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## GRAFTING ALKOXIDES ON THE SURFACE OF OXIDES

### A METHOD FOR PREPARING NEW CATALYSTS AND SUPPORTS

**The preparation of some catalysts and supports by using the grafting technique has been described.** The grafting technique consists in reacting metal alkoxides with the surface OH groups. The most relevant achieved results for both acid and redox catalysts prepared

**T**he grafting technique consists in putting in contact a metal alkoxide with the surface of an oxide rich of hydroxyls. This technique has recently been proposed and developed by different research groups, with encouraging results, for preparing new catalysts and supports [1-13]. A reaction occurs between the hydroxyls of the surface and the alkoxides. Alcohol is released, while, the metal remains strongly anchored to the surface through an oxygen bond. The strength of the formed bonds clearly depends on both the acid-base character of the surface and the properties of the reacting metal alkoxide. The residual organic groups remaining on the surface after the grafting reaction can then be eliminated by steaming the surface or

by burning the residual unreacted alkoxide groups from the surface during calcinations. In this last phase of preparation the surface is reconstructed and the dispersion of the anchored metal oxide is more or less lowered. However, with this procedure we can obtain:

- 1) a well dispersed metal oxide on the surface of another oxide by changing the acid-base or the redox character of the surface. In this case, a submonolayer of the metal alkoxide is deposited by contacting the solid with a dilute solution of the alkoxide;
- 2) a monolayer of the metal alkoxide anchored on the surface of the support by using an excess of alkoxide. In these cases we obtain surfaces that are chemically completely different with

respect to the original support, while, mechanical and structural properties of the support are normally retained. The resistance to thermal treatments is retained, too. This offer also the opportunity to obtain new supports with very interesting properties;

3) a multi-layered coating by repeating two or three times the grafting sequence. As in the previous case we obtain surfaces that are chemically completely different with respect to the original support, but retaining the mechanical and structural properties of the support. Silica coated with a multilayer of  $\text{TiO}_2$ , for example, has a specific surface area of about  $300 \text{ m}^2/\text{g}$  (the surface of silica) that is very high if compared with the specific surface area of pure  $\text{TiO}_2$  obtained by precipitation ( $70\text{-}100 \text{ m}^2/\text{g}$ ), and is more stable to the thermal treatments;

4) the possibility to change the hydrophilic-hydrophobic character of the surface.

Grafting is a very flexible technique and we can operate in such a way to obtain the optimal behaviour of a catalyst. We can change, for example, the alkoxide solvent (polar or apolar), the alkoxide concentration, the volume of the solution and the amount of solid to be grafted. It is then possible to modify opportunely also the chemical structure of the alkoxide to be grafted.

A systematic work has been performed by our research group for studying the preparation of catalysts and supports by using the grafting procedure. At this purpose, two groups of different catalysts have been prepared, characterised and tested in our laboratory. The first group is composed of more or less acid catalysts prepared by grafting alkoxides or modified alkoxides on different supports. The second group are redox catalysts. In particular, silica coated with titania has mainly been prepared and used as support for vanadia based catalysts. At last, selected test reactions have been considered for evaluating the performances of the different prepared catalysts and the most relevant obtained results are reviewed in this paper.

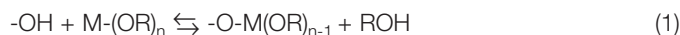
## Methods of preparing catalysts and supports by grafting

Preparation of catalysts and supports by grafting occurs through the following three steps:

- 1) grafting reaction, for anchoring the alkoxide on the surface;
- 2) steaming or burning, for eliminating residual unreacted alkoxide groups from the surface;
- 3) calcination, for stabilising the surface structure.

Grafting reaction is performed by contacting, under stirring, a solid powder of an oxide with a solution containing the alkoxide to be grafted in a given concentration. The solvent can be more or less polar giving place to a different degree of molecular complexity, because,

the apolar solvents favour the association of the alkoxide molecules. Very often the parent alcohol is used as a solvent, even if, this is detrimental for the grafting yields as a consequence of the equilibrium:

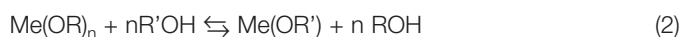


not favoured by the presence of the released alcohol. In these cases, a high initial alkoxide concentration or a continuous removal of the released alcohol are used to promote the reaction.

