ELSEVIER
Journal of Alloys and Compounds 408–412 (2006) 1108–1112
Journal of ALLOYS AND COMPOUNDS
www.elsevier.com/locate/jallcom

High-temperature stability of V_2O_5/TiO_2-WO_3-SiO_2 SCR catalysts modified with rare-earths

Marzia Casanova[a], Eliana Rocchini[a], Alessandro Trovarelli[a,*], Karl Schermanz[b], Irene Begsteiger[c]

[a] Dipartimento di Scienze e Tecnologie Chimiche, Università di Udine, 33100 Udine, Italy
[b] Department Chemistry R&D, Treibacher Industrie AG, A-9330 Althofen, Austria
[c] Porzellanfabrik Frauenthal GmbH, Catalyst Division, A-8523 Frauenthal, Austria

Received 30 July 2004; received in revised form 1 December 2004; accepted 15 December 2004

Abstract

The introduction of rare earth elements (RE = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Er and Yb) into a V_2O_5/TiO_2-WO_3-SiO_2 system leads to a catalyst which shows a significant improvement in thermal stability by hindering transformation of TiO_2 (anatase) into TiO_2 (rutile). As a consequence, these novel compounds show high removal efficiencies for NO_x even after aging at 1023 K, when the state of the art SCR catalysts loose activity and selectivity. This allows potential application of these catalysts in the removal of NO_x from diesel or lean-burn automotive engines in addition to stationary applications at high temperatures.

Keywords: SCR; deNO_x; Rare-earths; Vanadates; $TbVO_4$; $ErVO_4$

---

1. Introduction

Catalytic reduction of nitrogen oxide emissions represents one of the greatest challenges in environmental protection. Several approaches have been followed to reduce NO_x emissions for both mobile and stationary applications. Among these methods, the most widely employed technology for stationary applications is SCR [1,2]. It was introduced in the late 1970s for the control of NO_x emissions in stack gases for thermal power plants and other industrial facilities. SCR plants are currently operating in USA, Japan, Europe and Far East for a total capacity of the order of 180,000 MW. The SCR is based on the reduction of NO_x with NH_3 into water and nitrogen. Several types of catalysts have been tested which are active under different environments and conditions. The technology is operated commercially over metal-oxide SCR catalysts made of a homogeneous mixture of TiO_2 (80–90 wt.%), WO_3 (6–10 wt.%) and V_2O_5 (1–3 wt.%), which may contain some silica (0–10 wt.%) in the formulation. Titania in the form of anatase is used as a high surface area carrier to support the active component V_2O_5, which is responsible for the activity of catalysts for NO_x reduction. WO_3 (sometime also MoO_3) is employed as a chemical/structural promoter to enlarge the temperature window of application. Silica is often used to improve the catalyst strength.

In spite of the fact that SCR technology is used worldwide, there are still opportunities to improve catalytic performance especially in relation to the following issues: (i) to improve catalyst design in order to obtain at the same time a higher activity in NO_x removal and a lower activity in SO_2 oxidation; (ii) to limit ammonia slip and to improve the behaviour of the system under dynamic conditions; (iii) to avoid deactivation which occurs at present catalysts when treated at high temperatures. It is in fact known that the activity of a

---

[*] Corresponding author. Tel.: +39 0432558855; fax: +39 0432558803.
E-mail addresses: trovarelli@uniud.it (A. Trovarelli), karl.schermanz@treibacher.com (K. Schermanz), irene.begsteiger@frauenthal.net (I. Begsteiger).

0925-8388/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2004.12.128

$V_2O_5/TiO_2/SiO_2$ catalyst increases markedly with a rise in calcinations temperatures up to 873–923 K and then rapidly decreases [3]. This is mainly due to phase transformation of TiO_2 (anatase) into TiO_2 (rutile) and consequent loss of BET surface area with changes in the chemical state of surface vanadium species. Solving these issues will pave the road for use of SCR also in mobile applications; the process using urea as reducing agent is in fact investigated intensively for use in diesel or lean-burn engines [3]. The challenges for automotive applications are high SCR activity and improved thermal stability of vanadia-tungsta-titania catalysts in the temperature range 473–1000 K. Such extreme operating temperatures (compared to "classic" SCR applications where temperature range of the order of 573–773 K are often encountered) are certainly of short duration and may occur at very high power output (low rpm and high load).

