O}$ [20–0318]; $\text{Cr}_2\text{V}_4\text{O}_{13}$ [46–0061]; Cr_2O_3 [84–0313]
LaVO_4	LaVO_4 [70–0216]
BiVO_4	BiVO_4 [75–1866]

At the lowest vanadium contents (*i.e.* $\text{La}_{0.9}\text{V}_{0.1}$), the sample is found to be X-ray amorphous. Otherwise, high vanadium contents led to formation of crystalline V_2O_5 proportions. However, the $\text{La}_{0.5}\text{V}_{0.5}\text{O}_x$ catalyst shows intense and sharp reflections related to a crystalline and pure monoclinic phase of LaVO_4 (Fig. S1, ESI†).

The catalytic performance of these MVs was evaluated for the ammoxidation of MP in order to check the influence of catalyst composition, phase (bulk) and surface composition on the catalytic performance. The effect of the reaction temperature on the conversion and nitrile yield is shown in Fig. 1. It is obvious that the conversion of MP increases continuously with rise in temperature, however, the temperature required to obtain total conversion varies from 360–440 °C and depends on the type of the metal present in MV. Among all solids tested, the AlVO_4 sample is found to be highly active but less selective, which might be due to the presence of the crystalline V_2O_5 phase in major proportions. In addition, AlVO_4 displayed nearly 100% conversion of MP at relatively low reaction temperature (*i.e.* 340–360 °C) compared to others. On the other hand, the LaVO_4 solid exhibited the best performance with respect to conversion and selectivity. Nevertheless, this catalyst requires high reaction temperature (440 °C) to obtain 100% conversion of MP. Despite such high reaction temperature, there is no considerable loss of selectivity towards CP, which is indeed remarkable. Interestingly, the BiVO_4 catalyst displayed only 77% conversion of MP even at 440 °C, and is observed to remain more or less constant at this level with

further increase in temperature to 460 °C. However, the selectivity of CP obtained on BiVO_4 is considerably high. On the other hand, FeVO_4 and CrVO_4 catalysts showed comparable performance and lie in the middle of the series. These two solids required 380 °C to obtain total conversion of MP. The highest yield of CP (62%) was obtained on the LaVO_4 catalyst while the AlVO_4 material revealed the lowest yield of CP (~25%).

In general, the nature of the metal in the synthesized metal vanadate-containing catalysts is a crucial parameter, which appears to control both the conversion of MP and the distribution of products. Owen and Kung¹¹ have used different MVs (*e.g.* Cr, Fe, Mg *etc.*) for the ODH of butane and reported that the product distribution depends on the type of MV used. The authors also suggest that orthovanadate materials exhibit a high selectivity of the desired products when the VO_4 units are separated from each other by MO_x units and all the lattice oxygen ions are involved in the solid bridge (M–O–V) between V^{5+} and M^{n+} ions. The absence of V^{5+} –O– V^{5+} bonds in which the lattice oxygen can be readily removed due to the high reducibility of the two V^{5+} ions is the cause for the low combustion activity of the metal vanadates compared to V_2O_5 . A similar such situation can be expected from the present LaVO_4 and BiVO_4 catalysts due to the formation of well crystalline pure phases and hence the low combustion activity (*i.e.* high selectivity of CP). On the other hand, the reverse trend is observed in the case of AlVO_4 catalysts, where free V_2O_5 is present in major proportion. Interestingly, the yield obtained with this catalyst is lower than the values for pure V_2O_5 . The presence of Al cations is detrimental for the catalytic performance. The surface V/Me ratios obtained from XPS give good supporting evidence to the above results.

In all samples, pentavalent vanadium could be detected from XPS. The AlVO_4 catalyst with the largest portion of crystalline V_2O_5 shows the lowest amount of V in the near-surface region according to the XPS results. In contrast, LaVO_4 and BiVO_4 samples with no such visible crystalline V_2O_5 showed high enrichment of vanadium on the surface. Therefore, as already well known, bulk or crystalline V_2O_5 is detrimental for high product selectivity but a significant enrichment of vanadium in the near surface region as seen in more pure MVs exhibits the highest selectivity of CP at slightly decreased activity (Fig. 2). Wachs *et al.*⁹ also used different orthovanadate catalysts for the oxidation of MeOH and observed a clear surface enrichment of vanadium species on certain metal vanadates. They have shown that the V/Me ratio depends on the type of MV used and the differences in the nature of surface active sites of bulk MVs would also lead to a different product distribution.⁹ Wachs *et al.* analysing similar vanadates and molybdates have shown that the properties of the outermost surface layer are of prime importance for control of the catalytic performance.¹²

The catalytic performance of various LaVO_x catalysts with varying La/V ratios is presented in Fig. 3. As expected, pure La_2O_3 is almost inactive. However, the combination of La and V remarkably improved the performance. It is quite obvious that the performance of catalysts undeniably depends on the La/V ratio. The conversion of MP is observed to increase continuously with increase in the vanadium content

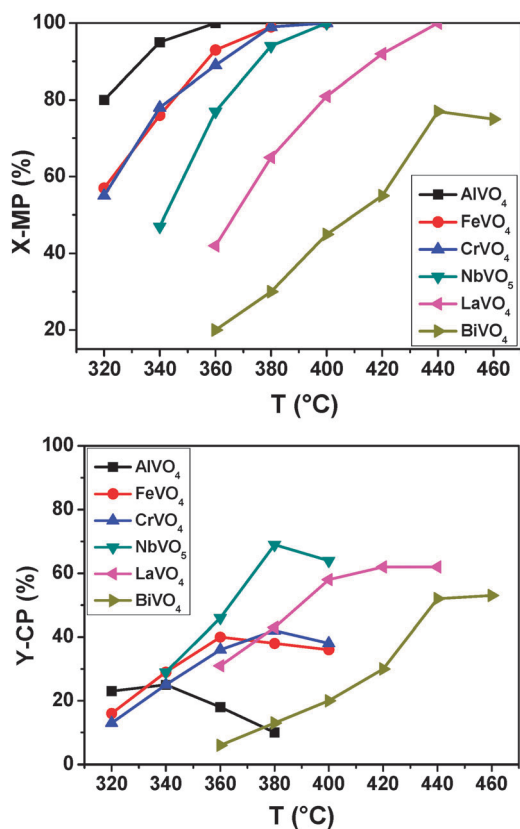


Fig. 1 Conversion of 2-methylpyrazine (top) and yield of CP (bottom) as a function of the temperature over various metal vanadate catalysts.

