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Adipic acid formation from cyclohexanediol using platinum and vanadium catalysts: elucidating the role of homogeneous vanadium species†

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Vanadium compounds have shown great potential alongside Pt/C for the oxidation of cyclohexanediol to adipic acid. However, the low stability of these materials often leads to ambiguity when considering the homogeneous or heterogeneous nature of the active species. In this article we describe our attempts to synthesise stable vanadium catalysts through the utilisation of vanadium bronze structures. By the addition of sodium, copper or silver into these structures, leaching could be decreased to 5% for $AgVO_3$, compared to 88.4% with V_2O_5. These reactions were run in aqueous conditions under 3 bar O_2. However, despite significant stabilisation of vanadium in the bronze structures, we show that as little as 7.6 ppm of a homogeneous vanadium species in the reaction solution can cause the selective oxidation of 2-hydroxycyclohexanone to adipic acid. Analysis of the speciation by ^{51}V NMR and UV-vis has revealed the active species to be in the +5 oxidation state in the form of a decavanadate compound with the presence of small amounts of monovanadate.

Introduction

The production of chemicals using the principles of green chemistry is becoming increasingly important.[1] Drives to cut emissions are at the forefront of government policy and as such the incentives for industry to follow suit are much greater. Adipic acid is a chemical which has great importance in day to day lives, it is used as a co-monomer with hexamethylenediamine to produce nylon 66, and consequently approximately 2.5 million tonnes is produced annually.[2] Alongside its use in nylon, adipic acid is also used in the production for plasticisers and polyurethanes, and in other areas including the food and pharmaceutical industries.[3]

Currently, adipic acid is produced predominantly from a cyclohexane-based feedstock.[3–5] In this process the use of nitric acid as the oxidant results in the release of N_2O, which has a global warming potential of 300 relative to CO_2.[6] The environmental impact of this adipic acid process has been diminished due to recent catalytic and thermal abatement of the N_2O emissions, resulting in significant reduction of

associated N_2O release. However the prospect of completely eliminating N_2O from the process would be beneficial.[7–9] This is gradually becoming more feasible due to the possibility of using cyclohexene as a substrate instead of cyclohexane. Cyclohexene is more easily oxidised and therefore, greener oxidants such as oxygen and hydrogen peroxide can be used, which can offer better atom economy.[1,10–12]

Oxidation starting from cyclohexene may need to be run in two steps. The first step would be an oxidation of cyclohexene to cyclohexanediol, which can be achieved using O_2, albeit with a maximum selectivity of 50%.[13] It is for this reason that a process which uses H_2O_2 in a first step, would be the most economically viable. However, this would likely only be economic at commercial scale if a stoichiometric amount of oxidant relative to substrate could be used.[14] This could then be followed by a second step to convert cyclohexanediol to adipic acid, which can be achieved using O_2.

The oxidative cleavage of vicinal diols is an important process in organic synthetic chemistry and is mostly achieved using expensive noble metal-based homogeneous catalysts. However, these catalysts suffer from a poor substrate range and do not offer reusability.[15–17] The Malaprade reaction[18] and the Criegee oxidation[19] offer classical examples of the cleavage of 1,2-diols, however, they require the use of stoichiometric oxidants, such as high-valent iodine or lead, resulting in large amounts of toxic waste.[20,21] Heterogeneous catalysts have also been used for vicinal diol cleavage, particularly, noble metals such as Pt, Ru, and Au have been

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4210 | *Catal. Sci. Technol.*, 2020, **10**, 4210–4218

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reported but these usually suffer from low activity.[22–24] It is rare that a non-noble metal shows activity for this reaction. However, Escande et al. found that a sodium–manganese oxide was active at 100 °C, albeit with a minimal substrate scope and, in particular, being inactive for the oxidation of cyclohexanediol.[25]

Brégeault and co-workers demonstrated the ability of various vanadium compounds to perform the aerobic oxidative cleavage of 2-hydroxycyclohexanone (2-HCO) to form adipic acid.[26] Rozhko et al. subsequently studied the ability of Keggin type P/Mo/V polyoxometalates for the oxidation of cyclohexanediol under acidic conditions. However, it was suggested that despite high initial selectivity, the adipic acid formed underwent further reaction with cyclohexane diol to form the corresponding ester, resulting in low overall yields of the acid.[27] More recently, Obara et al.[24] demonstrated the potential for a system utilising Pt/C and V_2O_5 that can selectively cleave the vicinal diol to adipic acid (Scheme 1). Using O_2 as oxidant and H_2O as solvent, a yield of over 90% can be reached when both catalysts were combined in a one-pot reaction over 48 h. Cyclohexanediol was converted to 2-HCO over Pt/C alone, whereas this reaction did not proceed with only V_2O_5. By using a V_2O_5 co-catalyst, the 2-HCO was then converted to cyclohexanediol. The main problem with such a system is the solubility of the V_2O_5 catalyst. The researchers highlighted that over each re-use approximately half of the vanadium leached into solution, although it was suggested that the remaining solid was responsible and sufficient for the observed catalysis. Nevertheless, a truly heterogeneous vanadium catalyst would mark a major advance in this field.