The present investigation is aimed to address the problem related to stability at high temperatures where state of the art V_2O_5/TiO_2-WO_3 (or V_2O_5/TiO_2-WO_3-SiO_2) catalysts still suffer strong deactivation. As a result, we have found that promotion of V_2O_5/TiO_2-WO_3-SiO_2 and V_2O_5/TiO_2-WO_3 catalysts with rare earth (RE) strongly improves activity even after aging at temperatures of 1023 K for several hours, when the activity of state of the art catalysts under comparable conditions drops to low values.

2. Experimental

2.1. Materials

The catalysts employed in this study were obtained starting from a commercial support material of composition 81%TiO_2-9%WO_3-10%SiO_2 (WTS). To this support, a combination of V and RE elements were added to provide a NO_x reduction catalysts represented by the formula $REVO_4$/WTS with RE = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Er and Yb. The content of the active phase was in the range 0–5 wt.% RE element, 0–2.1 wt.% vanadium and 0–2.7 wt.% oxygen, corresponding to a $REVO_4$ loading in the range 0–8.5 wt.% Preparation was carried out according to [4]. Briefly, a slurry containing the support and an aliquot of the complex $(NH_4)_2[VO(C_2O_4)_2]$ and rare-earth acetate is brought to dryness under continuous stirring at 353–373 K. The solid is then dried at 393 K overnight and calcined at 923 K for 2 h, pressed into pellet, crushed and sieved in the range 355–425 μm. This will be referred as fresh sample. Aging of samples was carried out in a tubular furnace at a temperature of 1023 K for 10 h under air. State of the art catalyst based on 3%V_2O_5/WTS was prepared according to [5]. The specific surface areas of oxide powders were measured by the BET method using N_2 adsorption/desorption at 77 K with a Sorptomatic 1990 instrument (Carlo Erba).

X-ray diffraction patterns were recorded with a Philips X'Pert Pro powder diffractometer equipped with an X'Celerator detector using Cu kα radiation.

Table 1
Reaction conditions and gas composition

Catalyst weight	100 mg
Particle size	350–425 μm
Total flow	0.3 l/min
Temperature	523–723 K
NO	200 ppm
NH_3	240 ppm
O_2	20000 ppm
H_2O	10%
N_2	Balance

2.2. Catalytic activity

Activity and selectivity of the catalysts were measured in a powder microreactor under stationary conditions in the temperature range 523–723 K; each temperature was maintained for at least 3 h after attainment of steady state. Reaction conditions and gas composition are reported in Table 1. A high space velocity of 150,000–180,000 h^{-1} was used in order to have NO conversion in the range 10–80% for the majority of samples investigated. Mass flow controllers were used to measure and control single gaseous streams, while an injection pump was used to feed water. The feed stream was preheated and premixed and ammonia was added to the gaseous mixture immediately before entering the reactor to avoid side reactions. A tubular quartz reactor was employed inserted in a furnace. Temperature was controlled by a thermocouple inserted in the catalyst bed. The gas exiting the reactor was scrubbed with an aqueous solution of phosphoric acid to trap unconverted ammonia and then cooled to condense water vapor. All gas lines were heated electrically to ca. 423 K. The inlet and outlet gases were analyzed by an FT-IR spectrometer (Biorad FTS-40) equipped with a gas cell.