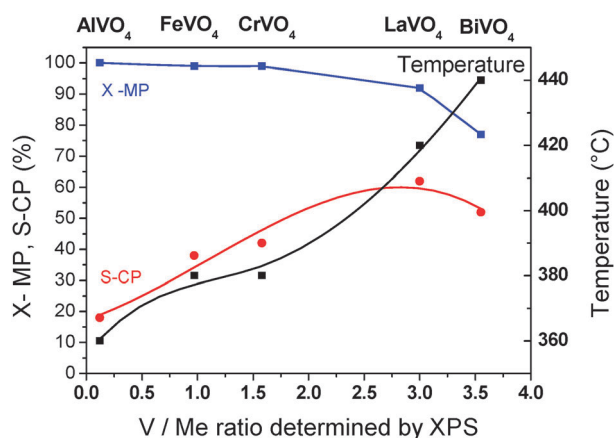


Fig. 2 Correlation between surface V/Me ratios and catalytic performance (X-MP: conversion of 2-methylpyrazine; S-CP: selectivity of 2-cyanopyrazine) and temperature at total conversion.

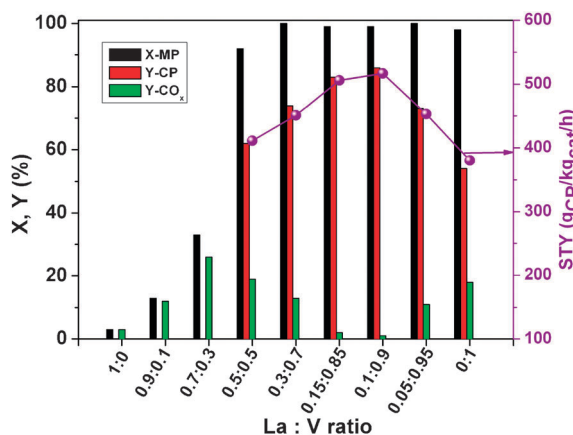


Fig. 3 Catalytic results of the ammoxidation of 2-methylpyrazine using various LaVO_x catalysts with varying La/V ratios; X-MP = conversion of 2-methylpyrazine; Y-CP = yield of 2-cyanopyrazine; Y- CO_x = yields of CO and CO_2 ; STY = space-time-yield.

and reached almost 100% on $\text{La}_{0.3}\text{V}_{0.7}\text{O}_x$ catalysts. Afterwards, the conversion remained unaltered, while the yield of CP has been substantially increased further with increase in the vanadium content of the catalyst up to 0.1:0.9 La:V mole ratio.

However, further increase in the vanadium content causes a decrease in the yield of CP. Among different $\text{La}_a\text{V}_b\text{O}_x$ solids, the catalyst with 0.1:0.9 La:V mole ratio (i.e. $\text{La}_{0.1}\text{V}_{0.9}\text{O}_x$) exhibited the superior performance. The best yield of CP is found to be 86% at almost total conversion of MP. Additionally, the best space-time-yield (STY) of CP of ca. $525 \text{ g}_{\text{CP}}^{-1} \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1}$ was obtained for the first time. This is the highest value obtained so far compared to all other existing literature on this reaction (e.g. 300^{13} and $140^7 \text{ g}_{\text{CP}}^{-1} \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1}$, respectively). Pyrazine, pyrazinamide, CO and CO_2 were observed as by-products. Pyrazine formation is from the demethylation of MP occurring usually on stronger acidic sites. Pyrazinamide formation is expected from hydrolysis of CP. CO and CO_2 are a result of unavoidable total oxidation.

The XRD of this catalyst (i.e. $\text{La}_{0.1}\text{V}_{0.9}\text{O}_x$) shows only the reflections typical for V_2O_5 (Fig. S2, ESI[†]), but less intense and sharp compared with pure V_2O_5 . The doping of V_2O_5

with La leads to a less crystalline and defect-rich V_2O_5 lattice which seems to be the best suited for this reaction. These results are in accordance to the XPS investigations showing a V-enriched surface offering the best catalytic performance.

In addition, the long-term behaviour of this catalyst was also tested for a period of 10 h on-stream. The conversion of MP is almost constant at 100% throughout. However, the yield of CP is slightly increased on-stream and then remained constant at around 86%, which indicates that the catalyst attained steady state conditions. Furthermore, it can be noticed that there is no deactivation over a period of 10 h.

In conclusion, it can be stated that different metal cations in the vanadates lead to different enrichment of V in the near surface region. Such variation of the surface composition clearly offered the possibility of enhancing the catalytic performance of the vanadates in terms of conversion and selectivity in the ammoxidation of MP. After proper optimization, very high yields of CP (86%) with remarkably high space-time-yields (ca. $525 \text{ g}_{\text{CP}}^{-1} \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1}$) at almost total conversion of MP could be successfully obtained, which is to our knowledge the best STY value reported so far for this reaction. The systematic optimization of the solids shows that La doped V_2O_5 is the best suitable system.

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