ELSEVIER

Catalysis Today 28 (1996) 381-389

CATALYSIS TODAY

On the mechanisms of light alkane catalytic oxidation and oxy-dehydrogenation: an FT-IR study of the *n*-butane conversion over $MgCr_2O_4$ and a Mg-vanadate catalyst

E. Finocchio [a], G. Ramis [a], G. Busca [a], V. Lorenzelli [a], R.J. Willey [b]

[a] *Istituto di Chimica, Facoltà di Ingeneria, Università, P. le J.F. Kennedy, I-16129 Genova, Italy*
[b] *Department of Chemical Engineering, Northeastern University, Boston, Ma 02115, USA*

Abstract

The interaction of *n*-butane, 1-butene, 1,3-butadiene and of C_4 oxygenates on the surface of oxidized Mg-chromite and Mg-vanadate catalysts has been studied by FT-IR spectroscopy. The results compare well with the catalytic behavior of these materials one of which is a combustion catalyst ($MgCr_2O_4$) and the other is a rather selective oxy-dehydrogenation catalyst (Mg-vanadate). A mechanism for these reactions is proposed.

Keywords: Mechanisms of light alkane catalytic oxidation; Oxy-dehydrogenation; FT-IR study of the *n*-butane conversion; $MgCr_2O_4$ catalyst; Mg-vanadate catalyst

1. Introduction

The increased availability of light alkanes from natural gas makes very attractive their use as the feedstocks for the synthesis of chemicals [1]. For this reason, the partial oxidation processes of light alkanes are the object of increasing interest. For several years *n*-butane has been used for the synthesis of maleic anhydride over vanadyl phosphate (VPO) catalysts. This reaction has been the object of several papers and reviews [2,3].

Recently, the VMgO system (V_2O_5-MgO) has been proposed as a promising one for the oxidative dehydrogenation of alkanes [4] such as butane to butene or butadiene [5,6]. The alkane oxy-dehydrogenation reaction has also been reported to occur promisingly over supported vanadias [6,7]. On the other hand, *n*-butane partial oxidation can also give rise to other products. According to the literature, acetic acid has been produced industrially by *n*-butane oxidation over V_2O_5-TiO_2 catalysts [8] but also furan, dihydrofuran [9], methyl-vinyl ketone, methyl-ethyl ketone and crotonaldehyde [10] can or could be produced.

Clearly, the main competitive reaction to be avoided in all partial oxidation processes is the catalytic combustion to CO_x. On the other hand, this reaction is of interest to abate butane if present in waste gases and as a test reaction for VOC abatement [11], and it has been investigated, e.g. in the field of automotive catalytic converters [12]. Knowledge on the activation mode of light alkanes and on the mechanisms of their catalytic oxidation over oxide catalysts is

PII S0920-5861(96)00051-X

still imperfect. As a development of our previous studies [13–15] we investigated comparatively the activation of *n*-butane and its oxidation over oxide catalysts having different catalytic behaviors by IR spectroscopy.

2. Experimental

The preparation and the solid state and surface characterization of the $MgCr_2O_4$ aerogel (53 m^2/g) have been described previously [16]. XRD and FT-FIR analyses show that the sample after calcination consists of the spinel-type phase $MgCr_2O_4$, very well crystallized, although with excess oxygen at the surface. The preparation and characterization of the $MgO-V_2O_5$ (Mg:V 3:2 atomic ratio; 8 m^2/g) catalyst has also been reported [13,17]. The catalyst looks amorphous to XRD analysis and appears to be predominantly constituted by a $Mg_2V_2O_7$-like phase to Raman analysis [17].

The IR spectra were recorded by a Nicolet Magna 750 and by a Nicolet 5ZDX Fourier transform instruments, using pressed disks of the pure powders, in an heatable cell connected to a conventional gas-handling system. Activation before adsorption experiments has been carried out by outgassing at 773 K.

