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Other catalytic properties

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Abstract

The behavior of fresh and aged EUROCAT V_2O_5–WO_3/TiO_2 SCR catalysts in the (I) oxidative dehydrogenation of light alkanes, and conversion of (ii) propan-2-ol, (iii) NO in the presence of propene and oxygen, (iv) propane and propene and (v) chloropropane is reported to analyse possible modifications of the catalyst properties during use and give a more comprehensive general picture of its surface and reactivity properties. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: EUROCAT V_2O_5–WO_3/TiO_2 samples; Oxidative dehydrogenation; Oxidising and non-oxidising conditions; Propan-2-ol conversion

1. Introduction

Vanadium possesses a polyfunctional catalytic behaviour as attested by its use as an active component in a variety of different catalytic reactions, from the selective reduction of NO_x to the oxidative dehydrogenation or selective oxidation of alkanes, the selective side chain oxidation of alkylaromatics or oxidation with rupture of the aromatic ring, and the ammoxidation of alkanes [1].

This broad range of applications, a unique characteristic of vanadium as an active element, derives from its electronic and coordination properties which can be tailored by interaction with the substrate and/or by its dispersion state on it or by adding a second element. The latter can (i) form a specific vanadium compound, (ii) modify its characteristics by electronic interaction, e.g., influencing its redox behaviour, (iii) stabilise a specific V coordination state or (iv) simply add a cocatalytic function, e.g., acid–base sites. Vanadium, thus, has potentially a rich surface catalytic chemistry, the complete understanding of which requires investigation of the behaviour not only of the main catalytic reaction (reduction of NO_x in the present case), but also of a series of additional reactions. For this reason, characterisation of the EUROCAT V_2O_5–WO_3/TiO_2 samples was extended to analysis of its reactivity in other catalytic reactions, in order to have a more complete picture of catalytic properties of this SCR catalyst.

It may be worth noting that the polyfunctional behaviour of vanadium has advantages related to the fact that this catalyst not only reduces NO_x to N_2, but also oxidises NH_3 to N_2 and SO_2 to SO_3 (Chapter 11) and is able to reduce NO_x and oxidise hydrocarbons at the same time. This observation has lead to the recent industrial development of a SCR process in which not only NO_x are converted to N_2, but also polychlorinated hydrocarbons such as dioxins are completely oxidised, even if present in ultra-low amounts. This is a significant technological improvement for applications such

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as those designed for the clean-up of emissions from incinerators [2] and shows the need to understand the oxidation characteristics of EUROCAT SCR catalysts too.

Due to the ultra-low amount of polychlorinated hydrocarbon present in the emissions as well as their health dangerous properties, a specific study of the reactivity of these chemicals on EUROCAT V_2O_5–WO_3/TiO_2 samples was not possible, but instead tests were made to compare the reactivity of propane, propene and chloropropane. Their comparison gives indication on how the presence of a C–Cl bond influences the reactivity and of the resistance of the catalyst towards HCl, the main chloro-containing product formed from chloropropane conversion.

Ageing during the SCR reaction can induce modifications in surface properties which can be monitored using some test catalytic reactions complementary to physico-chemical methods. Any modification in catalytic reactivity in test reactions can be more easily related to a change in SCR surface reactivity than structural or surface physico-chemical characterisation data. The present data could then be used to detect possible changes in surface reactivity properties between fresh and used EUROCAT V_2O_5–WO_3/TiO_2 SCR catalysts. Due to obvious limits, our choice was restricted to some specific examples.

For low vanadium loading on oxide supports (as in EUROCAT SCR catalysts), generally isolated vanadium species form vs. polyvanadium species with V–O–V bridging oxygen which dominate at higher vanadium loading. This change in the nature of vanadium species causes V-based catalysts [1] to have an oxidative dehydrogenation rather than an oxygen insertion character. For this reason, the oxidation behaviour of the EUROCAT SCR catalysts was investigated studying their properties in ethane and propane oxidative dehydrogenation. Their behaviour was compared with that of two optimised catalysts for these reactions in order to have more reliable comparison of the performances of the EUROCAT SCR catalysts. This reaction was investigated by the E-1 group. A summary of the experimental conditions used is outlined in Table 1.

Propan-2-ol conversion is a typical reaction test used to characterise both redox and acid–base properties of oxide catalysts [3–5], which can give useful information, additional to that learned from TPR (Chapter 3), IR (Chapter 5) and electrical conductivity (Chapter 8). The F-1 group has investigated the behaviour of fresh and used EUROCAT SCR catalyst in this reaction and, for comparison, the behaviour of binary oxides (V_2O_5/TiO_2 and WO_3/TiO_2). Experimental conditions for these tests are also summarised in Table 1.

Finally, a third test reaction studied was the conversion of NO by C_3H_6 in the presence of O_2. Many efforts have recently been focused on this reaction as a model reaction for the development of catalysts able to reduce NO in combustion emissions from lean burn gasoline or diesel engines [6], since current “three way catalysts” are not able to reduce NO_x in the presence of O_2. Within the present investigation, analysis of the reactivity of the EUROCAT SCR catalyst in this reaction, besides giving information about its behaviour using as the selective reductant a hydrocarbon instead of ammonia, also gives useful data on (i) the reactivity of the catalyst in hydrocarbon conversion, and (ii) its ability to oxidise NO to NO_2, a key step in the mechanism of reduction of NO by hydrocarbons [7], but which could also be a first step in an alternative pathway of reduction of NO by ammonia [8,9]. This reaction of NO conversion by C_3H_6 in the presence of O_2 was investigated by group F-3. The experimental conditions for these tests are also summarised in Table 1.

2. Oxidative dehydrogenation (ODH) of light alkanes

ODH of ethane. For comparative purposes, the tests were conducted in the temperature range 548–688 K, in the same reaction conditions used in a previous paper on the ODH of ethane over vanadium-containing oxides [10]. The results are shown in Fig. 1 for fresh and used EUROCAT V_2O_5–WO_3/TiO_2 SCR catalysts, marked EC in Fig. 1 for brevity. For further comparison, the behaviour of a NiVSb mixed oxide supported on alumina (28 wt.% supported components), which was found to be the most efficient in the cited work [10], is also described in Fig. 1.

