ELSEVIER

Applied Catalysis A: General 181 (1999) 77–85

APPLIED CATALYSIS A: GENERAL

Selective oxidation of *p*-methoxytoluene to *p*-methoxybenzaldehyde over V_2O_5/CaO–MgO catalysts

Benjaram M. Reddy*, M. Vijaya Kumar, K. Jeeva Ratnam

Inorganic Chemistry Division, Indian Institute of Chemical Technology, Hyderabad 500 007, India

Received 21 July 1998; received in revised form 20 October 1998; accepted 13 November 1998

Abstract

The vapour phase partial oxidation of *p*-methoxytoluene to *p*-methoxybenzaldehyde was investigated over various V_2O_5/CaO–MgO catalysts at 673 K and under normal atmospheric pressure. Among various catalysts the 14% V_2O_5/CaO–MgO sample exhibited good conversion and product selectivity. The CaO–MgO mixed oxide support was prepared by a homogeneous co-precipitation method using urea as hydrolysing agent. Ammonium metavanadate was used as source of V_2O_5 and the vanadia contents were varied from 2 to 14 weight per cent. The CaO–MgO support and various V_2O_5/CaO–MgO catalysts were characterized by means of X-ray diffraction, FT-infrared, electron spin resonance, scanning electron microscopy, NH_3 and CO_2 chemisorption, and BET surface area methods. Characterization results suggest that the vanadia does not form layer structures on the support surface, instead but interacts very strongly with the support oxide, in particular with MgO, and forms amorphous compounds. The NH_3 and CO_2 uptakes clearly distinguish the acid–base characteristics of the catalysts and correlate with catalytic properties.

Keywords: Vanadium oxide; CaO–MgO; V_2O_5/CaO–MgO; *p*-Methoxytoluene conversion; *p*-Methoxybenzaldehyde; CO_2 uptake; NH_3 uptake; Acidity; Basicity

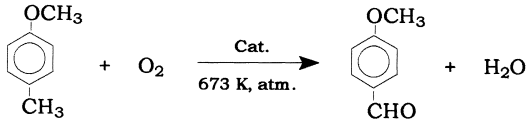
1. Introduction

Mixed oxides of CaO–MgO or Ca^{2+} doped MgO have been reported to show high activity and selectivity for oxidative coupling of methane (OCM) [1,2]. It is well known that CaO–MgO mixed oxide exhibits stronger basic properties than pure MgO alone [3,4]. In addition to more basicity, the CaO–MgO also exhibits some structural deformation, which may be involved in catalytic activity. When an MgO surface is doped with Ca^{2+}, rumpled regions co-exist with the non-reconstructed regions. The increased strain normally induces a large number of defects on the surface, which are also believed to participate in the catalytic reactions. Increased lattice strain, resulting in higher C_2 selectivity during the OCM, was already reported for MgO catalysts doped with Na^+ [5]. Structural distortion by addition of promoter atoms leads to oxygen species of low co-ordination. These low co-ordinated surface oxygen species are thought to be the reactive sites involved in OCM and related reactions [6,7].

Para-methoxybenzaldehyde (*p*-anisaldehyde) is an important chemical and chemical intermediate in the pharmaceutical and perfumery industry (Scheme 1).

*Corresponding author. Fax: +91-40-717-3387; e-mail: iict@ap.nic.in

0926-860X/99/$ – see front matter
PII: S0926-860X(98)00385-8



Scheme 1.

Substituted benzaldehydes are normally synthesized from the corresponding toluenes in the liquid phase in the presence of Co, Ce and Mn salts in acetic acid medium or by electrochemical methods [8]. However, efficiencies of these processes are not so high and the processes also produce to carrying out this reaction in the vapour phase with the involvement of a suitable heterogeneous catalyst system [9–12]. As per the literature reports, the selective oxidation reaction depends on both surface acid–base characteristics and redox properties of the catalysts [13–16]. Vanadium oxide, when supported on the basic oxides such as MgO (V–Mg–O), shows better performance than on the acid supports like alumina, titania, and titania–silica [17]. It is expected that an increase in the basicity of the catalysts will enhance the selectivity towards the anisaldehyde formation. Therefore, a systematic study was undertaken to gain more knowledge about the structure of vanadium oxide on CaO–MgO mixed support. The V_2O_5/CaO–MgO is also an interesting catalyst system with structural and catalytic importance. In this study, a series of V_2O_5/CaO–MgO catalysts containing various amounts of vanadium oxide were prepared, characterized by XRD, FTIR, ESR, SEM, O_2 and NH_3 uptake, and BET surface area methods, and evaluated for the title reaction.