3. Results and discussion

3.1. *n-Butane combustion over $MgCr_2O_4$*

The IR spectra obtained upon the interaction *n*-butane with the surface of oxidized $MgCr_2O_{4+x}$ are shown in Fig. 1. A reaction is observed starting from 423 K. At this temperature the strongest bands are observed near 1590 and 1440 cm^{-1} and, together with a weaker band at 1355 cm^{-1}, can be assigned to acetate species (COO^- asymmetric and symmetric stretching and CH_3 symmetric bending, respectively), in agreement with the spectra obtained upon the dissociative adsorption of acetic acid

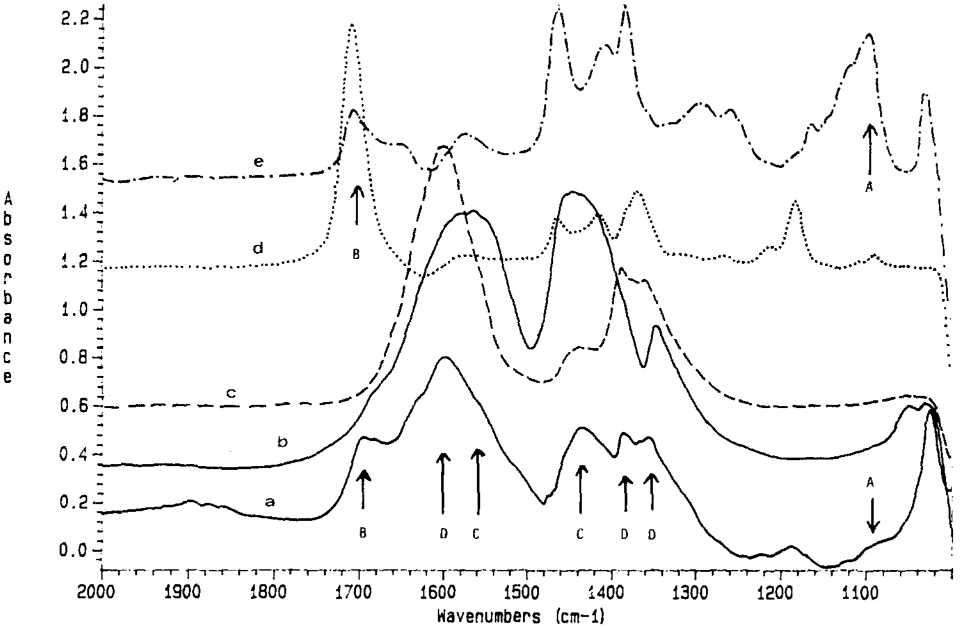


Fig. 1. FT-IR spectrum of the surface species arising from the interaction of the Mg-chromite catalyst with *n*-butane at 423 K (a), compared with the spectra of adsorbed acetates (b), formates (c), 2-butanone (d) and 2-butanol (e) over the same surface. Diagnostic bands: A, adsorbed 2-butoxide; B, adsorbed 2-butanone; C, adsorbed acetates; D, adsorbed formates.

(Fig. 1b). However, the sharp doublet at 1385 and 1355 cm^{-1} suggest that formate species are also present (CH deformation and COO$^-$ symmetric stretching), that participate also to the band near 1590 cm^{-1} (COO$^-$ asymmetric stretching). These species are again identified for comparison with the spectra of formates obtained by formic acid adsorption (Fig. 1c). Moreover, bands near 1690, 1475 (very weak), 1385 (sharp and rather strong) and 1175 cm^{-1} are also found and all correspond to evident features in the spectrum of adsorbed methyl-ethyl ketone (C = O stretching, asymmetric and symmetric CH_3 bendings, and C–C–C asymmetric stretching, respectively), that has also been adsorbed over the same surface, as shown in Fig. 1d. A further sharp band at 1025 cm^{-1} is assigned, together with a broader absorption in the range 1150–1100 cm^{-1} to C–O and C–C stretchings of 2-butoxy-species, by comparison with the spectrum of adsorbed 2-butanol (Fig. 1e). The above assignment finds support on the evolution of the spectra upon further heating. In fact, the bands assigned above to the ketone and to the alkoxide disappear by heating at near 473 K, while those associated to acetate species grow in intensity. The formation of *sec*-butoxy-species and of 2-butanone from *n*-butane oxidation is also substantiated by the observation that very similar spectra (but not identical) are found upon oxidation of 2-butanol (Fig. 2), 2-butanone (Fig. 3) and *n*-butane on this surface. Starting from the alcohol, the bands assigned to the 2-butoxy-species decrease strongly, although they are still visible, at 423 K when the bands due to adsorbed 2-butanone rise their maximum and those due to acetate species are already evident. Both starting from *n*-butane and from 2-butanol at 473 K the bands of adsorbed 2-butanone are still present, rather weak, while those due to acetate species grow at least up to 573 K, but later decrease with the appearance of water and CO_x in the gas phase and of water and carbonates on the surface. This agrees with the catalytic behavior of Mg chromite, that is an effective combustion cata-

