



1-BUTANOL DEHYDRATION AND DEHYDROGENATION OVER VANADIUM ALUMINIUM OXYNITRIDE CATALYSTS

Mihaela FLOREA,^{a*} Stephanie DELSARTE,^b Elisabeth van KEULEN^b and Paul GRANGE^{b**}

^aDepartment of Chemical Technology and Catalysis, Faculty of Chemistry, University of Bucharest, B-dul Regina Elisabeta 4-12, Bucharest 030018, Roumania

^bCatalyse et chimie des matériaux divisés, Université catholique de Louvain, Croix du Sud 2, Boite 17, Louvain-la-Neuve, 1348, Belgium

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Amorphous high surface area vanadium aluminium oxynitrides (VAION) are prepared by nitridation of vanadium aluminium oxide precursors. The acid-base and redox properties of VAION depend on their nitrogen content, as well as on the V/Al ratio of the reactive precursor. The influence of these parameters over the catalytic properties of VAION for 1-butanol dehydration/dehydrogenation was studied. For the studied samples, the only detected products were 1-butene, butane and butanal. The presence of butane as a major product could be explained by a hydrogen transfer mechanism.

INTRODUCTION

Oxynitride systems become extensively studied as a new class of catalysts because of their particular acid-base properties. Nitridation of amorphous oxide precursors induces a decrease of the number of acid sites and the creation of basic centers as is shown for aluminophosphate oxynitrides,¹ zirconophosphate oxynitrides^{2,3} and aluminogalliphosphate oxynitrides.⁴ It was shown previously⁵ that the vanadium aluminium oxynitrides catalysts - VAION - are active in the base-catalysed Knoevenagel condensation reaction between benzaldehyde and malononitrile. Several studies demonstrated a direct relation between the VAION basic properties and their catalytic activity for propane ammoxidation to acrylonitrile.⁶ The catalytic performances of the oxynitrides systems are strongly affected by their composition and the nitridation conditions. In the particular case of the V-Al oxynitride system, it was demonstrated that the modification of: i) the V/Al atomic ratio in the oxide precursor, ii) the degree of nitridation of the catalyst, iii) the nature and distribution of the

nitrogen species, may cause important differences in the catalytic behavior.⁶

The reactivity of 1-butanol over catalysts has been extensively used to evaluate the nature, the strength and the concentration of the acid-base sites⁷⁻¹⁰ since the product selectivities are influenced by the acid-base properties of the catalysts. Thus, the formation of 1-butene and dibutylether is favored by catalysts with a high density of acid sites of intermediate and weak strengths, whereas the isomerization of 1-butene to 2-butene is favored by catalysts which exhibit mainly Brønsted acid sites.¹¹

This study deals with: i) the study of the product distribution over oxynitride catalysts, with different V/Al ratio, and ii) the identification of the reaction mechanisms.

EXPERIMENTAL

1. Catalyst preparation

Vanadium aluminium oxide precursor, with V/Al ratios of 0.25, 0.7 and 0.9, was prepared by coprecipitation of solutions containing 10^{-2} M ammonium meta-vanadate and 10^{-2} M

* Corresponding author: mihaela.florea@g.unibuc.ro

** Deceased in 2003

aluminium nitrate with ammonia (25%) at pH = 5 and 60°C. The obtained precipitate was washed with ethanol and isopropanol and dried in a vacuum oven at 60°C under a pressure of 30 mbar. The thermal nitridation of the samples was carried out in a tubular rotating reactor under a flow of pure ammonia (30 L.h⁻¹) at 500°C for 5 h. The heating rate was 10°C min⁻¹. The system was subsequently cooled down to room temperature under a flow of pure nitrogen. The catalysts were labelled as follows: for the oxide samples VAION, where *n* is the V/Al molar ratio and for the oxynitrides VAION_n, where *n* is the V/Al molar ratio.

2. Physico-chemical characterization

The measurements of the BET surface area using single point method were performed on a Micromeritics Flow Sorb II 2300.

XPS spectra were collected with an SSX-100 Model 206 Surface Science Instrument spectrometer. The charge correction was made considering that the C1s signal of contaminating carbon was centred at 284.8eV. The C1s, V2p_{3/2}, Al2p, N1s and O1s bands were chosen for characterization, since they are the most intense and do not overlap.