Grafting reaction can be performed, at room temperature or alternatively at the boiling point of the solvent, according to the reaction kinetics. In some cases an inert and dry gaseous atmosphere is opportunely adopted. The stoichiometry of the reaction can change with the type of used alkoxide, the type of support and the operating conditions. The stoichiometry can also change during the reaction. The choice of the alkoxide concentration to be used can be made on the basis of the hydroxyls density on the solid surface.

Modifications can be introduced in the alkoxides to be grafted such as:

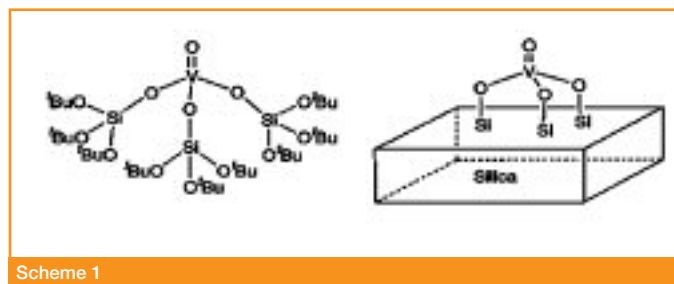
- 1) the exchange of one or more alkoxide groups with other alkoxide ones of particular chemical structure, having for example a long or a branched alkyl chain. The exchange reaction is an equilibrium reaction of the type:



and the equilibrium can be shifted to the right by boiling off the alcohol released;

- 2) introduction of other chemical elements or groups in the alkoxide molecule to modify the electron density of the metal. An example could be the reaction of an alkoxide with sulphuric acid in order to increase the acidity of the metal compound to be anchored;
- 3) synthesis of hetero-metallic alkoxide compounds to be anchored on the surface as in the impressive example reported in Scheme 1 [14].

The second step of the grafting procedure has the scope of elim-



Scheme 1

inating residual unreacted alkoxide groups from the surface. This can be done by steaming at 150-200 °C the catalyst. The following hydrolysis reaction occurs:



Residual alkoxide groups can be removed also by burning them with oxygen at a moderate temperature.

The last step, calcination, is normally performed at temperature greater than 500 °C in the presence of air with the scope of stabilizing the surface of the prepared supports or catalysts. During the calcination the surface could be subjected to a deep modification especially when the interaction bonds between the grafted compound and the surface are weaker than those between the grafted molecules that associate each other to give a compact film or small particles.

In order to prepare a new catalyst or a support we have to consider, first of all, the chemical properties and structure of both the alkoxide to be grafted and the solid surface. It is then important the choice of the alkoxide solvent (polar, apolar, none), the volume of the solution and its concentration, both related to the amount of used solid. Important are also the temperature of the reaction, the contact time and the stirring rate.

## Catalysts and supports characterization

Many techniques are available today for the characterisation of supports and catalysts and some are specifically useful for catalysts and supports prepared by grafting, even if, reaction tests would be considered the starting point for any kind of characterisation. The most commonly used characterisation technique for acid-base catalysts are:

- 1) chemical analysis of the anchored element for determining the grafting yields;
- 2) TGA in the range 500-1,000 °C to estimate the hydroxyls density of both the initial support and the solid obtained after grafting. A rough estimation of grafting stoichiometry can be made by comparing the obtained results;
- 3) potentiometric titration of the solids suspended in water to determine: the Isoelectric Point (IEP), the surface equilibria dissociation constants and a different estimation of surface hydroxyls density;
- 4) TPD (Thermal Programmed Desorption of different organic bases, such as: pyridine and lutidine to evaluate the number and strength of the acid sites of both Lewis and Brönsted type;
- 5) microcalorimetry with pyridine to evaluate the adsorption heats;
- 6) BET for determining specific surface area of both the support

and the catalyst prepared by grafting;

- 7) porosimetric measurements for determining the pore size distribution;
  - 8) XRD for observing the presence of crystalline domains;
  - 9) XPS to evaluate the relative energies of the new formed bonds.
- For the redox catalysts, together with some of the already mentioned characterisation techniques some other more specific are useful as:
- 1) TPR (Temperature Programmed Reduction) with hydrogen to evaluate the reducibility of the prepared catalysts;
  - 2) Pulse Oxygen Chemisorption performed on the reduced catalysts for determining the redox properties of the catalyst;
  - 3) Electron Microscopy SEM equipped with EDX for determining the uniformity of the grafting on the surface;
  - 4) Laser Raman Spectroscopy;
  - 5) FTIR Spectroscopy, FTIR diffuse reflectance (DRIFT) and DR-UV and Visible.