3. Results and discussion

Table 2 shows NO_x removal efficiency in the temperature range 523–723 K for catalysts containing 0–2.1 wt.% V and 0–5.0 wt.% RE on WTS support. For comparison, the activity of the state of the art reference catalyst based on 3 wt.% V_2O_5/WTS is also reported. The NO_x reduction activity of all the catalysts examined in the present study increased with increasing reaction temperature up to ca. 573–623 K where a maximum NO_x reduction activity was observed. At this point, the activity began to decrease due to ammonia oxidation reaction to NO_x, which is prevailing over its reaction to N_2. A strong effect is also shown with calcination temperatures. Particularly for the state of the art catalyst calcined at temperature above 923 K, strong deactivation is observed with conversion dropping at values between 5 and 20%. A similar strong deactivation is observed also with La-containing catalyst. All the other catalysts can be broadly divided in two groups: group A catalysts (comprising Y, Ce, Pr and Nd) which suffer a slight deactivation after ageing and group B catalysts (comprising Sm, Gd, Tb, Dy, Er; Yb is in the middle

Table 2
Activity of fresh and aged catalysts containing RE and V on TiO_2:WO_3:SiO_2 (81:9:10) matrix

Example no.				NO conversion (%)					
	RE	RE (%)	V (%)	Fresh (523 K)	Aged (523 K)	Fresh (593 K)	Aged (593 K)	Fresh (723 K)	Aged (723 K)
1	Y	3.7	2.1	49	25	70	49	55	29
2	La	4.6	1.7	31	0	51	0	38	3
3	Ce	4.6	1.7	67	20	86	31	46	21
4	Pr	4.6	1.7	51	25	74	37	35	16
5	Nd	4.7	1.7	40	20	62	30	43	11
6	Sm	4.8	1.6	40	55	64	61	43	29
7	Gd	4.9	1.6	50	48	61	68	47	60
8	Tb	1.4	0.5	22	68	53	90	50	65
9	Tb	2.8	0.9	40	63	68	81	51	45
10	Tb	4.9	1.6	32	52	49	80	40	49
11	Dy	4.9	1.5	48	52	64	75	50	48
12	Er	1.5	0.4	24	46	52	71	49	47
13	Er	5	1.5	40	47	65	80	54	53
14	Yb	5.1	1.5	45	47	72	49	48	25
(Reference)	–	–	1.7	85	5	91	17	17	7

of the two goups) in which deactivation has no effect or even causes an improvement of overall efficiency. The best performances are observed with Er and Tb containing catalysts where a substantial increase of conversion is observed after ageing in all temperature range examined. The overall picture detailing activity drop/improvement after aging is shown in Fig. 1, which also highlights a dependence of activity on position of the element in the periodic table.

Table 2 shows also the NO_x removal efficiency against RE and V loading. The loading amount was controlled by varying the amount of ammonium vanadate and rare earth acetate solutions in the impregnation. As listed in Table 2 (examples 8–10, 12–13), loading does not affect strongly activity after aging. For all the samples investigated, an unusual promotion of activity is observed after aging at 1023 K. Catalysts in the fresh state are less active at the lowest loading (especially at the lowest temperatures) consistently with the presence of a lower amount of active phase containing vanadium. Maximum of activity is observed always in the range 573–653 K.

Surface area analysis is reported in Tables 3 and 4. With all the catalysts examined, ageing procedure causes a drop in surface area which is proportional to the amount of RE and V deposited. This would suggest that aging induce an interaction between the active phase containing rare-earths and the support. However, by comparing the data of Tables 3 and 4, it is clearly evidenced that the presence of rare-earths lowers surface area drop caused by addition of vanadium to the support.

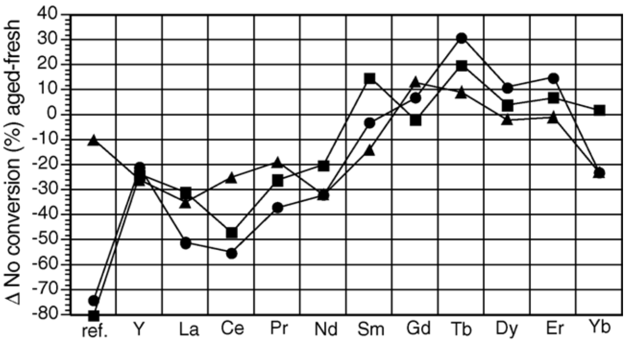

Fig. 1. Activity drop/increase after aging (%) for various elements at reaction temperatures of 523 K (■); 623 K (●); and 723 K (▲).