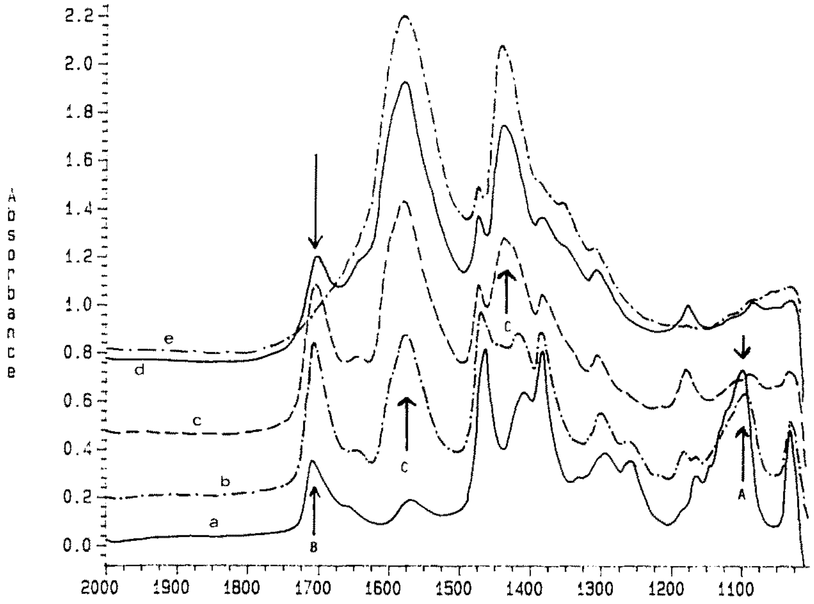


Fig. 2. FT-IR spectra of the surface species arising from the adsorption and oxidation of 2-butanol over the Mg-chromite catalyst at increasing temperature: outgassed at room temperature (a), 373 K (b), 423 K (c), 473 K (d), 523 K (e). Diagnostic bands: A, adsorbed 2-butoxide; B, adsorbed 2-butanone; C, adsorbed acetates.

lyst for several light alkanes in the range 620–770 K [15,18].

To verify the mechanism of *n*-butane oxidation, we also compared the spectra of C_4 oxygenates functionalized at C(1) (1-butanol, butyraldehyde and butyric acid) and of C_3 oxygenates functionalized at C(1) (1-propanol, propionaldehyde and propionic acid) and we did not find evidence of their presence among *n*-butane oxidation products.

On the other hand, the main difference between the spectra obtained upon *n*-butane oxidation and those obtained upon oxidation 2-butanol and 2-butanone is the detection, starting from butane only, of formate ions. These species are not detected from C_4 oxygenates functionalized at C(2). The presence of this C_1 fragment without a corresponding C_3 fragment, only from *n*-butane, can only be interpreted assuming that something occurs during the C–H activation step at C(2) (so before the production of the 2-butoxide from butane) that gives rise to a parallel way that can produce C_1 fragments.