## Test reactions for acid catalysts

Reactions suitable for testing the catalysts prepared by grafting can be distinguished for the catalytic action, that is, acid or redox. For testing acid catalysts we can consider, for example:

### Skeletal isomerization of 1-butene

This reaction occurs in two steps that are:

- a) double bond shifting, requiring weak acid sites;
- b) skeletal isomerization, requiring acid sites of medium strength, not too strong to avoid catalysts deactivation for carbon deposition (Scheme 2).



*Methanol dehydration* to dimethyl ether. A reaction requiring acid sites of medium strength and cooperative effects with vicinal basic sites.

*Cracking and isomerization of hydrocarbons* like n-hexane require



ing very strong acid sites (Scheme 3).

#### Test reactions for redox catalysts

Examples of test reactions for redox catalysts are:

a) Cyclo-octene epoxydation with cumene hydroperoxide, requir-

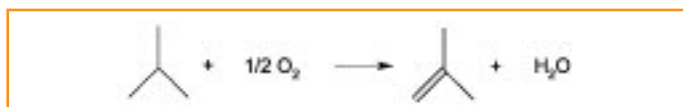


Scheme 4

ing redox sites containing titanium (Scheme 4);

b) Selective Catalytic Reduction (SCR) of  $\text{NO}_x$  with  $\text{NH}_3$  occurring on  $\text{V}_2\text{O}_5$  containing catalysts, preferably supported on  $\text{TiO}_2$ ;

c) Oxidative dehydrogenation (ODH) of propane, butane and isobutane (vanadium based catalysts). Examples of high tempera-



Scheme 5

ture redox reactions (Scheme 5);

d) Oxidative dehydrogenation (ODH) of methanol or ethanol to respectively formaldehyde and acetaldehyde. Examples of low temperature redox reactions.

The most relevant results obtained with the prepared catalysts for the mentioned reactions will be summarised in this paper.

## Most relevant obtained results

### Acid-base catalysts

System  $\text{ZrO}_2/\gamma\text{-Al}_2\text{O}_3$

Zirconium alkoxide is grafted on  $\gamma\text{-Al}_2\text{O}_3$  with relatively low yields for the equilibrium with the parent alcohol [8].

The IEP increases with the amount of

grafted  $\text{ZrO}_2$  and the obtained solids show more basic properties than the original support. The hydroxyls density increases with the amount of grafted  $\text{ZrO}_2$  suggesting that the grafting reaction stoichiometry involves one Al-OH group on the surface and one molecule of alkoxide. In the presence of zirconium oxide on the surface, there is an increase of the concentration of vicinal acid and basic sites, as a consequence the  $\text{ZrO}_2/\text{Al}_2\text{O}_3$  catalysts have shown a considerable increase of activity in the reaction of methanol dehydration as it can be appreciated in Tab. 1.

System  $\text{SiO}_2/\gamma\text{-Al}_2\text{O}_3$

Silicated alumina is a well known catalyst for the skeletal isomerization of 1-butene to isobutene [6, 15]. We have prepared different catalysts by changing the amount of grafted silica, as it can be seen in Tab. 2 [6]. The Isoelectric Point moderately decreases with the amount of grafted silica and the acidity increases. Nevertheless, we obtained strong differences in the catalytic performances. The best results have been obtained with AS4 catalyst prepared by contacting  $\gamma$ -alumina directly with silicon tetra-ethoxide without using any solvent. This catalyst shows high activity, high selectivity and very slow catalyst deactivation. It is interesting to observe that ASM catalyst, prepared by repeating two times the grafting procedure has shown slightly lower activity than AS4. The

Tab. 1 - Activity of grafted zirconia on alumina

Grafted Zr amount mmols/g	Reaction rate mmols/(g h)
0	4.0
0.01	5.2
0.02	6.3
0.08	8.0
0.14	4.0

Tab. 2- Catalyst prepared by grafting silicon alkoxide on  $\gamma$ -alumina [6]

