Catalysis Letters 38 (1996) 181–188

Platinum–tin and platinum–copper catalysts for autothermal oxidative dehydrogenation of ethane to ethylene ☆

C. Yokoyama,
Department of Applied Chemistry, Faculty of Engineering, The University of Tokyo,
Hongo 7-3-1, Bunkyo-ku, 113 Tokyo, Japan

S.S. Bharadwaj and L.D. Schmidt [1]
Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455, USA

Received 10 September 1995; accepted 11 January 1996

The addition of various metals to Pt-coated ceramic foam monoliths was examined for the autothermal oxidative dehydrogenation of ethane to ethylene at ~900°C at contact times of ~5 ms. The addition of Sn or Cu to Pt-monoliths enhanced both C_2H_6 conversions and C_2H_4 selectivities significantly, giving higher C_2H_4 yields. No deactivation or volatilization of the catalysts was observed. For Pt–Sn, an increase in the Sn/Pt ratio from 1/1 to 7/1 increased both the conversion and the selectivity. For Pt–Sn (Sn/Pt = 7/1) versus Pt alone the conversion increased by up to 6% and the selectivity up to 5% for an increase in optimal yield from 54.5% with Pt to 58.5% with Pt–Sn. XRD and XPS measurements showed that Pt existed in the form of PtSn and Pt_3Sn alloys. The 1/1 Pt–Cu catalyst showed comparable performance, with conversion increasing by 5% and selectivity by 3%. The addition of several other metals to Pt-monoliths decreased both C_2H_6 conversion and C_2H_4 selectivity in the order, Sn > Cu > Pt alone> Ag > Mg > Ce > Ni > La > Co. For oxidative dehydrogenation of *n*-butane and isobutane, Pt–Sn and Pt–Cu also showed higher conversion than Pt.

Keywords: oxidative dehydrogenation; catalytic alkane oxidation; olefin production; Pt–Sn catalysts

1. Introduction

Light alkanes are the preferred feedstocks for producing olefins by thermal pyrolysis. However, thermal dehydrogenation processes for olefin production are highly endothermic and require complex tube furnaces [1].

An alternate route to olefin production is oxidative dehydrogenation of alkanes which offers the advantages of faster and exothermic reactions. In earlier investigations of both catalytic and non-catalytic oxidative dehydrogenation [2–13], the conversions at the desired selectivity levels were too low to give acceptable product yields. However, in recent investigations in this laboratory, olefin production by catalytic oxidation of light alkanes was studied over Pt- and Rh-coated ceramic foam monoliths at contact times of the order of milliseconds [14,15]. Olefin selectivities in the range of 65–70% at > 80% conversion were observed on Pt-coated monoliths for ethane, propane, *n*-butane and isobutane. This very short contact time potentially allows the use of reactors 100 to 1000 times smaller than those currently used for the same yield. Also, unlike the thermal pyrolysis reactor, which must be externally heated, the catalytic oxidative dehydrogenation reactor operates autothermally and nearly adiabatically, thus further reducing operating costs.

In this study, we investigate the effect of addition of various metals to Pt-coated monoliths for autothermal oxidative dehydrogenation of ethane to ethylene. We also discuss the mechanism of oxidation of ethane, *n*-butane and isobutane.

2. Experimental

2.1. Catalyst

The Pt–M (M = Sn, Cu, Ag, Mg, Ce, La, Ni, Co, and Au) bimetallic catalysts were prepared as follows. First, Pt was added to α-Al_2O_3 foam monoliths (17 mm diameter×10 mm long, 45 pores per inch (ppi)) by impregnation with aqueous solutions of H_2PtCl_6. The samples were dried in vacuum at room temperature, followed by calcination at 100°C for 0.5 h and at 350°C for 2 h in oxygen. The second metal was then added by impregnation with aqueous solutions of corresponding metal salts: $SnCl_2$, $Cu(NO_3)_2$, $AgNO_3$, $Mg(NO_3)_2$, $Ce(NO_3)_3$, $La(NO_3)_3$, $Ni(OOCCH_3)_2$, $Co(OOCCH_3)_2$ and $AuCl_3$. The Pt–M monoliths were then dried in vacuum at room temperature, calcined at 100°C for 0.5 h and at 700°C for 1.5 h in oxygen, and then reduced at

---

☆ This research was partially supported by NSF under Grant CTS-9311295.