Supported vanadium oxides have been extensively used in oxidation reactions, notably in the selective oxidation of alkenes and alkanes and the oxidation of H_2S.[28–30] However, heterogeneous vanadium catalysts are well-known to leach in aqueous solutions. This can be alleviated to some extent by changing the support and reaction conditions as shown in work by Masumoto et al.[31] However, even the most successful attempt at mitigating leaching, a V/Al_2O_3 catalyst, still showed 37.6% leaching of vanadium into the solvent. The effect of leaching of vanadium catalysts in heterogeneous liquid phase reactions is also stated in studies by Ziolek et al., whereby V/MCM-41 leaches 71 wt% of vanadium into the reaction solution.[32] Interestingly, work by Tiwari et al. on polyoxometalate structures, specifically $H_5[PV_2Mo_{10}O_{40}]$, have shown that the dissolution of two reactive pervanadyl ions by H_2SO_4 is a reversible process, which can be controlled by the pH.[33]

Vanadium bronzes, which when combined with other metals such as sodium, copper or silver, can show stability in aqueous media and have various applications in areas such as, photocatalysts and in electrochemical energy storage,

however elemental analysis of aqueous media is not always reported.[34,35] In this report we show the synthesis of several vanadium bronzes with the aim of achieving stabilisation in aqueous media. However, we also demonstrate that even small amounts of leaching from these catalysts can have a great effect on reactivity. The filtrate of these reactions is also analysed to determine the likely active vanadium speciation.

Experimental

Chemicals

The following chemicals were used in this investigation without further purification. Vanadium oxide (V_2O_5, 99.95%), sodium sulfate ($NaSO_4$, 99.99%), copper(I) acetate (CuOAc, 97%), hydrogen peroxide (H_2O_2, 30 wt%), ammonium metavanadate (NH_4VO_3, 99.9%), vanadium carbide (99%), urea (99%), trans-1,2-cyclohexanediol (98%), 5 wt% Pt/C, 2-hydroxycyclohexanone dimer (97%) were all sourced from Sigma-Aldrich.

Catalyst preparation

NaV_6O_{15} with $NaSO_4$. Anhydrous Na_2SO_4 (3.6 mmol, 511 mg) and V_2O_5 (1.8 mmol, 328 mg) were dissolved in deionised water (30 ml). The mixture was then loaded into a 70 ml Teflon-lined stainless-steel autoclave. The autoclave was then heated to 200 °C under autogenous pressure for 24 h and allowed to cool to room temperature. The precipitate was collected by vacuum filtration, washed with distilled water and ethanol. The solid was then dried in a vacuum oven at 60 °C for 16 h.

CuV_2O_6. CuOAc (0.5 mmol, 61.3 mg) and V_2O_5 (2.0 mmol, 364 mg) were dissolved in deionised water (30 ml), Cu/V molar ratios were varied from 0.25–0.5. H_2O_2 (5 ml, 30%) was then added to this mixture and stirred at room temperature for 2 h. This mixture was then transferred to a 70 ml Teflon-lined stainless-steel autoclave and placed in an oven for 72 h at 175 °C under autogenous pressure. The resulting solid was washed with deionised water and dried at 40 °C for 16 h in a vacuum oven. The dried solid was then heat-treated at 500 °C in N_2 for 2 h at 10 °C min^{-1}.

$AgVO_3$. NH_4VO_3 (0.5 mmol, 58.5 mg) was dissolved in deionised water (30 ml). A solution of $AgNO_3$ (0.5 mmol, 84.9 mg, 10 ml) was added dropwise to the NH_4VO_3 solution. This mixture was stirred for 15 min and then transferred to a 70 ml Teflon-lined stainless-steel autoclave and heated at 180 °C under autogenous pressure for 18 h. The resulting precipitate was collected via vacuum filtration and rinsed with boiled deionised water and ethanol. The solid was then dried under vacuum at 60 °C.
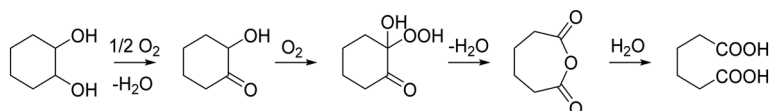
Scheme 1 Reaction scheme for oxidation of cyclohexanediol to adipic acid as proposed by Obara et al.

