DOI: 10.1002/adsc.200800313

Synthesis of a Novel Redox Material UDCaT-3: An Efficient and Versatile Catalyst for Selective Oxidation, Hydroxylation and Hydrogenation Reactions

Ganapati D. Yadav[a,]* and Haresh G. Manyar[a]

[a] Department of Chemical Engineering, University Institute of Chemical Technology (UICT), University of Mumbai, Matunga, Mumbai – 400 019, India
Fax: (+91)-22-2414-5614; phone: (+91)-22-2410-2121; e-mail: gdyadav@yahoo.com or gdyadav@udct.org

Received: May 20, 2008; Revised: July 20, 2008; Published online: October 1, 2008

Abstract: A novel, highly efficient and versatile redox catalyst, named UDCaT-3 (the acronym derived from **U**niversity **D**epartment of **C**hemical **T**echnology series catalyst # **3**) was developed by synthesizing manganese-vanadium ternary oxide within the framework of manganese oxide octahedral molecular sieve. This new composite material was characterized by elemental, X-ray diffraction, volumetric (N_2 adsorption-desorption) and transmission electron microscopic analyses as well as by electron spin resonance and framework infrared spectroscopy. In order to study its activity and selectivity, UDCaT-3 was used in the oxidation of alcohols to aldehydes, hydroxylation of phenol and acetophenone; and hydrogenation of *p*-nitroanisole to *p*-anisidine. It exhibited excellent activity and high selectivity towards the desired products. The active sites in UDCaT-3 are the lattice oxygens which get depleted during reaction followed by regeneration with the help of the oxidizing agent. UDCaT-3 is a stable, reusable and versatile catalyst.

Keywords: cryptomelane; hydrogenation; hydroxylation; octahedral molecular sieves; redox catalyst; selective oxidation

Introduction

Catalytic oxidations of organic molecules are most challenging. The chemical and allied industries continuously seek highly active and selective catalysts for partial and controlled oxidations to address technical, economical and environmental concerns. As a consequence, a large number of open-framework composites including zeolites, clays and silicates having vast structural diversity have been investigated for their specific properties.[1–4] Recently many smart catalytic oxidations have been reported.[5–14] However, most of them are based on noble metals like Pt, Pd and Ru, which are expensive and difficult to make. In this context, the octahedral molecular sieves (OMS) of manganese oxides are highly promising materials. Manganese oxide molecular sieves have a multivalent character and show high activity in oxidation reactions.[15,16] Son et al.[17] have reported the aerobic oxidation of aromatic alcohols with excellent conversions using hollandites. Recently, zirconium-doped OMS have been tested for the oxidation of ethylbenzene and benzyl alcohol.[18] The framework of manganese oxide molecular sieves consists of MnO_6 octahedral units sharing corners and edges. Cryptomelane, an octahedral molecular sieve (called OMS-2) in its K^+ ion form is a 2×2 edge-shared 1-D tunnel structure of dimension 4.6 Å. However, because of the small tunnel size of OMS, its application as an oxidation catalyst is restricted to organic molecules with smaller kinetic diameters. Thus, there is a tremendous scope to develop new types of materials, which would have the redox characteristics of OMS-2 as well as larger pore dimensions and which possess a stable open framework with the possibility of generating oxygen vacancies. Here we report for the first time the synthesis of a novel redox material using OMS-2 as the scaffold and it is named UDCaT-3. The catalytic activity and selectivity of UDCaT-3 were evaluated in the liquid-phase partial oxidation of alcohols as well as the direct ring hydroxylation of phenol and acetophenone. This paper also describes an interesting aspect of the hydrogenation of *p*-nitroanisole to *p*-anisidine. This material is being evaluated in many reactions.

Results and Discussion

Catalyst Synthesis

UDCaT-3 samples were synthesized by obtaining manganese-vanadium ternary oxide, $Mn(VO_3)_2$ over the OMS-2 framework. The vanadium precursor was adsorbed on the surface of OMS-2 by wet impregnation, dried and subjected to thermal treatment. During the calcination, the two oxides of vanadium (V_2O_5) and manganese (OMS-2) underwent a solid-state reaction to give manganese-vanadium ternary oxide. The formation of $Mn(VO_3)_2$ over the OMS-2 framework, during the solid-state interaction between manganese and vanadium oxides was studied by means of the powder X-ray diffraction patterns of samples prepared with average V/Mn atom ratios of 0.12, 0.31 and 0.65; and these were named accordingly as UDCaT-3(i)–(iii) (Table 1).

Catalyst Characterization

All materials called UDCaT-3 and the reference cryptomelane OMS-2 were characterized by elemental, X-ray diffraction, volumetric (N_2 adsorption-desorption) and TEM analyses as well as ESR and framework IR spectroscopy. All UDCaT-3 samples showed sharp X-ray diffraction patterns, with no evidence of any other manganese oxide crystalline phases except for pure OMS-2 (Figure 1). The *d*-spacing values match with the reported data of OMS-2[19] and the corresponding (h k l) values are (1 0 1), (0 0 2), (3 0 1), (2 1 1), (3 1 0), (1 1 4) and (6 0 0) at 2θ values of 12.7, 18.0, 28.7, 37.4, 41.8, 50.0, 55.3. The UDCaT-3(i) sample does not show the characteristic XRD pattern of vanadia. This may be because vanadia is dispersed in the form of small crystallites. However, UDCaT-3(ii), with a V/Mn ratio of 0.31, showed characteristic peaks for vanadia at 4.9579 and 2.410 Å. On further increasing the V/Mn ratio to 0.65 in UDCaT-3(iii), vanadia and manganese oxide undergo a solid-state reaction to form a ternary oxide, $Mn(VO_3)_2$ which is reflected in the characteristic peaks at 3.2486 Å and 3.0498 Å. The diffraction pattern of UDCaT-3(iii) indicates the presence of mixed phases of cryptomelane and $Mn(VO_3)_2$ ternary oxide.

