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Effect of carbon dioxide as oxidant in dehydrogenation of ethylbenzene over alumina-supported vanadium–antimony oxide catalyst

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Abstract

The dehydrogenation of ethylbenzene over alumina-supported vanadium–antimony oxide catalyst has been studied under different atmospheres such as inert nitrogen, steam, oxygen and carbon dioxide as diluent or oxidant. Among them, the addition of CO_2 gave the highest styrene yield (up to 82%) and styrene selectivity (up to 97%) along with stable catalytic performance. Carbon dioxide plays a beneficial role as a selective oxidant in improving the catalytic behavior through the oxidative pathway.

Keywords: Carbon dioxide; Oxidant; Dehydrogenation; Ethylbenzene; Styrene; Supported vanadium–antimony oxide catalyst

1. Introduction

Styrene is commercially producing by dehydrogenation of ethylbenzene (EBDH) over K-promoted iron oxide catalysts using a large excess of superheated steam. The main drawbacks of this long-time explored process are equilibrium limitations regarding conversion and large energy consumption. As an alternative way, the oxidative dehydrogenation of EB is free from thermodynamic limitations, operating at lower temperatures with an exothermic reaction. However, this process with use of strong oxidant, oxygen, suffers from loss of selectivity for styrene due to the production of carbon oxides and oxygenates [1].

Carbon dioxide, a main contributor to a greenhouse effect, could be utilized as non-traditional mild oxidant in the large-scale industrial EBDH process [2]. The effect of CO_2 on the EBDH was shown to be certainly dependent on the nature of the catalyst used. Almost solely on the supported FeO_x-[3] and VO_x-based [4–6] systems, the introduction of carbon dioxide into the reaction mixtures positively affects the reaction rate and styrene selectivity as well as partly hinders the coke formation.

Previously, we reported that alumina-supported V–Sb oxide system is highly active and selective catalyst for the CO_2-EBDH [5]. In this work, we investigate the catalytic behaviors of this system in the EBDH under different atmosphere such as nitrogen, steam, oxygen or carbon dioxide in order to clarify the effect of carbon dioxide.

2. Experimental

An alumina-supported vanadium–antimony oxide catalyst, $V_{0.43}Sb_{0.57}O_x/Al_2O_3$ (denoted as VSb/Al), was prepared by impregnation of activated alumina (Aldrich 19,996-6, $S_{BET} = 121\ m^2/g$) with aqueous solutions of ammonium metavanadate and antimony (III) chloride (Aldrich) along with tartaric acid [6]. Subscript numbers of V and Sb in the formulae of VSb/Al indicate the atomic percentages of the element in the supported binary system. The impregnated sample was dried at 120 °C and then calcined in air at 600 °C for 4 h. The total amount of the supported oxide component was 20 wt.%.

Calcined samples were characterized by means of XRD, H_2-TPR and CO_2 pulse methods. X-ray diffraction patterns were

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recorded on a Rigaku D/MAX-3B diffractometer using monochromatic Cu Kα radiation. Temperature-programmed reduction of the catalysts with hydrogen (H_2-TPR) was performed from 100 to 800 °C at a heating rate of 10 °C/min with a 5% H_2 in helium flow in a conventional flow system equipped with a thermal conductivity detector for monitoring of H_2-consumption. In order to estimate the re-oxidizability with carbon dioxide of the catalysts previously partially reduced at 600 °C in H_2/He flow for 30 min, CO_2 pulse experiments were conducted at 600 °C in the 1/4 in. outer diameter quartz reactor with 200 mg of the catalyst.

The EBDH reactions were carried out under atmospheric pressure at 500–650 °C in a micro-activity test unit (Zeton, MAT 2000) with a fixed bed isothermal reactor using 1 g of catalyst. The EB feed rate was 8.2 mmol/h and the total flow rate of the carrier gas mixture was 45 ml/min. The components of reaction mixtures were analyzed by on-lined gas chromatograph. Conversion of ethylbenzene, X(EB), yield of styrene, Y(ST) and styrene selectivity, S(ST), are expressed as mol% on a carbon atom basis.

3. Results and discussion

Fig. 1 represents the catalytic behaviors of VSb/Al in the different modes of the EBDH reactions. Styrene is a main product and benzene and toluene are obtained as by-products along with methane. Water, CO and CO_2 are also reaction products under the CO_2-EBDH and O_2-EBDH.