2. Experimental

2.1. Catalyst preparation

The CaO–MgO (1:1 molar ratio) mixed oxide support was prepared by a co-precipitation method using urea as hydrolyzing agent [18]. In a typical experiment, an aqueous solution containing the required quantities of calcium nitrate, magnesium nitrate and urea was heated to 368 K with vigorous stirring. In about 6 h of heating, as decomposition of urea progressed to a certain extent, the precipitate gradually formed and the pH of the solution increased to 7–8. The pH of the solution was further raised to 10–12 with dilute ammonia and heated for 6 h to felicitate aging. The precipitate was then filtered off, washed several times with deionized water to remove residual chloride ions, dried at 393 K for 16 h and calcined at 823 K for 6 h in a closed electrical furnace. The CaO–MgO mixed oxide which supported vanadia catalysts with various V_2O_5 loadings ranging from 2 to 14 wt% were prepared by a wet impregnation method with stoichiometric aqueous solutions of ammonium metavanadate dissolved in 1 M aqueous oxalic acid. After evaporation of excess water, the impregnated samples were dried again at 393 K for 12 h and calcined at 773 K for 5 h in a flow of dry oxygen.

2.2. Catalyst characterization

X-ray powder diffraction patterns were recorded on a Philips PW-1051 instrument, using monochromated Fe K_α radiation and standard recording conditions. XRD phases present in the samples were identified with the help of ASTM powder data files. Infrared spectra were recorded on a Nicolet 740 FTIR spectrometer, using KBr discs, with a nominal resolution of 4 cm^{-1}. ESR spectra were obtained on a Brucker ER 200D-SRC X band spectrometer with 100 kHz modulation. SEM investigations were made with a Hitachi model S-520 scanning electron microscope at an applied voltage of 10 kV.

A conventional standard static volumetric high vacuum (1×10^{-6} torr) system was used for both NH_3 and CO_2 uptake measurements. The catalyst sample was evacuated at 423 K for about 4 h (10^{-6} torr) before the ammonia chemisorption study. The amount of NH_3 chemisorbed was obtained from the difference between the two successive adsorption isotherms at 423 K [19]. Between the first and second adsorption isotherms, the sample was evacuated for 2 h at 423 K, the chemisorption temperature. A fresh catalyst sample was used for CO_2 adsorption and was evacuated at 298 K for 4 h (10^{-6} torr) before the measurements. The amount of CO_2 uptake was obtained from the two successive adsorption isotherms recorded at room temperature [20].

2.3. Activity studies

A fixed bed micro-reactor operating under normal atmospheric pressure was used to determine the activ-

ity and selectivity of the catalysts. Air from a pressure cylinder was used as carrier at a flow rate of 45 ml min^{-1} and the liquid reactant was fed through a metering pump at a rate of 1 ml h^{-1}. For each run, about 1 g of catalyst sample was used. The liquid products were collected in cold traps and were analysed by gas chromatography with a Carbowax 20 M column (2 m long) and flame ionization detector. The main reaction products observed were *p*-anisaldehyde, *p*-anisic acid, traces of CO and CO_2, and some unknown products. Conversion and product selectivity were calculated as follows:

$$\text{Conversion (\%)} = 100 \times \frac{\text{(no. of moles of 4-methylanisole reacted)}}{\text{(no. of moles of 4-methylanisole introduced)}}$$

$$\text{Selectivity (\%)} = 100 \times \frac{\text{(no. of moles of product formed)}}{\text{(no. of moles of 4-methylanisole reacted)}}.$$

3. Results and discussion

The N_2 BET surface area of the CaO–MgO support was found to be 81 $m^2\,g^{-1}$. The amount of V_2O_5 essential to cover this support surface as a single molecular layer can be estimated from the area occupied per $VO_{2.5}$ (10.3×10^4 pm^{-2}) unit of the bulk V_2O_5. This theoretical estimation renders a quantity of 0.145 wt% per m^2 of the support to cover its surface with a compact single lamella of the vanadium pentoxide structure [21]. However, in reality the maximum amount of metal oxide that can be formed as a two-dimensional monolayer depends not only on the support surface area but also on the concentration of reactive surface hydroxyl groups [22]. Therefore, the actual vanadium oxide content was always less than the theoretical monolayer capacity and ranged between 0.1 and 0.07 wt% per m^2 of support, depending on the above factors [23,24]. In view of these reasons, a range of V_2O_5 loadings from 2 to 14 wt% were selected in the present investigation. Table 1 lists the composition and the surface areas of various catalysts prepared in this study. The number in the catalyst label denotes the weight percentage of V_2O_5. As prepared, the colour of the catalyst ranged from white for CaO–MgO support and those of low vanadium content samples, to slightly yellow for those of high vanadium content. No appreciable change in the colour of the catalyst was observed even after reaction studies. With increase in vanadia loading one can note from Table 1 sharp decrease in the specific surface area of the catalyst. A more likely cause for this loss is the solid state reactions leading to formation of new phases between V_2O_5 and CaO–MgO.