On the EUROCAT SCR catalyst the main reaction products were ethene and carbon oxides. The apparent activation energy for the ethane depletion rate was $86\pm3\,\mathrm{kJ\,mol^{-1}}$ for the fresh sample, which was much

Table 1
Summary of the experimental conditions used in testing various catalytic properties of V_2O_5–WO_3/TiO_2 EUROCAT SCR catalysts

Laboratory	Reaction	Type of reactor	Experimental conditions	Analysis	Notes
E-1	Ethane ODH[a]	Fixed bed, quartz tube i.d. 7 mm[b]	$W/F = 7.8$ g cat. h mol^{-1} C_2H_6, C_2H_6:O_2:He = 17:41.5:41.5 molar ratio	GC with 13X molecular sieve and Poropak Q	XYS[c] normalised to carbon atom; carbon balance 100 ± 5%
E-1	Propane ODH[a]	Fixed bed, quartz tube i.d. 7 mm	$W/F = 27.2$ g cat. h mol^{-1} C_3H_8, C_3H_8:O_2:He = 4:8:88 molar ratio	GC with 13X molecular sieve and Poropak Q	XYS[c] normalised to carbon atom; carbon balance 100 ± 5%
F-1	Propan-2-ol conversion	Differential flow micro reactor	Total flow = 1.8 dm^3 h^{-1} N_2 or air + 3.3 kPa propan-2-ol 200 mg catalyst	FID–GC with Porapak Q and Cathar.-GC with Porapak columns	C balance: 100 ± 2%
I-1	C_3H_8, C_3H_6 and C_3H_7Cl conversion	Fixed bed reactor	Total flow = 21 l h^{-1} C_3H_8 or C_3H_6:O_2:He = 1.9:11.0:87.1 (% v/v) C_3H_7Cl:O_2:He = 0.1:0.5:99.4 (% v/v)	–	–
F-3	NO conversion with C_3H_6/O_2	Fixed bed flow reactor	Total flow = 10 l h^{-1} NO:C_3H_6:O_2:He = 0.02:0.02:5:94.96 212 mg catalyst	Dual Porapak-molecular sieve GC + IR and UV analysers	7% lack of N balance[d] NO_2 forms after the reactor

[a] ODH: oxidative dehydrogenation.

[b] Inside diameter (i.d.) 12 mm narrowed till an i.d. of 7 mm in the catalytic bed zone; there is an internal coaxial tube (o.d. = 4 mm) used as a thermocouple well. The upper zone of the reactor is filled with SiC which minimises the empty volume and allows the mixing of reactants and their preheating.

[c] X = conversion, Y = yield, S = selectivity.

[d] Lack of N balance due to reactions $NO_2 + NO \rightarrow N_2O_3$; $N_2O_3 + H_2O \rightarrow 2\ HNO_2$.

more active in this reaction than the supported mixed NiVSb oxide (Fig. 1a), although its specific surface area (SSA) was much lower (46 m^2 g^{-1} for the former vs. 75 m^2 g^{-1} for the latter). However, initial selectivity to ethene was around 48%, much lower than on the NiVSb catalyst (ca. 75%). In both cases, this selectivity decreased with the increase in conversion.

Nevertheless, the main difference resides in the formation of the carbon oxides. On the NiVSb oxide the main degradation product was CO_2 while selectivity to CO was low and remained practically unchanged with the increase in conversion. However, on the EUROCAT SCR catalyst, selectivity to CO_2 was low, initially decreasing and then remaining unchanged with the increase in conversion, while the much higher CO selectivity increased sharply with the increase in conversion at the expense of ethene selectivity. This seems to indicate that the reaction network might be different in each of the two cases. On the EUROCAT SCR catalyst, CO would be the product of the degradation of ethene, while CO_2 should be a primary product produced by a parallel route. On the NiVSb catalyst, CO_2 is produced in a parallel–consecutive scheme from ethane, ethene and CO [10]. Alternatively, the effect could also be explained by considering that the activation energy of CO formation on the EUROCAT SCR catalyst is higher than that of the formation of ethene or CO_2, because the selectivity–conversion graph (Fig. 1b) was obtained at increasing temperatures.

The used sample showed a higher activity than the fresh one (around 20–25% increase) (Fig. 1a), although the apparent activation energy was almost the same, say 76 ± 4 kJ mol^{-1}. Besides, very few differences were found in selectivity trends (Fig. 1b), just a small, but not negligible, change in initial selectivities to ethene and CO. This could indicate increased

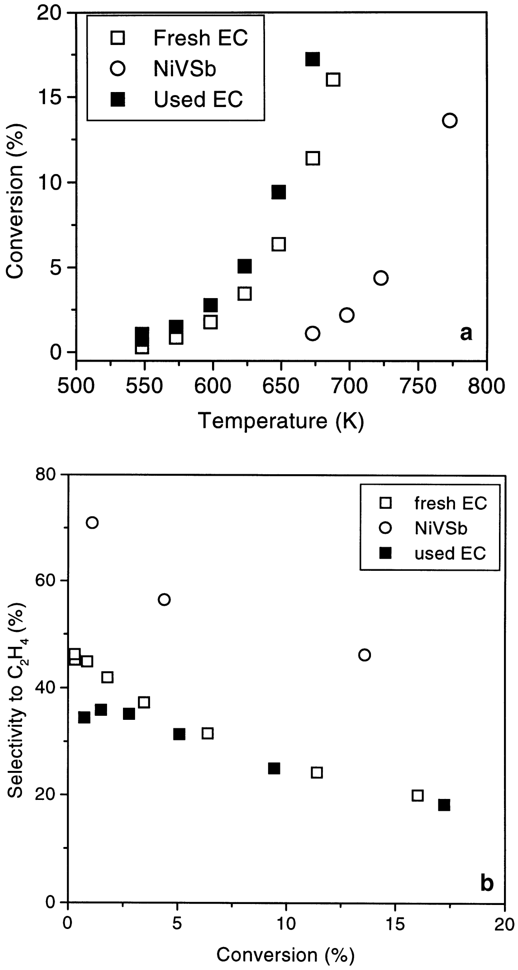

Fig. 1. Effect of temperature on ethane conversion (a) and selectivities to ethene (b) in the ODH of ethane over EUROCAT SCR and supported NiVSb oxide [7].