The total nitrogen content (N_T), including bulk and surface nitrogen, was determined using the method described by Guyader *et al.* [12] Briefly, this method consists in the measurement of ammonia produced by the reaction between melted potassium hydroxide and nitrogen (nitride N³⁻ or NH_x surface species), following the equation:



A mixture of 20 mg sample and 5g KOH was heated at 400°C. The released ammonia was carried away by a nitrogen flow (50 ml.min⁻¹) and the output was connected to a trap containing distilled water and titrated with a sulphuric acid solution of 10⁻² N.

3. Activity measurements

The dehydration and dehydrogenation reactions were carried out at atmospheric pressure, in a quartz fixed bed micro-reactor (i.d. 10 mm), in up flow mode. The reactor was placed in a vertical furnace with temperature control. The real reaction temperature was measured by a thermocouple situated in the middle part of the reactor, near the catalyst. Before reaction, the catalysts were sieved, and the particle size fraction of 100-200 μm was used. The catalyst mass was

100 mg, and the corresponding bed height was adjusted to 13 mm, by adding 200 to 500 μm glass balls.

Catalyst activation was performed in helium flow (30 ml.min⁻¹) (Indugas 4.5), at reaction temperature of 275°C for 2h. Helium was then saturated with 1-butanol (p.a. ACROS Organics) vapour by contact in a saturator. The 1-butanol partial pressure was 2.6 kPa. This helium/1-butanol gas reaction mixture supplies the reactor at a rate of 30 ml.min⁻¹ (WHSV=1.3 h⁻¹). To prevent the condensation of 1-butanol or reaction products, all lines from the saturator to the chromatograph were heated above 100°C.

Unconverted 1-butanol and the dehydration and dehydrogenation products were analysed by gas chromatography, using a Shimadzu Chrompac C-R3A chromatograph, equipped with a flame ionisation detector. A 50mx0.32 mm (RSL-160) capillary column was used for the separation of the various compounds. Water was not considered in the characterisation of the composition of the reaction mixture.

The reaction rate, *r*, was defined as the number of butanol moles transformed in one second per square meter of specific surface area of the catalyst. The yield for a product is defined as the number of moles of this product formed in one second per square meter of specific surface area of the catalyst. The conversion (%), was defined as the ratio of the amount of converted butanol to the amount of butanol supplied at reactor inlet. The selectivity for each product (molar %) was defined as the molar ratio of each of them to all the detected products. For quantitative comparison between the catalysts, care was taken to ensure that the data were controlled neither by external nor internal diffusion.

RESULTS

1. Chemical composition, textural and structural characteristics of the fresh catalysts

Samples with V/Al atomic ratios in the range of 0.25 to 0.9 were prepared by the co-precipitation method followed by nitridation in the presence of ammonia at 500°C for 5 hours. All the samples are X-ray amorphous before and after the catalytic test. Table 1 compiles the values of the nitrogen content and surface areas of the oxynitride powders before the reaction.

Table 1

Nitrogen content and surface areas of VAION catalysts

Catalyst	N _T (%wt)*	Surf. area m ² .g ⁻¹
VAIO0.25	n.a.	250
VAION0.25	5.35	153
VAIO0.7	n.a.	195
VAION0.7	3.28	122
VAIO0.9	n.a.	163
VAION0.9	2.26	143

*- total nitrogen content determined by the method described by Guyader *et al.*¹²; n.a. – not analyzed

The oxynitrides exhibit specific areas between 122 and 163 m².g⁻¹ depending on the V/Al ratio (Table 1). The surface area increases with decreasing the V/Al ratio; the highest surface area of 163 m².g⁻¹ being observed for the VAION0.25 sample. The nitrogen content of the nitrated powders before the catalytic test increases with decreasing the V/Al ratio the highest nitrogen content of 5.35% (wt) was obtained for VAION0.25.

The XPS technique provides information regarding the nature of the surface nitrogen species before and after catalytic test, as well as about the surface vanadium atoms. Table 2 shows the atomic composition for the oxynitrides before and after the catalytic test, as a function of V/Al ratio. In all the cases, the V/Al surface ratios calculated from the XPS data are smaller than the theoretical ones.