In our previous studies [14,15] we have proposed that C–H activation over Mg chromite occurs at surface O^{2-}–Cr^{6+}–O^{2-} centers with a 'concerted' mechanism giving rise to the breaking of the C–H bond with the consequent production of an OH and an alkoxide and the assumption of two electrons by the cation, so reduced (formally) to Cr^{4+}. This mechanism finds support in the present data. In this case CH activation occurs at C(2) in the case of *n*-butane because the C–H's at C(2) are those associated to the smaller dissociation energy.

The results discussed above (in particular with respect to the observation of formates upon *n*-butane oxidation) can be rationalized assuming that the mechanism is not a concerted one, but interaction of the alkane with the oxidizing centers can give rise first to the formation of a 'quasi free' carbenium ion that only later approaches to an oxide anion to produce the alkoxide. So, the 2-butyl cation is produced by *n*-butane oxidation, but it can later isomerize in part to the *tert*-butyl cation before to give rise to the alkoxide. As we have shown elsewhere [15] the *tert*-butoxy species (in this case pro-

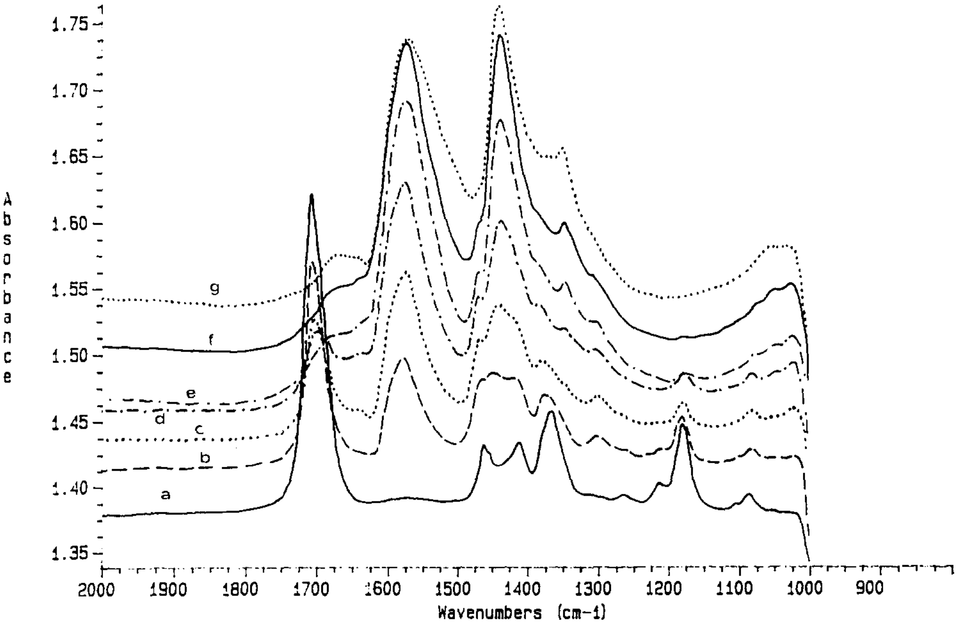
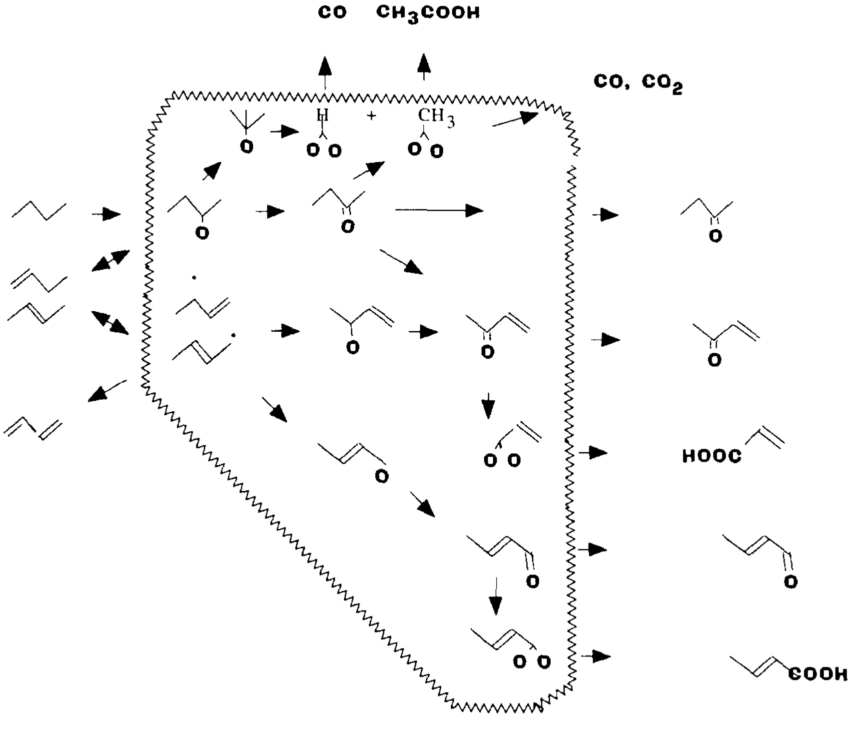