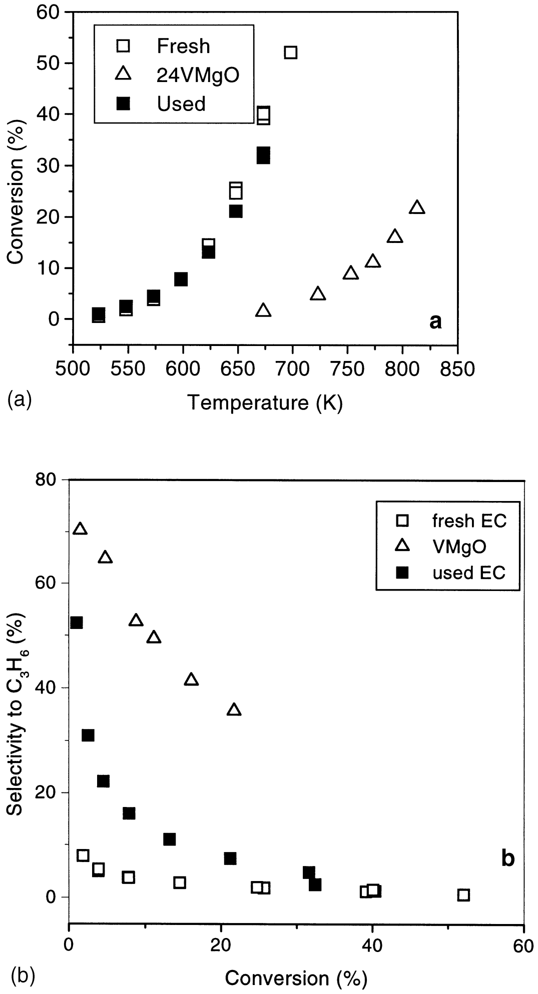

Fig. 2. Effect of temperature on propane conversion (a) and selectivities to propene (b) in the ODH of propane over EUROCAT SCR and VMg oxide [8].

dispersion of the active phases in the catalyst, developed during its use in SCR reaction conditions, or a change in their nature.

ODH of propane. Tests were conducted in the temperature range 523–698 K, in the same conditions as for previous studies of the ODH of propane over vanadium-containing oxide catalysts [11], except for the catalyst sample mass of 0.25 g instead of 0.1 g. The results are shown in Fig. 2, together with those obtained on a V–Mg–O catalyst with 24 wt.% V_2O_5.

Unlike the case of ethane oxidation, selectivity in propene formed from propane ODH was lower (e.g., ca. 15% against ca. 25% at 10% conversion), the main products being carbon oxides. The apparent activation energy equalled $80 \pm 3\,\mathrm{kJ\,mol^{-1}}$ for the fresh sample, which was much more active that the V–Mg–O catalyst (which has a SSA of $41.5\,\mathrm{m^2\,g^{-1}}$, nearly equal to that of the EUROCAT sample), but completely unselective.

Another significant difference is that the main oxidation product on the EUROCAT SCR catalyst is CO, whose selectivity increased with conversion (and temperature), in a similar pattern to that observed with ethane ODH. This implies that the reaction network should be the same as that observed for the reaction of ethane. Thus, the initially formed propene underwent consecutive oxidation, mainly to CO, whereas carbon dioxide was mainly formed by a parallel route. Grabowski et al. [12] reported the same trends when studying the ODH of propane on a V–Ti–O catalyst prepared by depositing one theoretical monolayer of vanadia on a titania (anatase) support. It should be noted that these authors also obtained the selectivity vs. conversion graph at variable reaction temperatures, as the data in Fig. 2b indicate. So, a possible influence of the different activation energies for the various reaction steps, as pointed out above, cannot be completely ruled out.

The activity of the used EUROCAT SCR sample was similar or slightly lower than that of the fresh one. The main difference here was a higher initial selectivity to propene, which increased to nearly 60%, for the used sample. However, this improvement in selectivity decreased sharply with increasing conversion, which seems to suggest that the differences only affect the initial reaction steps and not the subsequent oxidation of propene to CO. In fact, this increase in propene selectivity is mostly at the expense of the parallel formation of CO_2, as its selectivity decreased by 50% at the lower conversions.

It is worth noting that in propane ODH the selectivity in propene was larger for the used sample vs. the fresh one, in contrast with what was observed for ethane ODH (compare Fig. 1b and Fig. 2b). Propene possesses allylic H and can form alkoxy species more easily than ethene and thus its further oxidation is also easier than that of ethene, whereas ethane, on the other hand, is activated with more difficulty than propane (compare Fig. 1a and Fig. 2a).

Conclusions on ODH of light alkanes. In the ODH of light alkanes the EUROCAT SCR catalyst behaved like a typical vanadia–titania catalyst. It is active, but not very selective for alkenes. Since the reaction conditions used for ethane and propane ODH are different, caution should be exercised in comparisons, but the greater selectivity to alkene in ethane than in propane ODH is not in question and greater than that observed for other V-oxide on titania catalysts. This is possibly a consequence of the change in acidic properties and the presence of a V–W ion pairs in the EUROCAT V_2O_5–WO_3/TiO_2 SCR catalyst, in agreement with literature data illustrating the role of the acidic character of the catalyst [13] in alkane ODH. Thus, it is safe to assume that the higher selectivity for ethene than for propene may be explained by the acidic properties of the EUROCAT SCR catalyst.