Table 2

Atomic compositions derived from the XPS analysis for the fresh and used samples

Sample	N (%bulk*)	Al (%)	O (%)	V (%)	N (%)	V/Al ratio
<u>VAION0.25</u>						
fresh	5.4	28.7	65.5	4.2	2.6	0.15
used	4.8	31.0	61.5	4.1	2.3	0.13
<u>VALON0.7</u>						
fresh	3.28	20.9	66.8	8.9	1.2	0.42
used	2.6	22.9	64.9	8.10	1.0	0.35
<u>VALON0.9</u>						
fresh	2.26	23.34	67.80	8.20	1.64	0.35
used	1.93	32.45	62.71	5.90	1.50	0.18

*- Total nitrogen content determined by the method described by Guyader *et al.*¹²

An increase of the amount of aluminum at the surface was observed for the used catalyst, and, as a consequence, the V/Al ratio diminished for the tested catalysts. More details about XPS analysis for these catalysts are reported elsewhere.¹³

2. Catalytic activity

2.1. Influence of nitridation on activity and selectivity

The effect of nitridation on the initial conversion and selectivity for 1-butanol dehydration and dehydrogenation was studied on oxides and oxynitrides possessing variable V/Al ratios and the results are presented in Table 3. Conversions and selectivities obtained with reference catalysts (MgO and SiO₂-Al₂O₃), tested in the same conditions are also presented in Table 3.

Conversion of 1-butanol is affected by the insertion of nitrogen in the oxide structure, and increases by approximately 25% after nitridation. For the studied samples, the only detected products were 1-butene, butane and butanal. 1-butene is the intramolecular dehydration product (elimination reaction), butanal is the dehydrogenation product, and butane could be formed as the results of the

hydrogenation reaction of 1-butene, but this aspect will be elucidated later in the discussion part of this work. It is worth to mention that no consecutive isomerization of 1-butene was observed on the VAIO and VAION catalysts.

The selectivities are not much affected by the nitrogen insertion, and the same proportions of products are formed in the presence of oxides and oxynitrides, this behaviour being unexpected for the two series of catalysts. The carbon balance deficit upon the transformation of 1-butanol could come from the yellow deposits on the quartz balls and on the cold part walls of the reactor. The analysis of the deposits by mass spectrometry shows that the products not detected by GC were the butylbutyrate and the 2-ethyl hexanal.

2.2. Influence of the V/Al ratio on activity and selectivity

The catalytic properties of the VAION catalysts depend on the V/Al ratio. The evolution of the yields for but-1-ene, butane and butanal as a function of the V/Al ratio are presented in Fig. 1.

Table 3

Activity results for the oxide and oxynitride catalysts, as well as for reference oxides

Catalyst	Butanol conversion (%)	Selectivities				C balance (%)
		1-butene(%)	Butane (%)	Butanal (%)	Dibutylether (%)	
VAIO0.25	33	9	47	44	traces	80
VAION0.25	42	8	45	45	traces	72
VAIO0.9	34	6	48	46	traces	94
VAION0.9	42	8	48	44	traces	78
SiO ₂ -Al ₂ O ₃ (6.38 wt.% Al)	100	46*	traces	traces	traces	>95
MgO	3	traces	traces	100	traces	>95

* For this sample, cis-2-butene and trans-2-butene are also detected (cis-2-butene selectivity 26 %; trans-2-butene selectivity =28%).

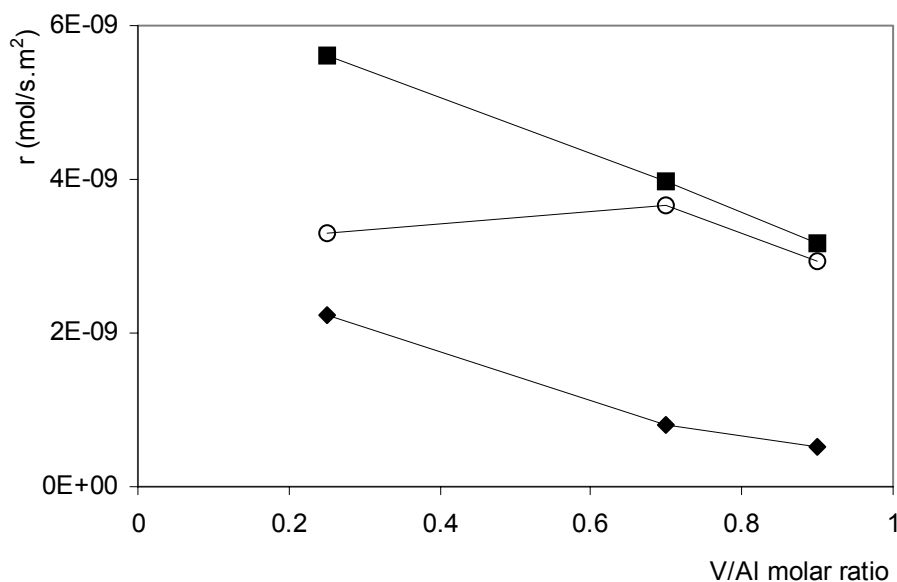


Fig. 1 – (◆)1- butene; (■) butane; (○) butanal yields over VAION catalysts as a function the V/Al ratio.

