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Synthesis of C4 olefins from n-butane over a novel $VO_x/SnO_2–ZrO_2$ catalyst using CO_2 as soft oxidant

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ABSTRACT

Oxidative dehydrogenation (ODH) of n-butane was investigated over ZrO_2, SnO_2 and $SnO_2–ZrO_2$ mixed oxide supported vanadium oxide catalysts with the aim of utilizing CO_2 as the soft oxidant, and to study the effect of mixed oxide support on the ODH activity and C4 olefins selectivity. The acid–base properties, reducibility, surface area and morphology of the $SnO_2–ZrO_2$ mixed oxide and its individual component oxide supported vanadium oxide samples were thoroughly studied. The mixed oxide supported vanadia sample exhibited superior acid–base bifunctionality; in particular, more numbers of medium strength acid–base sites were observed. The reduction temperature of the vanadia was observed to decrease in the case of mixed oxide supported vanadia catalysts. The mixed oxide supported vanadia sample exhibited a high conversion and product selectivity than its individual component oxide supported vanadia samples. A significant difference in the catalyst activity was noted in the presence and absence (He) of CO_2 feed gas. Among various catalysts evaluated, the $VO_x/SnO_2–ZrO_2$ catalyst exhibited excellent performance (22.34 and 36.63% conversion of n-butane and selectivity of C4 olefins, respectively), which is attributed to a high specific surface area, superior acid–base bifunctionality and easily reducibility of the dispersed vanadium oxide.

1. Introduction

The rising level of carbon dioxide (CO_2) in the atmosphere has a detrimental effect on the environment, mainly contributing to global warming [1]. Reducing the release of CO_2 and implementing CO_2 recycling techniques have therefore become increasingly important. On the other hand, conversion of CO_2 via catalytic reactions is considered as one of the most promising approaches for CO_2 abatement. Recently, much attention has been devoted toward utilization of CO_2 as an oxygen source or non-traditional (soft) oxidant and oxygen transfer agent [2,3]. In our previous studies, we have investigated the soft oxidant nature and promotional effect of CO_2 in various reactions [3–6]. The utilization of CO_2 as a soft oxidant will provide several potential advantages, which are normally encountered in conventional processes such as deep oxidation, low product selectivity and the formation of CO_2 greenhouse gas as a by-product [7]. Moreover, the utilization of CO_2 in the ODH process can encompass several prominent features like alleviating the thermodynamic equilibrium limitations, minimizing the hot spot phenomenon on the catalyst surface, poisoning the nonselective sites of the catalysts, accelerating the reaction rate, enhancing the selectivity and suppressing the total oxidation products [4,8–11]. On the other hand, such consumption of CO_2 shows a significant positive impact on the global carbon balance.

The unsaturated hydrocarbons are most important building block chemicals in the industry. Among the paraffins, n-butane is the least intensively studied alkane in the ODH processes where CO_2 is used as an oxidant. In the dehydrogenation of higher alkanes, generally the produced olefins contain allylic hydrogen. The bond dissociation energy of allylic hydrogen is much lower than that of the starting substrate. Thus, the abstraction of hydrogen from the allylic position may proceed more rapidly to produce coke precursors. Therefore, avoidance of the deactivation of the catalyst is very difficult, which consequently results low yields of olefins [12,13]. Moreover, the formed alkenes are approximately four times more reactive than butane. The high reactivity of alkenes causes the lower selectivity to the desired products with increasing the conversion of butane [14]. Therefore, design of a selective catalyst with high yields of alkenes remained a challenge in catalysis. Vanadium oxide based materials are very often used as catalysts in the ODH reactions [15]. We have also studied various vanadium oxide based catalysts for the ODH of aromatic hydrocarbons [4–6,8,16,17]. Various vanadium oxide catalytic systems such as VMgO [18], VO_x/SiO_2 [19], VO_x/Al_2O_3 [20], V_2O_5/ZrO_2 [21], VO_x/SBA-15 [22] and VO_x/USY [23] were reported in the literature for the synthesis of C4 olefins (1-butene, trans-2-butene,

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