Fig. 3. FT-IR spectra of the surface species arising from the adsorption and oxidation of 2-butanone over the Mg-chromite catalyst at increasing temperature: outgassed at room temperature (a), 373 K (b), 423 K (c), 473 K (d), 523 K (e), 573 K (f), 623 K (g).

duced by skeletal isomerization) gives rise, by further oxidation, to two formate and one acetate species, so justifying the formation of formate species from *n*-butane too (Scheme 1).

We have also investigated the interaction of 1-butene and butadiene over the same surface, but the observed spectra are very different (see Figs. 4 and 5) from those observed upon interaction with butane. In fact, the spectra obtained from 1-butene contain bands that can be assigned to 1-buten-2-oxide species (C–O stretching at 1019 cm^{-1}) and to methyl-vinyl ketone (bands at 1667, 1634 and 1173 cm^{-1}, C = O, C = C and C–C stretchings, respectively). The detection of these species can be interpreted as an evidence of the allylic oxidation mechanism occurring, also in this case, with the breaking of the weakest C–H bond (the allylic one) and the formation of the corresponding allylic alkoxide species. This species can later be oxidatively dehydrogenated to the corresponding carbonyl compound, methyl-vinyl ketone. The behavior of $MgCr_2O_4$ with respect to 1-butene oxidative transformation is similar to that previously found for $FeCrO_3$ [19], an active industrial oxy-dehydrogenation catalyst for butene [20]. On the other hand also $MgCr_2O_4$ is active for the synthesis of butadiene from butene oxy-dehydrogenation although with lower selectivity than $FeCrO_3$ and than ferrite and chromite-ferrite spinels [20]. In any case the above data strongly imply that olefins are not intermediates in the combustion way of *n*-butane, because adsorbed allylic species are not found upon *n*-butane oxidation.

These data support the previous ones concerning propane and propene combustion over this catalyst [14] as well as those reported by Yao [21] that showed that olefins and alkanes burn with different mechanisms over chromia. The following reaction scheme is proposed for *n*-butane combustion over Mg chromite.



Scheme 1. Proposed reaction pathway for butane and butene oxidations over $MgCr_2O_4$ and Mg-vanadate.