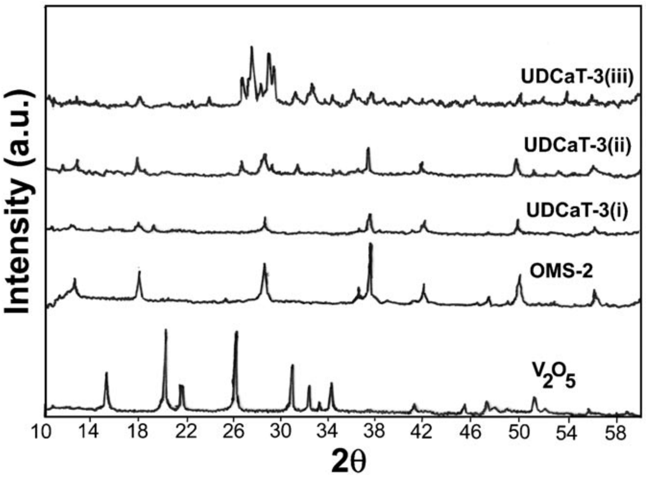

Figure 1. X-ray diffraction patterns.

Textural characteristics of all three UDCaT-3 materials are given in Table 2. The nitrogen adsorption-desorption isotherms obtained for all samples were similar and a typical one is shown for UDCaT-3(iii) in Figure 2, **A**. It is a type III isotherm, suggesting a porous structure. The BET surface area of OMS-2 is 67.84 m^2/g. When vanadium is dispersed in the form of fine V_2O_5 crystallites, there is a linear decrease in surface area from 67.84 to 44.14 m^2/g. However, in the case of UDCaT-3(iii), there is a substantial reduction in the surface area. The inspection of pore volumes in Table 2 shows that it was 0.4 cm^3/g for OMS-2, where-

Table 1. Average elemental composition based on energy dispersive X-ray spectroscopy.

Material	K [w/w, %]	V [w/w, %]	Mn [w/w, %]	V/Mn ratio
UDCaT-3(i)	8.8	10.1	81.1	0.12
UDCaT-3(ii)	14.1	20.5	65.5	0.31
UDCaT-3(iii)	4.4	37.6	58.0	0.65

Table 2. Textural Characteristics of UDCaT-3.

Sample	Single point surface area [m^2/g]	BET surface area [m^2/g]	Langmuir surface area [m^2/g]	BJH adsorption cumulative pore volume [cm^3/g]
OMS-2	69.3	67.8	102.4	0.4
UDCaT-3(i)	26.5	44.1	41.0	0.37
UDCaT-3(ii)	16.3	15.6	26.0	0.35
UDCaT-3(iii)	7.6	7.2	12.0	0.31

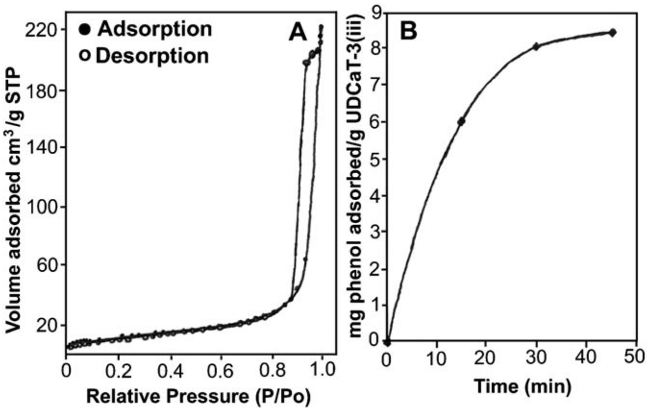

Figure 2. (**A**) Adsorption-desorption isotherm of UDCaT-3-(iii), (**B**) phenol adsorption isotherm.

as that in all three UDCaT-3 materials the pore volumes decreased from 0.37 to 0.31 cm^3/g for (i)–(iii) as the V/Mn ratio increased. The pore size distribution of UDCaT-3(iii) showed the presence of mesopores. The broad peak at about 25 Å is evidence for the presence of mesopores in UDCaT(iii). Pore diameters are in the range of 16 to 64 Å with the maximum contribution of pore volume by mesopores in the range of 21 to 28 Å. Phenol adsorption studies were thus conducted to provide evidence that mesopores are intra-particle and there was no artifact of inter-particle porosity being measured. The adsorption and desorption of phenol from an aqueous solution of concentration (1000 ppm) at room temperature on UDCaT-3(iii) were studied to find that phenol was indeed chemisorbed on UDCaT-3(iii) (Figure 2, **B**).

The ESR measurements were used to study the chemical environments of Mn in the ternary oxide, $Mn(VO_3)_2$ in UDCaT-3(iii). The ESR spectra of the UDCaT-3(iii) and OMS-2 are shown in Figure 3. At room temperature, the ESR spectra of UDCaT-3(iii) showed a broad single line signal centered at $g=2.0$ and no hyperfine or other resonances were found. Both Mn^{2+} and Mn^{4+} can give similar ESR spectra. However, Mn^{4+} shows g values less than 2. Mn^{2+} ions show purple to violet color whereas Mn^{4+} ions are yellow colored.[20,21] The color of the samples and g value at 2.0 suggest the presence of Mn^{2+} in an octahedral co-ordination structure. However, both the OMS-2 structure and $Mn(VO_3)_2$ have Mn ions at close distances, which may lead to antiferromagnetic interactions and a loss of the ESR signal. Thus, it was very difficult to conclude if the signal was obtained from Mn sites of the OMS-2 framework or from Mn of $Mn(VO_3)_2$. The TEM of OMS-2 and UDCaT-3(iii) are compared in Figure 4. They show the presence of mixed phases of the tunnel structure of OMS-2 and new $Mn(VO_3)_2$ ternary oxide particles finely dispersed on the rod-like morphology of OMS-2. The size of the OMS-2 crystals was observed to decrease which can be attributed to the solid-state reaction with V_2O_5 crystallites.