The butane and 1-butene yields diminish with increasing the V/Al ratio, while butanal formation is maximal for a V/Al ratio of 0.7.

In Fig. 2, the catalytic activity of the VAION series is expressed per mol of vanadium in order to normalize the catalytic results. We observed that the amount of 1-butanol transformed per mole of vanadium increased with the decreasing of the vanadium loading.

2.3. Stability of the catalysts

The evolution of the catalytic activity of VAION0.25 with time on stream is presented in

Fig. 3. The initial conversion of 1-butanol was about 42% and stayed constant during the 10 hours of the reaction. The butane selectivity was almost constant with time on stream, while the selectivity to butanal diminished and the selectivity to 1-butene increased slightly.

The consecutive isomerization of 1-butene was not observed during the 10 hours of reaction and no deactivation of the catalyst was noted during this period. For the catalysts with different V/Al ratios, the trends were similar to that presented in Fig. 3.

XPS spectroscopy was used for the characterization of the catalysts after 1-butanol dehydration and dehydrogenation catalytic tests

(10 hours on stream). The results obtained for the VAION0.25 sample are presented in Table 2. The

nitrogen content diminished slightly for the used catalyst.

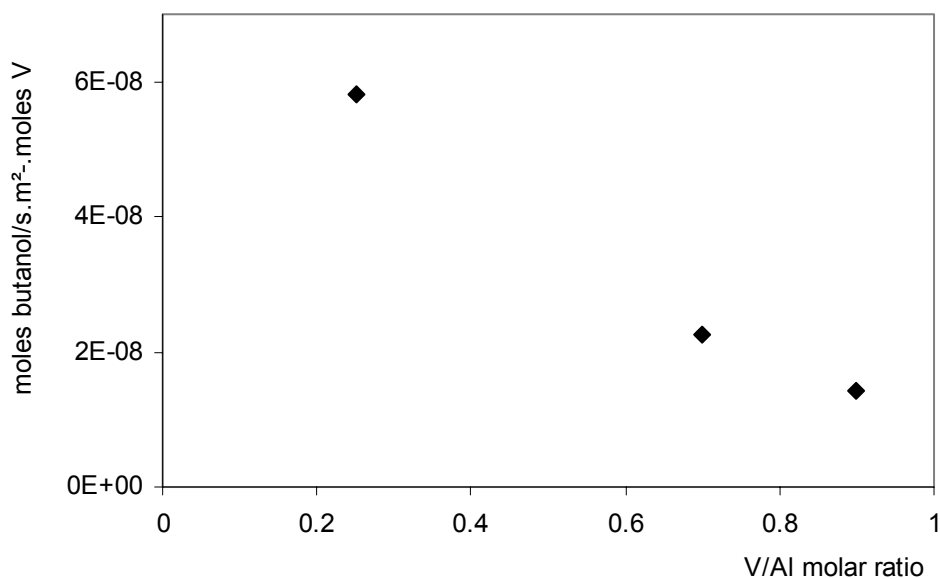


Fig. 2 – Reaction rates, expressed as mol of butanol/s.m².mol of V as a function of the V/Al molar ratio.

