

## Dehydrogenation of Ethylbenzene with Carbon Dioxide as Oxidant over Mg-modified Alumina-supported V–Sb Oxide Catalysts

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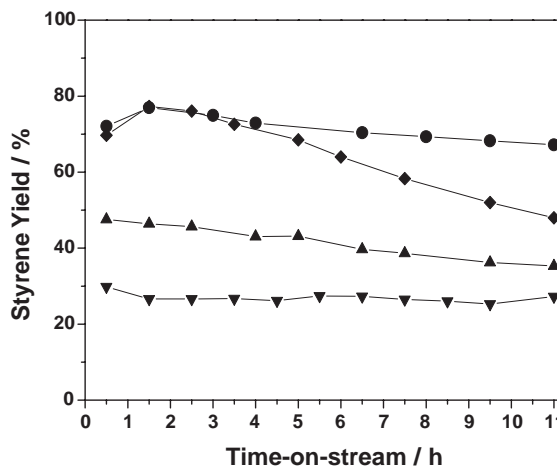
Modification of alumina support with an appropriate amount of magnesia (Mg/Al = 0.1) leads to the stable activity of the supported vanadium–antimony oxide catalyst for the dehydrogenation of ethylbenzene into styrene in the presence of carbon dioxide as oxidant. Correlation between catalytic performance and surface acidity has been found.

Catalytic dehydrogenation of ethylbenzene in the presence of carbon dioxide (CO<sub>2</sub>-EBDH) has recently been attempted to explore a new technology for producing styrene selectively because it could provide us with an energy-saving and environmentally friendly process to utilize CO<sub>2</sub>, a greenhouse gas, as a mild oxidant.<sup>1–3</sup> Several families of the catalysts, mainly based on supported or mixed oxides of Fe, V, or Cr were found to be active and selective in the CO<sub>2</sub>-EBDH.<sup>2–14</sup> However, most of the catalysts have usually shown strong deactivation for this reaction during even a few hours on stream. As a typical example, over Mg–Al–V mixed oxides, the initial styrene yield, 64% after 1 h on stream, decreased to 40% after 7 h.<sup>7</sup> The similar deactivation rate was observed also for VO<sub>x</sub>/MgO catalyst.<sup>3</sup> We have proposed a very active and selective catalyst, V<sub>0.43</sub>Sb<sub>0.57</sub>O<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> (VSb/Al), but its deactivation was also significant mainly owing to coke formation although the deactivation rate was less than other reported catalysts.<sup>12,13</sup>

Since the coke precursors are easily formed through the oligomerization of olefins, facilitation of olefins desorption from a catalyst surface could minimize the carbon accumulation. Taking into consideration a basic character of electron-rich olefins including styrene, lower surface acidity of the catalyst appears to induce easier desorption of olefins from the catalyst surface. VO<sub>x</sub> catalysts loaded on MgAl oxide support exhibited a decreased adsorption and rapid desorption of propylene as compared with those on alumina.<sup>14,15</sup> Based on these considerations, an attempt has been made to stabilize the activity of VSb/Al catalyst in the CO<sub>2</sub>-EBDH by the modification of the alumina support with a basic MgO component.

MgO-modified alumina (Mg<sub>n</sub>Al) supports were obtained by impregnation of an activated alumina with aqueous solutions containing a certain amount of Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Mg<sub>n</sub>Al; *n* is an atomic ratio of Mg/Al = 0.1, 0.3, or 0.5) followed by calcination at 670 °C. Alumina (Al)- or Mg<sub>n</sub>Al-supported vanadium–antimony oxide catalysts were prepared by impregnation with the solutions of NH<sub>4</sub>VO<sub>3</sub> and SbCl<sub>3</sub> followed by calcination at 650 °C. The loading of the supported V<sub>0.43</sub>Sb<sub>0.57</sub>O<sub>x</sub> component (20 wt %) was the same for all samples. The catalyst supports and supported catalysts were characterized by BET specific surface area (S<sub>BET</sub>) measurements (Micrometrics model ASAP

2400), X-ray diffraction (XRD) (Rigaku D/MAX-3B diffractometer) and the NH<sub>3</sub>-temperature-programmed-desorption method (NH<sub>3</sub>-TPD) (Micrometrics, TPD/TPR 027 Option). The catalytic tests were performed with 1 g of catalyst at 595 °C under atmospheric pressure in an isothermal fixed bed flow reactor of the continuous micro-activity test unit. The ethylbenzene feed rate was 8.2 mmol/h, molar ratio CO<sub>2</sub>/EB = 5, total flow rate of the gas mixture of CO<sub>2</sub> and N<sub>2</sub> was 45 mL/min. The components of reaction mixtures were analyzed by on-line gas chromatograph.

