

## 이소부탄의 산화탈수소반응에 대한 여러 담지체에 따른 V-Sb 산화물 촉매 성능 효과

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### Effect of Various Supports on the Catalytic Performance of V-Sb Oxides in the Oxidative Dehydrogenation of Isobutane

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**요약.** 이소부탄의 산화탈수소반응(ODH)에 대한  $V_{0.9}Sb_{0.1}O_x$  촉매계의 5가지 담지체의 촉진효과를 조사하였다. 사용된 5가지 담지체는 감마-알루미나, 알파-알루미나, 실리카-알루미나, 실리카겔, 마그네슘 산화물이다. 촉매는 사용된 담지체에 따라 그 효과가 다르게 나타났다:  $\gamma\text{-Al}_2\text{O}_3 > \alpha\text{-Al}_2\text{O}_3 > \text{Si-Al-O} > \text{SiO}_2 \approx \text{MgO} \gg \text{unsupported}$ . V-Sb-O 비율은 별로 촉매 활성과 선택성에 영향을 미치지 않았다. 촉매 성분들이 담지체에 골고루 잘 분포된 이유로 인해 감마-알루미나에 담지된  $V_{0.9}Sb_{0.1}O_x$  촉매계가 성능이 제일 뛰어났다.

**주제어:** 바나듐-안티몬 산화물 촉매, 담지체, 산화탈수소반응, 이소부탄, 이소부텐

**ABSTRACT.**  $V_{0.9}Sb_{0.1}O_x$  systems, bulk and deposited on different supports (five types of  $\gamma$ -aluminas,  $\alpha$ -alumina, silica-alumina, silica gel, magnesium oxide), have been tested in the oxidative dehydrogenation (ODH) of iso-butane. Catalytic performance of V-Sb oxides has shown to be highly dependent on the support and the nature of the support decreasing in a series:  $\gamma\text{-Al}_2\text{O}_3 > \alpha\text{-Al}_2\text{O}_3 > \text{Si-Al-O} > \text{SiO}_2 \approx \text{MgO} \gg \text{unsupported}$ . Variation of the V-Sb-O-loading in the studied range of coverage (0.5-2 theoretical monolayer) only slightly influences the catalysts' activity and selectivity. The best catalytic performance of  $\gamma$ -alumina-supported  $V_{0.9}Sb_{0.1}O_x$  systems can be explained by the optimal surface interaction between support and supported components resulting in the formation of well-spread amorphous active  $VO_x$ -component with vanadium in a high oxidation state.

**Keywords:** Vanadium-antimony oxide catalysts, Supports, Oxidative Dehydrogenation, Isobutane, Isobutene

## INTRODUCTION

Among a relatively large number of reported and reviewed studies on the oxidative dehydrogenation (ODH) light paraffins over vanadium oxide-based catalysts,<sup>1,2,4-8,9-13</sup> only few of them are specifically devoted to the ODH of isobutane to isobutene,<sup>14-17</sup> despite the potentially industrial importance of this process.<sup>18-21</sup> Some particular examples dealing with isobutane were also published in a few papers and patents mainly devoted to the ODH of other light paraffins.<sup>1,22-24</sup>

Complex V-Sb oxides (either bulk or supported) with excess antimony are well known as highly efficient catalysts for several prospective industrial processes such as ammoxidation of propane and alkylbenzenes to correspond-

ing nitriles,<sup>3,11,21,22</sup> partial oxidation of toluene<sup>23,24</sup> and  $H_2S$ ,<sup>25</sup> selective reduction of NO with ammonia.<sup>26</sup> It was mentioned in<sup>27</sup> that  $V_1Sb_{10}O_x$  mixed oxide is active in the ODH of isobutane to isobutene.

The effects of support and loading for V-Sb oxide catalysts have been reported in several papers but only for the ammoxidation of propane (including the propane ODH occurring in the course this reaction)<sup>21,22,28,29</sup> and the partial oxidation of toluene.<sup>24</sup> However, activity of different supported  $VO_x$ -species depends not only on their nature, but also on the catalysed reaction. So, this issue remains relevant but has not been still addressed in the case of isobutane ODH.