A second important observation deriving from the study of alkane ODH on the EUROCAT SCR catalyst is that in the used catalyst, compared to the fresh one, there is a clear change in reactivity properties, possibly the acid–base character, which in ethane reflects an enhanced rate of alkane depletion, and in propane enhanced selectivity. Note that the IR study (Chapter 5) has demonstrated that the only minor differences between fresh and used samples, corresponded to a small decrease in Lewis acid site strength and the appearance of some nucleophilic (basic) centres for the used sample. Both reactions, however, conclusively indicated a minor but real change in surface reactivity properties of the EUROCAT V_2O_5–WO_3/TiO_2 SCR catalyst during plant operations in NO_x conversion.

3. Conversion of propan-2-ol

The conversion of propan-2-ol is a model reaction widely used to characterise and differentiate between acid, basic and redox properties of metal oxide catalysts [3–5]. In the absence of oxygen, propan-2-ol is dehydrated to propene and diisopropylether on acid sites and dehydrogenated to acetone on basic sites. In the presence of oxygen, oxydehydrogenation to acetone may also occur on redox centres.

The conversion of propan-2-ol was used previously to characterise the EUROCAT V_2O_5/TiO_2 (ELV1) catalysts [14] and it was shown that with N_2 as a carrier gas, hydrogenating properties did not depend on V content whereas dehydrating properties increased with it. Then basic (or redox) properties were correlated to highly dispersed vanadia species and acidic properties to the presence of microcrystallized V_2O_5.

Non-oxidising conditions. The variations of the specific rates of product formation with time on stream, at 423 K, are shown in Fig. 3 for propene (PRO), diisopropylether (DIPE) and acetone (ACE), respectively, at less than 4% conversion of propan-2-ol. For the fresh and used catalysts, a very drastic deactivation was observed followed by a pseudo-stationary state, the used catalyst being only slightly less active than the fresh catalyst. For the two catalysts, selectivities at the pseudo-stationary state, were about 55% for ACE, 35% for PRO and 10% for DIPE. In contrast, the

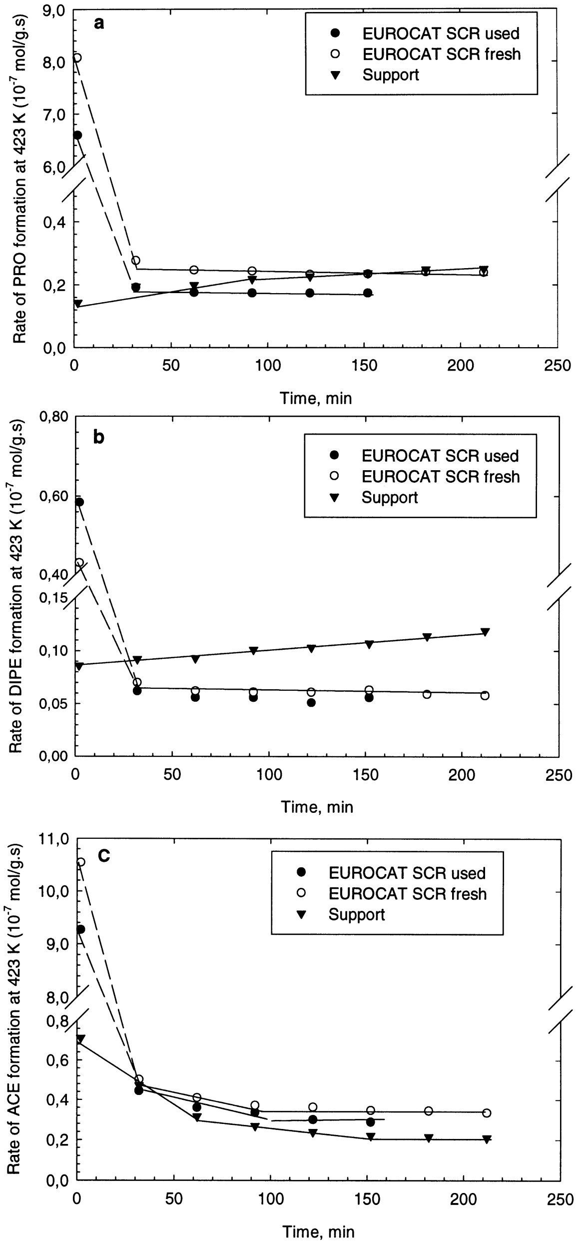

Fig. 3. Rate of formation of products at 423 K in propan-2-ol conversion in the absence of oxygen in the feed over fresh and used V_2O_5–WO_3/TiO_2 EUROCAT SCR and for comparison over the WO_3/TiO_2 support: (a) propene (PRO), (b) diisopropylether (DIPE), and (c) acetone (ACE).

initially scarcely active WO_3/TiO_2 support remained stable and its activity reached that of fresh and used catalysts at the pseudo-stationary state. Its activity for DIPE formation was higher by a factor of two and slightly increased with time on stream. Selectivities were about 40% for ACE, 40% for PRO and 20% for DIPE.

Oxidising conditions. Fig. 4 shows the time dependence of the rate of formation of PRO, DIPE and ACE in oxidising conditions. For the fresh and used samples, the rates of PRO formation slightly increased over about 100 min, whereas those of ACE formation decreased and those of DIPE formation remained constant. At the pseudo-stationary state, the same selectivities of about 45% for ACE, 52% for PRO and 3% for DIPE were observed for both samples.

The used sample was about 5% less active than the fresh sample while the activity of the WO_3/TiO_3 support was only 10% that of the fresh sample and selectivities amounted to 26% for ACE, 58% for PRO and 16% for DIPE, showing that the dehydration pathway was favoured.

It is striking to note that the initial activities for PRO and ACE measured in non-oxidising conditions are approximately equal to those obtained in oxidising conditions, showing that the activities are certainly strongly dependent on the oxidation state of the samples.

In order to confirm this observation, the fresh sample was stabilised in oxidising conditions and then the air flow was replaced by the N_2 flow. The first analysis in non-oxidising conditions took place 2 min after the change of carrier gas and is indicated in Fig. 5 by the first arrow. After stabilisation in non-oxidising conditions, the carrier gas nature was inverted and the first analysis took place 2 min later (second arrow). These results show that (i) the catalyst was very rapidly reduced by propan-2-ol in the absence of oxygen, (ii) the reduced catalyst was scarcely active, and (iii) the redox process was reversible.