The X-ray powder diffractograms of CaO–MgO and various V_2O_5/CaO–MgO catalysts are shown in Fig. 1. Characteristic lines due to CaO, MgO and the hydroxides of both (in traces) are observed in the case of CaO–MgO support alone. However, in the case of V_2O_5/CaO–MgO catalysts, only the characteristic lines due to CaO are noted, most importantly, the intensity of these peaks decreases with increase in vanadia content. The XRD patterns of V_2O_5/CaO–MgO catalysts did not show any lines due to crystalline vanadium pentoxide phase or any compound of the same with the support. The absence of characteristic peaks of V_2O_5 indicates that the vanadia is either in microcrystalline state or is dissolved in the support. However, the absence of crystalline V_2O_5 phase and decrease in the intensity of CaO lines with increase in

Table 1
NH_3 uptake, CO_2 uptake, and BET surface areas of various V_2O_5/CaO–MgO catalysts obtained on a volumetric high vacuum system

Catalyst	NH_3 uptake (μ mol g^{-1} cat.)	CO_2 uptake (μ mol g^{-1} cat.)	BET SA ($m^2\,g^{-1}$)
CaO–MgO	0	69.0	81.5
2% V_2O_5/CaO–MgO	24.9	66.3	77.2
4% V_2O_5/CaO–MgO	25.8	60.2	71.8
6% V_2O_5/CaO–MgO	26.0	54.8	69.4
8% V_2O_5/CaO–MgO	26.5	46.2	60.2
10% V_2O_5/CaO–MgO	27.4	44.9	57.3
12% V_2O_5/CaO–MgO	28.6	41.3	54.2
14% V_2O_5/CaO–MgO	30.6	38.2	48.1

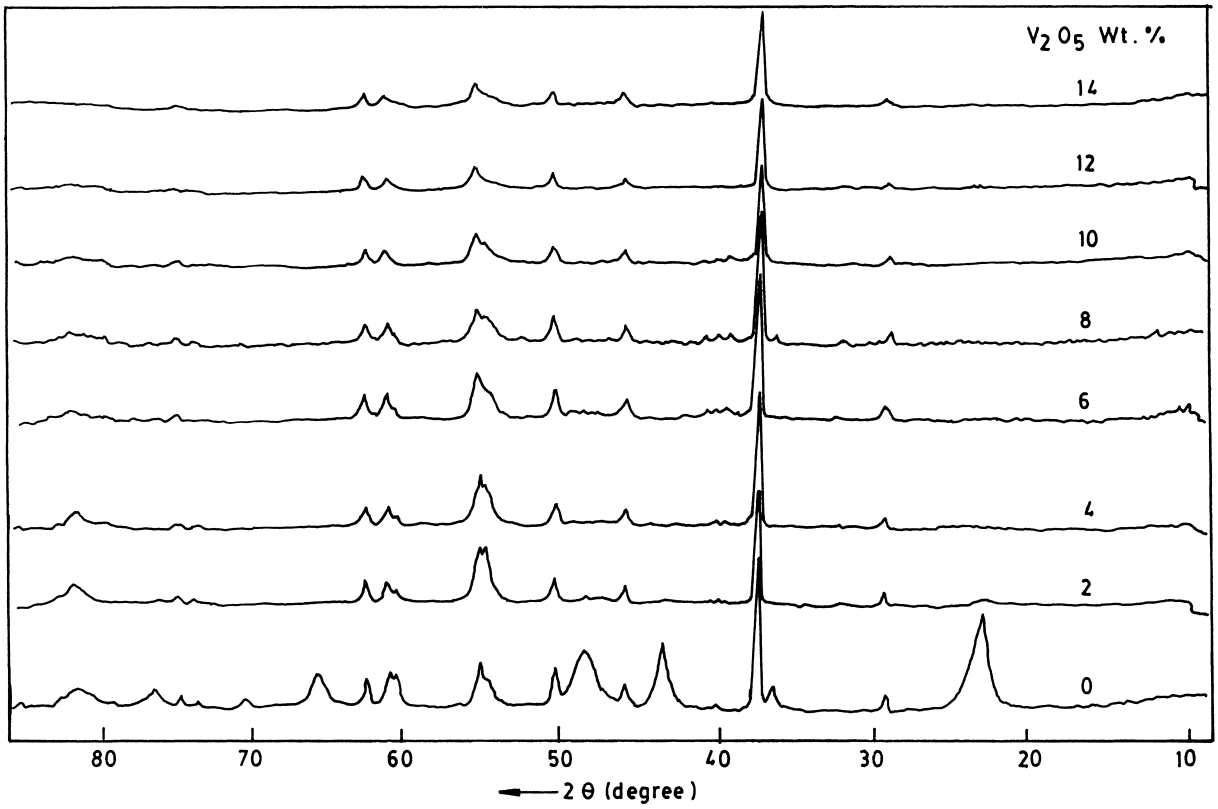


Fig. 1. X-ray powder diffraction patterns of CaO–MgO mixed oxide support and various V_2O_5/CaO–MgO catalysts