We have shown recently that, despite the poor efficiency of bulk V-Sb mixed oxides for the ODH of isob-

utane, their catalytic activity and olefin selectivity can be dramatically improved by depositing them on various oxide supports.<sup>30,31</sup> A further development of the isobutane ODH process requires the new knowledge about factors controlling the efficiency of these supported V-Sb-O catalysts.

## EXPERIMENTAL

### Catalyst Preparation

All bulk and supported V-Sb oxide catalysts were prepared by the citrate method<sup>32</sup> with a constant atomic ratio V/Sb = 8.8, previously found to be optimal for the target reaction.<sup>31</sup> Appropriate amounts of  $\text{NH}_4\text{VO}_3$  (Merck) and  $\text{SbCl}_3$  (Aldrich) were dissolved separately in water under heating (in the latter case of  $\text{SbCl}_3$ , hydrochloric acid was added to suppress the hydrolysis). The resulting transparent solutions were cooled to ambient temperature and subjected to ultrasonic treatment for 5 min. Then aqueous solutions of citric acid monohydrate ( $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ , Merck) were added separately to each of the above solutions (1.1 equivalent-gram of acid function per valence-gram of metal cation). The resulting solutions were stirred for 1 h, mixed together and then stirred again for 8 h. The mixture was then evaporated at 40 °C under reduced pressure in Rotavapor apparatus to form a syrup-like liquid, and dried in a vacuum oven at 80 °C for 24 h. The resulting solid precursor was decomposed at 300 °C for 16 h and calcined at 550 °C for 8 h in a static air to give the final bulk

catalyst.

Supported catalysts were prepared by impregnation of support materials using an incipient wetness method with a mixed V-Sb citrate solution obtained in the same way as described above. Impregnated samples were left at room temperature for 2 h, then dried and calcined in accordance with a procedure described for bulk catalysts.

The textural and other characteristics of support materials used in this work are summarized in Table 1. Among them, are four types of  $\gamma$ -aluminas (Aldrich) with very similar textural characteristics, but carrying different trade marks: "acidic", "weakly acidic", "neutral", and "basic", further denoted as A(a), A(wa), A(n), and A(b), respectively. The main difference between these  $\gamma$ -aluminas consists in the surface Na content varied from 0.15 at.% for A(a) to 0.6 at.% for A(b), according to the data of XPS analysis (Table 1). The other supports were: a microspheric alumina, A(ms),  $\alpha$ -alumina ( $\alpha$ A), silica-alumina (SA), silica gel (SG) and magnesium oxide (M). Samples with V-Sb-O component having surface coverage corresponding to  $n = 0.5, 1$  and  $2$  theoretical monolayers (ML) of the support were prepared and denoted as  $n\text{VSb/support}$ , e.g.  $0.5 \text{ VSb/A(wa)}$ , where  $n$  is the number of ML of the supported phase. Being vanadium oxide the main component of the active phase, the theoretical coverage of the support was calculated referred to vanadium oxide. The amount of vanadia required to obtain nominal monolayer coverage is considered to be  $4.98 \cdot 10^{18}$  formal  $\text{V}_2\text{O}_5$  molecules per square meter of support surface.<sup>33-36</sup>