The same experiment was performed on the support, but only small and slow effects were observed (Fig. 5b). This indicates that these properties must be related to the presence of vanadium ions. A very similar effect as for V_2O_5–WO_3/TiO_2 EUROCAT SCR sample was also observed when the same experiment was performed on the V_2O_5/TiO_2 EUROCAT ELV1 catalyst (1 wt.% V_2O_5) (Fig. 5c). However, it is to be

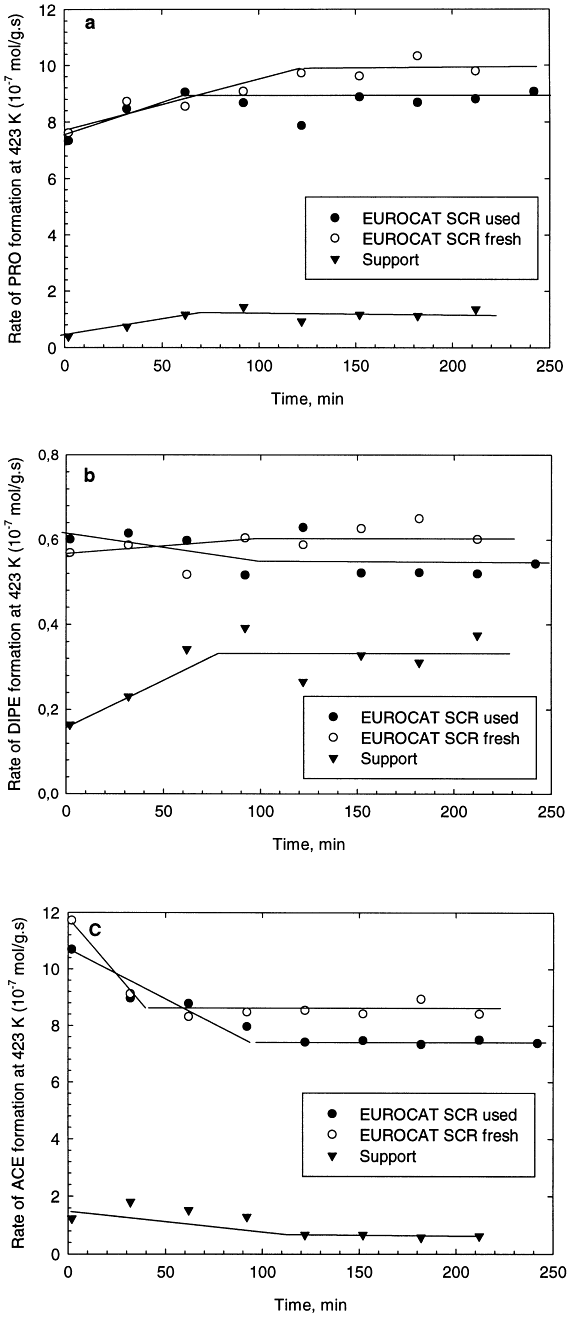

Fig. 4. Rate of formation of products at 423 K in propan-2-ol conversion in the presence of oxygen in the feed over fresh and used V_2O_5–WO_3/TiO_2 EUROCAT SCR and for comparison over the WO_3/TiO_2 support: (a) propene (PRO), (b) diisopropylether (DIPE), and (c) acetone (ACE).

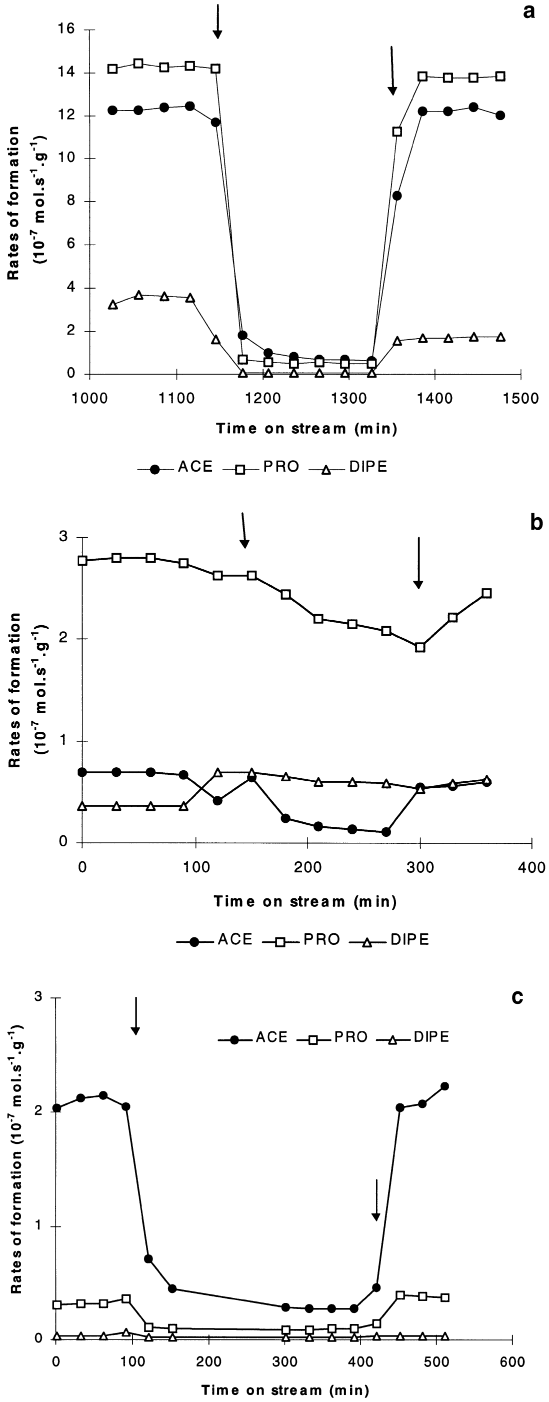

Fig. 5. Influence of the carrier gas on catalytic performances at 423 K of fresh V_2O_5–WO_3/TiO_2 EUROCAT SCR (a), WO_3/TiO_2 support (b) and for comparison on EUROCAT ELV1 catalyst (c). See text for an explanation of the arrows.

noted that V_2O_5/TiO_2 in oxidising and non-oxidising conditions is much less selective to propene than V_2O_5–WO_3/TiO_2 catalyst.