Catalyst-Solvent	Grafted silicon (mmol/g)	ZPC	Surface OH (mmol/g) potentiometric	pKa <sub>1</sub>	pKa <sub>2</sub>	Surface OH by TGA (mmol/g)
$\gamma$ -alumina	-	7.5	1.05	5.7	9.3	1.05
$\text{SiO}_2\text{-Al}_2\text{O}_3$	-	4.5	1.08	2.6	6.2	-
$\text{SiO}_2$	-	2.2	2.50	0.6	3.5	2.20
AS1-Ethanol	0.07	7.4	1.01	5.3	9.1	-
AS2-Ethanol	0.14	7.1	0.95	4.9	8.8	1.50
AS3-Ethanol	0.28	6.6	0.82	4.1	8.1	-
AS4 (no solvent)	0.50	5.6	0.97	3.4	7.6	1.40
ASM-Two steps grafting as AS4	0.71	5.2	0.91	3.2	7.5	-

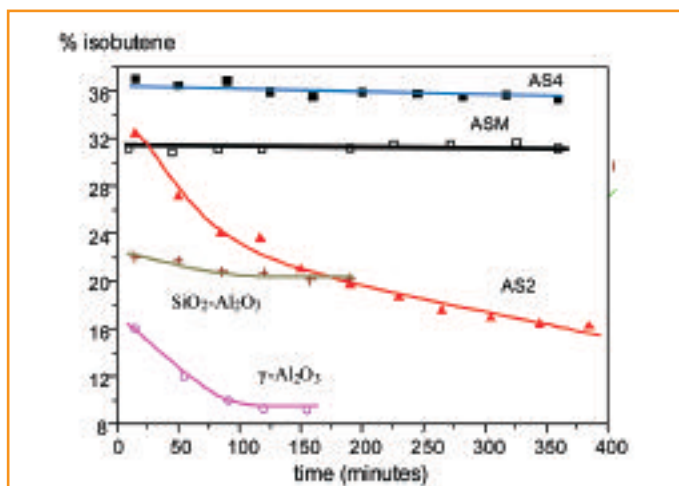


Fig. 1 - Comparison of the activities of different catalysts in the skeletal isomerization of 1-butene to isobutene 1-butene=5mL/min., N2=50 mL/min., T=430 °C, Catalyst amount=2 g

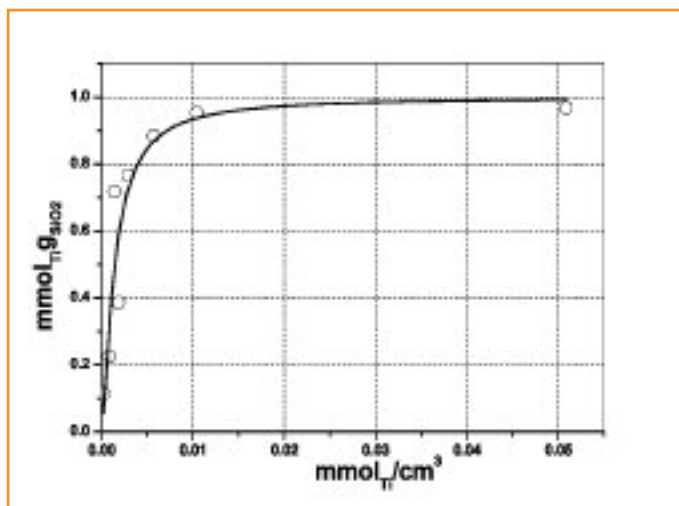


Fig. 2 - Adsorption isotherm of titanium isopropoxide dissolved in dioxane on silica Grace S432 ( $S_{BET}=282 \text{ m}^2/\text{g}$ ; hydroxyls density =  $0.92 \text{ mmolOH/g}$ )

explanation of this behaviour supported by XPS analyses and other characterization techniques is that silica does not cover completely alumina surface giving place to coating islands. By repeating the grafting step silica islands grow only in height and consequently the activity poorly changes. We suggest that the active sites are located at the border line of the silica islands where the opposite charges of aluminium atoms (positive) and of the terminal oxygen of the silica clusters (negative) can cooperate in promoting the reaction. The best results obtained with the catalysts prepared in the absence of ethanol solvent can be explained by considering the possible competition of ethanol and alkoxide molecule in the adsorption on the Lewis acid sites of alumina. As a consequence, in the presence of ethanol these sites responsible

for catalyst deactivation are not completely neutralized. In Fig. 1, the activities obtained for silicated alumina AS4 compared with the activity of the corresponding alumina support and some other prepared catalysts are reported.

### System $\text{TiO}_2/\text{SiO}_2$ a new catalyst and a new support

Titanium alkoxide can be grafted in a single step on silica, in different amounts, until to reach the monolayer, when the scope is that of preparing a well dispersed catalyst, while, for preparing a support a multistep grafting procedure must be adopted in which the grafting procedure is repeated two or three times [7, 16-24].