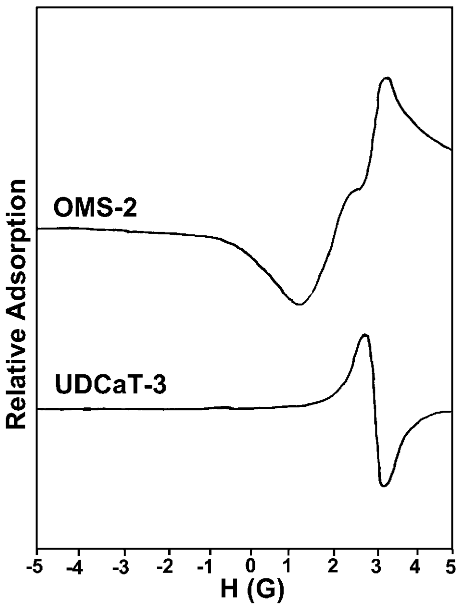

Figure 3. ESR spectra of OMS-2 and UDCaT-3(iii).

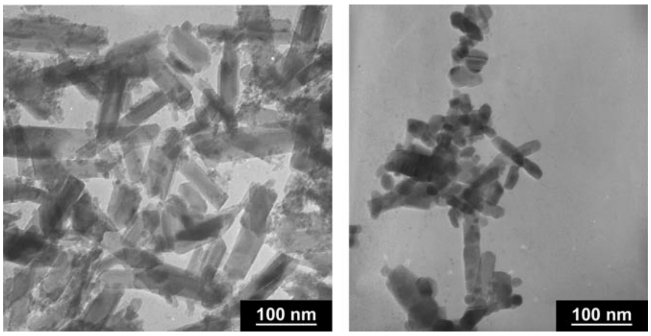

Figure 4. TEM of OMS-2 (*left*)and UDCaT-3(iii) (*right*).

The IR spectra of UDCaT-3(iii) and OMS-2 showed no prominent differences, other than enhanced intensities (Figure 5). Peaks at wave numbers 600 and 520 cm^{-1} are characteristics of OMS-2. Peaks in the region 3400–3600 cm^{-1} belong to −OH groups of sorbed water molecules present in the framework. The bending vibration bands of water molecules were seen at ~1640 cm^{-1}. The bands in the region of 700–760 cm^{-1} are due to vibrations of Mn−O bonds.

Catalytic Activity of UDCaT-3

Of the three materials, UDCaT-3(iii), showed great promise as a catalyst. It was examined in three different types of reactions, namely, oxidation of cinnamyl alcohol to cinnamaldehyde, oxidation of benzyl alco-

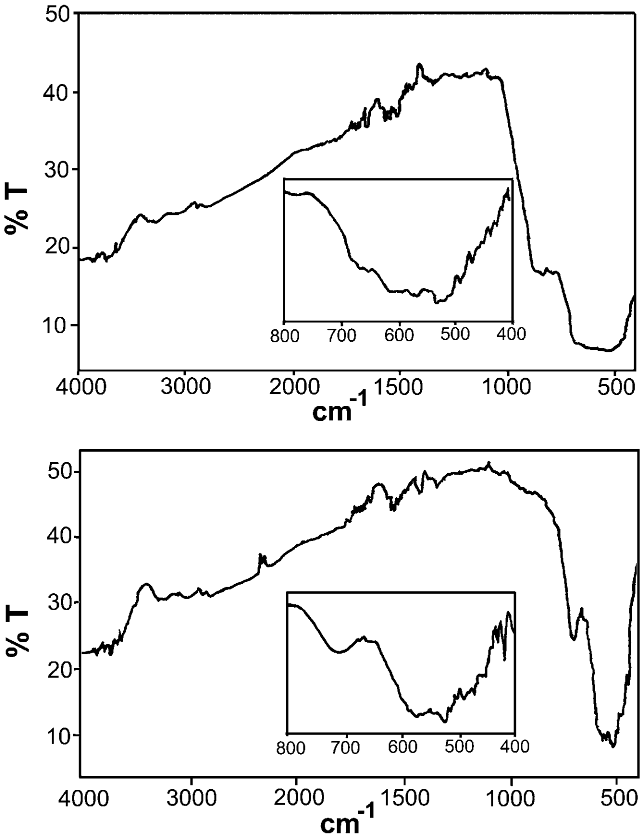

Figure 5. IR spectra of OMS-2 and UDCaT-3(iii).

hol to benzaldehyde, hydroxylation of phenol to dihydroxybenzenes as well as hydroxylation of acetophenone to *p*- and *o*-hydroxyacetophenones, and hydrogenation of *p*-nitroanisole to *p*-anisidine.