In non-oxidising conditions, the total activities were, respectively, 0.6 and 0.4×10^{-7} mol s^{-1} g^{-1} for V_2O_5–WO_3/TiO_2 (which contains 3.4 wt.% V_2O_5) and V_2O_5/TiO_2 (which contains 1 wt.% V_2O_5), that is to say that they roughly followed the V content. However, in oxidising conditions, total activities were, respectively, 20 and 2.5×10^{-7} mol s^{-1} g^{-1} for V_2O_5–WO_3/TiO_2 and V_2O_5/TiO_2 samples, suggesting that W plays a direct role in the oxydehydrogenation process, in agreement with the conclusions derived from alkane ODH experiments.

The activities measured at 393 K (conversion level <4%), at the pseudo-stationary state, and the apparent activation energy values are shown in Table 2. The behaviour of the V_2O_5–WO_3/TiO_2 catalysts in their fresh and used forms and, regardless of conditions, was quite similar. They have almost equal dehydrogenating and dehydrating properties in oxidising conditions and are more dehydrogenating than dehydrating in reducing conditions. This contrast with the conclusions obtained in alkane ODH (Section 2), probable because propan-2-ol conversion is less sensitive than ODH to minor changes in surface properties. Moreover, in the absence of air in the feed, reduction of the surface did occur in propan-2-ol reaction as attested by rapid deactivation and by UV–Vis and EPR characterisation, making it hard to detect an initial difference in surface reactivity between the fresh and used EUROCAT SCR samples.

Comparison with V_2O_5/TiO_2 EUROCAT catalysts, clearly showed that properties were not exclusively due to the vanadium content and differences in surface area (factor of four in favour of V_2O_5–WO_3/TiO_2 catalyst). In particular, the dehydrating properties in oxidising conditions are related to the presence of W.

The most important observation concerns the apparent activation energy values which considerably differed depending on the oxidising/reducing conditions. This implies a change in the nature of the catalytic species and/or in the reaction mechanisms.

Conclusions on propan-2-ol conversion. Investigation of the conversion of propan-2-ol produces the following conclusions:

- In the presence of air as a carrier gas (oxidising conditions) the dehydrogenating properties of both fresh and used V_2O_5–WO_3/TiO_2 samples were similar to those of V_2O_5/TiO_2 EUROCAT ELV1 catalyst, while V/W association conferred some important additional dehydration (acid) properties with respect to the WO_3/TiO_2 support or V_2O_5/TiO_2 EUROCAT ELV1 catalyst. This demonstrates the synergetic effect of V/W association on acid properties in agreement with IR data for pyridine absorption (Chapter 5).
- In the absence of air (reducing conditions) rapid deactivation was observed while the catalysts were clearly reduced. This indication was confirmed by additional UV–Vis and ESR spectroscopic data not given here and which showed the formation of V^{4+} and presumably W^{5+} with the formation of V^{4+}–W^{5+} ion pairs. This behaviour was observed to be completely reversible.
- Fresh and used samples behaved quite similarly, which indicates that selective reduction of NO_x did not appreciably modify the catalyst, even after

Table 2
Activities, selectivities at 393 K and apparent activation energy values in non-oxidising and oxidising conditions

Conditions	Samples	Specific rates (10^{-7} mol s^{-1} g^{-1})			Selectivities (%)			Apparent activation energies (kJ mol^{-1})		
		PRO	DIPE	ACE	PRO	DIPE	ACE	PRO	DIPE	ACE
Non-oxidising	EC SCR fresh	0.033	0.025	0.177	14	11	75	97	45	14
	EC SCR used	0.039	0.026	0.154	18	12	70	86	47	24
	V_2O_5/TiO_2 (EC ELV1)	0.106	0.028	0.078	50	13	37	128	91	68
	WO_3/TiO_2 support	0.87	0.27	0.15	67	21	12	132	85	70
Oxidising	EC SCR fresh	0.93	0.61	1.71	29	19	52	114	89	80
	EC SCR used	0.93	0.71	1.55	29	22	49	104	93	80
	V_2O_5/TiO_2 (EC ELV1)	0.026	0.020	0.379	6	5	89	126	68	90
	WO_3/TiO_2 support	0.235	0.169	0.117	45	32	22	114	68	90

9000 h on stream, with V and W cations at their high oxidation state. However, this conclusion differs from that drawn from alkane ODH (Section 3), probably because propan-2-ol conversion is less sensitive to minor surface modifications.

- From a mechanistic point of view, apparent activation energy values for acetone formation in the absence of air were much lower than in the presence of air. This indicates that the mechanisms governing acetone formation are different in both cases. It may be supposed that in the former case the active sites are basic while they have redox (dehydrogenating) properties in the latter case.
- If one takes into account the data for the EUROCAT ELV1 V_2O_5/TiO2 and the WO_3/TiO_2 support samples, it seems probably that the active sites for the propan-2-ol reaction in the presence of air on V_2O_5–WO_3/TiO_2 samples are isolated V cations for acetone formation and V^{4+}–W^{5+} cation pairs and protons for propene formation (dehydrating feature).

