V–$BaCO_3$ catalysts for the oxidative dehydrogenation of ethane

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A new type of supported vanadium oxide catalyst V–$BaCO_3$, which consists of barium orthovanadate $Ba_3(VO_4)_2$ and $BaCO_3$ phases, has been used in the oxidative dehydrogenation of ethane. The catalyst with the ratio of V/Ba from 0.1 to 0.3 exhibited high catalytic activity for oxidative dehydrogenation of ethane, with particularly high activity for ethene production.

Keywords: supported vanadium oxide catalyst, V–$BaCO_3$, oxidative dehydrogenation, light alkane, ethane, barium orthovanadate $Ba_3(VO_4)_2$, $BaCO_3$

1. Introduction

Vanadium oxide-based catalysts have become an important class of catalytic materials because of their numerous industrial applications in heterogeneous catalytic selective oxidation reactions and their use as model systems for fundamental catalyst studies [1–3]. It has been demonstrated that vanadium oxide-based catalysts, particularly containing the crystalline phases of orthovanadate, pyrovanadate and metavanadate, exhibit a significant catalytic activity for the oxidative dehydrogenation of light alkanes [3,4]. For instance, V–Mg–O catalysts, which coexist with MgO and $Mg_3(VO_4)_2$ phases, show particularly high activity for the oxidative dehydrogenation of ethane, propane and butane [4]. Recently, however, we have developed a new type of supported vanadium oxide catalyst, V–$BaCO_3$, which consists of barium orthovanadate $Ba_3(VO_4)_2$ and $BaCO_3$ phases, and have successfully applied the V–$BaCO_3$ catalyst for the oxidative coupling of methane with a particularly high activity for ethene and ethane production [5]. The conclusion from catalytic activity and characterization of the catalysts with X-ray diffraction was that the active phase can be attributed to the co-operation of $BaCO_3$ and small amounts of $Ba_3(VO_4)_2$ phases, and that the selective production of ethene and ethane is due to the absence of V=O groups and the basic properties of the catalysts.

Oxidative dehydrogenation of ethane to ethene is a potentially important process to utilize ethane. To date, however, there are a few vanadium-containing catalysts developed for the oxidative dehydrogenation of ethane [6–12]. Kung and colleagues have applied the V–Mg–O catalyst, containing $Mg_3(VO_4)_2$ and MgO phases, to the oxidative dehydrogenation of ethane, but the selectivity for ethane was low [4]. We now report that V–$BaCO_3$ catalysts, which have been previously used in oxidative coupling of methane in this laboratory [5], have been applied to the oxidative dehydrogenation of ethane to produce ethene, with a particularly high activity for ethene production.

2. Experimental

The preparation of these catalysts has been described previously [5]. Briefly, the catalysts with V/Ba atomic ratios varying from 0.0 to 1.0 were prepared by a conventional impregnation method: i.e., $BaCO_3$ powder was added to a hot aqueous solution containing an appropriate amount of NH_4VO_3 with constant stirring for an hour, then the mixture was evaporated to dryness and followed by drying at 110 °C. The final step was the calcination at 820 °C in air for 4 h.

The phase identification of the catalysts was performed by X-ray diffraction on a D/MAX-RB Rigaku powder diffractometer using Cu Kα radiation. The XRD results of the catalysts are shown in table 1. Three phases are identifiable: $BaCO_3$, $Ba_3(VO_4)_2$ and $Ba_2V_2O_7$. The ratio $I_{Ba_3(VO_4)_2(110)}/I_{BaCO_3(111)}$ was used to indicate the relative amounts of $Ba_3(VO_4)_2$ and $BaCO_3$ phases.

To measure catalyst activity, 0.5 ml of the catalyst from 30 to 60 mesh was placed in a flow microreactor with verti-

Table 1
Identification of V–$BaCO_3$ catalysts by X-ray diffraction.

V/Ba ratio	Phase identified	I_V/I_{Ba} [a]
0.00	$BaCO_3$	0.0
0.05	$BaCO_3 + Ba_3(VO_4)_2$	0.16
0.10	$BaCO_3 + Ba_3(VO_4)_2$	0.22
0.25	$BaCO_3 + Ba_3(VO_4)_2$	0.31
0.50	$Ba_3(VO_4)_2 + BaCO_3 + (Ba_2V_2O_7)$ [b]	1.25
0.70	$Ba_3(VO_4)_2 + BaCO_3 + Ba_2V_2O_7$	2.05
1.00	$Ba_2V_2O_7 + (BaCO_3)$ [b]	–

[a] Indicating the ratio of $I_{Ba_3(VO_4)_2(110)}$ to $I_{BaCO_3(111)}$.
[b] Very weak diffraction patterns were detected.