Table 1. Supports Characteristics

Support	Support code	Origin	Particle size (mm)	N <sub>2</sub> Phisorption				XPS Na content at%	XRD
				SSA (m <sup>2</sup> /g)	D (Å)	Vp (ml/g)	V <sub>μp</sub> (ml/g)		
$\gamma$ -Al <sub>2</sub> O <sub>3</sub> "acidic"	$\gamma$ A(a)	Aldrich 19,996-6	0.1	183	58	0.23	0.09	0.15	Amorphous
$\gamma$ -Al <sub>2</sub> O <sub>3</sub> "weakly acidic"	$\gamma$ A(wa)	Aldrich 26,774-0	0.1	165	58	0.23	0.09	0.2	Amorphous
$\gamma$ -Al <sub>2</sub> O <sub>3</sub> "neutral"	$\gamma$ A(n)	Aldrich 19,997-4	0.1	179	58	0.23	0.1	0.3	Amorphous
$\gamma$ -Al <sub>2</sub> O <sub>3</sub> "basic"	$\gamma$ A(b)	Aldrich 19,444-3	0.1	148	58	0.25	0.08	0.6	Amorphous
$\gamma$ -Al <sub>2</sub> O <sub>3</sub> microspheric	$\gamma$ A(ms)	Katalizator Co., Novosibirsk (Russia)	0.3-0.8	85	175	0.37	-	n.d.	Almost amorphous, $\gamma$ -Al <sub>2</sub> O <sub>3</sub> (small amount) +corundum (traces)
$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	$\alpha$ A	Catalyst & Chemical Europe, S.a.	0.1-0.2	35	190	0.22	0.001	n.d.	Corundum
Si-Al-O (SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> =9.5)	SA	Aldrich 34.335-8	0.07-0.25	468		0.67	0.25	n.d.	Amorphous
Silica gel	SG	Aldrich 24.398-1	0.07-0.25	290	150	1.21	0.12	n.d.	Amorphous
Magnesium oxide	M	Jansenn 22,253.40	0.1-0.2	33		0.18	0.02	n.d.	Periclase + $\text{Mg}(\text{OH})_2$ brucite

### CATALYTIC ACTIVITY TESTS

Catalytic tests were performed under atmospheric pressure in a continuous gas flow system. A fixed-bed, straight down-flow tubular quartz reactor (i.d.15 mm) was used. Quartz chips were placed above and below the catalyst bed to reduce the reactor void volume and to diminish the possibility of homogeneous reaction in the free gas space. According to the results published elsewhere,<sup>34</sup> such filling substantially decreases the contribution of heterogeneously initiated homogeneous reaction in the presence of active V-Sb catalysts if not excludes it totally. Isobutane conversion in a catalyst free reactor filled with quartz chips was ~1% at 550 °C and ~3% at 600 °C.

The catalyst bed temperature (typically 550 °C) was monitored by a thermocouple placed into the centre of the catalyst bed and isolated with a coaxial thermo-well. A gas mixture (20 vol.% isobutane, 12 vol.% oxygen, nitrogen - balance) was fed into the reactor at a total flow of 1 cm<sup>3</sup>/s (formal contact time  $\tau = 4$  s). On-line GC analysis of the reaction mixture was carried out using a TC detec-

tor and two packed columns: with heptadecane-impregnated diatomite to separate CO<sub>2</sub>, C<sub>2</sub>-C<sub>4</sub> hydrocarbons and with molecular sieve NaX for O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, CO separation. Measurements were made 1 h after the desired reaction temperature was reached. A typical catalytic run lasted approximately 4-6 h without substantial activity loss, and catalytic performances are compared at 2.5 h on stream. Isobutane conversion (X), product yields (Y) and olefin selectivity (S) are expressed as mol.%. In all tests, calculated carbon and mass balances were within 100 ± 5%.

### RESULTS AND DISCUSSION

Supported V-Sb-O systems are, by far, more efficient in the target reaction than the bulk binary oxide. Catalytic performances of the supported V-Sb-O systems in the isobutane ODH are influenced only slightly by the V-Sb-O-loading in the studied range of coverage (0.5 - 2 theoretical monolayer) but strongly depend on the chemical nature of the oxide carriers and decrease in a series:

**Table 2.** Oxidative conversion of isobutane over nVSb/support and bulk VSb catalysts (V/Sb = 8.8, at.) Reaction conditions: 550 °C, P<sup>0</sup>iC<sub>4</sub>H<sub>10</sub> = 20 kPa, P<sup>0</sup>O<sub>2</sub> = 12 kPa,  $\tau = 4$  s

