

## Dehydrogenation of Ethylbenzene with Carbon Dioxide over Supported Vanadium-Antimony Oxide Catalysts: Effect of Zirconia Modification in Alumina Support

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Styrene, an important monomer for synthetic polymers, is commercially produced by the ethylbenzene catalytic dehydrogenation (EBDH) process, which is thermodynamically limited and energy consuming. Alternative methods using oxygen as an oxidant are free from these disadvantages but have their own sets of challenges related to safety (the operations with potentially explosive oxygen-hydrocarbons mixtures) and substantial loss of styrene selectivity due to hydrocarbons total oxidation by this strong oxidant.<sup>1</sup>

Dehydrogenation of ethylbenzene in the presence of soft oxidant, carbon dioxide (CO<sub>2</sub>-EBDH), allows to produce styrene selectively with an energy-saving and environmentally friendly process as well as to effectively utilize CO<sub>2</sub>, a greenhouse gas.<sup>2-4</sup> Several catalysts, mainly based on supported (on active carbon, alumina, MgO, TiO<sub>2</sub>, silicates, ZSM-5, MCM-41) or mixed oxides of Fe, Cr, and V were found to be efficient in the CO<sub>2</sub>-EBDH.<sup>2-14</sup> Among the best catalytic systems for this reaction, alumina supported V-Sb oxide catalyst demonstrates a very high styrene selectivity (97-98%) at high and stable time-on-stream activity.<sup>12-14</sup>

Zirconium oxide has received considerable attention not only as a promising catalyst for a number of reactions including hydrocarbons oxidative dehydrogenation (see Refs. in<sup>15,16</sup>), but also as an active and "tunable" support with practically important chemical, thermal, and mechanical features. ZrO<sub>2</sub> has bifunctional properties of acid and base along with reducing and oxidizing ability. Its high thermal stability is important as the CO<sub>2</sub>-EBDH is performed at high temperature of about 550-600 °C. Like  $\gamma$ -alumina, zirconia is an excellent support for the synthesis of highly dispersed oxides, including VO<sub>x</sub>-species.<sup>16,17</sup> Also, in contrast with weaker interacting supports, zirconia inhibits the sintering of supported oxides in the presence of water at high temperatures.<sup>17</sup> In general, zirconia has low surface area<sup>15,18</sup> which, nevertheless, can be substantially increased by use of some special preparation methods.<sup>17,19-22</sup> However, zirconia is more expensive than the traditional oxide materials such as alumina, silica, etc., and this is one of the reasons why attempts were made to explore the inherent favorable properties of both alumina and zirconia supports in a mixed Al-Zr oxide.<sup>15,21-27</sup> There are several examples when Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> supported catalysts exhibited better catalytic properties

than the catalysts supported on pure Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub>.<sup>21,22,26</sup>

We have reported that zirconia shows noticeable activity in the CO<sub>2</sub>-EBDH at high temperatures. At 600 °C, monoclinic zirconia displayed the ethylbenzene conversion of 40% whereas ZrO<sub>2</sub> with high content of structurally stable tetragonal phase prepared by high-temperature aging method showed even better activity, mainly due to higher surface area.<sup>20</sup> However, taking into account relatively low styrene selectivity over ZrO<sub>2</sub>-catalyst (~90%<sup>20</sup>) and its high price, in the current work it has been decided to use zirconia not as a catalyst but as an active co-component of the alumina support for more selective and substantially more active V<sub>0.43</sub>Sb<sub>0.57</sub>O<sub>x</sub> catalytic system.<sup>4,12,13</sup>

### Experimental Section

$\gamma$ -Alumina (Al) from Kureha Co. (Japan) was used as starting catalyst support. The zirconia-modified alumina materials (nZrAl where n is nominal wt.% of ZrO<sub>2</sub> = 3, 5, 10 and 20 wt.%; the rest is Al<sub>2</sub>O<sub>3</sub>) were prepared by impregnation at room temperature of Al with proper amount of aqueous solution of zirconyl nitrate (20 wt.% as ZrO<sub>2</sub>) from MEL Chemicals (UK) followed by calcination in air at 500 °C for 4 h. For catalyst preparation of the supported VSb/Al and VSb/nZrAl catalysts (VSb is the V<sub>0.43</sub>Sb<sub>0.57</sub> oxide, where subscript numbers indicate the atomic percentages of the element), the Al and nZrAl supports were impregnated with aqueous solutions (along with tartaric acid) of NH<sub>4</sub>VO<sub>3</sub> and SbCl<sub>3</sub> from Aldrich. The loading of V<sub>0.43</sub>Sb<sub>0.57</sub>O<sub>x</sub> component, 20 wt.%, was the same for all samples. The catalysts were calcined in air at 650 °C for 4 h. The resulting catalysts were crushed and sieved to a size between 300 and 710  $\mu$ m.