Oxidation of Cinnamyl Alcohol

The partial oxidation of cinnamyl alcohol to cinnamaldehyde was studied by using aqueous H_2O_2 (30% w/v) and *tert*-butyl hydroperoxide as the oxidizing agent. Since the organic phase and aqueous H_2O_2 are mutually immiscible, a phase-transfer agent, cetyl(trimethyl)ammonium bromide (CTAB) was used in the H_2O_2 oxidation experiment. Due to the decomposition of H_2O_2 the oxidation methodology was designed in a semi-batch process instead of batch-type process. The reaction conditions were optimized by performing a series of preliminary experiments and a separate blank experiment. The following preliminary experiments were performed for the oxidation of cinnamyl alcohol; (a) using OMS-2 (support) as a catalyst and H_2O_2 as an oxidizing agent, (b) V_2O_5 as a catalyst and H_2O_2 as an oxidizing agent, (c) UDCaT-3(iii) as a catalyst and H_2O_2 as an oxidizing agent, and (d) a blank experiment, reaction without any catalyst using only H_2O_2 as an oxidizing agent. There was no noticeable conversion of alcohol in all four preliminary experiments. This observation proved that there was no contribution from the OMS-2 support towards the catalytic activity and there was no oxidation with the oxidizing agent in the absence of a catalyst. A typical experiment was performed with UDCaT-3(iii) as a catalyst and H_2O_2 as an oxidizing agent in conjunction with CTAB as a phase-transfer agent and the reaction proceeded smoothly to give a cinnamyl alcohol conversion of 92% with cinnamaldehyde as the major product (97% selectivity). This observation confirmed the synergistic action of the heterogeneous catalyst UDCaT-3(iii) and CTAB as a phase-transfer agent. In the case of *tert*-butyl hydroperoxide as the oxidizing agent (without CTAB), the conversion of cinnamyl alcohol was limited to 48% with cinnamaldehyde as the major product with 97% selectivity. The effect of composition of UDCaT-3 with varying V/Mn ratios was studied by using aqueous H_2O_2. At the very low V/Mn ratio of 0.125 in UDCaT-3(i), vanadium metal is dispersed in the form of very small crystallites over the tunnels of the octahedral molecular sieve, as evident from the X-ray diffraction analysis. However, oxidation of cinnamyl alcohol does not take place. On increasing the V/Mn ratio to 0.31, in UDCaT-3(ii), the reaction proceeded with a cinnamyl alcohol conversion of 39% to yield cinnamaldehyde (98% selectivity). X-ray diffraction reveals the formation of Mn-V ternary oxide over the tunnels of OMS-2. On further increasing the V/Mn ratio to 0.65, larger domains of Mn-V ternary oxide are formed. This reaction proved to be an interesting example of partial oxidation as there is no carboxylic acid formation even if an excess of peroxides was used and the C=C bond remained intact without any intramolecular hydrogen transfer. The catalytic performance of UDCaT-3(iii) was compared with those of other state-of the-art catalysts (Table 3).[22–26] The UDCaT-3(iii) catalyst showed higher catalytic activity and selectivity towards cinnamaldehyde in comparison with transition metal peroxo complexes, $[PPh_4]_2[MoO_3(O_2)_4]$ (entry 5) and $RuCl_2(PPh_3)_3$ (entry 7). UDCaT-3(iii) exhibited similar yield and selectivity as compared with the noble metals, Pt and Ru supported on alumina (entries 1 and 4). The economically cheaper and easier synthesis of UDCaT-3(iii) made it an attractive alternative to noble metal catalysts. The oxidation of cinnamyl alcohol seems to conform to the Mars van Krevelen mechanism. The reduced site is regenerated by oxygen transferred from oxidizing agent brought to the site by the phase-transfer agent. In the literature, Makwana et al.[27] have reported a two-step Mars van Krevelen model involving an exchange between the gas phase and lattice oxygen for the oxidation of benzyl alcohol by molecular O_2 in the liquid phase using OMS-2.

Table 3. Comparison of activities and selectivities of different catalysts with UDCaT-3(iii) in oxidation of cinnamyl alcohol to cinnamaldehyde.

No.	Catalyst	Temp. [K]	Solvent	Oxidizing agent	TOF [h^{-1}]	Y [%]	S [%]	Ref.
1	5% Pt-0.8% Bi/Al_2O_3	313	H_2O + detergent	O_2	144	94	98	[22]
2	PMA/VAMO	333	$PhCH_3$	H_2O_2	87	97	100	[23]
3	UDCaT-3(iii)[a]	333	EDC	H_2O_2	31	92	97	–
4	1.4% Ru/Al_2O_3	356	$PhCF_3$	O_2	27	98	98	[22]
5	$[PPh_4]_2[MoO_3(O_2)_4]$	RT	MDC	H_2O_2	–	45	–	[24]
6	Diphenyl selenide	Reflux	benzene	*t*-BuOOH	–	87	–	[25]
7	$RuCl_2(PPh_3)_3$	298	MDC	$Me_3SiO\text{-}OSiMe_3$	–	80	–	[26]

[a] *Reaction conditions:* cinnamyl alcohol 0.0166 mol, H_2O_2 0.05 mol, catalyst loading 0.02 $g\,cm^{-3}$, CTAB 1.66 mmol, speed of agitation 1200 rpm, temperature 60 °C, time 40 min, rate of addition of peroxide 0.021 mmol/s.

Oxidation of Benzyl Alcohol

The partial oxidation of benzyl alcohol to benzaldehyde was studied by using aqueous H_2O_2 (30% w/v) and *tert*-butyl hydroperoxide as the oxidizing agents. Due to the immiscibility of the organic phase and aqueous H_2O_2, CTAB was used as phase-transfer agent in the H_2O_2 oxidation experiment. In the case of H_2O_2 as the oxidizing agent there was no reaction in the presence of either CTAB or UDCaT-3(iii) alone. However, in the presence of both of them, the reaction proceeded smoothly to give a benzyl alcohol conversion of 42% with benzaldehyde as the major product (90% selectivity). In the case of *tert*-butyl hydroperoxide as the oxidizing agent (without CTAB), the conversion of benzyl alcohol was limited to 22% with benzaldehyde as the major product with 89% selectivity. In a separate experiment, with an objective to avoid the use of CTAB, the oxidation of benzyl alcohol was performed with H_2O_2 and UDCaT-3(iii) in the solvent mixture of acetonitrile and 1,2-dichloroethane, without using CTAB, but there was no reaction. When this experiment was repeated in the presence of CTAB, the reaction proceeded with a benzyl alcohol conversion of 15% to yield benzaldehyde (96% selectivity), hence the use of CTAB was unavoidable. Higher conversions of benzyl alcohol were obtained when aqueous H_2O_2 was used as the oxidizing agent in conjunction with CTAB as phase-transfer agent in 1,2-dichloroethane as a solvent. UDCaT-3(iii) showed higher reactivity in the benzyl alcohol oxidation with H_2O_2 and CTAB as compared to *tert*-butyl hydroperoxide as the oxidizing agent. This may be attributed to the higher steric constraint within the catalyst pores when using a bulkier oxidant (*tert*-butyl hydroperoxide) as compared to H_2O_2 and the subsequent availability of a higher active oxygen content from the synergistic combination of H_2O_2 and CTAB as compared with *tert*-butyl hydroperoxide.