The catalysts prepared by grafting sub-monolayers amounts of titanium alkoxides are active in promoting two different reactions, that are: cyclo-octene epoxidation and transesterification of triglycerides with methanol for preparing biodiesel. The activity in both cases seems to be strictly related to the occurrence of Lewis acid sites of medium strength increasing with the amount of grafted titania. It is possible to evaluate exactly the amount of titanium alkoxide that can be grafted by previously determining a Langmuir adsorption isotherm like the one reported in Fig. 2 [16, 17].

The amount of  $\text{TiO}_2$  corresponding to the anchored alkoxide monolayer is about 8% by weight ( $2.2 \text{ Ti atoms}/\text{nm}^2$ ) in agreement with the Langmuir relation  $K=(1/C^{eq})/(\Gamma^\infty/\Gamma^\infty-\Gamma^{eq})$  where  $K=710, 89 \text{ [L/mol]}$  e  $\Gamma^\infty = 1.02 \text{ mmol}_{\text{Ti}}/\text{g}_{\text{SiO}_2}$  [16].

It is interesting to observe that by using these catalysts in both the already mentioned reactions, i.e. the epoxidation of cyclo-octene with cumene hydroperoxide and the transesterification of triglycerides with methanol the activity increases with the amount of grafted titania until reaching a monolayer of coating and then rapidly decreases, as it can be seen in the plots of Fig. 3 and 4, while, in Fig. 5 it can be seen the evolution of the Lewis acid sites

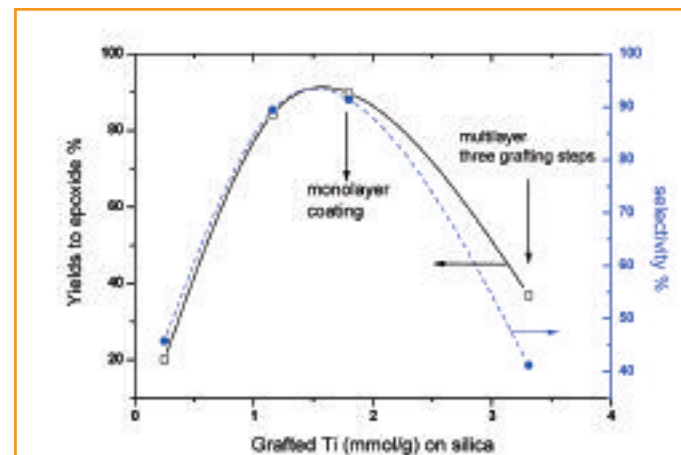


Fig. 3 - Cyclooctene epoxidation by cumene hydroperoxide in the presence of  $\text{TiO}_2/\text{SiO}_2$  [18]

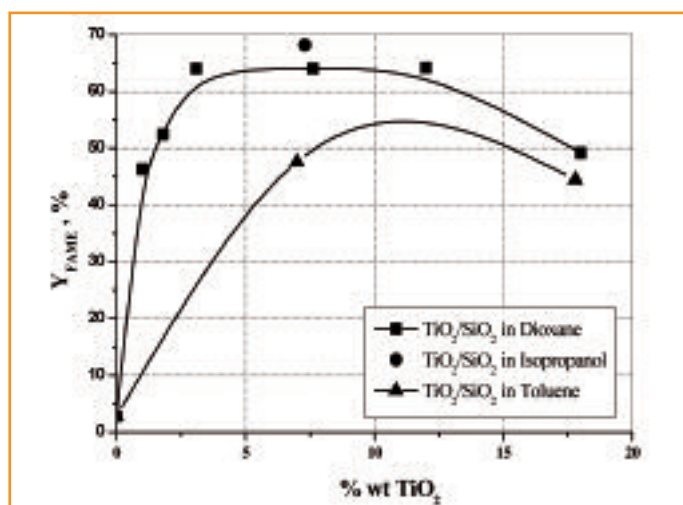


Fig. 4 - Catalytic activity of the  $\text{TiO}_2/\text{SiO}_2$  catalysts in the transesterification of a refined oils with methanol [19]

density as a function of the amount of grafted titania [18]. The maximum of Lewis acid site density corresponds to about the monolayer of alkoxide grafted, while, 17% of grafted  $\text{TiO}_2$  has been obtained by repeating three times the grafting procedure. At last, it is important to point out that pure  $\text{TiO}_2$  obtained by precipitation is not active in both the mentioned reactions.