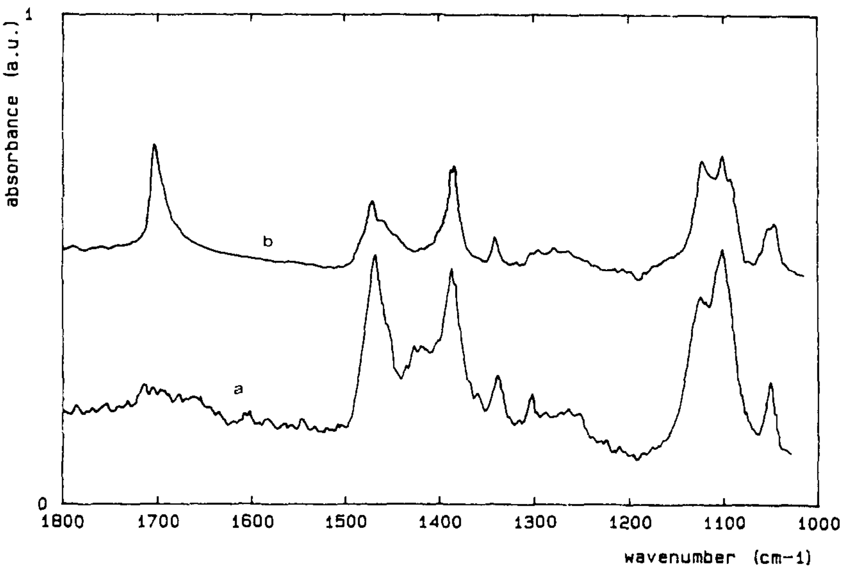


Fig. 4. FT-IR spectra of the surface species arising from the adsorption and oxidation of 2-butanol over the Mg-vanadate catalyst at increasing temperature: at 373 K (a) and 453 K (b).

The results discussed here, concerning oxidation of C_4 compounds, support the previous proposal on alkane combustion mechanism [14,15]. C–H activation occurs on both *n*-butane and 1-butene at the weakest C–H bond, that in both cases is that in secondary position. So, *sec*-butoxy species are formed from *n*-butane and 1-buten-2-oxides from 1-butene. The alkoxides rapidly oxidatively dehydrogenate to the ketones that later undergo a C–C bond breaking

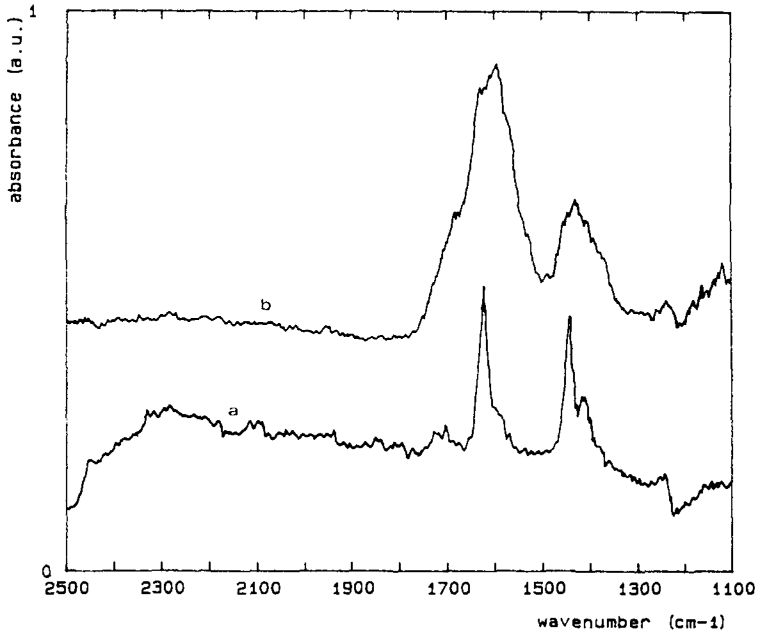


Fig. 5. FT-IR spectra of the surface species arising from the adsorption and oxidation of 1-butene at room temperature (a) and at 523 K (b) over the Mg-vanadate catalyst.

giving rise carboxylate species, acetates from *n*-butane and, likely, mainly acrylates from 1-butene. This can occur in the temperature range 300–473 K, so it represents a fast sequence at the combustion temperature of near 773 K. Acetate species, instead, are stable up to 573 K, and burn in the range 573–773 K; this agrees with the light-off temperature of near 623 K for light alkane combustion over this catalyst.

A secondary way from *n*-butane involves previous skeletal isomerization to give rise *tert*-butoxide that later are oxidized to give rise to two formate and one acetate species. Formates decompose fast giving rise to CO while acetates behave as reported above.

3.2. *n-Butane oxy-dehydrogenation over Mg-vanadates*

The interaction of Mg-vanadates with butane does not give detectable adsorbed species, although it is certainly effective above 623 K according to the formation of gas-phase carbon oxides and to the decrease of transmittance of the sample likely due to its reduction.