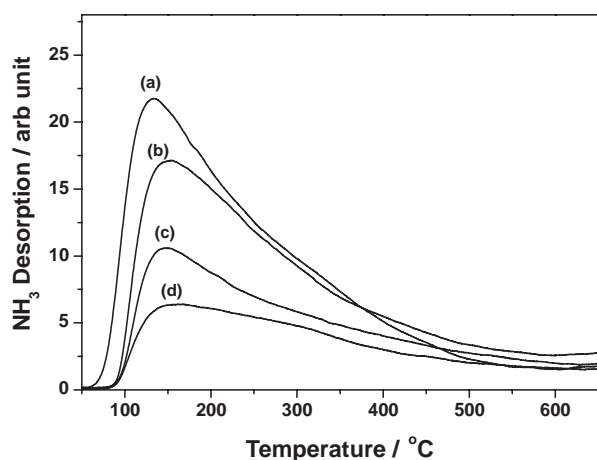


**Figure 1.** Catalytic dehydrogenation of ethylbenzene with carbon dioxide as oxidant over supported V–Sb oxide catalysts at 595 °C: VSb/Al (◆) and VSb/Mg<sub>n</sub>Al with *n* = 0.1(●), *n* = 0.3(▲), or *n* = 0.5(▼).

VSb/Al and VSb/Mg<sub>n</sub>Al catalysts are highly selective with respect to styrene (>95%). The VSb/Al and VSb/Mg<sub>0.1</sub>Al sample showed similar initial styrene yield, *Y*<sub>ST</sub> ≈ 75 mol % after 1 h on-stream. However, considering the difference in their *S*<sub>BET</sub> values (87 and 67 m<sup>2</sup>/g, respectively), the VSb/Mg<sub>0.1</sub>Al catalyst can be regarded as a little more active one due to its higher specific yield based on the *S*<sub>BET</sub> value (*Y*<sub>ST</sub>/*S*<sub>BET</sub>), 1.1%/m<sup>2</sup> against 0.9%/m<sup>2</sup> for the VSb/Al. The VSb/Mg<sub>0.3</sub>Al and VSb/Mg<sub>0.5</sub>Al catalysts displayed substantially lower styrene yield (≈45 and 30%, respectively) due to their reduced specific surface areas (48 and 38 m<sup>2</sup>/g, respectively) but their *Y*<sub>ST</sub>/*S*<sub>BET</sub> values (0.9–0.8%/m<sup>2</sup>) are very close to that for the VSb/Al catalyst. Thus, the specific surface areas of the catalysts decrease with an increase of MgO-content, affecting only slightly their specific activities. The activities of the supported V–Sb oxide catalysts in the CO<sub>2</sub>-EBDH are mainly determined by the sup-

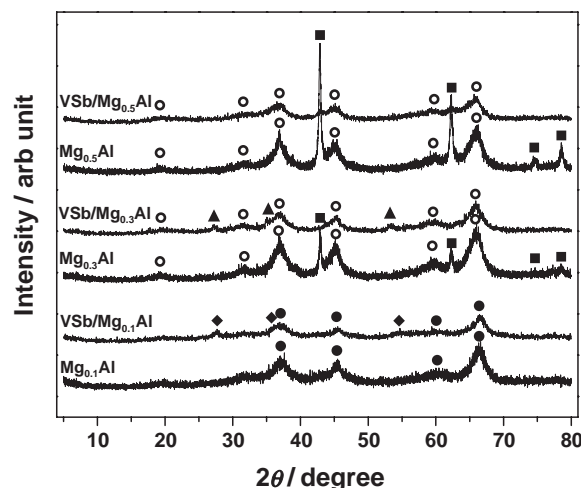
ported  $\text{VO}_x$  species whereas the presence of  $\text{SbO}_x$  positively affects the catalyst stability through the facilitation of the redox cycle.<sup>12,13</sup> Moreover, it is noted that the Mg-containing catalysts studied exhibit much stable catalytic behavior compared to the VSb/Al (Figure 1). When we checked the content of carbon formation on each catalyst after 12 h on stream, we observed that Mg-modified catalysts reveal less carbon formation (4.4–6.0 wt %) as compared with VSb/Al (13.1 wt %), indicating that modification of alumina support with magnesia leads to the stable activity, at least partly, due to strong resistance against carbon formation.