By repeating grafting steps, after three grafting steps silica resulted completely covered with more than a monolayer, as it can be demonstrated by DRIFT spectra where silanols absorption band completely disappears as a consequence of titanium alkoxide three steps grafting [21]. As before mentioned, this system has mainly been studied as a possible support for vanadium based catalysts. Vanadyl tri-isopropoxide can easily be grafted on the surface of this support. By using an apolar solvent the reaction is almost quantitative, while, less favoured is the reaction in the presence of the parent alcohol isopropanol for the negative effect of the solvent on the reaction equilibrium. However, an advantage in using isopropanol as solvent is that vanadium dispersion can further be increased. In Tab. 3 the properties of different  $\text{TiO}_2\text{-SiO}_2$  prepared supports are summarised together with the solids obtained during multistep titanium alkoxide grafting on silica [20].

### Redox catalysts

#### System $\text{V}_2\text{O}_5$ on $\text{TiO}_2/\text{SiO}_2$ support

Vanadyl tri-isopropoxide grafted on silica coated with titanium dioxide gives place to a well dispersed and stable catalyst [20, 22-31]. When vanadyl alkoxide is grafted directly on a silica support the mobility of the grafted vanadium oxide on the surface is relatively high and a less dispersed catalysts are obtained as a consequence. The most dispersed catalysts are the ones obtained by using  $\text{TiO}_2/\text{SiO}_2$  supports

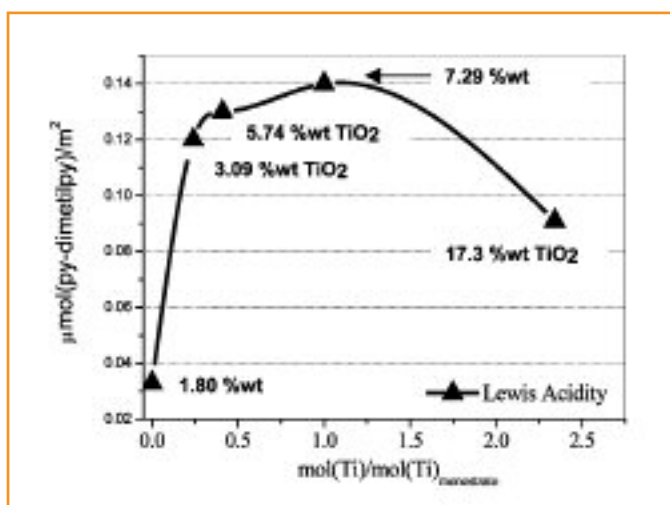


Fig. 5 - Lewis acid sites densities as a function of titanium oxide loaded on silica support [20]

prepared by grafting titanium alkoxide on silica and repeating three time the operation. In Fig. 6 are reported for comparison the adsorption isotherms respectively obtained by contacting a solution of vanadyl tri-isopropoxide dissolved in dioxane with respectively silica,  $\text{TiO}_2/\text{SiO}_2$  obtained by coating in one step silica with a monolayer of titanium alkoxide,  $\text{TiO}_2/\text{SiO}_2$  obtained by repeating three times the grafting procedure, respectively [16]. The properties of the different mentioned supports are summarised in Tab. 3.

Vanadium based catalysts prepared by grafting have shown better performances for both activities and selectivities than the impregnated catalysts containing the same amount of vanadium pentoxide in different reactions. In particular we have obtained good results in the Selective Catalytic Reduction (SCR) of  $\text{NO}_x$  with  $\text{NH}_3$  [22] in the Oxidative dehydrogenation (ODH) of propane [23, 24], butane [16, 27] and isobutene [25, 26] and in the Oxidative dehy-

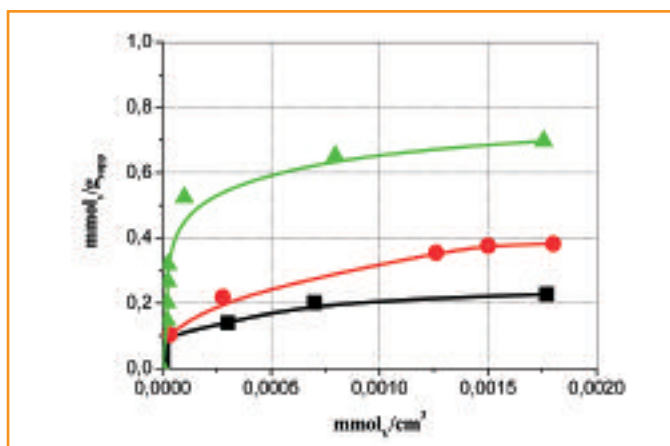


Fig. 6 - Adsorption isotherms obtained by contacting vanadyl isopropoxide with silica,  $\text{TiO}_2/\text{SiO}_2$  supports prepared by grafting in one step (TS1) and in three steps (TS3) titanium alkoxide on silica