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Catal. Sci. Technol., 2020, **10**, 4210–4218 | **4211**

V–C$_3$N$_4$. Urea (0.2 mol, 12.0 g) was dissolved in water (100 ml). Ammonium metavanadate (NH$_4$VO$_3$, 4.36 mmol, 510 mg) was then added to this mixture. The solution was then heated to 100 °C to remove water. The dried catalyst underwent a heat treatment at 300 °C for 2 h at 3 °C min^{-1} under N$_2$. The temperature was subsequently increased to 550 °C for 4 h at 3 °C min^{-1} under N$_2$.

Catalytic testing

Oxidation of cyclohexanediol to adipic acid under O$_2$. A solution of cyclohexanediol (5 ml, 10 000 ppm) was loaded into a low-pressure glass reactor. When required, Pt/C (10 mg) and the vanadium co-catalyst (2 mg) were then added to the vessel. The reactor was purged with O$_2$ and then charged with 3 bar O$_2$. The reactor was then stirred at 80 °C for 4 h. Samples were centrifuged and filtered using PTFE syringe filters (0.45 μm) before HPLC analysis.

Oxidation of 2-hydroxycyclohexanone. A stock solution of vanadium was prepared by stirring V$_2$O$_5$ (2.20 mmol, 400 mg) in water (50 ml) for 16 h. The resulting solution was then centrifuged, and the supernatant was collected. After filtration using PTFE syringe filters (0.45 μm) an accurate concentration was then determined by using MP-AES. A solution of 2-hydroxycyclohexanone (5 ml, 4000 ppm) was loaded into a low-pressure glass reactor. The required volume of vanadium solution was then added to the vessel. The reactor was purged with O$_2$ and then charged with 3 bar O$_2$. The reactor was then stirred at 80 °C for 4 h. Samples were centrifuged and filtered using PTFE syringe filters (0.45 μm) before HPLC analysis.

HPLC analysis. Analysis was carried out using an Agilent 1260 Infinity HPLC equipped with ultraviolet and refractive index detectors. Reactants and products were separated using a Metacarb 67H column. The mobile phase was an aqueous solution of H$_3$PO$_4$ (0.01 M) and the flow rate was 0.5 ml min^{-1}. For the quantification of the amounts of reactants consumed and products generated, an external calibration method was used. The conversion, selectivity and mass balance were calculated as follows:

$$\text{Conversion (\%)} = [(\text{mol of consumed substrate})/(\text{mol of initial substrate})] \times 100$$

$$\text{Selectivity (\%)} = [(\text{mol of product})/(\text{mol of consumed substrate})] \times 100$$

$$\text{Mass balance (\%)} = [(\text{mol of product final} + \text{mol of final substrate})/(\text{mol of initial substrate})] \times 100$$

Catalyst characterisation

MP-AES. Samples of the catalyst testing solution after reaction were tested without dilution. If samples exceeded 100 ppm then samples were diluted as required using deionised water and then filtered using PTFE syringe filters (0.45 μm). For solid samples, 10 mg of catalyst was dissolved in freshly prepared aqua regia (5 ml) and left for 24 h. The solution was then diluted up to 50 ml. Elemental composition was determined using an Agilent MP-AES 4100, quantification was achieved by calibration of the instrument using commercial calibration standards.

NMR spectroscopy. NMR spectroscopy was conducted on a Bruker Avance III 500 MHz (11.7 Tesla) spectrometer equipped with a Prodigy cryoprobe, chemical shifts are reported in ppm. When required, reaction samples were diluted by 10% with D$_2$O and ^{51}V NMR measurements acquired over 512 scans at a frequency of 131.55 MHz over the spectral range −100 ppm to −900 ppm.

XRD. Powder X-ray diffraction was carried out using a Panalytical X'Pert diffractometer equipped with a Cu X-ray source operating at 40 kV and 40 mA. The ICDD standard database was used for phase identification where possible or checked against examples in the literature.

Results and discussion

Obara *et al.*[24] have demonstrated the potential for Pt/C and vanadium to operate catalytically in tandem offering a highly selective route to adipic acid from cyclohexanediol. Firstly, the results (Table 1 – entry 1) show that the blank reaction displayed no activity. The use of V$_2$O$_5$ (Table 1 – entry 2) as the sole catalyst resulted in little activity, with only a small amount of conversion observed. This is followed by Pt/C (Table 1 – entry 3), which showed a conversion of 39.4% and a selectivity of 59.4% towards 2-HCO. This is accompanied by low selectivity to other oxidation products, such as glutaric acid and succinic acid at 2.7% and 1.4%, respectively. When a vanadium catalyst is added to the Pt/C catalyst, selectivity towards adipic acid was observed, as shown in entry 4. In this system selectivity to adipic acid increases to 76.1% and conversion remains at a similar level of 49.5%. This reaction is likely a largely homogeneous reaction, as most of the vanadium oxide catalyst has been measured by MP-AES to be dissolved in the reaction media. Obara *et al.* suggested that despite losing approximately half the solid vanadium on each use, the remaining catalyst is responsible for the activity observed.[24] In either case, this leached homogeneous vanadium makes the system far less industrially viable due to the poor stability, and therefore lifetime, of the vanadium oxide under reaction conditions in addition to the possible contamination of the product with toxic vanadium species. If a stable heterogeneous vanadium catalyst could be prepared, then this would be more practical industrially. For this purpose, we therefore prepared a range of vanadium bronzes incorporating Na, Cu or Ag to increase stability, as they have commonly been used previously as heterogeneous catalysts in aqueous reactions, albeit with V leaching not being reported.[34–37]