vanadia loading supports the latter observation. The absence of characteristic MgO lines also gives one the impression that the vanadia is forming V–Mg–O compounds of amorphous nature [17].

To examine the influence of the support on the V=O bond strength and surface structure of vanadium oxide species, FTIR spectra were recorded. Fig. 2 represents the FTIR spectra of CaO–MgO support and of various V_2O_5/CaO–MgO catalysts. As can be seen from Fig. 2, the CaO–MgO support shows characteristic but broad peaks at 1000, 1450, and 3600 cm^{-1}. As per the literature, the calcined samples of CaO–MgO produce absorption bands at around 1000 cm^{-1} caused by crystal lattice vibrations [25,26]. No OH stretching bands of residual surface hydroxyl groups were detected on MgO-rich samples, whereas on CaO and 50% MgO/CaO a weak band at 3640 cm^{-1} was found. In another study it was observed by deuterium exchange reaction that even after outgassing MgO at 1273 K a measurable number of surface hydroxyls remained on the surface [27]. Very interestingly, in line with XRD observations, the characteristic IR bands due to the support were also found to decrease with increase in V_2O_5 content. The IR spectrum of pure V_2O_5 shows sharp characteristic peaks at 1025 and 824 cm^{-1}. The peak at 1025 cm^{-1} is attributed to the stretching vibrations of the short V=O bonds and the 824 cm^{-1} peak to the deformation modes of V–O–V, respectively [23]. However, the IR spectra of V_2O_5/CaO–MgO catalysts did not indicate the formation of V_2O_5 phase or any compounds of the same with support oxides.

As presented in Fig. 3, the V_2O_5/CaO–MgO catalysts showed strong ESR signals with well-resolved eight-fold splitting resulting from the interaction of the unpaired electron associated with V^{4+} ($3d^1$) with the nuclear spin of ^{51}V (I=7/2 and abundance 99.75%). The ESR parameters are calculated as per the procedure described in the earlier publication [28] and listed in Table 2. The spectrum of 2% catalyst

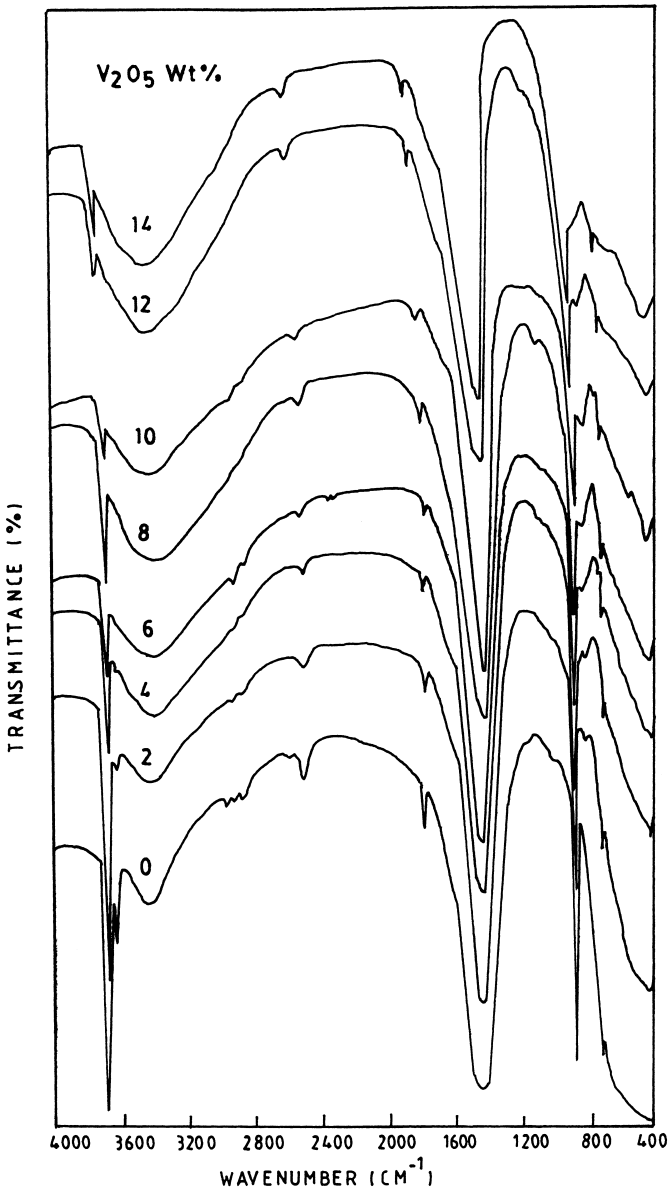


Fig. 2. FTIR spectra of CaO–MgO support and V_2O_5/CaO–MgO catalysts.