However, the surface of this catalyst is reactive towards oxygenate compounds even at very low temperatures. In Fig. 4 the spectra of *sec*-butanol adsorbed on the Mg vanadate catalyst are reported. The adsorption of the alcohol is almost completely dissociative, as shown by the almost complete absence of the OH deformation mode near 1280 cm^{-1} typical of coordinated *sec*-butanol, and to the presence of the strong C–O/C–C modes near 1100 cm^{-1} due to *sec*-butoxy-species. The bands near 1460 and 1380 cm^{-1} are assigned to the asymmetric and symmetric deformations of methyl groups, that near 1420 cm^{-1} to the scissoring mode of the methylene group and that at 1335 cm^{-1} is the deformation mode of the methyne group. The alcoholates are progressively destroyed with the appearance of small amounts of methyl-ethyl ketone near 450 K, evidenced by the sharp band near 1700 cm^{-1}, but disappear completely at near 523 K. On the other hand, also the interaction of 1-butene and of butadiene over this surface is extremely weak. The interaction with 1-butene is molecular at room temperature (Fig. 5a) and, in these conditions, the adsorbed butene molecules is characterized by a weakening of the C = C bond, whose stretching is found at 1630 cm^{-1} with respect to 1643, 1647 cm^{-1} for the two conformers in the gas. Reactive adsorption is observed only near 523 K (Fig. 5b), with the formation of carboxylate species, characterized by bands at 1590 and 1420 cm^{-1}, due to the asymmetric and symmetric –COO stretchings. However, these adsorbed carboxylate species disappear by further heating at 673 K, due their complete combustion and/or desorption of partly oxidized fragments. The same bands observed after contact with 1-butene are also found after contact with 1,3-butadiene but at significantly lower temperatures.

These results show that polar molecules like the alcohols do react with the surface of Mg vanadates, giving raise to dissociative adsorption, while further dehydrogenation also can occur (although perhaps to a limited extent). However, the reactivity of this surface is by far weaker than that of Mg-chromite where the alcohols are oxidized to ketones in part already at room temperature, ketones are very strongly bonded and further transform to carboxylate species and finally completely decompose.

The behavior observed upon butane interaction with Mg-vanadate is justified by the fact that at the temperature at which this interaction really occurs (above 623 K) the resulting partially oxidized surface species desorb or further transform very fast. The behavior observed upon 2-butanol adsorption suggests that the main way of its transformation is its dehydration to *n*-butene, that should occur completely already near 523 K, giving rise to gas-phase olefin and adsorbed water. This agrees with the very weak reactivity of the olefin with Mg-vanadate, that does not give rise to any detectable reaction (including the hydration observed fast over other catalysts like vanadia-titania) up to 550 K. So, over Mg-vanadate the butane activation could occur just with the same mechanism as on the Mg chromite, i.e. with the formation of an 2-butoxide as the result of the weakest C–H bond scission. However, at the temperature at which this reaction occurs over this very poorly active catalyst, the alkoxide very rapidly dehydrates to the olefin *n*-butene. Being the olefins rather unreactive towards Mg-vanadates they can be recovered as the main useful product, while in part they produce CO_x via ketone-acetates. The key step determining selectivity is the evolution of the alkoxides that over the vanadate can in part decompose to the olefin while over the chromite are mainly oxy-dehydrogenated to the ketone.

4. Conclusions

The above experiments allow us to propose a reaction pathway for *n*-butane oxidation and oxy-dehydrogenation over Mg-chromite and Mg-vanadate respectively. The data are consistent with the hypothesis that the reaction mechanism is the same on the two catalysts. If this is true, the different behavior of the two catalysts is explained by the different rates of two alternative steps on the two surfaces, i.e. the dehydration or the oxy-dehydrogenation of the 2-butoxide intermediate. So, the evolution of the surface intermediate 2-butoxide is proposed to play the role of 'selectivity determining step', using an expression proposed by Kung and co-workers [6], where the oxy-dehydrogenation route diverges from the combustion route. The low activity in oxidation and the significant basicity with absence of Brønsted acidity typical of Mg vanadate are likely main factors favoring the production of butene from the 2-butoxy-species. On the contrary, the weak Brønsted acidity of oxidized Mg-chromite [16] is likely responsible for blocking on the surface the 2-butoxide species and the high oxidizing power of Cr^{6+} causes its rapid oxy-dehydrogenation to the ketone and the following C–C bond breaking that finally produces CO_x.