**Tab. 3 - Catalyst prepared by grafting silicon alkoxide on  $\gamma$ -alumina [6]**

Sample	Acronym	Grafting atep	TiO <sub>2</sub> % by weight	Metal Initial mount mmol/g	S <sub>SA</sub> m <sup>2</sup> /g	Pore Volume cm <sup>3</sup> /g	OH density mmols/g
SiO <sub>2</sub>	S	0	-	-	282	1.02	0.92
TiO <sub>2</sub> -SiO <sub>2</sub>	TS1 <sub>1</sub>	1	7.0	1.37		-	
TiO <sub>2</sub> -SiO <sub>2</sub>	TS2 <sub>1</sub>	2	13.7	1.37		-	
TiO <sub>2</sub> -SiO <sub>2</sub>	TSM <sub>1</sub>	3	17.8	1.37	289	-	
TiO <sub>2</sub> -SiO <sub>2</sub>	TS1	1	5.9	0.95	237	0.23	0.71
TiO <sub>2</sub> -SiO <sub>2</sub>	TS2	2	9.7	0.95	267	0.26	0.79
TiO <sub>2</sub> -SiO <sub>2</sub>	TSM	3	11.3	0.95	299	0.27	0.82
TiO <sub>2</sub> -SiO <sub>2</sub>	T <sub>sm</sub> S	1	2.3	0.30	245	0.81	-

drogenation (ODH) of methanol [30, 31] or ethanol [29, 31] to respectively formaldehyde and acetaldehyde.

In Fig. 7, it is possible to appreciate the difference between the performance of a catalyst prepared by grafting and another prepared by impregnation in the SCR of NO<sub>x</sub> with NH<sub>3</sub>. As it can be seen the catalyst prepared by grafting is active at lower temperatures and is much more selective.

In the case of the ODH of alkanes to alkenes the activity is related to the amount of grafted vanadium until the monolayer coating is reached, then, the activity remains unchanged (see Fig. 8) [16]. On the contrary the selectivity is greater for the lower amounts of grafted vanadium suggesting that isolated vanadium sites are the most selective ones (see Fig. 9) [16].

Similar results have been obtained also for the ODH of propane and isobutane, that is, (i) catalysts prepared by grafting have performances better than catalysts prepared by impregnation; (ii) activity increase with the amount of loaded vanadium oxide until a grafted amount corresponding to about a monolayer is reached; (iii) selectivity is positively affected by vanadium oxide dispersion.

The ODH of hydrocarbons follows a classic Mars and Van Krevelen

reaction mechanism involving the surface oxygen that actively intervenes in the dehydrogenation reaction and is then restored by reaction of the surface with gaseous oxygen fed to the reactor. This last reaction occurs at temperatures greater than 320 °C.

The same mechanism cannot be assumed for the ODH of methanol or ethanol occurring in the range 150-250 °C. In these cases the dehydrogenation of an adsorbed alcohol molecule occurs as a first step with the formation of an hydride specie that is successively oxidized by molecular oxygen so closing the catalytic cycle. However, there is a great difference in the mechanism of reaction for the ODH of methanol with respect to ethanol. As a matter of fact, while ethanol gives place directly to acetaldehyde as the main reaction product (see Fig. 10) [29], methanol forms before all dimethoxy methane that is successively hydrolysed to formaldehyde (see Fig. 11) [30].

All the kinetic runs have been made on the best catalyst founded after a screening test. This catalyst contained about 5% of V<sub>2</sub>O<sub>5</sub> grafted on TiO<sub>2</sub>/SiO<sub>2</sub> [30].