(Fig. 3) is rather diffused, which may be due to a distortion at low vanadium loadings. The spectra of 4% catalyst and above are well resolved into eight-fold splitting, the resolution increases with increase in vanadia loading. A comparison of the "g" and hyperfine tensor of V^{4+} species with the literature data [23,27,28] permits one to assign them to the vanadyl groups (VO^{+2}) well dispersed in the oxide matrix. The paramagnetic vanadium species in the catalysts have different signal intensities, and the relative ratios between lines and the magnitude of hyperfine tensor indicate a different surrounding ligand field. In any case, the experimental observation that the $g_{\|}<g_{\perp}$ in the electronic ground state indicates a tetragonal distortion, the geometry of the vanadyl complexes corresponding to an approximate C_{4V} symmetry. The

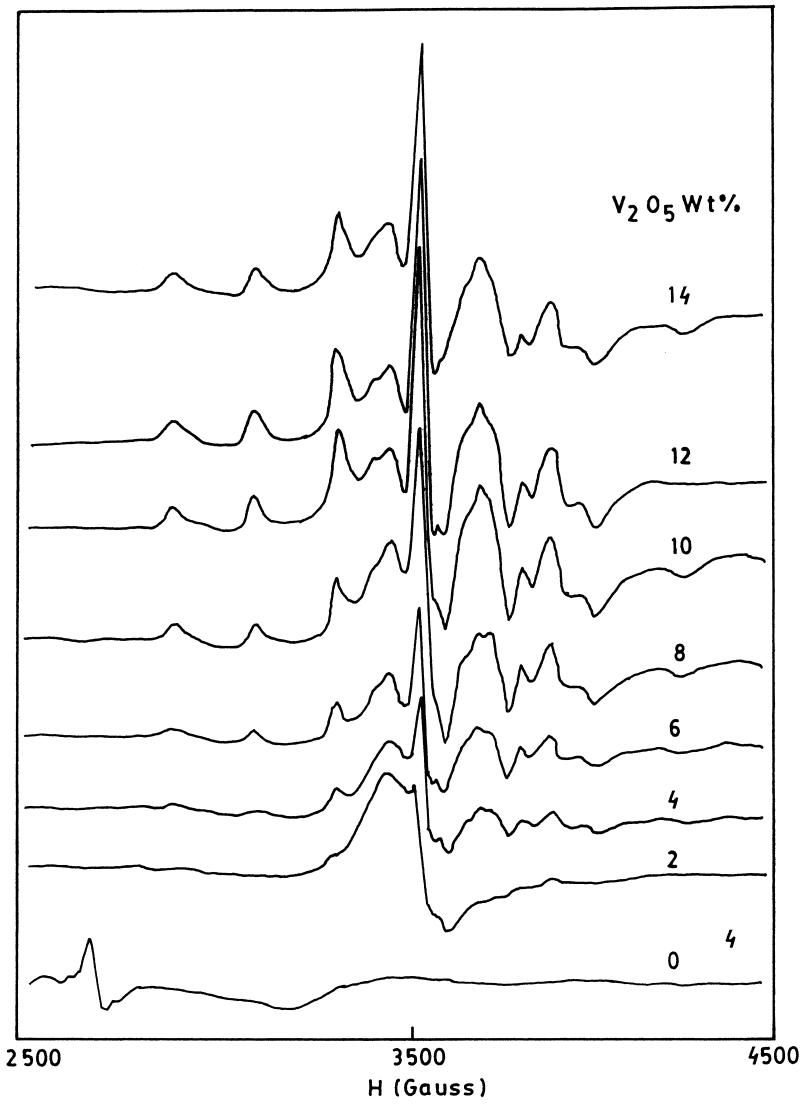


Fig. 3. ESR spectra of CaO–MgO support and V_2O_5/CaO–MgO catalysts.

quantity of $\beta=\Delta g_{\parallel}/\Delta g_{\perp}$ is a sensitive indicator of the tetragonal distortion; an increase of β indicates a shortening of V=O bond, or a lengthening of the distance to the oxygen ligand in the basal plane, the limit of undistorted octahedral symmetry being $\beta=1$. Any geometry changes consistent with an increase in β could correspond to a strengthening of the V=O bond. That the ESR signals of V_2O_5/CaO–MgO are more intense than the corresponding V_2O_5/MgO catalysts suggests that the V^{4+} species are more stabilized in V_2O_5/CaO–MgO catalysts than in the V_2O_5/MgO catalyst [17].