Under inert nitrogen, the catalyst reveals initially, at 1 h on-stream, high activity ($X(\mathrm{EB}) = 73\%$) with good styrene selectivity, $S(\mathrm{ST}) = 94\%$. The activity increases slightly until 2.5 h on-stream and then decreases significantly. The catalyst deactivation stems mainly from the coke formation because intense CO_x evolution was monitored during the re-oxidation of the spent catalyst in air stream. Under steam diluent, the catalyst exhibits rather low activity, $X(\mathrm{EB}) < 60\%$, and poor selectivity, $S(\mathrm{ST}) < 85\%$. The poor selectivity might be due to the enhancement of hydrocracking or steam reforming reaction of ethylbenzene. The activity increases initially but remains stable after 2.5 h on-stream different from under nitrogen. No coke was observed on the surface of the spent catalyst. In the presence of oxygen, the initial catalytic activity is similar to that under nitrogen decreasing rapidly with the same deactivation trend. The styrene selectivity in the O_2-EBDH (~83%) is lower than that under nitrogen due to the total oxidation of ethylbenzene to CO_x, resulting in the significant decrease of styrene yield (Fig. 1). Moreover, fast catalyst deactivation due to coke deposition was found to be unavoidable in the presence of oxygen over VSb/Al catalyst even though O_2 is known to be strong oxidant for coke burning. Under carbon dioxide, the catalyst exhibits the highest styrene yield and styrene selectivity (up to 97%) along with the relatively stable catalytic performance (Fig. 1). Coke formation was also observed on the surface of the spent catalyst but in much lower amount in comparison with the simple EBDH and O_2-EBDH.

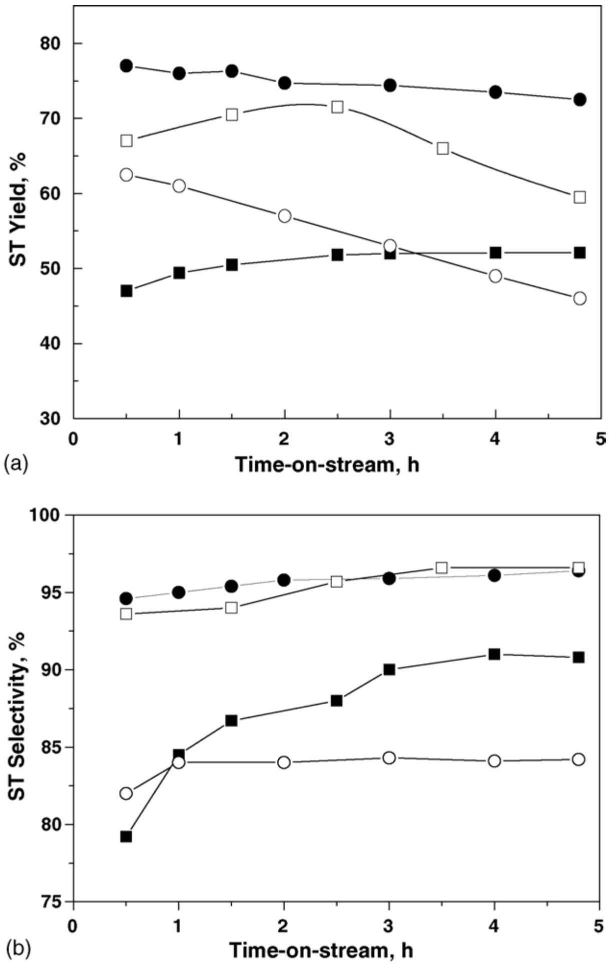

Fig. 1. Styrene yields (a) and styrene selectivities (b) in the EBDH reactions under different atmospheres over VSb/Al catalyst at 595 °C. Molar ratios: N_2/EB = 12.8, steam/EB = 10, O_2/EB = 1 and CO_2/EB = 1. Symbols: (●) CO_2, (□) N_2, (○) O_2, (■) H_2O.