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cal quartz tubes as described in [13], but the internal diameter of the external tube was 8 mm and the external diameter of the internal tube was 4 mm. Reaction temperatures were monitored by a thermocouple adjacent to the quartz tube. The reacting gas mixture consisted of 13% ethane, 10% oxygen and nitrogen as diluent. The conversion of ethane in the empty reactor increased with increasing temperature, but was negligible ($<2\%$) even though reaction was carried out at 650 °C. All reactants and products were analyzed using two gas chromatographs with thermal conductivity detectors. A Porapak Q column was used for CO_2, CH_4, C_2H_4 and C_2H_6 separation and a 5A molecular sieve column for O_2, N_2 and CO separation. The catalysts were allowed to equilibrate under reaction conditions for at least 30 min. The ethane conversion and product selectivity were defined as described in [4].

3. Results

The results of catalytic activity of V–$BaCO_3$ catalysts for the oxidative dehydrogenation of ethane are presented in table 2. Under the conditions used, the catalysts are catalytically active for oxidative dehydrogenation of ethane, but the activity decreases with increasing V/Ba ratio and increases with increasing temperature. When the V/Ba ratio is <0.5, the catalysts have small amounts of a $Ba_3(VO_4)_2$ phase together with a great amount of the $BaCO_3$ phase and exhibit particularly high activity for ethene production. The activity of these catalysts is higher than that of the well-known V–Mg–O catalyst reported by Kung and co-workers in the oxidative dehydrogenation of ethane [4]. When the V/Ba ratio is >0.5, large amounts of the $Ba_3(VO_4)_2$ phase are formed together with small amounts of the $BaCO_3$ phase and new phase of barium pyrovanadate $Ba_2V_2O_7$. These catalysts are of relatively weak activity for ethane conversion. By comparison, however, the pure $BaCO_3$ catalyst shows some activity for ethene production. In addition, it is interesting to note that the behaviour of these catalysts for the oxidative dehydrogenation of ethane is quite similar to that for the oxidative coupling of methane [5], i.e., the catalysts with V/Ba ratio <0.5 are particularly active for oxidative coupling of methane and oxidative dehydrogenation of ethane.

Kung and co-workers have used barium orthovanadate $Ba_3(VO_4)_2$ in the oxidative dehydrogenation of butane and observed that the catalytic activity declined with time on stream due to the decomposition of the $Ba_3(VO_4)_2$ phase to $BaCO_3$ [14]. The XRD results confirmed the presence of the $BaCO_3$ phase in used catalysts. In our case, however, V–$BaCO_3$ catalysts are stable even after reaction for 20 h. The XRD results still showed the presence of the $Ba_3(VO_4)_2$ phase and no other new phase was formed. The $Ba_3(VO_4)_2$ phase in these V–$BaCO_3$ catalysts decomposes less readily. It is obvious that the chemical equilibrium of decomposition reaction of the $Ba_3(VO_4)_2$ phase would play one role in the stability of the $Ba_3(VO_4)_2$ phase in these V–$BaCO_3$ catalysts.

The dependence of activity and selectivity of the catalysts on reaction temperature is shown in table 2. The reac-

Table 2
The results of catalytic activity of V–$BaCO_3$ catalysts for oxidative dehydrogenation of ethane.[a]

V/Ba ratio	Reaction T (°C)	C_2H_6 conv. (mol%)	Selectivity (mol%)			C_2H_4 yield (mol%)
			CO	CO_2	C_2H_4	
0.00	550	3.2	–	22.0	78.0	2.5
	600	6.2	–	26.5	72.5	4.6
	650	18.6	2.7	19.3	78.0	14.5
0.05	550	3.2	–	27.4	72.6	2.2
	600	8.6	–	20.9	79.1	6.8
	620	9.9	3.0	17.5	79.5	7.9
	650	23.1	3.5	14.2	82.3	19.0
0.10	550	3.2	–	25.9	74.1	2.4
	600	9.2	–	18.5	81.5	7.5
	620	19.3	5.7	15.0	79.3	15.3
	650	32.5	7.0	14.9	78.1	25.4
0.25	550	3.0	–	37.5	69.5	2.5
	600	11.0	–	22.7	77.3	8.5
	620	22.0	4.9	17.1	77.9	17.1
	650	34.0	7.0	16.5	76.5	26.0
0.50	550	1.5	–	46.7	53.3	0.8
	600	4.5	–	29.0	71.0	3.2
	650	15.4	4.5	17.5	77.9	12.0
0.70	550	0.7	–	42.8	57.2	0.4
	600	3.0	–	26.6	73.4	2.2
	650	6.9	–	22.1	76.9	5.3
1.00	550	1.2	–	–	100.0	1.2
	600	3.4	–	17.7	82.3	2.8
	650	9.3	6.4	15.6	77.4	7.2

[a] Reaction conditions: GHSV $= 0.6 \times 10^3$ h^{-1}; $C_2H_6 = 13\%$, $O_2 = 10\%$.

tion temperature has a marked effect on the catalytic activity and product distribution. At low temperature, the ethane conversion is low. Significant conversion of ethane takes place at temperature >600 °C, leading to the high yield of ethene. That conversion of ethane increases with reaction temperatures is consistent with that in other vanadium-containing oxide catalysts [6–12].