The technique of SEM was also used to determine the shape and size of the catalyst particles. The scanning electron micrographs revealed that the CaO–MgO support particles are porous, spherical, bright and shiny. Addition of small amounts of vanadium oxide to the mixed oxide support resulted in samples containing particles of less uniform size and shape. With increase of vanadium content, a gradual increase in the

Table 2
ESR parameters of various V_2O_5/CaO–MgO catalysts

Catalyst	$g_{\parallel}$	$A_{\parallel}$	$g_{\perp}$	$A_{\perp}$
2% V_2O_5CaO–MgO[a]	–	–	–	–
4% V_2O_5CaO–MgO	1.952	174	1.946	48
6% V_2O_5CaO–MgO	1.958	169	1.947	47
8% V_2O_5CaO–MgO	1.946	180	1.967	45
10% V_2O_5CaO–MgO	1.921	175	1.981	47
12% V_2O_5CaO–MgO	1.946	181	1.995	44
14% V_2O_5CaO–MgO	1.945	172	1.947	51

[a]The g_{av}=2.001 and A_{av}=40.

size of the particles was also noted. The SEM results thus support the observations from other techniques.

The NH_3 and CO_2 uptakes on various catalysts are presented in Table 1. These measurements are expected to provide some information on the acid–base nature of V_2O_5/CaO–MgO catalysts. Pure CaO–MgO support apparently has no acidic sites, as evidenced by a zero NH_3 uptake and a high CO_2 uptake. As vanadium content of these catalysts increases, the NH_3 uptake also increases and the CO_2 uptake decreases. Therefore, it can be concluded that vanadium oxide is well covered on the surface of the support or strongly interacts with it. A comparison of the NH_3 and CO_2 uptake results on V_2O_5/CaO–MgO samples with those of MgO, Al_2O_3, SiO_2, TiO_2 supported V_2O_5 catalysts suggest that the former contain more basic sites than any of these systems [17]. In the case of MoO_3/Al_2O_3 catalysts, Segawa and Hall [29] showed that CO_2 chemisorbs selectively on the hydroxyls of the Al_2O_3 support surface, but does not show any chemical interaction with surface molybdena species. Similar phenomena are apparent in the present case as evidenced by a decrease of CO_2 uptake with increase in V_2O_5 content and also the observation of residual hydroxyls from IR measurements. Bezouhanova and Al-Zihari [30] used cyclohexanol conversion as a test reaction to investigate the acid–base properties of different metal oxide catalysts. They observed a direct correlation between Bronsted acid sites and the amount of cyclohexene, the dehydration product, formed. The dehydrogenation product, cyclohexanone, was directly correlated with the basic sites. The present uptake results also support their classification of acid–base oxides.

The activity and selectivity of various V_2O_5/CaO–MgO catalysts were investigated between 523 to 723 K at normal atmospheric pressure. The activity and selectivity trends on various catalysts followed the same pattern with temperature and with contact time. In general, an increase in the conversion with an increase of temperature was observed. The formation of some additional side products with traces of CO and CO_2 was also occasionally noted at higher temperatures. The activity was slightly high in the first few minutes and dropped (about 1%) to a level where it remained constant up to the 12 h duration studied. There was no substantial change in the conversion and product selectivity during the 12 h time-on-stream. In order to provide a better comparison, the activity and selectivity results obtained at 673 K after 3 h of reaction and at a fixed optimum contact time are shown in Table 3. The pure CaO–MgO did not show any conversion under the experimental conditions used in this study. The activity of the V_2O_5/CaO–MgO catalyst was found to increase with increase of vanadium loading. A comparison of the activity and selectivity results with the literature reports suggests that the 14% V_2O_5/CaO–MgO is much superior to the earlier systems reported [17].

According to Maitra et al. [31] the primary role of catalyst in OCM reaction is the abstraction of hydrogen atom from methane, which is an acid–base reaction.

$$CH_4 + \text{base} = CH_3^- + \text{base}\,H^+$$

This stoichiometric reaction can proceed in a catalytic mode because of the subsequent thermal decomposition of the protonated base, which regenerates the base catalyst and completes the catalytic cycle. The effectiveness of a catalyst thus depends on its strength as a base. Following the hydrogen abstraction, the residual carbanion generates a methyl radical by reaction with molecular oxygen, as suggested by Garrone et al. [32]:

$$CH_3^- + O_2 = CH_3^\bullet + O_2^-$$

Thus freshly generated $CH_3^\bullet$ either dimerizes to ethane or undergoes excessive oxidation, leading to CO/CO_2, presumably from encounters with gaseous oxygen or the catalyst surface. Therefore, the V_2O_5/CaO–MgO catalyst's basicity is expected to influence greatly the selective oxidation of *p*-methoxytoluene to anisaldehyde.