Hydroxylation of Phenol

The catalytic activity of UDCaT-3(iii) was tested in the hydroxylation of phenol by using aqueous H_2O_2 (30% w/v) that led to a mixture of *para*- and *ortho*-dihydroxybenzenes. In this reaction, selectivity to hydroquinone (*para*-dihydroxybenzene) is desired.[28,29] We obtained 15% conversion of phenol with the very high *p*/*o* ratio of 2.84. No *p*-benzoquinone (BQ) was detected. The phenol hydroxylation reaction was very clean and there was no formation of black tarry material in the reaction mixture, which was usually observed in some cases. The efficacy of UDCaT-3(iii) in phenol hydroxylation was compared with other state-of-the-art catalysts (Table 4).[30–35] Dawson-type heteropoly acids (entry 2) or metal oxides (entry 4) show either a low catalytic activity or undesirable product selectivity. $Fe(NO_3)_3$ salt and Fe-MCM-41 (entries 5 and 6) exhibit very high activity with 70 and 60% conversion of phenol, respectively. However, effective conversion to dihydroxybenzene was only 29 and 38%, respectively, and a large amount of tar was formed. Titanium-substituted molecular sieves such as TS-1 (entry 8) exhibited unique catalytic behavior including fairly high activity and *p*-selectivity in phenol hydroxylation. The UDCaT-3(iii) catalyst showed good results with a very high *p*-selectivity similar to that of TS-1. Once again, the economically cheaper and easier synthesis of UDCaT-3(iii) made it a very promising hydroxylation catalyst.

Hydroxylation of Acetophenone

The catalytic activity of UDCaT-3(iii) was also studied for the direct ring hydroxylation of acetophenone. The methods so far reported in the literature mention very low yields of *para*-hydroxyacetophenone and very high yields of *ortho*-hydroxyacetophenone, which is commercially less important than *para*-hydroxyacetophenone. UDCaT-3(iii) was employed for the direct ring hydroxylation of acetophenone to get 31% con-

Table 4. Comparison of activities and selectivities of different catalysts with UDCaT-3(iii) in the hydroxylation of phenol.

No.	Catalyst	Temp. [K]	Phenol Conv. [%]	Product distribution [wt%]				Ref.
				HQ	CAT	others	HQ/CAT	
1	UDCaT-3(iii)[a]	333	15	74	26	–	2.84	–
2	$(Cpyr)_9P_2W_{15}V_3O_{62}$	333	7.4	43.0	17.2	39.8	2.5	[30]
3	0.2Cu-VSB-5	333	47.7	28.4	19.3	–	1.5	[31]
4	V_2O_5-Nd_2O_3	353	12	28.9	65.3	5.8	0.44	[32]
5	$Fe(NO_3)_3$	343	70	9	20	71	0.45	[33]
6	Fe-MCM-41	343	60	12.2	25.8	62	0.47	[33]
7	CuO-MCM-48	333	21.8	33.4	52	14.6	0.64	[34]
8	TS-1	333	37.4	56.2	30.5	13.4	2.3	[35]

[a] *Reaction conditions:* phenol 0.01 mol, methanol 26 mL, H_2O_2 0.03 mol, catalyst loading 0.02 g cm^{-3}, speed of agitation 1200 rpm, temperature. 60 °C, time 5 h, rate of addition of peroxide 0.0017 mmol/s.

version of acetophenone with *para*-hydroxyacetophenone as the major product (65% selectivity) and *ortho*-hydroxyacetophenone as the minor product (35% selectivity). UDCaT-3(iii) was found to be a better alternative to the corrosive and difficult to handle Lewis acid salts. The reaction methodology with UDCaT-3(iii) was very clean and environment friendly.

Hydrogenation of *p*-Nitroanisole

In the hydrogenation of *p*-nitroanisole to *p*-anisidine, the selective reduction of the nitro group to an amino group is highly desirable. The efficacy of the UDCaT-3(iii) catalyst was finally tested in the hydrogenation of *p*-nitroanisole to obtain 100% conversion of *p*-nitroanisole with *p*-anisidine as the only product. The catalytic activity of UDCaT-3(iii) was compared with the activity of other reported catalysts as shown in Table 5.[36] It is evident that UDCaT-3(iii) is highly active and showed excellent catalytic activity in hydrogenation of *p*-nitoanisole to *p*-anisidine. This made UDCaT-3(iii) a highly versatile, selective and promising catalyst in comparison to the noble metal catalysts.

Table 5. Hydrogenation of *p*-nitroanisole to *p*-anisidine using different catalysts.

Catalyst	Conversion [%]	Selectivity [%]
UDCaT-3(iii)[a]	100	100
5% Pd/C[a,b]	100	100
Raney nickel[a,b]	55	100
2% Rh/C[a,b]	9	100

[a] *Reaction conditions:* 100-mL Parr autoclave, *p*-nitroanisole 0.02 mol, solvent 2-propanol, hydrogenation pressure 0.5 MPa, catalyst loading 0.015 g cm^{-3}, speed of agitation 1000 rpm, temperature 100 °C.