[1] To whom correspondence should be addressed.

700°C for 1.5 h in hydrogen. Pt loadings of all samples were either 2 or 5 wt%. The other metal loadings are summarized in table 1.

2.2. Apparatus and procedure

The reactor used was essentially identical to those described previously for the oxidative dehydrogenation of alkanes [14,15]. The catalyst was sandwiched between two inert α-Al_2O_3 monoliths which act as radiation shields. These monoliths were sealed in the quartz tube by silica–alumina cloth, and the reactor was insulated by wrapping the quartz tube with high-temperature insulation. The temperature at the back of the catalyst was measured by a Pt–Pt/Rh thermocouple placed between the catalyst and the downstream radiation shield.

The reactions examined were the oxidative dehydrogenation of ethane, *n*-butane, and isobutane. Gas flows into the reactor were controlled by mass flow controllers. The feed flow rate was 5 standard liters per minute (slpm), corresponding to 37 cm/s superficial velocity (feed gases upstream from the catalyst) at room temperature and atmospheric pressure and ~250 cm/s in the monolith at reaction conditions. For ethane oxidation the C_2H_6/O_2 ratio was varied from 1.5 to 2.1 at a fixed nitrogen dilution (30%). For butane oxidation, C_4H_{10}/O_2 ratio was changed from 0.8 to 1.4 at 50% nitrogen dilution. In all experiments, the reactor pressure was maintained at 1.4 atm.

The product gases were analyzed by a gas chromatogragh equipped with a single Hayesep DB packed column. For quantitative determination of concentrations, standards were used for all species except for H_2O, which was obtained most reliably from an oxygen atom balance. Nitrogen was used as an internal GC calibration standard. The selectivity data shown was calculated on a carbon atom or a hydrogen atom basis, as described previously [14].

2.3. Light-off

In all experiments the catalysts were operated autothermally and the heat generated by the reaction was sufficient to sustain reactions. However, heat was needed initially to ignite the reaction. For ignition, a mixture of alkane and oxygen was fed to the reactor, and the reactants were heated using a Bunsen burner. After light-off, the external heat source was removed, and the reaction parameters were adjusted to the desired conditions. For situations where catalyst was not ignited in the mixture of alkane and oxygen, a NH_3/O_2 mixture was used for light-off and NH_3 was then gradually exchanged for the alkane.

The effect of preheat of reaction gases was examined for the best catalyst. The preheat temperature was measured in absence of reaction by a thermocouple located immediately before the upstream shield by flowing only $N_2 + O_2$ through the reactor.

Shutdown of the reactor was accomplished by turning off oxygen before alkane.

3. Results

3.1. Ethane

For C_2H_6 oxidation, the major products over all catalysts were C_2H_4, CO, CO_2, CH_4, H_2, and H_2O. Traces of C_2H_2, C_3H_6, C_3H_8, and C_4H_8 were observed, usually with selectivities < 2%. The conversions of oxygen were always above 97%, so reactions always go to completion.

3.1.1. Pt, Pt–Sn, and Pt–Cu

Figs. 1a, 1b and 1c show the C_2H_6 conversion, C_2H_4 selectivity, and C_2H_4 yield for oxidative dehydrogenation of ethane over Pt, Pt–Sn (Sn/Pt = 7/1), and Pt–Cu

Table 1
Comparison of metals [a]

Catalyst	Atomic ratio (metal/Pt)	Reaction temp. (°C)	Conv. of C_2H_6 (%)	$S_{C_2H_4}$ (%)	S_{CO_x} (%)	$Y_{C_2H_4}$ (%)	Max. $Y_{C_2H_4}$ (at C_2H_6/O_2)
Pt	0	920	69.7	64.9	26.9	45.3	52.7 (1.5)
Pt–Sn	1	912	71.5	68.2	24.1	48.8	55.3 (1.5)
Pt–Sn	3	905	72.8	68.0	24.4	49.5	55.4 (1.5)
Pt–Sn	7	920	75.7	69.0	21.9	52.3	57.4 (1.7)
Pt–Cu	1	928	74.4	68.1	23.8	50.7	55.0 (1.7)
Pt–Cu	3		extinguished in $C_2H_6 + O_2$				
Pt–Ag	1		62.6	64.3	26.4	40.2	51.6 (1.7)
Pt–Mg	3	943	65.1	60.6	33.6	39.5	43.4 (1.7)
Pt–Ce	3	905	60.2	49.7	47.7	29.9	31.2 (1.7)
Pt–La	3	905	56.0	41.7	56.0	23.4	24.8 (1.7)
Pt–Ni	1	905	58.7	46.3	50.4	27.2	29.3 (1.7)
Pt–Co	1	873	50.8	26.8	71.4	13.1	15.3 (1.7)
Pt–Au	1		extinguished in $C_2H_6 + O_2$				

[a] All conversions, selectivities, and temperatures at C_2H_6/O_2 = 1.9 and 5 slpm without preheat. Pt loadings of all catalysts are 2 wt%.