Table 3
Surface area of fresh and aged catalysts containing RE and V on TiO_2:WO_3:SiO_2 (81:9:10) matrix

Example no.	RE	RE (%)	V (%)	Surface area	
				Fresh	Aged
1	Y	3.7	2.1	62	28
2	La	4.6	1.7	68	22
3	Ce	4.6	1.7	62	17
4	Pr	4.6	1.7	60	28
5	Nd	4.7	1.7	66	24
6	Sm	4.8	1.6	64	28
7	Gd	4.9	1.6	64	28
8	Tb	1.4	0.5	80	56
9	Tb	2.8	0.9	76	45
10	Tb	4.9	1.6	67	35
11	Dy	4.9	1.5	68	19
12	Er	1.5	0.4	70	38
13	Er	5.0	1.5	68	33
14	Yb	5.1	1.5	70	11

Table 4
Surface area of fresh and aged V containing catalysts on TiO_2:WO_3:SiO_2 (81:9:10) and TiO_2/WO_3 (90:10) matrix

Sample	Surface area	
	Fresh	Aged
V_2O_5 on Ti/W/Si (81:9:10)	65	8
Ti/W/Si (81:9:10)	88	70
V_2O_5 on Ti/W (90:10)	24	6
Ti/W (90:10)	59	29

X-ray diffraction analysis of the support showed that TiO_2 (anatase) is the only phase detected after aging at 1023 K under air for 10 h, indicating that transformation to rutile does not occur. A comparison with the diffraction profile of a support not containing Si, of composition 90% TiO_2–10%WO_3 (WT), indicates that the presence of silica has no effect on X-ray diffraction profile under these conditions. Aging under more severe conditions (1123 K, 10 h) induces a modification of the diffraction profile. Segregation of crystalline WO_3 is observed in both WTS and WT while for supports not containing silica, TiO_2 in the form of rutile is clearly evidenced. The introduction of SiO_2 strongly stabilizes anatase against its transformation to rutile. Adding of vanadium modifies this picture by accelerating segregation of WO_3-containing phases and transformation of anatase to rutile. Peaks characteristic of V_2O_5 are not seen in both supports indicating that V_2O_5 is either amorphous when supported on TiO_2 or that the particle size is below the detection limits of X-ray technique. This is in agreement with the fact that crystalline V_2O_5 on TiO_2 is observed only at higher loading [6]. In the presence of V_2O_5, the anatase to rutile phase transformation is initiated at lower temperature, as a consequence for WT support after calcinations at 1023 K for 10 h, approximately 50% of TiO_2 is in the form of rutile. The presence of V_2O_5 also accelerates segregation of crystalline WO_3 phase, in accordance with previous observations [6,7]. A more accurate analysis of X-ray diffraction profiles indicate that modification of WO_3 by introduction of foreign cations into the oxide lattice could be responsible of small differences in the peak positions. Formation of mixed $Ti_xW_yO_3$ or $M_xW_yO_3$ (with M being an impurity present in the support) could be a possibility although no evidence can be found from existing XRD patterns. The presence of residual Ca from commercial additives was responsible of formation of $CaWO_4$ in structured catalysts of similar composition treated at comparable temperatures [7]. Reaction of supported vanadia with TiO_2 to yield $V_xTi_{1-x}O_2$ in which vanadium is incorporated into the titania support in the form of rutile has been previously observed. In our case, lattice parameters of TiO_2 (rutile) stabilized in the presence and in the absence of vanadia are coincident, indicating that formation of TiVO solid solution does not occur. SiO_2-containing support shows a similar behaviour although the transformation of TiO_2 (anatase) to rutile is slower, in agreement with what observed in the absence of V_2O_5.