[b] Yadav and Goel.[36]

Evaluation of the Nature of the Catalytic Activity: Heterogeneous vis-à-vis Homogeneous

Catalysts based on vanadium oxides are known for leaching of V into solution in the presence of H_2O_2 giving rise to homogeneous catalytic species. In order to understand the true nature of the catalytic activity of UDCaT-3(iii), we performed the following experiments using the oxidation of benzyl alcohol as a model reaction. In the first experiment, H_2O_2 (0.021 mmol/s) was slowly added to the reaction mixture that consisted of benzyl alcohol (0.0166 mol), in 1,2-dichloroethane (20 mL). Keeping a PMA/VAMO catalyst loading of 0.02 g cm^{-3}, the reaction was carried out at 60 °C for 30 min. The reaction mixture was filtered hot to separate the catalyst particles. The reaction was further continued at the same temperature for the next 30 min in the absence of solid catalyst particles. It was observed that the reaction stopped in the absence of solid catalyst particles (Figure 6).

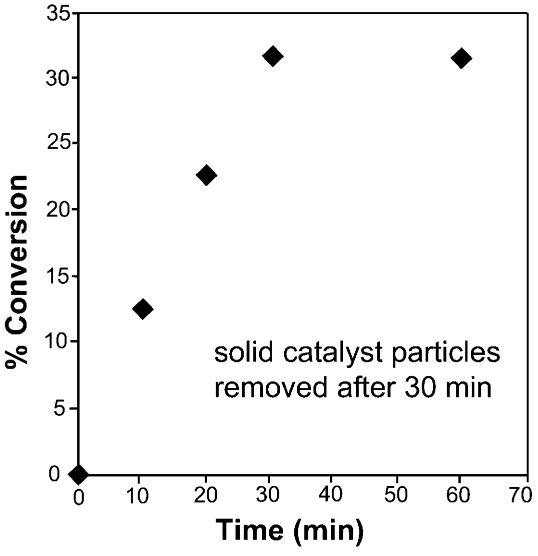

Figure 6. Evaluation of leaching from UDCaT-3(iii).

A second experiment was performed to reconfirm the absence of any active homogeneous V or Mn species present in the solvent in the dissolved state. UDCaT-3(iii) catalyst was subjected to vigorous stripping in 1,2-dichloroethane for 1 h. The catalyst was filtered and the filtrate was used as the reaction medium. No noticeable transformation of alcohol confirmed the heterogeneous behavior of the catalyst. We did not find any evidence of leached homogeneous V or Mn species responsible for the homogeneous catalytic activity. This can be attributed to the formation of the Mn-V ternary oxide, which did not leach Mn or V species into the solution under the reaction conditions used in this study, or the leaching was so negligible that it effectively did not contribute towards the catalytic activity and as a result we attribute the observed catalytic activity of UDCaT-3(iii) as heterogeneous.

Reusability of Catalyst

The partial oxidation of benzyl alcohol was arbitrarily selected as a model reaction to study the reusability of the catalyst. The catalyst reusability was studied three times, including the use of fresh catalyst (Figure 7). The catalyst was filtered, washed with 1,2-dichloroethane and subsequently dried at 200 °C for 2 h before being reused in subsequent batches. In the presence of the fresh catalyst, the conversion of benzyl alcohol was 32.8%. During the third run the conversion decreased to 31.5% while the selectivity towards benzaldehyde remained unchanged. This might be because of the observed losses due to attrition during filtration of catalyst particles, as no make-up quantity of catalyst was added. UDCaT-3 thus showed a very good reusability.

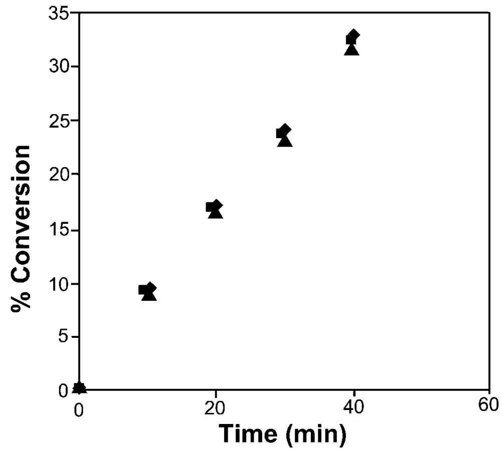

Figure 7. Reusability of catalyst: ◆ – fresh use, ■ – first reuse, ▲ – second reuse; BnOH 0.0166 mol, 30% w/v aqueous H_2O_2 0.033 mol, UDCaT-3(iii) 0.02 g cm^{-3}, CTAB 1.66 mmol, speed of agitation 1000 rpm, temperature 60 °C.

Conclusions

The synthesis and characterization of a novel redox catalyst system, UDCaT-3, is reported for the first time and it is based on OMS-2 by using different Vn/Mn ratios. The material with a ratio of 0.65 is found to be the best. X-ray diffraction studies reveal the formation of a manganese-vanadium ternary oxide by the solid-state interaction between vanadia and manganese oxide during the thermal treatment. The framework of UDCaT-3 possesses lattice oxygen vacancies. UDCaT-3 proved to be a very versatile and selective catalyst in the wide array of redox reactions and its reusability with consistent performance makes UDCaT-3 a promising candidate to develop an economically viable high-performance industrial catalyst.

Experimental Section

Chemicals and Catalysts

Cinnamyl alcohol, 30% w/v aqueous hydrogen peroxide, acetophenone, *p*-anisidine, 2-propanol, 1,2-dichloroethane, methanol and carbon tetrachloride were procured from M/s s. d. Fine Chemical Ltd., Mumbai, India. Phenol was obtained from Merck, Mumbai., Ltd. *p*-Nitroanisole was obtained from Fluka, Germany. 5% w/w Pd/C was obtained from M/s s. d. Fine Chemical Ltd., Mumbai, India. Raney nickel and 5 w/w% Ru/C were obtained from Kallin Industries, Mumbai. 20% w/w Ni/SiO_2 and 2% Rh/C were procured from M/s Filtra Specialty Chemicals, Mumbai. All chemicals used in this work were analytical grade reagents and used without further purification. The hydrogen cylinder was obtained from Industrial Oxygen Co. Ltd., Mumbai.