4. Conversion of NO in the presence of C_3H_6/O_2

In contrast to Cu-based catalysts such as Cu–ZSM5 [9], V_2O_5–WO_3/TiO_2 the EUROCAT SCR sample showed negligible activity in NO conversion up to temperatures of 783 K. It did not form N_2 and minimal amounts of N_2O (not more than 10–20 ppm) with a maximum at temperatures in the 673–723 K range. NO_2 was detected in the 150–200 ppm range, nearly independent of reaction temperature, indicating that it probably formed mainly downstream in the pipes of the reactor apparatus. This indicates that the EUROCAT SCR catalyst was unable to oxidise NO in the full range of reaction temperatures, in contrast to Cu-based catalysts, e.g., which oxidise NO to NO_2 in an amount nearly equivalent to the thermodynamic equilibrium for reaction temperatures above 573–623 K. Therefore, notwithstanding the fact that the EUROCAT SCR catalyst has an oxidising property as shown in the previous tests and is able to oxidise SO_2 to SO_3 (Chapter 11), it did not oxidise NO. This behaviour is probably connected to the negligible chemisorption of NO over the EUROCAT SCR, as shown by IR spectroscopy (Chapter 5) and further confirms mechanistic data [8] indicating that on this catalyst NO conversion does not involve the formation of NO_x adspecies, unlike other types of SCR catalysts. The negligible formation of NO_x adspecies may also be the cause of the absence of conversion using propene as a reducing agent instead of ammonia, which supports previous observations indicating that the formation of NO_x adspecies is the first stage in the mechanism of NO reduction by hydrocarbons.

The conversion of propene started at 472 K and became complete at temperatures above 723 K, a relatively broad temperature range indicating low activation energy. CO was the main product of oxidation and CO_2 formation became higher than that of CO only at temperatures higher than 773 K. There are small hysteresis phenomena in analysing catalytic behaviour at increasing or decreasing temperatures in the 473–783 K temperature range, due to a slight lack of C balance at increasing temperatures probably connected to a partial strong chemisorption of propene over the catalyst, especially in the 473–623 K temperature range.

In conclusion, the V_2O_5–WO_3/TiO_2 EUROCAT SCR sample is not a suitable catalyst for the reduction of NO by propene in the presence of oxygen, and furthermore propene is mainly oxidised into CO in spite of the excess of oxygen. The first characteristic is associated with the inability of this catalyst to oxidise NO, whereas the second characteristic indicates a low oxidising power towards alkene conversion.

5. Conversion of C_3H_8, C_3H_6 and C_3H_7Cl

The reaction conditions of the tests are summarised in Table 1. Catalytic tests were made on fresh V_2O_5–WO_3/TiO_2 EUROCAT sample at two different contact times, e.g., using 0.15 or 0.5 g sample and a total flow rate (STP) of 21 l h^{-1}.

Propane and propene conversion. Reported in Fig. 6a is the behaviour of EUROCAT SCR catalyst in propane conversion. The hydrocarbon starts to be converted at a temperature of around 500 K and reaches 22% at 730 K. By increasing the contact time (Fig. 6b), the conversion increases, as expected, reaching 80% at 670 K. The only detectable products are propene, CO and CO_2. Propene is the main product at low conversions, CO_2 has a maximum (40%) in correspondence with a propane conversion of 5% and CO becomes the

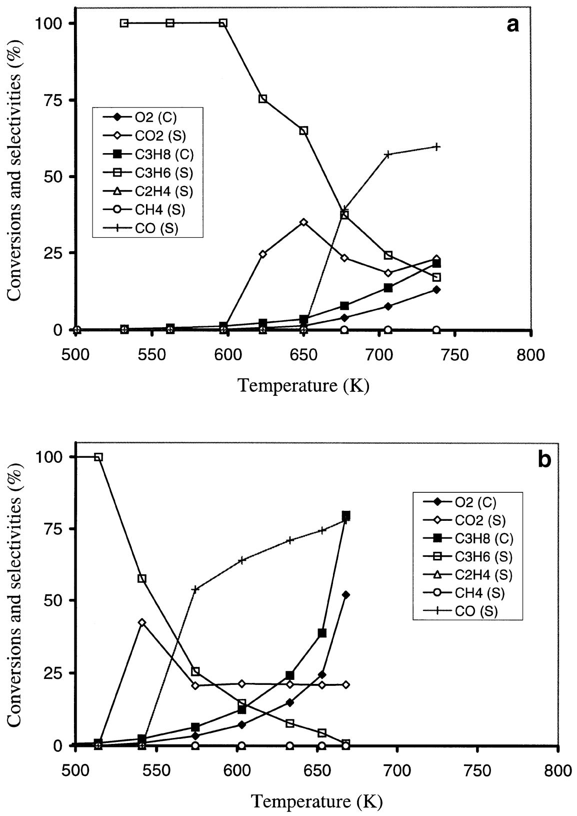

Fig. 6. Propane conversion on V_2O_5–WO_3/TiO_2 EUROCAT SCR catalysts: (a) 0.154 g catalyst, (b) 0.5 g catalyst. Other reaction conditions in Table 1.

main product (80% in correspondence of 80% conversion) at the highest conversions. In comparison with the results of group E-1 (see Section 4 and Fig. 2), comparable data were obtained, notwithstanding minor differences due to the different reaction conditions used in the tests.

Propene conversion (Fig. 7) is complete already at 680 K. The largely predominant products are carbon oxides with CO as main product (70%) at high conversions. Traces of oxygenated compounds such as phthalic and maleic anhydrides are detectable. These data are consistent with those obtained with propane where selectivity to propene decreases between 500 and 600 K giving rise to CO and CO_2.

Chloropropane conversion. The conversion of 1- and 2-chloropropane, as model compounds for chloro-containing hydrocarbons, is reported in Fig. 8a and b, respectively. 1-Chloropropane is completely

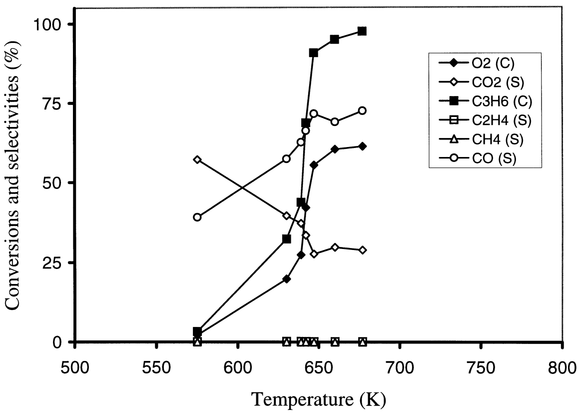

Fig. 7. Propene conversion on V_2O_5–WO_3/TiO_2 EUROCAT SCR catalysts: 0.154 g catalyst. Other reaction conditions in Table 1.