Catalyst support	n	SSA (m <sup>2</sup> /g)	iC <sub>4</sub> H <sub>10</sub> conversion, X (%)	Selectivity (%)			iC <sub>4</sub> H <sub>8</sub> yield, Y (%)
				iC <sub>4</sub> H <sub>8</sub>	C <sub>1</sub> -C <sub>3</sub>	CO <sub>x</sub>	
No (bulk)	-	7.0	12.7	11.0	6.1	82.9	1.4
$\gamma$ A(wa)	0.5	143	30.0	65.0	3.6	31.4	19.5
	1	125	34.5	65.0	4.1	30.9	22.4
	2	107	31.2	63.8	3.5	32.7	19.9
$\gamma$ -A(n)	0.5	149	30.8	65.8	3.0	31.2	20.3
	1	131	34.4	64.3	5.0	30.7	22.1
	2	109	34.0	63.3	4.6	32.1	21.5
$\gamma$ -A(b)	0.5	131	29.6	66.7	1.7	31.6	19.7
	1	114	34.3	65.9	4.0	28.9	22.6
	2	100	31.6	67.5	2.6	29.9	21.3
$\gamma$ -A(ms)	0.5	73	35.3	68.0	6.0	26.0	24.0
	1	69	36.5	70.2	6.2	23.6	25.6
	1.7	65	39.9	72.1	6.2	21.6	28.8
$\alpha$ A	0.5	35	18.2	51.7	3.5	44.8	9.4
	1	32	20.7	52.0	4.2	43.8	10.8
	2	31	24.6	55.9	4.5	39.7	13.8
SA	0.5	299	22.4	45.5	6.6	47.3	10.2
	1	232	19.4	44.6	4.8	50.6	8.6
	2	133	17.6	38.3	5.7	56.1	6.7
SG	0.5	206	20.5	49.2	5.7	45.1	10.0
	1	183	16.3	35.8	5.0	59.3	5.8
	2	142	17.7	41.1	3.6	55.3	7.3
M	0.5	30	15.2	35.6	10.3	54.0	5.4
	1	29	15.0	36.7	9.6	53.7	5.5
	2	28	17.3	44.6	5.7	49.7	8.1

$\gamma\text{Al} > \alpha\text{Al} > \text{SiAl} > \text{Si} \approx \text{Mg} > \text{unsupported}$

Except VSb/ $\alpha$ Al sample, which displays moderate catalytic properties, the studied systems containing VSb mixed oxide component supported on oxide carriers can be separated into two groups on the basis of their catalytic behaviour in the isobutane ODH:

- efficient catalysts - supported on  $\gamma$ -aluminas ( $Y = 17 - 29\%$  at OS = 61 - 72%);
- non-efficient catalysts - supported on MgO and silica-containing supports ( $Y = 5.4 - 10\%$  at OS = 36 - 49%).

The characterization data presented above shed a new light on the influence of the nature of oxide supports on catalyst efficiency.

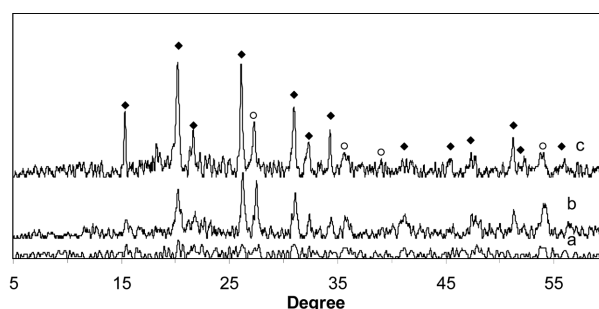
No clear trend can be found when catalytic properties are compared with the values of specific surface area of the samples. Among the equally non-efficient catalysts (VSb/M, VSb/SA, VSb/SG), there are samples with low ( $\sim 30 \text{ m}^2/\text{g}$ ), as well as with very high ( $\sim 200\text{-}300 \text{ m}^2/\text{g}$ ) SSA values. The VSb/aA catalyst is twice as efficient as VSb/M which has the same SSA. All VSb/ $\gamma$ A systems exhibit similar efficiencies, although the best among them (VSb/A(ms) with moderate SSA and large pore diameter) differs significantly in the SSA value from the catalysts on Aldrich  $\gamma$ -aluminas. So, the catalyst SSA and pore structure are not the main or principal factors controlling the catalytic performance in the isobutane ODH. Also, since the variations of the type of  $\gamma$ -alumina (from "acidic" to "basic") has almost no effect on the catalytic performance, one may conclude that surface Na content in the initial support plays no significant role in the formation of the final efficient catalytic system.