The supports and supported V-Sb catalysts were characterized by BET specific surface area (S<sub>BET</sub>) measurements (Micromeritics Tristar 3000), X-ray diffraction (XRD) (Rigaku Miniflex diffractometer), hydrogen temperature-programmed reduction (H<sub>2</sub>-TPR) (Micromeritics Pulse Chemisorb 2705 system) and carbon dioxide temperature-programmed desorption method (CO<sub>2</sub>-TPD) (Micromeritics Pulse Chemisorb 2705 system).

The catalytic tests were carried out in an isothermal fixed bed flow reactor (continuous micro-activity test unit) using 1

g of catalyst at 550 °C under atmospheric pressure. The ethylbenzene feed rate was 8.2 mmol/h (weight hourly space velocity, WHSV = 1 h<sup>-1</sup>), molar ratio CO<sub>2</sub>/EB = 5, total flow rate of the gas mixture was 45 mL/min. Nitrogen was used as inert diluent component as well as the internal standard for gas analysis. Products formed during reaction were analyzed by on-line gas chromatograph equipped with TCD and FID. The ethylbenzene conversion, X<sub>EB</sub>, styrene yield, Y<sub>ST</sub>, and styrene selectivity, S<sub>ST</sub>, are expressed as mol. % on a carbon atom basis.

## Results and Discussion

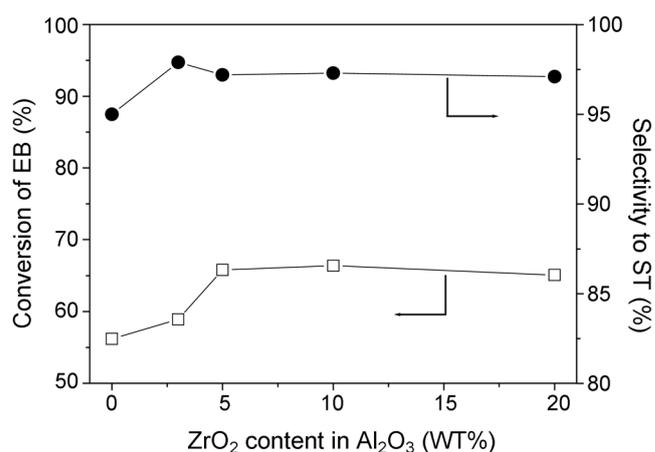
Table 1 and Figure 1 present the catalytic properties of the VSb/Al and VSb/nZrAl oxide systems in the CO<sub>2</sub>-EBDH. For studied catalysts, styrene, together with H<sub>2</sub>, CO and water, was a main product, and benzene and toluene along with methane were obtained as cracked by-products in much lower amounts. All these catalysts demonstrate similar high selectivity to styrene, S<sub>ST</sub> ~ 95-97%; however, S<sub>ST</sub> for the catalysts on ZrO<sub>2</sub>-modified support is a little higher compared to the selectivity over VSb/Al catalyst. At the same time, the VSb/nZrAl catalysts demonstrate substantially higher activity (in terms of the ethylbenzene conversions X<sub>EB</sub> ~ 60-66%) than V-Sb-O system on unmodified alumina (56%). Although the leveling off of X<sub>EB</sub> values is observed for the catalysts containing in their binary ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support more than 5 wt.% of zirconia, well-pronounced beneficial effect of the modification of alumina with zirconia on the catalyst activity and styrene yield has been revealed. Contribution of the inherent catalytic activity of zirconia into this effect, evidently, cannot be considered as substantial one because fourfold increase of the content of zirconia in the Al-support from 5 to 20 wt.% did not cause any increase of the ethylbenzene conversions.