The same mechanism proposed for the combustion catalyst Mg-chromite apply also to catalysts that allow important yields in acetic acid from *n*-butane, like vanadia-titania [8,13] that accordingly also show a medium-high Brønsted acidity. Being acetate ions intermediates in the combustion way it seems reasonable that the production of acetic acid can be favored by addition of steam in the reactant mixture and by adjusting the reaction conditions, such as, e.g. by increasing space velocity.

Acknowledgements

This work has been supported in part by MURST (Rome, Italy) and by NATO (CRG grant 900463).

References

[1] K. Weissermel and H.J. Arpe, Industrial Organic Chemistry, 2nd ed., VCH, Weinheim, 1993.

[2] G. Centi, F. Trifirò, J. Ebner and V. Franchetti, Catal. Rev., 88 (1988) 55.

[3] G. Centi, Editor, Catal. Today, 16(1) (1993).

[4] M.A. Chaar, D. Patel and H.H. Kung, J. Catal., 109 (1988) 463.

[5] D. Bhattacharyya, S.K.Bej and M.S. Rao, Appl. Catal. A General, 87 (1992) 29.

[6] P.M. Michalakos, M.C. Kung, I. Jahan and H.H. Kung, J. Catal., 140 (1993) 226.

[7] J.G. Eon, R. Olier and J.C. Volta, J. Catal., 145 (1994) 318.

[8] J. Schulze and M. Homann, C_4-Hydrocarbons and Derivatives, Springer Verlag, Berlin, 1989, p. 73.

[9] V.A. Zazhigalov, J. Haber, J. Stoch, G.A. Komashko, A.I. Pyatniskaya and I.V. Bacherikova, in V. Cortes Corberan and S. Vic Bellon, Editors, New Developments in Selective Oxidation II, Elsevier, Amsterdam, 1994, p. 265.

[10] A. Bielanski and J. Haber, in Oxygen in Catalysis, Marcel Dekker, New York, 1991.

[11] M.T. Vandersall, S.G. Maroldo, W.H. Brendley, K. Jurkzyk and R.S. Drago, in J.N. Armor, Editor, Environmental Catalysis, ACS, Washington, 1994, p. 331.

[12] J.M. Bart, A. Pantenero and M.F. Prigent, in R.G. Silver, J.E. Sawyer and J.C. Summers, Editors, Catalytic Control of Air Pollution, ACS, Washington, 1992, p. 42.

[13] G. Busca, V. Lorenzelli, G. Oliveri and G. Ramis, in V. Cortes Corberan and S. Vic Bellon, Editors, New Developments in Selective Oxidation II, Elsevier, Amsterdam, 1994, p. 253.

[14] E. Finocchio, G. Busca, V. Lorenzelli and R.J. Willey, J. Chem. Soc., Faraday Trans., 90 (1994) 3347.

[15] E. Finocchio, G. Busca, V. Lorenzelli and R.J. Willey, J. Catal., 151 (1995) 204.

[16] R.J. Willey, P. Noirclerc and G. Busca, Chem. Eng. Commun., 123 (1993) 1.

[17] G. Ramis, G. Busca and V. Lorenzelli, J. Chem. Soc., Faraday Trans., 90 (1994) 1293.

[18] E. Finocchio, G. Busca and R.J. Willey, work in progress.

[19] G. Busca and V. Lorenzelli, J. Chem. Soc., Faraday Trans., 88 (1992) 2783.

[20] R.J. Rennard and W.L. Kehl, J. Catal., 21 (1971) 282.

[21] Y. Yu Yao, J. Catal., 28 (1974) 139.