4212 | *Catal. Sci. Technol.*, 2020, **10**, 4210–4218

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Table 1 Reproduction of work by Obara et al.[24] for the oxidation of cyclohexanediol. Reaction conditions: 80 °C, 3 bar O_2, 4 h, 10 000 ppm cyclohexanediol in water (5 ml), 10 mg 5% Pt/C, 2 mg V_2O_5
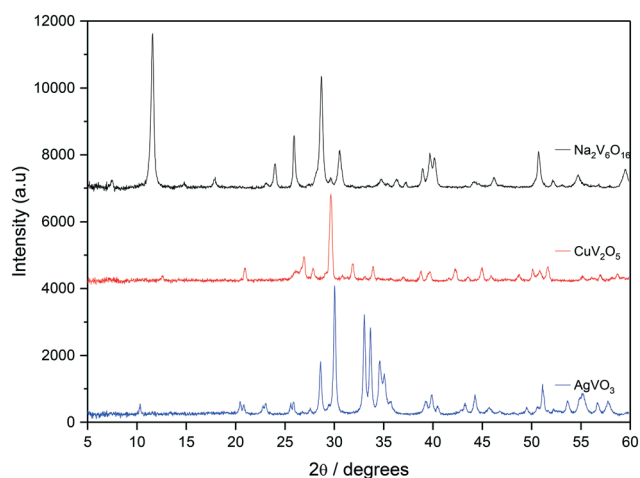
Entry	Catalyst	Conversion/%	Selectivity/%					Vanadium leaching/%	Vanadium concentration/ppm	Mass balance/%
			Adipic acid	2-HCO	Glutaric acid	Succinic acid	Unknowns			
1	Blank	0.0	0.0	0.0	0.0	0.0	0.0	—	—	100
2	V_2O_5	3.0	0.0	0.0	0.0	0.0	0.4			97.5
3	Pt/C	39.4	0.0	59.4	2.1	1.3	9.2	—	—	90.4
4	Pt/C + V_2O_5	49.5	76.1	1.2	4.5	1.4	5.4	88.4	168	96.2

All bronze catalysts in this study were synthesised using a hydrothermal technique and the XRD patterns are shown in Fig. 1. The $Na_2V_6O_{16}$ bronze was synthesised according to a previous method described by Xu et al.,[38] using V_2O_5 and $NaSO_4$ as precursors. The XRD pattern (black) can be referenced to the monoclinic $Na_2V_6O_{16}$ phase with a $P21/m$ space group with reflections at 2θ = 11.70, 25.93, 28.35, 29.77, 40.06, 46.26 and 50.83° all indicative of this phase.[39,40] This is accompanied by a high degree of crystallinity. Included in Fig. 1 is the XRD pattern for $Cu_{0.5}V_2O_6$ (red), which shows reflections that would be indicative of a CuV_2O_6 phase with peaks at 2θ = 20.7, 26.7, 33.6, 42.1, 42.2 and 44.8°. However, there also appear to be reflections which can be identified as related to the monoclinic β-$Cu_{0.261}V_2O_5$ phase, which is characterised by reflections at 2θ = 29.16, 12.15, 26.39, 31.16, 33.09, 37.25, 39.73, 40.93 and 46.23°.[29,36] The XRD pattern for $AgVO_3$ (blue) shows strong similarities to that of the β-$AgVO_3$ phase with the monoclinic structure and $I2/m$ space group.[35,41] There were no other detectable reflections in the sample suggesting the sample was mainly composed of the β-$AgVO_3$ phase.

When used for the oxidation of cyclohexanediol, the $Na_2V_6O_{16}$ catalyst (Table 2 – entry 1) demonstrates a similar conversion and adipic acid selectivity to the Pt/C + V_2O_5 system, achieving 36.7% and 70.1% respectively. However, the main drawback of this catalyst was the amount of

leaching observed. MP-AES analysis of the vanadium bronze post reaction solution revealed a total of 67 ppm V which amounts to 41.8% of the overall vanadium present in the bronze. This level of leaching was still distinctly lower than that for a Pt/C + V_2O_5 catalytic reaction which leached 88.4%, however it is still an unsustainable amount. This level of leaching was consistent even after catalysts were washed with 1 L boiling water prior to the catalytic testing and also after multiple reuse experiments. These results show that sodium is not a suitable metal substitute to stabilise the leaching of vanadium species in the mixed metal oxide.