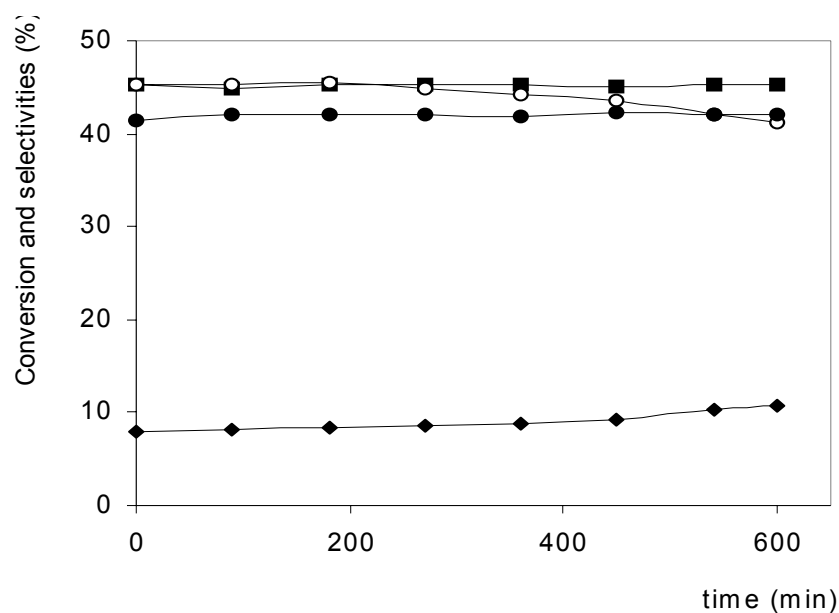


Fig. 3 – Evolution of the activity and selectivity of 1-butanol dehydration and dehydrogenation over VAION0.25 as a function of time on stream: (●) conversion; (◆) 1-butene selectivity; (■) butane selectivity; (○) butanal selectivity.

DISCUSSION

The reactivity of 1-butanol over catalysts has been extensively used to evaluate the nature, the strength and the concentration of the acid-base sites⁷⁻¹⁰ since the product selectivities are influenced by acid-base properties of the catalysts. We will first discuss the product distribution over the VAION catalysts. Scheme 1 summarizes the

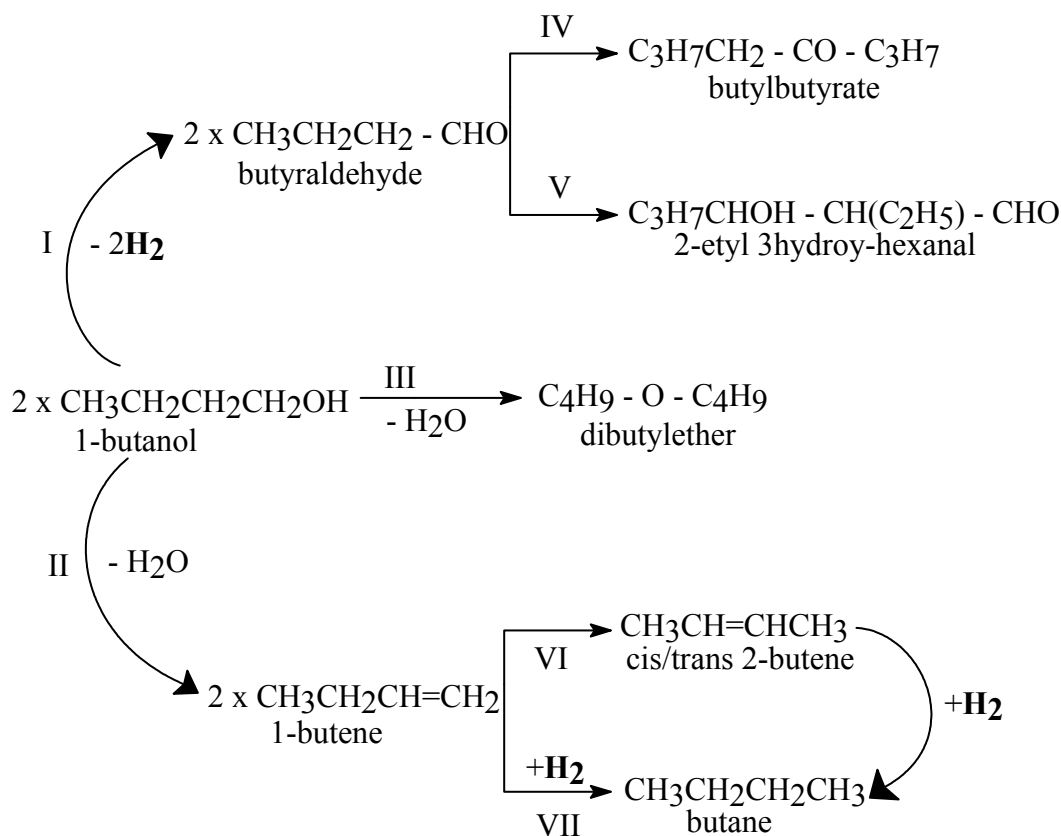
reactions that are observed on VAION catalysts at 275°C.