Synthesis of UDCaT-3

OMS-2 was synthesized by a sol-gel route.[16] For the synthesis of the ternary oxide in the UDCaT-3 series, the vanadium precursor was adsorbed on the surface of OMS-2 by wet impregnation. A known amount of ammonium metavanadate was dissolved in 25 mL of 1 M oxalic acid solution. This precursor solution was then added to OMS-2 (3 g) and the temperature was raised to 65 °C. The mixture was stirred continuously until it was nearly dry. The product so obtained was further dried at 120 °C for 10 h, crushed to a powder form and subsequently calcined at 450 °C for 6 h to get a brown-colored powder. This material is named UDCaT-3. Three atomic ratios of V/Mn, namely 0.125, 0.31 and 0.65, were used to synthesize UDCaT-3(i), UDCaT-3(ii), and UDCaT-3(iii), respectively.

Structural Characterization

All the synthesized materials, UDCaT-3(i-iii) and OMS-2 were characterized by X-ray diffraction (XRD), surface area and pore size measurements, elemental analysis, electron spin resonance (ESR), infrared (IR) spectrosocopic and scanning electron microscopic (SEM) analyses. The X-ray scattering measurements were done with Cu-Kα radiation by using a Siemens D 500 diffractometer. The scattered intensities were collected from 10° to 60° (2θ) by scanning at 0.025° (2θ) steps. Surface area, pore volume and pore sizes were calculated from BET nitrogen adsorption/desorption isotherms obtained at liquid nitrogen temperature by using a Micromeritics ASAP 2010 analyser. SEM images were recorded with a Cameca SU 30 microscope. FT-IR spectra were recorded by using Perkin- Elmer Paragon 500 FT-IR spectrometer.

Adsorption of Phenol on UDCaT-3(iii)

In order to ascertain that the organic molecules are chemisorbed on to the surface of the pores of the catalyst, phenol was chosen as the adsorbate. The adsorption of dilute phenol from aqueous solution (1000 ppm) was studied by using catalyst UDCaT-3(iii) at 30 °C. For this purpose, 1 g UDCaT-3(iii) was used with 50 mg phenol in 50 mL water in an agitated vessel. The experiment was performed in a fully baffled, 5-cm inner diameter, cylindrical vessel made of glass (capacity 100 mL, flat bottom). It was equipped with a standard six-blade pitched turbine impeller of 1.6 cm diameter. The mixture was well agitated at 400 rpm. Samples were withdrawn periodically from the aqueous solution of phenol and analyzed by a Chemito 2100 Scanning UV spectrophotometer at 271 nm. A calibration curve was prepared. The decrease in the concentration of phenol was measured and the adsorption isotherm of phenol on UDCaT-3(iii) was prepared. Adsorption of phenol on UDCaT-3(iii) was further confirmed by subsequent desorption. UDCaT-3(iii) catalyst particles were filtered from the aqueous solution, washed four times with distilled water and subsequently the particles were mixed with 50 mL methanol. The slurry was sonicated for 30 min. Sampling was done periodically to monitor the phenol concentration in methanol. The intensity of the peak obtained at 271 nm on UV spectrophotometry corresponded to a 49.5 ppm phenol concentration (2.48 mg in 50 mL). This also demonstrated that phenol gets chemisorbed on UDCaT-3(iii).

Liquid-Phase Oxidations

The partial oxidation of cinnamyl alcohol and benzyl alcohol was carried out by using 30% w/v of aqueous hydrogen peroxide in the mechanically agitated reactor described earlier. It was also equipped with a reflux condenser. The assembly was maintained at 60 °C. Alcohol (0.0166 mol), PTC (0.00167 mol) and UDCaT-3(iii) (0.02 $\mathrm{g\,cm^{-3}}$) in 1,2-dichloroethane (20 mL) as solvent was stirred at 1000 rpm. The required amount of peroxide (0.05 mol, 5.67 mL) was added using a peristaltic pump, at a rate of 0.021 mmol/s over 40 min. In the experiment where a solvent mixture was used as reaction medium, the solvent composition was 30% acetonitrile (6 mL) and 70% 1,2-dichloroethane (14 mL). Samples were withdrawn periodically, filtered and analyzed on a Chemito 8510 gas liquid chromatograph with FID. A 2 m × 1/8 in stainless steel column, packed with Chromosorb W loaded with 10% OV-17 (80–100 mesh size) was used. Synthetic mixtures were used to quantify the data.

Liquid-Phase Hydroxylations

The hydroxylation of phenol by hydrogen peroxide was performed in the same reactor, as mentioned before, under reflux at 60 °C for 5 h with UDCaT-3(iii) as the catalyst to get dihydroxybenzenes. A reaction mixture of 0.01 mol phenol and 26 mL methanol, with a catalyst loading of 0.02 $\mathrm{g\,cm^{-3}}$ liquid volume was uniformly stirred. 0.03 mol of aqueous solution of hydrogen peroxide (30% w/v) was added by using a peristaltic pump at a constant rate of 0.0017 mmol/s over 5 h. The total volume of aqueous H_2O_2 added was 3.4 mL. The liquid-phase samples were analyzed by HPLC (Tosoh) by using an RP C-18 column and UV detector at 280 nm.

For the hydroxylation of acetophenone to hydroxyacetophenones, the reaction mixture consisted of 0.01 mol acetophenone, UDCaT-3(iii) (0.02 $\mathrm{g\,cm^{-3}}$) and 10 mmol of acetic acid at 80 °C. To this 0.05 mol aqueous hydrogen peroxide (30% w/v) was added using a peristaltic pump, at a rate of 0.0028 mmol/s over 5 h. The analysis was done by gas chromatography over a 10% OV-17 (2 m × 3.2 mm) column.