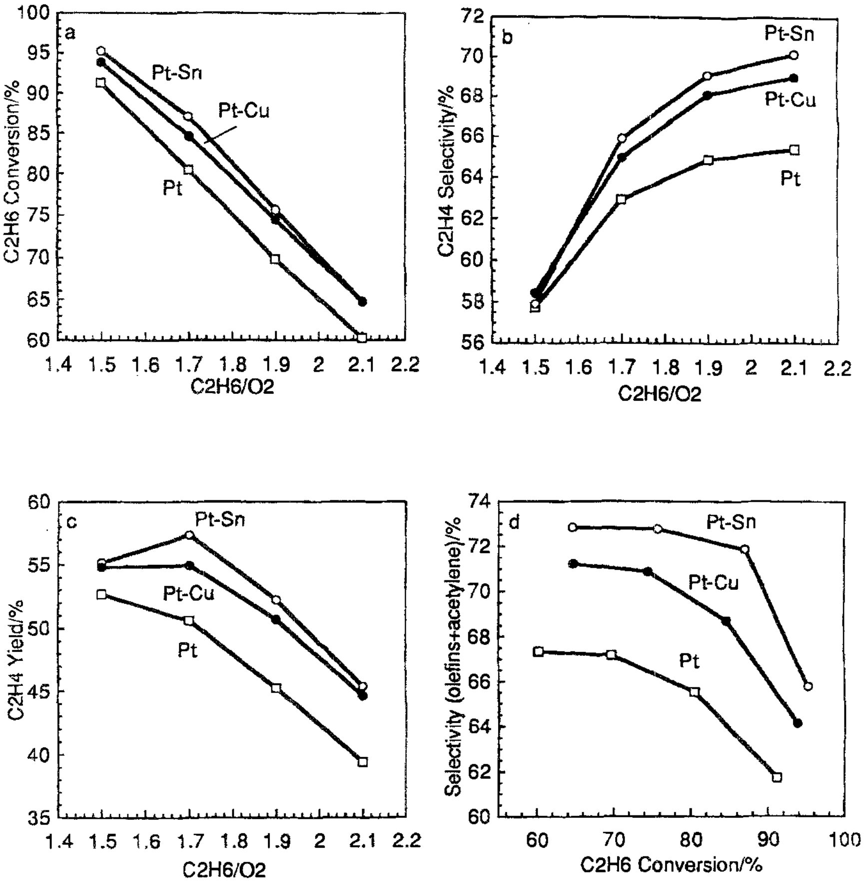

Fig. 1. Comparison of (a) C_2H_6 conversion, (b) C_2H_4 selectivity, and (c) C_2H_4 yield for oxidative dehydrogenation of ethane over Pt-, Pt–Sn- (Sn/Pt = 7), and Pt–Cu- (Cu/Pt = 1) coated α-Al_2O_3 monoliths (Pt loadings are all 2 wt%). (d) Correlation between C_2H_6 conversion and sum of the selectivities to olefins.and acetylene. Total flow rate = 5 slpm at 25°C feed; 30% N_2 diluent.

(Cu/Pt = 1/1) as a function of the feed composition (2.0 is the ethylene stoichiometric ratio). With increasing feed composition, the conversion decreased while the selectivity increased over the three catalysts. The addition of Sn significantly enhanced both the conversion (by ~7%) and the selectivity (by ~5%), which produced the highest C_2H_4 yield of 57% for 25°C feed in this study. The Pt–Cu also showed higher conversion and higher selectivity than Pt, the maximum yield being 55%. As shown in fig. 2, both Pt–Sn and Pt–Cu showed 5–9% lower CO selectivity and 1–2% higher CO_2 selectivity than Pt. It is interesting that CH_4 selectivity was nearly the same on the three catalysts. Among minor products, more C_2H_2 and C_4H_8 were formed on both Pt–Sn and Pt–Cu than on Pt. Thus, the addition of Sn or Cu inhibited CO production and promoted the formation of olefins and acetylene without significant change in CH_4 selectivities. The sum of the selectivities to olefins and acetylene plotted against C_2H_6 conversion in fig. 1d clearly shows that Pt–Sn produced much more olefins and acetylene than Pt.