The dehydrogenation reaction (I) occurs on strongly basic catalysts like MgO, CaO or mixed oxides like mixed aluminum and magnesium oxide that possess strong basic sites.

The intramolecular dehydration (II) to 1-butene is an elimination reaction and occurs through the E1, E2 or E1cB mechanisms as a function of the

acid or basic character of the catalyst.¹⁴ To differentiate between E1, E2 and E1cB eliminations and to determine the properties of the VAION catalyst it is necessary to study the distribution of 1-butene, *trans*-2-butene and *cis*-2-butene:¹⁵ i) on strong acid, catalyzing the intramolecular dehydration of 1-butanol through an

E1 mechanism, 1-butene isomerises rapidly to 2-butene (the *cis/trans* ratio being close to 1) and 2-butene will be the major reaction product; ii) on amphoteric or basic catalysts, catalyzing the intramolecular dehydration through an E2 or E1cB mechanism, 1-butene will be the major product.



Scheme 1 – 1-butanol transformation reactions on VAION catalysts.

Hence, from the distribution of butenes (1-butene and 2-butene proportions, *cis/trans*-2-butene ratios), one can deduce the mechanism dominating the reaction. The mechanism for VAIO and VAION catalysts is most probably the direct transformation of 1-butanol to 1-butene through a bifunctional E2 mechanism.

The intermolecular dehydration of two molecules of 1-butanol to dibutylether (III) necessitates the co-operation of acid and basic surface sites.¹¹ This was clearly established by Jain and Pillai¹⁶ by the selective poisoning of catalysts by acid (phenol) and basic (pyridine) molecules. Our tests on reference catalysts (Table 3) clearly confirm their findings: dibutylether neither is formed on very basic solids (MgO), neither on very acid solids (SiO₂-Al₂O₃).

From a strictly acid-base point of view, the dehydrogenation reaction of alcohols occurs on strongly basic catalysts like MgO (see Table 1). The conversion of 1-butanol into butanal (I) on VAION is not surprising, since it was shown previously,¹⁷ that these catalysts possess basic properties. Surprising is the fact that the same selectivities in aldehyde were obtained for the oxide and oxynitride catalyst, while just the oxynitride possesses basic properties.

However, the dehydrogenation of an alcohol can also be considered as an oxidation of the carbon atom bound to the hydroxyl group, since it becomes doubly bound to an oxygen atom. Therefore, a redox mechanism could be envisaged to explain the reactivity observed on the VAIO and VAION.

The 2-ethyl, 3-hydroxy hexanal (IV) could be formed in two stages: first the autocondensation of 2 molecules of butanal and secondly the hydrogenation of the unsaturated aldehyde, produced through aldolic condensation. The butylbutyrate (V) could be formed from the acylation of 1-butanol with butyric acid. The butyric acid could come from the oxydation of 1-butanol in butanal, then in acid.

Nevertheless, the major product of the 1-butanol transformation is butane (VII), the selectivity to butane over the VAIO and VAION catalysts being around 45% (see Table 3). This reaction product is not obtained directly from the dehydration or dehydrogenation of 1-butanol.

This result is quite different than that observed over the nitrated phosphates, AIPON, AlGaPON and ZrPON.¹⁸ Dibutylether is the main reaction product for AIPON and AlGaPON, both acting as bifunctional acid-base catalysts for this reaction. For ZrPON catalyst, 1-butene is the main reaction product, and the reaction rate is much lower.

1. Origin of the butane formation from 1-butanol over VAION catalysts

Alkane formation upon alcohol activation over oxides or nitrides has already been reported in the literature. For instance: i) Noller *et al.*,¹⁹ assumed the formation of butane from 1-butanol over TiO₂ occurred through the nucleophilic substitution (SN2) of OH⁻ by H⁺ coming from the water formed at the surface of the catalyst; ii) Tanabe *et al.*,²⁰ studied the reaction of 2-butanol over Fe₂O₃ and suggested that the OH⁻ from the alcohol is substituted (SN1) by H⁺ formed on an oxygen vacancy of the catalyst; iii) Lee *et al.*²¹ suggested a hydrogen transfer when octane is obtained from 2-octanol over VN, without other details. The formation of about equal molar quantities of n-octane and n-octanone supports this view.