As an attempt to further decrease the vanadium leaching, the effect of using copper or silver as stabilising metals in the vanadium bronze structure was investigated. Metals such as Cu and Ag are commonly substituted in these materials, due to the resulting enhanced electrochemical properties and increased activity in the oxidation of H_2S.[29,41–43] For the copper bronzes, shown in Table 2 entries 2–4, different molar ratios of copper to vanadium were prepared to investigate any effect that copper had on the stability of the vanadium bronze. The molar ratios of copper to vanadium studied were 0.25, 0.33, and 0.5. From Table 2 it can also be seen that vanadium leaching is reduced dramatically on inclusion of copper to 5.8% for $Cu_{0.33}V_2O_6$. This contrasted with $Cu_{0.25}V_2O_6$ and $Cu_{0.5}V_2O_6$, which showed vanadium leaching of 16.6% and 19.8% respectively. This is a drastically lower leaching level than that observed with the $Na_2V_6O_{16}$ bronzes, demonstrating that the copper successfully increases the stability of the bronze. As seen in Table 2, the copper bronzes achieve lower conversions than observed with $Na_2V_6O_{16}$. However, this level of conversion is mostly influenced by Pt/C and therefore it is more useful to compare selectivity to adipic acid. It is evident from the data that $Cu_xV_2O_6$ showed lower selectivity to adipic acid. This may be due to copper atoms occupying active sites at the surface of the catalyst, or due to the additional copper affecting the electronic structure of vanadium at the surface, making it more stable but potentially less reactive. Another explanation for this change in selectivity may also be a result of less leaching in the reaction solution highlighting the role of homogeneous vanadium. These bronzes show similar selectivities towards adipic acid, despite there being a lower vanadium concentration present in the $Cu_{0.33}V_2O_6$ reaction solution. However, this may be due to only low concentrations of homogeneous vanadium being required to have this marked effect on selectivity.

Fig. 1 XRD patterns for synthesised bronzes: NaV_6O_{15} (black), CuV_2O_5 (red), $AgVO_3$ (blue).

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Catal. Sci. Technol., 2020, **10**, 4210–4218 | **4213**

Table 2 Reaction data for the oxidation of cyclohexanediol. Reaction conditions: 80 °C, 3 bar O_2, 4 h, 10 000 ppm cyclohexanediol in water (5 ml), 10 mg 5% Pt/C, 2 mg vanadium catalyst

Entry	Catalyst	Conversion/%	Selectivity/%					Vanadium leaching/%	Vanadium concentration/ppm	Mass balance/%
			Adipic acid	2-HCO	Glutaric acid	Succinic acid	Unknowns			
1	Pt/C + $Na_2V_6O_{16}$	36.7	70.1	4.0	6.5	1.6	1.5	41.8	67	96.0
2	Pt/C + $Cu_{0.25}V_2O_6$	32.0	64.0	4.9	0.0	0.0	4.3	16.6	35	91.2
3	Pt/C + $Cu_{0.33}V_2O_6$	27.2	60.4	9.0	0.0	0.0	0.0	5.8	11	91.2
4	Pt/C + $Cu_{0.5}V_2O_6$	25.1	63.7	9.5	0.0	2.2	5.2	19.8	33	95.5

Table 3 Reaction data for the oxidation of cyclohexanediol. Reaction conditions: 80 °C, 3 bar O_2, 4 h, 10 000 ppm cyclohexanediol in water (5 ml), 10 mg 5% Pt/C, 2 mg vanadium catalyst

Entry	Catalyst	Conversion/%	Selectivity/%					Vanadium leaching/%	Vanadium concentration/ppm	Mass balance/%
			Adipic acid	2-HCO	Glutaric acid	Succinic acid	Unknowns			
1	$AgVO_3$	18.4	41.6	21.3	0.0	2.1	0.0	5.0	9	92.8
2	V–C_3N_4	24.7	59.3	5.3	0.0	1.7	33.7	—	33	91.4
3	VC[a]	19.4	55.0	—	0.0	0.0	16.0	1.2	17	91.3

[a] Reaction conditions: 80 °C, 3 bar O_2, 4 h, 4000 ppm 2-hydroxycyclohexanone in water (5 ml), 5 mg vanadium carbide after washing with 5 L water.