In comparing some vanadium-containing oxide catalysts such as V–P–O, Mo–V–O and V–Mg–O catalysts, however, it seems in our case that V–$BaCO_3$ catalysts have a high reaction temperature for obtaining significant conversion of ethane. The VPO catalysts, being completely different from V–$BaCO_3$ and V–Mg–O catalysts in structure and phase composition, are well known to be highly active and selective in the oxidation of n-butane to maleic anhydride. These catalysts, however, have been used to the oxidative dehydrogenation of ethane [4,7]. At the mild reaction temperature, a considerable high selectivity (up to 80%) to ethene over pure $(VO)_2P_2O_7$ phase catalyst was obtained by Kung's group [4]. At the high reaction temperature (about 500 °C) a high selectivity (>80%) to ethene at 12% conversion of ethane over the V–P–O catalysts of a high P/V ratio of 1.15 were obtained by Merzouki and colleagues [7]. The Mo–V–O catalysts are important catalysts for selective dehydrogenation of light alkanes [21]. However, when the other components, especially the niobium, are added to the system, the catalyst exhibits high activity and selectivity for ethene production. The pioneering work by Thorsteinson et al. [6] reported that MoVNb oxide catalysts were active at reaction temperature as low as 200 °C. Furthermore, these catalysts were found to give selectivity to ethene of 100% at 10% conversion. Their data, however, have not been confirmed by the recent studies on the same catalysts [8]. The active phase for oxidative dehydrogenation of ethane is still a controversial subject [6,8]. Nevertheless, the presence of niobium in V–Mo–O catalysts is important for enhancing the ethene selectivity in the oxidative hydrogenation of ethane. V–Mg–O catalysts, quite similar to V–$BaCO_3$ in structure and phase composition, have been applied to the oxidative dehydrogenation of ethane. However, very low ethene selectivity (20–30%) was obtained at the reaction temperatures of 500–570 °C [4].

Figure 1 shows the dependence of selectivity on conversion for V–$BaCO_3$ catalysts with V/Ba atomic ratio of 0.05–0.25 at 620 °C. All samples were tested in similar experimental conditions. The space velocity GHSV was varied from 0.6×10^3 to 6.8×10^3 h^{-1}. As expected, the ethene selectivity decreases with increasing ethane conversion, but the decrease is very slow. All the catalysts in figure 1 exhibit a similar performance. The results in table 1, however, indicate that the catalysts with V/Ba ratio of 0.05–0.25 in figure 1 also have a similar phase composition, i.e., these catalysts have small amounts of a $Ba_3(VO_4)_2$ phase and a great amount of the $BaCO_3$ phase. The catalysts with a similar phase composition exhibit a similar performance in oxidative dehydrogenation of ethane.

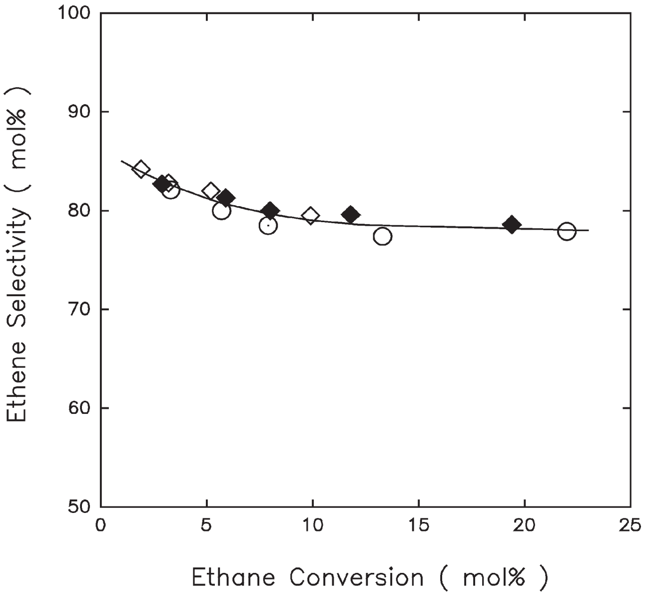

Figure 1. Ethene selectivity as a function of ethane conversion on V–$BaCO_3$ catalysts with V/Ba ratio: (◇) 0.05; (◆) 0.1; (○) 0.25. Reaction conditions: $T = 620\,°C$, $C_2H_6 = 13\%$, $O_2 = 10\%$. GHSV = $0.6–6.8 \times 10^3$ h^{-1}.