Table 3
Activity and selectivity of various V_2O_5/CaO–MgO catalysts after 3 h of reaction at 673 K and normal atmospheric pressure for the vapour phase oxidation of *p*-methoxytoluene (the catalyst amount 1.0 g, air flow rate 45 ml min^{-1} and *p*-methoxytoluene flow rate 1.0 ml h^{-1})

Catalyst	Conversion (%)	Selectivity (%)	
		p-Methyoxybenzaldehyde	*p*-Methoxybenzoic acid
CaO–MgO	0	0	0
2% V_2O_5/CaO–MgO	15	46	52
4% V_2O_5/CaO–MgO	18	48	51
6% V_2O_5/CaO–MgO	21	49	49
8% V_2O_5/CaO–MgO	22	50	48
10% V_2O_5/CaO–MgO	25	52	45
12% V_2O_5/CaO–MgO	28	53	45
14% V_2O_5/CaO–MgO	30	55	43

In V_2O_5/CaO–MgO catalysts, the support normally decreases the acidic nature of V_2O_5 and also modifies the reactivity of V=O groups to produce more oxygenated products. The CO_2 as a side product formed in the reaction can decrease the activity of these catalysts; this is because CO_2, being acidic in nature, attacks the catalyst basic sites. In fact, a small drop in the activity was noted in the first few minutes of the reaction. The effect of catalyst inhibition by CO_2 results in the formation of weakly bound basic carbonates. The carbonate decomposition temperature is, therefore, an important factor in determining the selectivity of these catalysts. In the case of more basic oxides, the intensity of the catalytic oxide–carbon dioxide interaction is likely to be stronger and the resultant carbonate will be more stable. Therefore, a temperature of 673 K as used in this study was necessary to overcome the excessive CO_2 adsorption and to obtain good product yields.

The anisaldehyde selectivity over V_2O_5/CaO–MgO catalysts was observed to be more than on the V_2O_5/MgO catalyst [17]. The different catalytic behaviour of V_2O_5/CaO–MgO and V_2O_5/MgO catalysts suggest that MgO and CaO–MgO oxides stabilize vanadium oxide species quite differently [33]. In fact, the ESR results also supported these observations. Although it is very difficult to envisage the exact mechanism of this reaction, however, one gets the impression that the oxidation of *p*-methoxytoluene to *p*-anisaldehyde and *p*-anisic acid proceeds through a nucleophilic addition of O^{2-} species from the surface of the V_2O_5/CaO–MgO catalyst [34,35]. Thus, the electron-rich oxygen species extracts hydrogen atom from the hydrocarbon reactant [36], while neutral (O_2) or electron deficient oxygen species, such as V_2O_5, tend to combine with hydrocarbon species to give oxygenated products or carbon dioxide [37]. In the present case, the increased basicity of MgO, which is caused by incorporation of a Ca^{2+} ion could increase the electron density of oxygen species on the surface and thus promote its ability of radical formation. However, further studies are required to understand the role of acid–base properties of the catalyst and the microscopic mechanism of this reaction.

4. Conclusions

The following conclusions can be drawn from this study:

1. When impregnated on the CaO–MgO, vanadia interacts strongly with the support and does not form layer structures on the support surface. Additionally, the vanadia also forms amorphous V–Mg–O compounds, leaving the CaO portion of the oxide.
2. In terms of CO_2 and NH_3 uptakes, the CaO–MgO support is basic oxide and the V_2O_5 is an acid oxide. Impregnation of V_2O_5 on CaO–MgO results in the formation of more acid sites, as evidenced by an increase in the quantity of NH_3 uptake and a decrease in the CO_2 uptake.
3. The 14% V_2O_5/CaO–MgO catalyst exhibits good conversion and product selectivity for the vapour phase oxidation of *p*-methoxytoluene to *p*-methoxybenzaldehyde.

To obtain good conversion and product selectivity, both acid–base functions coupled with the redox

properties of the catalyst are essential. Finally, further studies are required to fully understand the mechanism of this reaction and role of acid–base properties of the catalyst on the conversion and product selectivity.

Acknowledgements

Financial support for this work came from the Council of Scientific and Industrial Research, New Delhi, under a CSIR Young Scientist Award Scheme to BMR.