The activities and selectivities of the vanadium based catalysts prepared by grafting resulted largely competitive with the catalysts usually employed for promoting the ODH of both ethanol and methanol

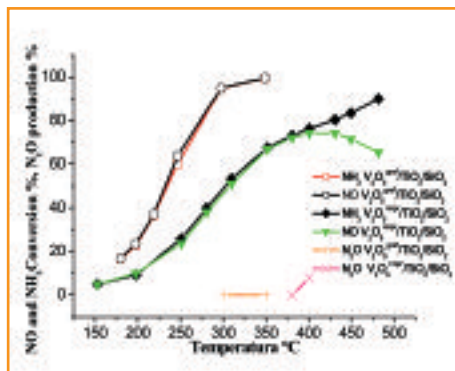


Fig. 7 - NO and NH<sub>3</sub> conversion values vs. temperature in NO SCR reaction for impr/TiO<sub>2</sub>/SiO<sub>2</sub> and Vgraf /TiO<sub>2</sub>/SiO<sub>2</sub> catalysts [22]

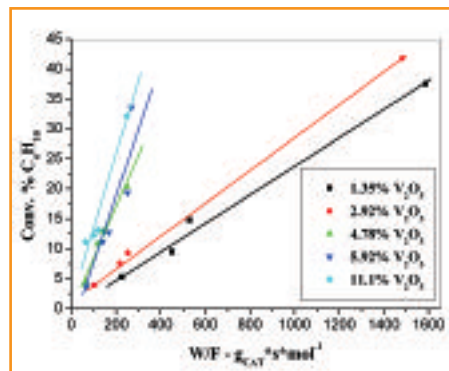


Fig. 8 - Activities shown by catalyst containing increasing amount of vanadium as a function of contact times. Runs performed at T=500 °C

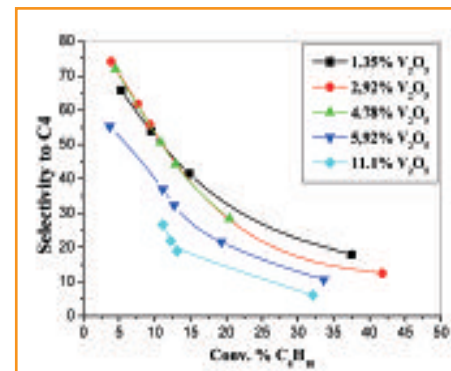


Fig. 9 - Selectivity to butenes as a function of butane conversion on the same catalysts of Fig. 8

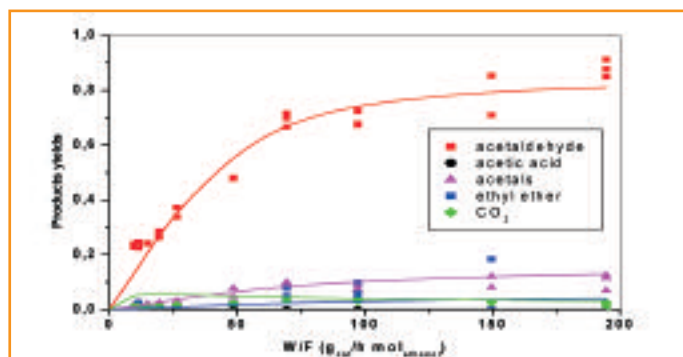


Fig. 10 - Acetaldehyde yields and by-products distribution as a function of residence time for a feed with variable molar ratio ethanol/oxygen, at temperature of 160 °C [29]

in particular the reaction temperatures are considerably lower.

## Conclusions

We have shown that the grafting procedure allows: (i) to prepare new supports having optimal chemical and textural properties; (ii) to prepare well dispersed catalysts by adopting opportune experimental conditions; (iii) to create the most favourable environ-

ment to the reaction in a simple and tailored way by modifying opportunely the precursor; (iv) to prepare more simply and in a more controlled way bifunctional or multi-functional catalysts.

The properties of the surfaces obtained by coating an oxide with another oxide are not foreseeable giving place to unsuspected performances.

Very encouraging results have been obtained in several reactions of industrial interest and new scientific insights in catalysis have been individuated.

**Acknowledgements:** Thanks are due to MIUR (PRIN- 2005038244\_001) for the

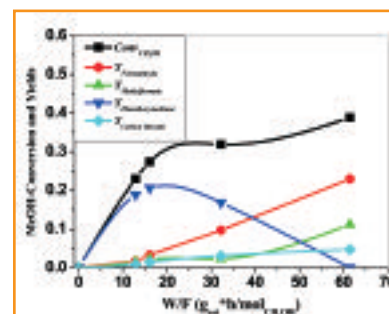


Fig.11- Formaldehyde yields and by-products distribution as a function of residence time for a feed with variable molar ratio ethanol/oxygen, at temperature of 160 °C [30]

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