We have attempted to explain butane formation from 1-butanol over VAION catalysts. Two additional tests were performed in the same reactions conditions used for 1-butanol dehydration and dehydrogenation: i) hydrogenation of 1-butene over VAION and ii) addition of propylene in the reaction feed.

In the first experiment, we reacted 1-butene (10% in He) and H₂ (5% in He) at 275°C over a VAION catalyst (V/Al ratio = 0.25; N wt.% = 5.35). No butane was observed in the effluents. This test

demonstrated that the formation of butane among 1-butanol dehydration/dehydrogenation products could not be explained by the hydrogenation of 1-butene with hydrogen resulting from the dehydrogenation of other alcohol molecules.

In the second case propylene (10% in He) was added in the reaction feed on top of 1-butanol and reacted at 275°C over a VAION catalysts (V/Al ratio = 0.25; N wt.% = 5.35). Propylene was converted to propane, demonstrating a coupling between the dehydrogenation/dehydration step of 1-butanol and the formation of alkanes from alkenes (butane from butene and propane from propylene). One possible explanation for this coupling could be the formation of a metallic hydride intermediates on the VAION surface during the catalytic cycle; the active hydrogen atoms in the metallic hydride being able to hydrogenate efficiently 1-butene (as well as propylene).

This phenomenon was referred as a catalytic transfer hydrogenation by Imamura *et al.*²² who used catalysts such as LaNi₅, CaNi₅ and LaNi₄Al to obtain butane and acetone from a mixture of 2-butene and 2-propanol.

The reactions with hydrogen transfer are catalyzed most often by noble metals.²³ It has been extensively demonstrated that the nitridation of transition metal oxides confers them properties similar to those of noble metals.²⁴ Once nitrated they become active in reaction necessitating a hydrogen transfer like the NH₃ synthesis²⁵ or the dehydrogenation of small alkanes. The noble metal character of vanadium atoms in VAION catalysts was recently demonstrated using XAS.²⁶

2. Effect of nitrogen content on the VAION catalytic properties

Conversion of 1-butanol is affected by the insertion of nitrogen in the oxide structure, and increases by approximately 25% after nitridation (Table 3). This could be due to the fact that the reduction degree of vanadium increases with the amount of nitrogen incorporated during the nitridation process.²⁷ Indeed, it has been shown previously²⁸ for the dehydrogenation of alcohols on chromium-containing catalysts that the coordination of transition metal cations in catalysts had an influence on the alcohol conversion and that lower oxidation states induced higher conversions.

3. Effect of the V/Al ratio on the VAION catalytic properties

The quantity of the 1-butanol transformed over the VAION catalysts increases with decreasing the vanadium content, and, in parallel, butane and 1-butene yields are increased (Fig. 1). The butanol yield is maximum for an intermediate V/Al molar ratio.

From the characterization data of the VAION catalysts, reported elsewhere,¹³ a correlation can be made between the nature of the vanadium oxide species and the V/Al ratio. For higher V/Al ratios, the V-O-V bonds of polymeric vanadium oxide species are predominant which impeaches nitrogen incorporation, while for the lower V/Al ratios there is a predominance of the V-O-Al bonds of isolated vanadium oxide species type which favours higher nitrogen contents (see Table 1). As the reduction state of vanadium atoms decreases with nitrogen incorporation, and as this decrease in the vanadium reduction state has a positive influence on the 1-butanol conversion rate, the observed increase of the 1-butanol conversion rate with the decrease of the V/Al ratio can be explained.

4. Stability of the VAION samples under reaction test conditions

The sensitivity of phosphate-based oxynitride catalysts to the presence of water was previously mentioned for AIPON system.²⁹ Water, as reaction product, could hydrolyse the surface NH_x species, generating M-OH acid sites and progressively modifying the catalytic properties of oxynitrides during time on stream. This phenomenon was observed for AIPON catalysts.²⁹ In the case of the VAION catalysts the 1-butanol conversion is stable for at least 10 hours (Figure 3). Moreover, the nitrogen content measured by XPS before and after the catalytic test for VAION (V/Al=0.25) diminished very slightly, which underlines the fact that for this system the hydrolysis of the NH_x species does not take place and is an important way under the chosen operating conditions.