References

[1] J. Counigham, C. Healy, D.Mc. Namara, S. O'Brien, Catal. Today 2 (1988) 557.
[2] K. Omata, A. Aoki, K. Fujimoto, Catal. Lett. 4 (1990) 241.
[3] K. Tanabe, T. Shibata, J. Kitagawa, Bull. Chem. Soc. Jpn. 47 (1974) 1064.
[4] T. Jin, H. Hattori, K. Tanabe, Bull. Chem. Soc. Jpn. 55 (1982) 2279.
[5] E. Iwamatsu, T. Moriyama, N. Takasaki, K. Aika, J. Catal. 113 (1988) 25.
[6] V.R. Choudhary, S.T. Chaudhari, A.M. Rajput, V.H. Rane, J. Chem. Soc., Chem. Commun., (1989) 555.
[7] E. Ruckenstein, B.M. Reddy, Catal. Lett. 29 (1994) 217.
[8] T. Tzedakis, A.J. Savall, Ind. Eng. Chem. Res. 31 (1992) 2475.
[9] B. Crzybaoska, M. Czerwenka, J. Sloczynski, Catal. Today 1 (1987) 157.
[10] S. Noboru, N. Saito, M. Veshima, Stud. Surf. Sci. Catal. 44 (1989) 131.
[11] M. Ueshima, N. Saito, Chem. Lett. (1992) 1341.
[12] B.M. Reddy, I. Ganesh, B. Chowdhury, Chem. Lett. (1997) 1145.
[13] H.H. Kung, Ind. Eng. Chem. Prod. Res. Dev. 25 (1992) 171.
[14] J. Kijenski, A. Baiker, Catal. Today 5 (1989) 1.
[15] M. Ai, J. Mol. Catal. A 114 (1996) 3.
[16] D. Martin, D. Duprez, J. Phys. Chem. 100 (1996) 9429.
[17] B.M. Reddy, E.P. Reddy, I. Ganesh, M.V. Kumar, Ind. J. Chem. Technol. 4 (1997) 256.
[18] B.M. Reddy, B. Manohar, S. Mehdi, J. Solid State Chem. 97 (1992) 233.
[19] B.N. Reddy, B.M. Reddy, M. Subrahmanyam, J. Chem. Soc., Faraday Trans. 87 (1991) 1649.
[20] B.M. Reddy, E.P. Reddy, S.T. Srinivas, J. Catal. 136 (1992) 50.
[21] F. Roozeboom, T. Fransen, P. Mars, P.J. Gellings, Z. Anorg. Allg. Chem. 449 (1979) 25.
[22] K. Segawa, T. Soeya, D.S. Kim, Res. Chem. Intermed. 15 (1991) 129 and references therein.
[23] G.C. Bond, S.F. Tahir, Appl. Catal. 71 (1991) 1 and references therein.
[24] B.M. Reddy, S. Mehdi, E.P. Reddy, Catal. Lett. 20 (1993) 317.
[25] M. Rusiecka, B. Brazybowski, M. Gasior, Appl. Catal. 10 (1984) 101.
[26] D. Cordischi, B. Vielhaber, H. Knoezinger, Appl. Catal. 30 (1987) 265.
[27] V.K. Sharma, A. Wokaun, A. Baiker, J. Phys. Chem. 90 (1986) 2715.
[28] K.V.R. Chary, B.M. Reddy, N.K. Nag, V.S. Subrahmanyam, C.S. Sunandana, J. Phys. Chem. 88 (1984) 2622.
[29] K. Segawa, W.K. Hall, J. Catal. 77 (1982) 221.
[30] C.P. Bezouhanova, M.A. Al-Zihari, Catal. Lett. 11 (1991) 245.
[31] A.M. Maitra, I. Campbell, R.J. Taylor, Appl. Catal. A 85 (1992) 27.
[32] E. Garrone, A. Zecchina, F.S. Stone, J. Catal. 62 (1980) 396.
[33] A. Gervasini, G. Formasari, G. Bellussi, Appl. Catal. A 83 (1992) 235.
[34] J. Haber, in: P. Ruiz, B. Delmon (Eds.), New Developments in Selective Oxidation by Heterogenous Catalysts, Stud. Surf. Sci. Catal., vol. 72, Elsevier, Amsterdam, 1992, p. 279.
[35] A. Bielanski, J. Haber, Oxygen in Catalysis, Marcel Dekker, New York, 1991.
[36] K. Otsuka, Y. Murakami, Y. Wada, A. Said, A. Morikawa, J. Catal. 121 (1990) 122.
[37] R. Pitachi, K. Klier, Catal. Rev.-Sci. Eng. 28 (1986) 13.