It is seen from Table 1 that the supporting of the V-Sb-O component on all supports results in small decrease in BET surface areas. Among modified supports and supported catalysts, S<sub>BET</sub> values for ZrO<sub>2</sub>-containing samples are comparable, and are found to be only slightly less than those for, respectively,

**Table 1.** Textural and catalytic properties of VSb/Al and VSb/nZrAl oxide systems in the CO<sub>2</sub>-EBDH reaction

Catalyst or support	S <sub>BET</sub> , m <sup>2</sup> /g	Pore volume (mL/g)	Pore size (Å)	Y <sub>ST</sub> <sup>a</sup> , %
Al	240	0.76	126	—
VSb/Al	200	0.61	122	54.6
3ZrAl	206	0.60	117	—
VSb/3ZrAl	165	0.54	115	57.2
5ZrAl	222	0.75	136	—
VSb/5ZrAl	186	0.56	120	62.9
10ZrAl	214	0.78	147	—
VSb/10ZrAl	194	0.60	124	64.1
20ZrAl	219	0.63	114	—
VSb/20ZrAl	184	0.59	128	62.6

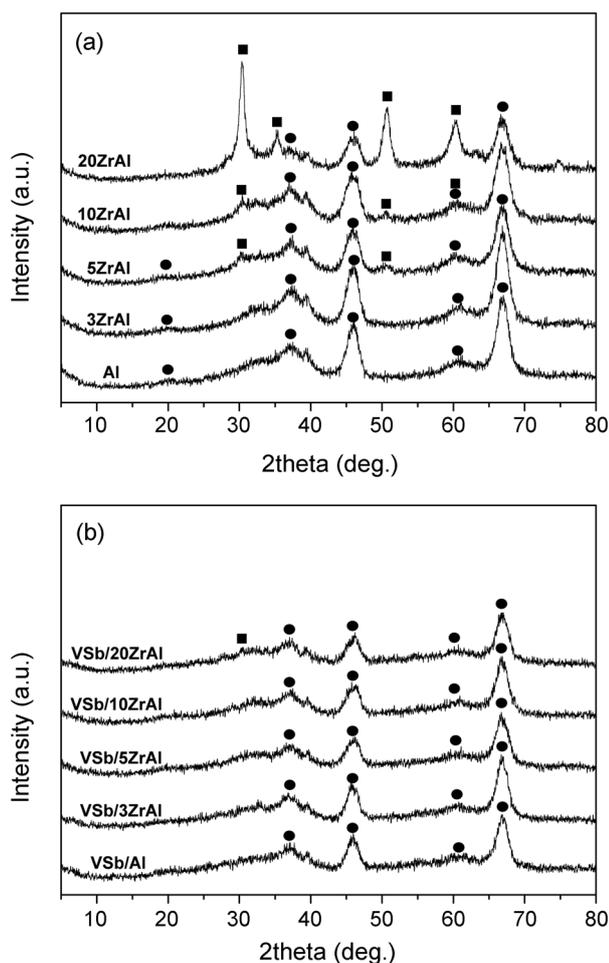
<sup>a</sup>styrene yield after 2 h reaction at T = 550 °C, molar ratio CO<sub>2</sub>/EB = 5 and WHSV = 1 h<sup>-1</sup>.



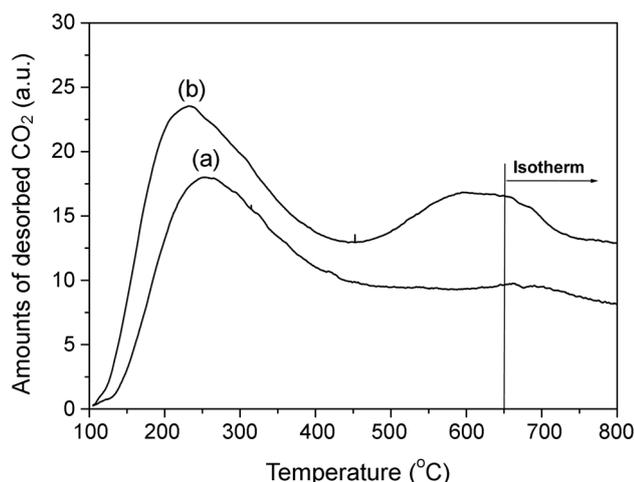
**Figure 1.** Dehydrogenation of ethylbenzene with carbon dioxide over VSb/Al and VSb/nZrAl catalysts. Reaction conditions: T = 550 °C, molar ratio CO<sub>2</sub>/EB = 5, WHSV = 1 h<sup>-1</sup>, time-on-stream = 2 h.

Al-support and VSb/Al catalyst. The differences in the pore volume and the average pore diameter for all supports and corresponding catalysts are also not great. So, there is no relationship between the enhanced activities of ZrO<sub>2</sub>-containing catalysts and their textural characteristics.