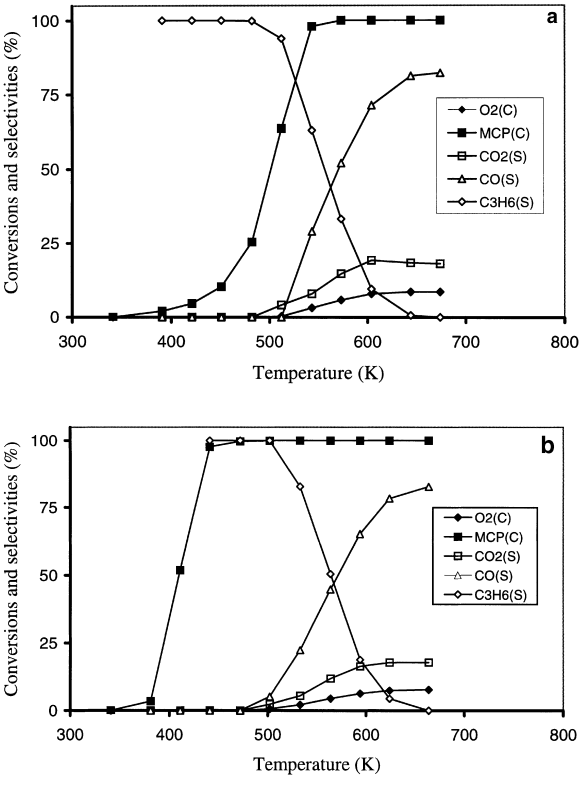

Fig. 8. Chloropropane conversion on V_2O_5–WO_3/TiO_2 EUROCAT SCR catalysts: (a) 1-chloropropane, (b) 2-chloropropene. 0.5 g catalyst; other reaction conditions in Table 1.

converted at 570 K, while 2-chloropropane reacts completely already at 480 K. The products are propene and carbon oxides, in both cases. Since propene selectivity decreases from 100 to 0% in favour of CO and CO_2, it is evident that the catalyst accelerates the elimination of HCl from the chlorinated alkane. Thus, propene is produced and later oxidised, as expected considering the direct oxidation obtained over this catalyst. This is consistent with an E1 mechanism of elimination of HCl from chloropropanes: 2-propyl carbenium ion is more stable than 1-propyl carbenium ion and for this reason is formed more quickly. The fact that the complete combustion of propylene can be obtained after the elimination of HCl shows that this catalyst is resistant to HCl itself.

6. Conclusions

Investigation of the behaviour of V_2O_5–WO_3/TiO_2 EUROCAT SCR catalyst in (i) ethane and propane oxidative dehydrogenation (ODH), (ii) propan-2-ol conversion, and (iii) NO conversion by propene/O_2 indicates a series of characteristics of this catalyst, both fresh and used, which integrate well with other physico-chemical characterisation data to give a more comprehensive general picture of its surface and reactivity properties.

A relevant observation deriving from these studies concerns the question of the modifications of the properties of the EUROCAT SCR catalyst during use. Propan-2-ol data indicate a negligible modification, whereas alkane ODH tests indicate minor but appreciable changes.

Finally, tests of NO conversion with C_3H_6/O_2 clearly showed the inability of the EUROCAT SCR catalyst to oxidise NO and the absence of possible surface pathways of transformation involving the formation of NO_x adspecies. Comparison with V_2O_5/TiO_2 catalyst clearly showed that WO_3 has introduced more acidic properties to the V_2O_5/TiO_2 catalyst as detected by all reactions studied above. This is quite in agreement with general conclusions drawn from other chapters, particularly from IR study (Chapter 5).

References

[1] B. Grzybowska-Swierkosz, F. Trifirò, J.C. Vedrine (Eds.), Vanadia catalysts for selective oxidation of hydrocarbons and their derivatives, Appl. Catal. A 157 (1997) 1.

[2] A. Bassetti, R. Ricci, F. Jensen, in: G. Centi, S. Perathoner, C. Cristiani, P. Forzatti (Eds.), Environmental Catalysis, SCI Pub., Rome, 1995, p. 25.

[3] V.I. Parvulescu, P. Grange, B. Delmon, Catal. Today 46 (1998) 233.

[4] J. Cunningham, B.K. Hodnett, M. Ilyas, J. Tobin, E.L. Leahy, J.L.G. Fierro, Faraday Discussions 72 (1981) 283.

[5] B. Grybowska-Swierkosz, Mater. Chem. Phys. 17 (1987) 121.

[6] A. Ouqour, G. Coudurier, J.C. Vedrine, J. Chem. Soc., Faraday Trans. 89 (1993) 3151.

[7] H. Kato, C. Yokoyama, M. Misono, Catal. Today 45 (1998) 93–102.

[8] G. Busca, L. Lietti, G. Ramis, F. Berti, Appl. Catal. B 18 (1998) 1.

[9] G. Centi, S. Perathoner, Appl. Catal. A 132 (1995) 179.

[10] R. Juárez López, N.S. Godjayeva, V. Cortés Corberán, J.L.G. Fierro, E.A. Mamedov, Appl. Catal. A 124 (1995) 281.

[11] R.X. Valenzuela, E.A. Mamedov, V. Cortés Corberán, React. Kinet. Catal. Lett. 55 (1995) 213.

[12] R. Grabowski, B. Grzybowska, K. Samson, J. Sloczynski, J. Stoch, K. Wcislo, Appl. Catal. A 125 (1995) 129.

[13] P. Concepción, A. Dejoz, J.M. López Nieto, M.I. Vázquez, in: Proceedings of the XIV Iberoamerican Symposium On Catalysis, Concepciön, Chile, 1994, p. 769.

[14] B. Gryzybowska-Swierkosz, Catal. Today 20 (1994) 165.