The final bronze of the series of vanadium catalysts was $AgVO_3$, which is shown in Table 3 – entry 1. This bronze catalyst shows the highest stability with regards to vanadium leaching with only 5.0% V leached into solution. This corresponds to a total of 9 ppm V present in the reaction solution, the lowest levels of vanadium leaching from the bonzes. Unfortunately, this catalyst also showed a noticeably lower cyclohexanediol conversion than $Na_2V_6O_{16}$ and $Cu_xV_2O_6$. It can be observed (Table 3 entry 1) that there is still 21.3% of 2-HCO in the solution so this had not been completely converted to adipic acid. This may be due to less active vanadium sites or also it could be attributed to the lower concentration of homogeneous vanadium in solution.

Efforts to probe the heterogeneity of this reaction extended to synthesising a support that had a strong interaction with vanadium, to minimise leached vanadium in solution. In previous studies Ding et al.[44] had shown that vanadium supported on carbon nitride can be a promising catalyst in liquid phase reactions for the synthesis of phenol from benzene. The purpose of carbon nitride as a support to stabilise vanadium was predominantly due to basic NH and NH_2 groups on the surface which help to bind to the acidic vanadium species. These acid–base interactions have also been shown to decrease leaching to a negligible amount in vanadium-substituted molybdophosphoric acid, due to the strong interactions between the heteropolyacid and amine groups on SBA-15.[45] The V–C_3N_4 material was successfully synthesised and tested in the oxidation reaction (Table 3 – entry 2). However, after a hot wash prior to the catalytic testing, 32.6 ppm V was still leached into the reaction solution. An accurate measure of vanadium leaching from V–C_3N_4 was not obtained, due to the difficulty of dissolving graphite and carbon nitride in aqua regia. In addition to the

synthesised vanadium catalysts, a commercial vanadium carbide, which is insoluble in aqueous solutions,[46] was tested (Table 3 – entry 3). However, under reaction conditions leaching was observed for this material as well. The leaching continued even after a pre-wash of the catalyst with 5 L of boiling water. However, after this treatment only 1.2% of total vanadium leached from the catalyst, giving a total concentration of 17.0 ppm vanadium in the reaction mixture. To observe whether this level of vanadium leaching was significant for cyclohexanediol oxidation a further study using solutions with known quantities of homogeneous vanadium was conducted.

Effect of homogeneous vanadium on the oxidation of cyclohexanediol

To elucidate the role of homogenous vanadium, a series of reactions using low concentrations of vanadium in solution were conducted. A time online study was also undertaken to assess the effect of conversion on selectivity, as conversion is largely controlled by Pt/C. As there is a slight correlation between conversion and selectivity (Fig. 2a), 2-HCO was used as the starting material for these reactions, and therefore the addition of Pt/C was unnecessary.

To study the effect of homogeneous vanadium, a solution of 4000 ppm 2-HCO in water was used as the starting solution. A stock solution of V_2O_5 in water was prepared with a concentration of 200 ppm. This was then inserted into the reaction as required to obtain vanadium concentrations within the range of 0 to 45 ppm. The final concentration post reaction was then analysed by MP-AES. The results can be seen in Fig. 2b. These solutions contained only soluble vanadium species so any reaction observed would be
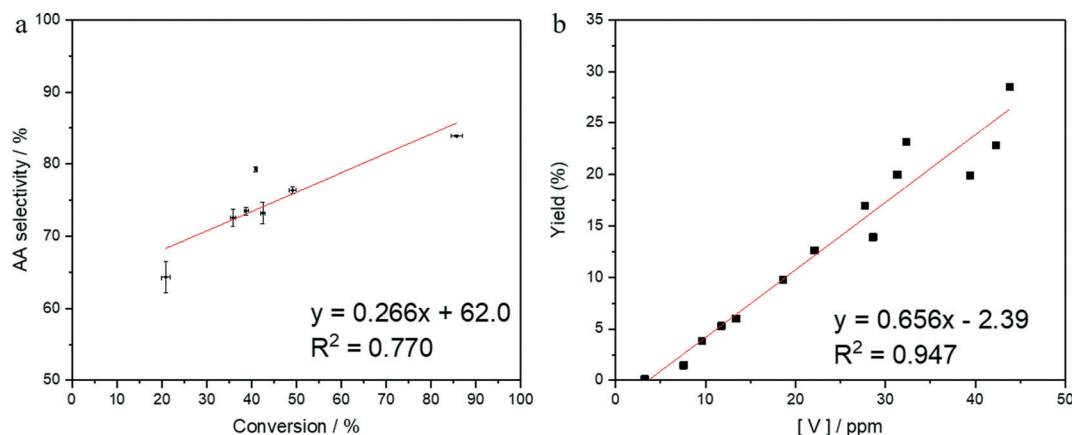
4214 | *Catal. Sci. Technol.*, 2020, **10**, 4210–4218