Only broad and weak lines of alumina (no diffraction peaks from zirconia) were observed in the XRD pattern of the 3ZrAl-support (Figure 2). A very small quantity of poorly crystallized zirconia corresponding to reflections at  $2\theta \sim 30, 50$  and  $60^\circ$  were seen in the 5ZrAl- and, more reliably, in the case of 10ZrAl-supports. But for 20ZrAl-support, a well-crystallized phase of tetragonal ZrO<sub>2</sub> was definitely detected. No detectable phase(s) of vanadium oxide or mixed vanadium-antimony oxide were observed in all supported catalysts. It is noteworthy to mention that previously we several times reliably determined by XRD the presence of the V<sub>1.1</sub>Sb<sub>0.9</sub>O<sub>4</sub> phase in the same V<sub>0.43</sub>Sb<sub>0.57</sub>O<sub>x</sub> system but supported on the Aldrich alumina with smaller specific surface area of 87 m<sup>2</sup>/g.<sup>4,12,13</sup> The presented XRD results indicate that catalytic active V-component is very well dispersed in the zirconia-modified and unmodified Kureha alumina. Zirconia (up to 10 wt.%) is also very well dispersed on alumina. Earlier investigations proved that vanadia disperses very well on zirconia particles.<sup>16,17</sup> For equal vanadia loading, the dispersion of vanadia on mixed Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> support was found to be better than that of vanadia supported on pure zirconia or alumina.<sup>26,27</sup> Another important observation from the XRD investigation is the disappearance of the V<sub>0.43</sub>Sb<sub>0.57</sub>O<sub>x</sub> component. This result implies the strengthening of interaction between supported acidic V-Sb oxide and the support whose basicity apparently would be increased while using a large content of rather basic zirconia in mainly acidic alumina. The formation of bulk ZrV<sub>2</sub>O<sub>7</sub> compound through the reaction of V<sub>2</sub>O<sub>5</sub> and ZrO<sub>2</sub> at temperatures ~600 °C was already reported.<sup>16,17</sup> However, in this study, zirconia vanadate compound is probably two-dimensional and thus it is XRD-undetectable phase.



**Figure 2.** XRD patterns of (a) Al and  $n\text{ZrAl}$  supports and (b) VSb/Al and VSb/ $n\text{ZrAl}$  catalysts: (●)  $\text{Al}_2\text{O}_3$ ; (■) tetragonal  $\text{ZrO}_2$ .



**Figure 3.**  $\text{CO}_2$ -TPD profiles of the (a) VSb/Al and (b) VSb/5ZrAl catalysts.

Efficient redox properties of the VSb/Al system is known to be crucial for its activity in the  $\text{CO}_2$ -EBDH.<sup>4,12,13</sup> Meanwhile, the  $\text{H}_2$ -TPR profiles for the VSb/3ZrAl, VSb/5ZrAl and VSb/10ZrAl catalysts were found to be practically identical

to the profile for the VSb/Al catalyst (not included here). Moreover, at the same shape and peaks positions, the  $\text{H}_2$ -consumption for VSb/20ZrAl catalyst was substantially lower as compared to other samples. This could be related with the formation of zirconia vanadate compound, whose vanadia species are less reducible than amorphous V-species highly dispersed on the support surface. Thus, there is no obvious relationship between beneficial effect of the addition of  $\text{ZrO}_2$  on the activity and redox properties of the catalysts.

Previously we have concluded for the  $\text{CO}_2$ -EBDH over VSb/Al catalyst that carbon dioxide plays a beneficial role as a selective oxidant improving the catalytic behavior; the efficient reduction of  $\text{CO}_2$  to CO was revealed.<sup>4,12-14</sup> This indicates the catalyst ability for the dissociative adsorption of  $\text{CO}_2$  on moderately strong basic sites. Such ability of zirconia to adsorb  $\text{CO}_2$  efficiently<sup>20</sup> and promote  $\text{CO}_2$  dissociation<sup>28</sup> is already reported. The  $\text{CO}_2$ -TPD profiles for starting VSb/Al system and VSb/5ZrAl system (Figure 3) show the substantially higher capability of the latter catalyst to adsorb carbon dioxide than that of the VSb/Al one. Moreover, the  $\text{ZrO}_2$ -containing catalyst also contains stronger surface basic sites that might favor the more efficient dissociative adsorption of  $\text{CO}_2$ . The observed  $\text{CO}_2$ -adsorption behavior is consistent with the improvement of activity in the  $\text{CO}_2$ -EBDH of the catalyst on zirconia-modified alumina.

In summary, modification of alumina support with zirconia (3-20 wt.%) improved dispersion of active  $\text{VO}_x$ -species and enhanced the  $\text{CO}_2$ -adsorption capacity related with the surface basicity of the supported  $\text{V}_{0.43}\text{Sb}_{0.57}$  oxide system. As a result, a significant increase of its catalytic activity in the dehydrogenation of ethylbenzene has been achieved.

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