CONCLUSIONS

In summary, according to the experimental results obtained in the present study, amorphous

VAIO(N) system exhibits good activity in 1-butanol dehydration and dehydrogenation. The catalytic transformation of 1-butanol over these surfaces has revealed that the main change induced by nitrogen was an increase in the activity. We can conclude also, that the transformation of 1-butanol into butanal can be considered as an oxidation of the C-O bond rather than an acid-base catalysed reaction. The presence of butane as a major product can be explained by a hydrogen transfer mechanism.

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REFERENCES

1. A. Massinon, J. Odriozola, P. Bastians, R. Conanec, R. Marchand, Y. Laurent and P. Grange, *Appl. Catal. A*, **1996**, *137*, 9-23.
2. N. Fripiat, R. Conanec, R. Marchand, Y. Laurent and P. Grange, *J. Eur. Ceram. Soc.*, **1997**, *17*, 2011-2015.
3. N. Fripiat, R. Conanec, A. Auroux, Y. Laurent and P. Grange, *J. Catal.*, **1997**, *167*, 543-544.
4. S. Delsarte, V. Peltier, Y. Laurent and P. Grange, *Stud. Surf. Sci. Catal.*, **1998**, *118*, 869-878.
5. H. Wiame, L. Bois, P. L'Haridon and P. Grange, *J. Eur. Ceram. Soc.*, **1997**, *17*, 2017-2020.
6. M. Florea, R. Prada Silvy and P. Grange, *Catal. Lett.*, **2003**, *87*, 63-66.
7. P. Berteau, S. Ceckiewicz and B. Delmon, *Appl. Catal. A*, **1987**, *31*, 361-383.
8. P. Berteau, M.A. Kellens and B. Delmon, *J. Chem. Soc. Faraday Trans.*, **1991**, *87*, 1425-1431.
9. P. Berteau, B. Delmon, J.L. Dallons and A. Van Gysel, *Appl. Catal.*, **1991**, *70*, 307-323.
10. G. Guiu and P. Grange, *J. Catal.*, **1995**, *56*, 132-138.
11. P. Berteau and B. Delmon, *Catal. Today*, **1989**, *5*, 121-137.
12. J. Guyader, F.F. Grekov, R. Marchand, and J. Lany, *Rev. Chim. Miner.*, **1978**, *15*, 413-423.
13. M. Florea, R. Prada Silvy and P. Grange, *Appl. Catal. A*, **2005**, *286*, 1-10.
14. S. Delsarte and P. Grange, *Appl. Catal.*, **2004**, *259*, 269-279.
15. H. Noller, J. A. Lercher and H. Vinek, *Mater. Chem. Phys.*, **1988**, *18*, 577-593.
16. J.R. Jain and C.N. Pillai, *J. Catal.*, **1967**, *9*, 322-330.
17. H. Wiame, C. Cellier and P. Grange, *J. Catal.*, **2000**, *190*, 406-418.
18. S. Delsarte, M. Florea and P. Grange, *Ceram. Sci. Techn.*, **2004**, *69*, 69-75.
19. J. A. Lercher, H. Vinek, H. Noller and J. Stoch, *Appl. Catal.*, **1984**, *12*, 293-307.

20. T. Jin, H. Hattori and K. Tanabe, *Bull. Chem. Soc. Jpn.*, **1983**, *56*, 3208-3215.
21. J.H. Lee, C. E. Hamrin and H.D. Burton, *Catal. Today*, **1992**, *15*, 223-241.
22. K. Soga, H. Imamura and S. Ikeda, *J. Catal.*, **1979**, *56*, 119-126.
23. F. Zaera and C.R. French, *J. Am. Chem. Soc.*, **1999**, *121*, 2236-2243.
24. S.T. Oyama, *Catal. Today*, **1992**, *15*, 179-200.
25. L. Volpe, and M. Boudart, *J. Phys. Chem.*, **1986**, *90*, 4874-4877.
26. G. Silversmit, H. Poelman, R. De Gryse, W. Bras, S. Nikitenko, M. Florea, P. Grange and S. Delsarte, *Catal. Today*, **2006**, *118*, 344-352.
27. M. Florea, R. Prada Silvy, P. Grange and S. Delsarte, *Progress in Catal.*, **2004**, *13*, 13-28.
28. L. Nondeck and J. Sedlacek, *J. Catal.*, **1975**, *40*, 34-39.
29. M. A. Centeno and P. Grange, *J. Phys. Chem., B*, **1999**, *103*, 2431-2438.