The catalytic activity increases with the increase of molar ratio of CO_2/EB in the reaction feed (Fig. 2). At $CO_2/\mathrm{EB} = 10$, the styrene yield is about 82%, increasing by 12.5% as compared with that under nitrogen diluent. It is noteworthy that the molar ratio H_2O/H_2 reflecting the correlation between oxidative and non-oxidative dehydrogenation of ethylbenzene increases almost linearly with the increase of CO_2/EB ratio. These results indicate that addition of carbon dioxide into the

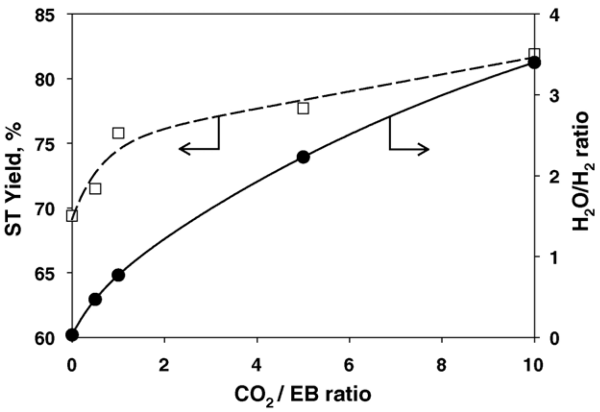

Fig. 2. Styrene yields and H_2O/H_2 molar ratios over VSb/Al catalyst at 595 °C as a function of CO_2/EB molar ratio in the reaction mixture.

reaction mixture leads to the profound effect on the catalyst activity and stability in parallel with the increase of contribution to the oxidative dehydrogenation route at the expense of non-oxidative one.

Among the factors determining the catalytic properties of vanadium oxide-based catalysts, the redox behavior of vanadium oxide is known to play a key role in oxidative dehydrogenation, oxidation and ammoxidation of hydrocarbons in accordance with Mars-van-Krevelen mechanism [7]. It can consequently be proposed that facile redox cycle between fully oxidized and reduced vanadium species yields the more effective catalyst. Likewise, the CO_2-EBDH is expected to follow the same mechanism. The oxidation products are formed in the reduction step on V-active sites to generate the reduced sites with oxygen vacancy followed by re-oxidation with the proper oxidant, carbon dioxide in the CO_2-EBDH. On the basis of catalytic and characterization results, the similar redox mechanism could be reasonably proposed for the CO_2-EBDH over the VSb/Al catalyst. The effective redox cycle of the catalyst would be likely to occur between V^{5+} and V^{4+} because after the CO_2-EBDH run, average oxidation state of surface vanadium species of the VSb/Al catalyst was shown (XPS) to be almost highest, namely 4.84, without any contribution from V^{3+} [6].

The XRD patterns of the VSb/Al catalyst do not reveal crystalline vanadium oxides before and after the reaction. Instead, an intermediate phase of mixed vanadium–antimony oxide, $V_{1.1}Sb_{0.9}O_4$, is newly appeared in the XRD pattern of the fresh VSb/Al. This result implies that vanadium oxides are well dispersed in the Sb-promoted catalysts and the mixed phase of V–Sb oxide can be formed at an optimal ratio of V/Sb. The catalytic activity of the VSb/Al in the CO_2-EBDH is mainly determined by the supported VO_x species whereas the presence of SbO_x positively affects the catalyst stability through the facilitation of the redox cycle as evidenced by H_2-TPR and subsequent CO_2-pulse reoxidation to confirm the vanadium redox cycle in the reaction [6]. Thus, the H_2-TPR analysis of the VSb/Al catalyst revealed that the addition of antimony to the V/Al catalyst increases the reducibility of vanadium oxide. The subsequent CO_2-pulse experiments showed that the dissociative adsorption of CO_2 on the reduced vanadium oxide of the catalysts produces CO and surface oxygen and re-oxidizability of the VSb/Al catalyst with oxygen species originated from CO_2 is much higher than that of the V/Al catalyst.

In the O_2-EBDH, the total oxidation of styrene might be caused by an electrophilic molecular form of adsorbed oxygen species on isolated reduced sites, O_2^{-}. The formation of atomic lattice oxygen, O^{2-}, which is useful for selective oxidations of hydrocarbons, needs at least two oxygen vacancies in the vicinity. The deficit of pair neighboring oxygen vacancies can hinder the re-oxidation step with dioxygen. In contrast, carbon dioxide might be adsorbed dissociatively on an accessible single oxygen vacancy. As a result, oxygen species generated from CO_2 can re-oxidize the reduced vanadium site and keep the surface vanadium ions at high oxidation state improving thus the catalyst performance.

In conclusion, carbon dioxide among carrier gases was utilized as the selective and soft oxidant through an oxidative pathway of the EBDH, leading to the highest catalytic activity and styrene selectivity along with the relatively stable catalytic performance.

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