The diffraction profiles of materials after introduction of rare earth elements revealed the presence of weak signals due to formation of rare earth vanadates. These can be seen from the majority of RE elements investigated. Calcinations at 1023 K clearly evidence formation of crystalline $REVO_4$ for all elements with the exception of La. Interestingly, the presence of lanthanides seems to positively influence the degree of rutilization of the support and the process of segregation/formation of WO_3. For silica containing support rutile is seen only at calcinations temperatures above 1023 K and the appearance of crystalline WO_3 is also retarded (this is true except for Tb, Ce and Pr-containing catalysts where the formation of WO_3 is not affected if compared with V_2O_5-only samples). In the absence of silica, segregation of WO_3 and transformation to rutile occur already at temperature of 1023 K, although the presence of RE slows down their formation. Fig. 2 shows the effect of aging treatment at temperatures in the range 923–1123 K for Tb-V-O/WTS.

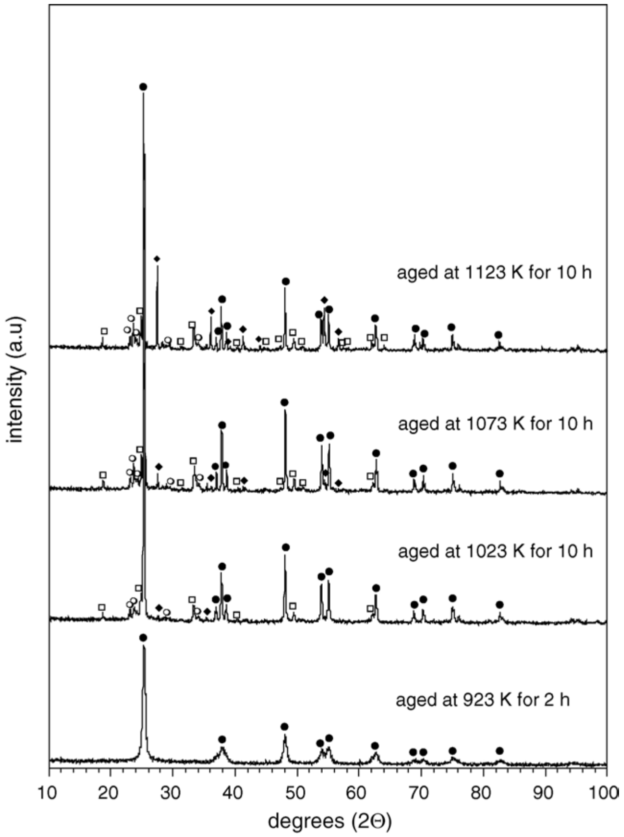

Fig. 2. X-ray diffraction profiles of Tb-V-O/WTS aged at different temperatures; rutile (♦); anatase (●); WO_3 (○); $TbVO_4$ (☐).

4. Summary

In summary, a new class of RE-based SCR catalysts for potential application in mobile systems has been developed. They show: (i) improved surface area stability after aging at temperatures up to 1023 K; (ii) lower degree of transformation of TiO_2 (anatase) into TiO_2 (rutile) if compared to traditional SCR catalysts; (iii) a higher $deNO_x$ activity after aging which might be related to the higher thermal stability but also to beneficial interaction between surface vanadium and rare earth elements.

References

[1] V.I. Parvulescu, P. Grange, B. Delmon, Catal. Today 46 (1998) 233.
[2] P. Forzatti, Appl. Catal. A: General 222 (2001) 221.
[3] G. Madia, M. Elsener, M. Koebel, F. Raimondi, A. Woukan, Appl. Catal. B: Environ. 39 (2002) 181.

[4] I. Begsteiger, E. Rocchini, K. Schermanz, A. Trovarelli, Applied for Austrian Patent under AZ 1831/2003.
[5] A. Schafer-Sindlinger, A. Burkardt, H. Van der Tillaart, T. Kreuzer, E. Lox, W. Weisweller, Eu Patent Application EP 1 145762 A1.
[6] R.Y. Saleh, I.E. Wachs, S.S. Chan, C.C. Chersich, J. Catal. 98 (1986) 102.
[7] I. Nova, L. dall'Acqua, L. Lietti, E. Giamello, P. Forzatti, Appl. Catal. B: Environ. 35 (2001) 31.