Hydrogenation

Hydrogenation was carried out in a 100-mL stainless steel Parr autoclave. The reaction mass consisting of 0.02 mol *p*-nitroanisole in s-propanol as solvent (40 mL) and 0.6 g UDCaT-3(iii) was charged into the autoclave and it was pressurised with hydrogen to 0.5 MPa and agitated. The pressure inside the autoclave was maintained at 0.5 MPa throughout the course of the reaction. Clear samples were withdrawn periodically and analyzed by gas chromatography over 10% SE-30 on a Chromosorb (2 m × 3.2 mm) column.

Identification and Isolation of Products

Product identification in all cases was done by TLC, GC and GC-MS. The retention times of the reaction products were also found to match those of the authentic compounds.

Acknowledgements

Partial funding was made available through CSIR-NMITLI project. GDY also acknowledges support from the Darbari Seth Professor Endowment for a personal chair. He also thanks the Purdue University for inviting him as Distinguished Visiting Scholar under their President's Asian Initiative Program, which allowed him to indulge in creative pursuits.

References

[1] C. S. Cundy, P. A. Cox, *Micro. Meso. Mater.* **2005**, *82*, 1.
[2] G. Oye, J. Sjoblom, M. Stocker, *Adv. Colloid Inter. Sci.* **2001**, *89–90*, 439.
[3] Q. Huo, D. I. Margolese, *Nature* **1994**, *368*, 317.
[4] S. L. Suib, *Chem. Rev.* **1993**, *93*, 803.
[5] G. Brink, I . W. C. E. Arends, R. A. Sheldon, *Science* **2000**, *287*, 1636.
[6] D. R. Jensen, J. S. Pugsley, M. S. Signam, *J. Am. Chem. Soc.* **2001**, *123*, 7475.

[7] M. Pagliaro, S. Campestrini, R. Ciriminna, *Chem. Soc. Rev.* **2005**, *34*, 837.
[8] V. D. Makwana, Y.-C. Son, A. R. Howell, S. L. Suib, *J. Catal.* **2002**, *210*, 46.
[9] H.-B. Ji, K. Ebitani, T. Mizugaki, K. Kaneda, *Catal. Commun.* **2002**, *3*, 511.
[10] R. A. Sheldon, J. K. Kochi, *Metal-Catalyzed Oxidation of Organic Compounds*, Academic Press, New York, **1981**, pp 350–357.
[11] E. Takezawa, S. Sakaguchi, Y. Ishii, *Org. Lett.* **1999**, *1*, 713.
[12] B. Hinzen, R. Lenz, S. V. Ley, *Synthesis* **1998**, 977.
[13] K. Kaneda, Y. Fujie, K. Ebitani, *Tetrahedron Lett.* **1997**, *38*, 9023.
[14] K. Ebitani, Y. Fujie, K. Kaneda, *Langmuir* **1999**, *15*, 3557.
[15] S. L. Suib, *Stud. Surf. Sci. Cat.* **1996**, *102*, 47.
[16] N. Duan, S. L. Suib, C.-L. O'Young, *Chem. Commun.* **1992**, 1213.
[17] Y.-C. Son, V. D. Makwana, A. R. Howell, S. L. Suib, *Angew. Chem. Int. Ed. Engl.* **2001**, *40*, 4280.
[18] R. Jothiramalingam, B. Viswanathan, T. K. Vardarajan, *J. Mol. Cat. A: Chem.* **2006**, *252*, 49.
[19] *Database of powder diffraction patterns; JCPDS File 34–168*, International Centre for Diffraction Data, Newtown Square, PA 19073, **1994**.
[20] D. Goldfarb, *Zeolites* **1989**, *9*, 509.
[21] H. G. Manyar, G. S. Chaure, A. Kumar, *Green Chem.* **2006**, *8*, 344.
[22] T. Mallat, A. Baiker, *Chem. Rev.* **2004**, *104*, 3037.
[23] H. G. Manyar, G. S. Chaure, A. Kumar, *J. Mol. Cat. A: Chem.* **2006**, *243*, 244.
[24] N. J. Campbell, A. C. Dengel, C. J. Edwards, W. P. Griffith, *J. Chem. Soc. Dalton Trans.* **1989**, 1203.
[25] I. Kuwajima, M. Shimizu, H. Urabe, *J. Org. Chem.* **1982**, *47*, 837.
[26] S. Kanemoto, S. Matsubara, K. Takai, K. Oshima, K. Utimoto, H. Nozaki, *Bull. Chem. Soc. Jpn.* **1988**, *61*, 3607.
[27] V. D. Makwana, Y.-C. Son, A. R. Howell, S. L. Suib, *J. Catal.* **2002**, *210*, 46.
[28] C. Perego, A. Carati, P. Ingallina, M. A. Mantegazza, G. Bellussi, *Appl. Catal. A: Gen.* **2001**, *221*, 63.
[29] K. Weisermel, J.-H. Arpe, *Industrial Organic Chemistry*, VCH, Weinheim, **1993**, p 358.
[30] J. Yu, P. Yang, Y. Yang, T. Wu, J. R. Parquette, *Catal. Commun.*, **2006**, *7*, 153.
[31] Y. Jiang, Q. Gao, *Materials Lett.* **2007**, *61*, 2212.
[32] S. Shylesh, T. Radhika, K. Sreeja Rani, S. Sugunan, *J. Mol. Cat. A: Chem.* **2005**, *236*, 253.
[33] J.-S. Choi, S.-S. Yoon, S.-H. Jang, W.-S. Ahn, *Catal. Today* **2006**, *111*, 280.
[34] L.-L. Lou, S. Liu, *Catal. Commun.* **2005**, *6*, 762.
[35] T. Yokoi, P. Wu, T. Tatsumi, *Catal. Commun.* **2003**, *4*, 11.
[36] G. D. Yadav, P. K. Goel, *Clean Tech. Environ. Policy* **2003**, *4*, 227.