As illustrated in  $\text{NH}_3$ -TPD profiles (Figure 2), the VSb/ $\text{Mg}_n\text{Al}$  catalysts contain smaller amounts of surface acid sites compared with the un-modified VSb/Al catalyst. Thus, the higher Mg-content leads to the lower acidity. Therefore, the better stability of the MgO-containing catalysts is ascribed to their reduced surface acidities.



**Figure 2.**  $\text{NH}_3$ -TPD profiles of (a) VSb/Al and VSb/ $\text{Mg}_n\text{Al}$  catalysts: (b)  $n = 0.1$ , (c)  $n = 0.3$ , and (d)  $n = 0.5$ .

According to XRD patterns (Figure 3), both  $\text{Mg}_{0.1}\text{Al}$  support and VSb/ $\text{Mg}_{0.1}\text{Al}$  catalyst do not contain a free crystalline MgO phase. Instead they showed a fully incorporated into spinel-like binary oxide phase,  $\text{MgAl}_2\text{O}_4$ . However, a crystalline MgO is distinctively observed in the  $\text{Mg}_{0.3}\text{Al}$  and  $\text{Mg}_{0.5}\text{Al}$  whose major phase is  $\text{MgAl}_2\text{O}_4$ . Trace of free MgO particles is also detectable when the V–Sb oxide is loaded on these support materials. However, taking into account no detectable phase of vanadium oxide in XRD, a catalytically active V-component appears to be well dispersed on the support materials. It was found that XRD peaks of  $\text{VSbO}_4$ -like phases, which are well detectable in the VSb/Al<sup>12,13</sup> and VSb/ $\text{Mg}_{0.1}\text{Al}$  catalysts, are very weak in the VSb/ $\text{Mg}_{0.3}\text{Al}$  and, moreover, they fully disappear in the VSb/ $\text{Mg}_{0.5}\text{Al}$  catalyst. This result implies the stronger interaction between acidic V–Sb oxide and  $\text{Mg}_n\text{Al}$  support materials while using a large content of basic MgO in catalyst preparation. The increased acid–base interaction might lead to the formation of magnesium vanadate(s) with the lower specific surface area, which is probably two-dimensional and un-detectable phase in XRD. It is reasonably assumed that a decrease in an amount of active V-species exposed at the catalyst surface diminishes the EB-conversions compared with those over VSb/Al and VSb/ $\text{Mg}_{0.1}\text{Al}$  samples.



**Figure 3.** XRD patterns of  $\text{Mg}_n\text{Al}$  supports and VSb/ $\text{Mg}_n\text{Al}$  catalysts: (●)  $\text{MgAl}_2\text{O}_4$ ; (○)  $\text{MgAl}_2\text{O}_4$ ; (■) MgO; (◆)  $\text{V}_{1.1}\text{Sb}_{0.9}\text{O}_4$ ; (▲)  $\text{V}_{0.95}\text{Sb}_{0.95}\text{O}_4$ .

In summary, this work demonstrates that a favorable balance between the decreased acidity of the V–Sb oxide catalyst supported on MgO-modified alumina and an amount of V–Sb oxide species is needed for the stable and active catalytic performance in the  $\text{CO}_2$ -EBDH. As a result, modification of alumina support with an appropriate amount of magnesia ( $\text{Mg}/\text{Al} = 0.1$ ) leads to the stable activity of the VSb/ $\text{Mg}_{0.1}\text{Al}$  catalyst for the reaction.

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