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Fig. 2 a) Effect of conversion on selectivity taken over reactions from 2 h to 22 h. Reaction conditions: 80 °C, 3 bar O_2, 5 ml 10 000 ppm cyclohexanediol in water, 10 mg Pt/C, 2 mg V_2O_5 b) oxidation of 2-HCO to adipic acid using solutions of vanadium between 0 and 45 ppm. Reaction conditions: 80 °C, 3 bar O_2, 4 h, 4000 ppm 2-hydroxycyclohexanone in water (5 ml), vanadium added as a stock solution of 200 ppm V_2O_5 in water. Vanadium concentrations are obtained using MP-AES analysis which are run in triplicate and averaged.

completely homogeneous. Fig. 2b demonstrates that at these low concentrations, a linear trend can be observed between vanadium in solution and yield to adipic acid. Interestingly, it is only very minimal amounts of vanadium that are required to promote conversion of 2-HCO to adipic acid. A concentration of 7.6 ppm is sufficient to observe an effect on the reaction and yield 1.5% adipic acid. This suggests that even a small amount of leaching from the above vanadium materials would likely result in catalytic activity. These vanadium species can also be determined to be acting catalytically and not as stoichiometric oxidants (SI). Higher concentrations above 45 ppm proved difficult to prepare under these reaction conditions, despite seeing concentrations above 150 ppm previously when using the bronzes as catalysts. High concentrations above 50 ppm seems to be achievable only under certain reaction conditions, which were not present in the study of 4000 ppm 2-HCO. As such, a study was undertaken to probe which conditions would induce leaching of vanadium in reaction solution and the results are illustrated in Fig. 3.

Fig. 3 shows the effect of reaction conditions on vanadium leaching, specifically the effect of the presence of Pt/C and the effect of different reaction mixtures. The reactions containing both Pt/C and V_2O_5 showed consistently more leaching than their counterpart which only included V_2O_5. The effect of the Pt/C on the leaching may have been due to the Pt activating the oxygen causing it to destabilise the vanadium structure and promote leaching of the V_2O_5 more readily. The most drastic decrease in leaching of V_2O_5 is observed in 4000 ppm 2-HCO where only 4.7% was homogeneous. This is compared to 38.8% in 10 000 ppm cyclohexanediol. The main reason for this could be the polarity of the different substrates affecting the solubility of vanadium.

Since we have shown that adipic acid selectivity was mainly reliant on homogeneous vanadium, UV-vis and ^{51}V NMR studies were undertaken to determine the speciation of

vanadium present in the reactions. The UV-vis is shown in Fig. 4, and shows the reaction filtrate from $Na_2V_6O_{16}$ (green) and the V_2O_5 reaction mixture (blue) as well as the V_2O_5 stock solution (pink) used for the vanadium homogeneous reactions (Fig. 2). From the UV-vis spectra of these mixtures it can be concluded that the vanadium oxidation state is +5 with no other oxidation states present.[47] From the UV-vis spectra we do not see V(III) or V(IV) so the catalytic V(v) must have a closed catalytic cycle. The spectra for ^{51}V NMR studies are shown in Fig. 5. By comparing the NMR spectrum with data published by Andersson et al.[48] the vanadium species can be identified as a vanadium decavanadate, which has 3 chemical environments as shown by the spectra. These shifts can be observed at −424 ppm, −508 ppm, −526 ppm for Vc,
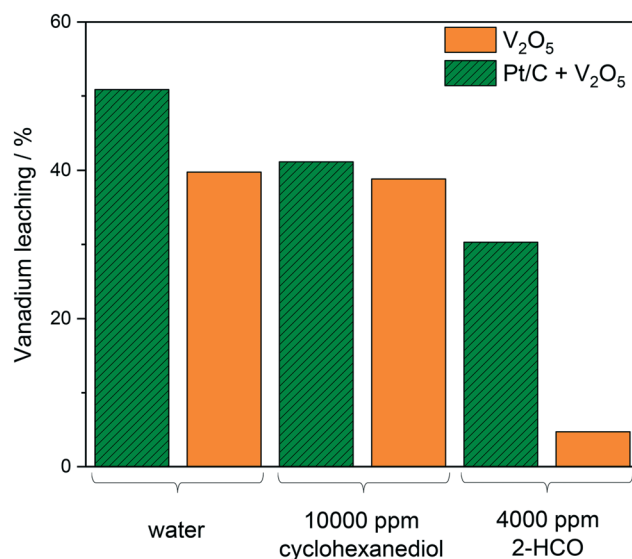