4. Discussion

It is well known that V–Mg–O catalysts are efficient for the oxidative dehydrogenation of light alkanes [3,4]. There are three magnesium vanadate phases, i.e., orthovanadates, pyrovanadates and metavanadates in this working catalyst which depend on vanadium concentration and calcination temperature. Although two isolated phases have been proposed to be responsible for the selective oxidation of light alkanes [14–16], one can note from these studies that in V–Mg–O working catalysts, the coexistence of more than one phase has been identified. Thus it is reasonable to suggest that the active phases for oxidative dehydrogenation of light alkane could be attributed to at least more than one phase. This conclusion has been further promoted by Delmon and co-workers [17]. However, in the present studies, V–$BaCO_3$ catalysts, which consist of $BaCO_3$ and $Ba_3(VO_4)_2$ phases, are quite similar to the V–Mg–O catalysts which consist of MgO and $Mg_3(VO_4)_2$ phases [4,15]. Thus it is reasonable to assume that the $BaCO_3$ and $Ba_3(VO_4)_2$ phases in V–$BaCO_3$ catalysts could be contributed to the active phases in selective oxidation. This has been proposed in our previous work on oxidative coupling of methane [5]. The present results indicate that pure $BaCO_3$, a relatively large amount of the $Ba_3(VO_4)_2$ phase and the barium pyrovanadate $Ba_2V_2O_7$ phase exhibit a relatively weak activity for ethane conversion. However, the V–$BaCO_3$ catalysts, which consist of $BaCO_3$ and small amounts of $Ba_3(VO_4)_2$ phases, exhibit a particularly high activity for oxidative dehydrogenation of ethane. Therefore, it is proposed that the observed activity results from the co-operation of $BaCO_3$ and small amounts of $Ba_3(VO_4)_2$ phases.

By comparison, it is interesting to note that V–Mg–O and the V–$BaCO_3$ catalysts of this paper are very different from TiO_2-, Al_2O_3- and SiO_2-supported V_2O_5 catalysts [1]. The high density of V=O groups on the surface of the latter three supported V_2O_5 catalysts, which tend to form C–O bonds in the reaction due to their stronger nucleophilicity [18], have been proposed to be responsible for the selective oxidation to oxygenation or combustion products, for example, partial oxidation of methane to formaldehyde and methanol, and partial oxidation of alkane to alcohols and aldehydes [12,20]. On the other hand, both V–Mg–O and V–$BaCO_3$ catalysts possess orthovanadate phase in which there are only isolated tetrahedral VO_4 groups and no V=O or V–O–V groups, and these are relatively basic [4,19]. Thus, the lattice oxygen ions in the V–O–M bridging bonds are relatively less reactive, and the tendency for the formation of C–O bonds is low. Consequently, the oxidative dehydrogenation of alkane is predominant on these catalysts.

For the oxidative dehydrogenation of ethane there are two reaction mechanistic routes proposed in literature [22]. One is that ethyl radicals are generated by catalysts and then catalyze the homogeneous gas-phase conversion of ethane to ethene; the other is that ethene is formed via surface ethoxide species which are generated by the surface lattice oxygen of catalysts. Moreover, it is generally accepted that the relative importance of these two mechanisms will be dependent on reaction temperature and the nature of catalysts [8]. A high reaction temperature may result in a greater tendency for generating ethyl radicals to desorb into gas phase; the reducible oxide catalysts may result in a greater tendency to form ethoxide species on the surface of the catalysts. Thus, it is worth noting in our case that the reaction over V–$BaCO_3$ catalysts at relatively high reaction temperatures would be a surface-catalyzed reaction or a surface-generated free-radical reaction. Based on the consideration mentioned above, it is suggested that the use of the relatively high reaction temperature in our case does not eliminate the possibility that this reaction might be mainly a surface-generated ethyl radical reaction even though the presence of reducible oxide catalysts and the absence of a significant conversion in an empty reactor at relatively high temperatures. However, a further detailed study on reaction mechanism, which is excess the subject of this paper, is necessary to confirm this assumption.

5. Conclusion

V–$BaCO_3$ catalysts have high activity and selectivity for the oxidative dehydrogenation of ethane. The active phase is attributed to the co-operation of $BaCO_3$ and small amounts of $Ba_3(VO_4)_2$ phases. The selectivity could be a result from the absence of V=O groups and the basic properties of the catalysts. Similar to the performance of V–Mg–O catalysts, one can expect that V–$BaCO_3$ catalysts can also be used in oxidative dehydrogenation of propane and butane.

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