The surface of VSb/ $\alpha$ A catalyst is strongly enriched in catalytic inactive antimony ions, and this could be the reason of its lower activity and selectivity in comparison with VSb/ $\gamma$ A systems. On the contrary, the surface of silica-containing catalysts is impoverished in both V and Sb. This could be due to two factors: the formation of bulky deposits leaving bare support areas uncovered, or deposit of a substantial part of these ions inside the support pores instead of on the outer surface. The latter may explain this impoverishment as well as the biggest drop in the SSA upon supporting the active V-Sb-O component (compare SSA values for SA and SG and corresponding catalysts in Tables 1 and 2).

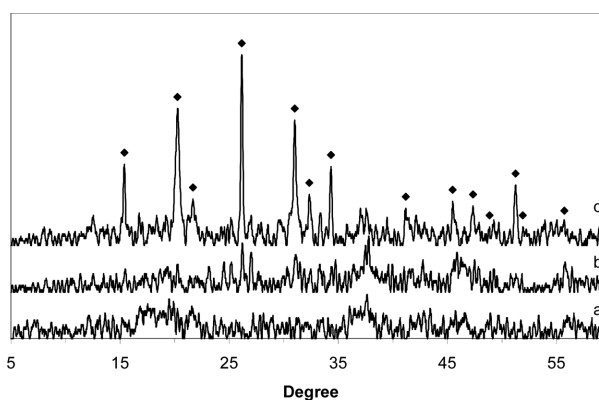
The surface V/Sb ratios in catalysts on these supports are higher than nominal ones. This may indicate that Si-containing supports preferably interact with antimony and non-bound vanadium ions from the supported component

concentrates on the surface. A substantial fraction of vanadium ions, which are not properly spread on the surface, remain mostly in a separate highly-crystalline  $\text{V}_2\text{O}_5$ -like phase (XRD).<sup>36</sup> As a result, poor catalytic performances of SG- and SA-supported samples is due to two main factors: high content of bulk V- and VSb-oxides displaying low efficiency in the isobutane ODH and low coverage of support surface with V-containing active component. Both these factors originate from low chemical affinity between silica-containing supports and VSb oxide.<sup>35</sup>

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**Fig. 1.** XRD patterns of silica-supported catalysts: (a) 0.5VSb/SG, (b) 1VSb/SG, and (c) 2VSb/SG.



**Fig. 2.** XRD patterns of alumina-supported catalysts: (a) 0.5VSb/A(wa), (b) 1VSb/A(wa), and (c) 2VSb/A(wa).

between silica-containing supports and VSb oxide.

One may conclude that catalytic performance of supported V-Sb-O systems in the isobutane ODH strongly depends on the type of structures that a supported component forms. In its turn, the type of such structure is controlled by the chemical affinity between the supported component and the support, as follows:

- if the interaction between V-Sb-oxide and support is weak (like in the case of SiO<sub>2</sub>) or excessively strong (as in the case of MgO), the supported catalysts exhibit low ODH activity and selectivity;
- an optimum surface interaction between components (in the case of  $\gamma$ -aluminas) results in the formation of well-dispersed (spread) active component, efficient for the isobutane ODH reaction.

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