Fig. 3 Leaching of vanadium induced by differing sets of reaction conditions. Reaction conditions: 80 °C, 3 bar O_2, 4 h, 5 ml reaction solution (as specified), 10 mg Pt/C (when required), 5 mg V_2O_5 (when required).
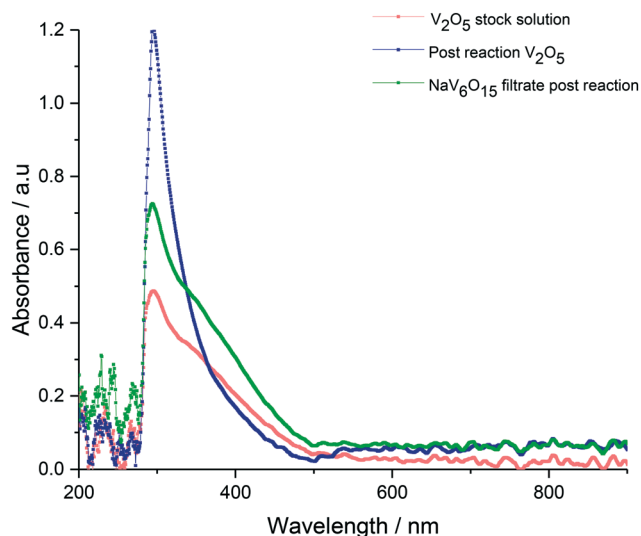
Fig. 4 UV-vis spectra of reaction filtrate from bronze reactions showing presence of only vanadium +5. V_2O_5 stock solution (pink), post reaction mixture of V_2O_5 (blue), post reaction filtrate of NaV_6O_{15} (green).

Vb and Va respectively. An additional signal, which can be attributed to the monovanadate species, can also be seen in the NMR spectrum.[49] To confirm that the spectrum observed for the reaction mixture in Fig. 5a was as a result of a V_{10} species (Fig. 5c), a sample of the decavanadate was prepared

from an acidified solution of sodium orthovanadate.[49–51] As can be seen in the spectrum the signals overlay perfectly, with the only exception of the vanadium environment signified by Va. For this environment there is a small shift from −526 ppm to −529 ppm for the reaction filtrate and the acidified sodium orthovanadate V_{10} species, respectively. This shift may result from a binding of Va with reaction products. There also appears to be a stronger monovanadate peak in the ^{51}V NMR spectrum of V_{10}, which may be a consequence of the lower pH of this sample.

Conclusions

A range of vanadium bronzes were assessed for the oxidation of cyclohexanediol to adipic acid. Initial sodium containing bronzes demonstrate promising activities, however this is accompanied by high degrees of leaching. This leaching can be significantly mitigated by the incorporation of Cu or Ag. However, even the low levels of leaching, observed with the $Cu_{0.33}V_2O_6$ and $AgVO_3$, enable the conversion of 2-HCO to adipic acid. In addition, efforts to reduce leaching using a carbon nitride as a support proved unsuccessful despite strong acid–base interactions being reported as stabilising the vanadium onto the surface of the support. In subsequent studies it was shown that even trace levels of vanadium leached from these materials was enough to catalyse the reaction homogeneously. ^{51}V NMR studies have revealed that
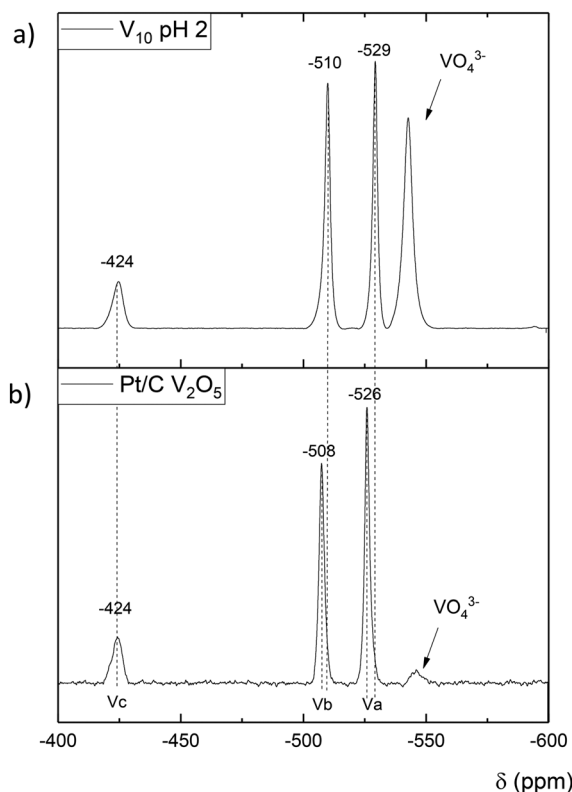

Fig. 5 ^{51}V NMR of a) vanadium decavanadate which is present at low pH with presence of monovanadate also b) reaction sample of Pt/C and V_2O_5 with 4000 ppm 2-HCO solution c) V_{10} compound with labelled vanadium sites corresponding to the shifts shown in the NMR spectra.

4216 | *Catal. Sci. Technol.*, 2020, **10**, 4210–4218

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the speciation in these homogeneous reactions to be in the form of a decavanadate.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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