The reaction temperatures decreased from 1000 to 900°C as the C_2H_6/O_2 ratio increased from 1.5 to 2.1 and temperatures were same to within ±20°C on these three catalysts.

No deactivation or volatilization of the catalysts were observed for several hours. No significant coke formation on the catalysts was observed.

3.1.2. Other metals

The results on the catalysts containing the various metals are summarized in table 1. Pt–Ag exhibited comparable conversion and C_2H_4 selectivity to Pt. Experiments were identical to those described previously [16], but experiments were less extensive for poor catalysts. The addition of the other metals lowered both conversion and C_2H_4 selectivity in the order of Sn > Cu > Pt alone > Ag > Mg > Ce > Ni > La > Co. With lower C_2H_4 selectivity, syngas (CO + H_2) formation became predominant. Pt–Au could not be ignited with $C_2H_6 + O_2$. NH_3 and O_2 were used for light-off. However, the catalyst extinguished quickly when C_2H_6 was introduced in spite of the presence of NH_3 [16].

3.1.3. Loadings of Pt, Sn, and Cu

Fig. 3 shows plots of C_2H_6 conversion and C_2H_4 selectivity as functions of Sn/Pt ratio at a feed near the oxidative dehydrogenation stoichiometry ($C_2H_6/O_2 = 1.9$). The conversion increased with increased Sn/Pt ratio. On the other hand, the addition of a small

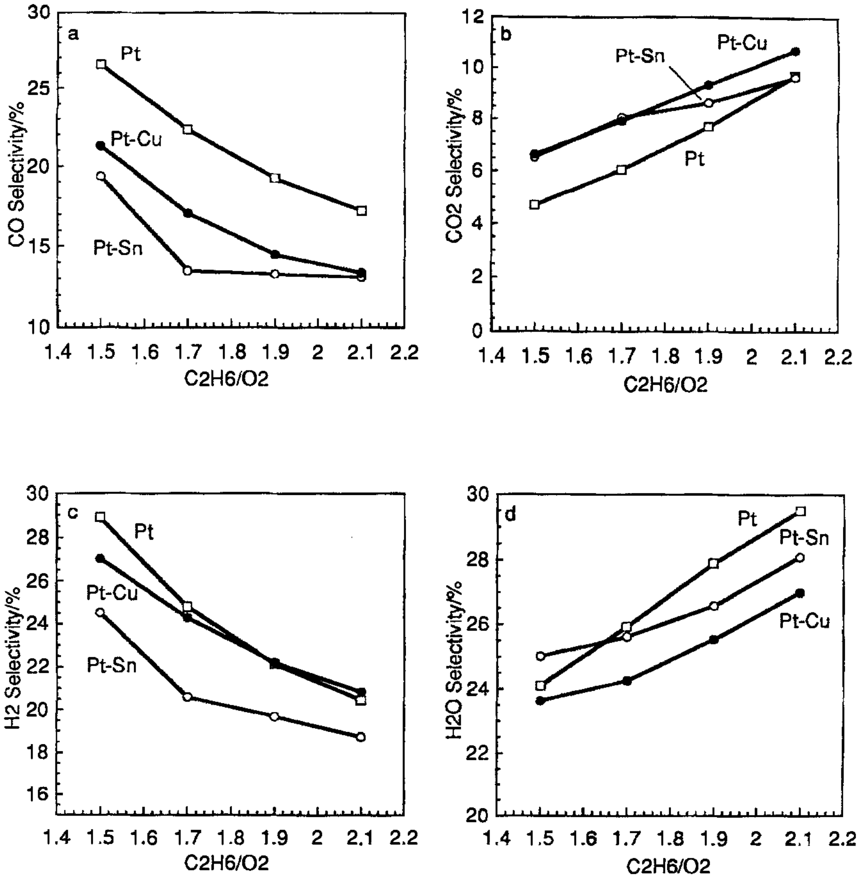

Fig. 2. Comparison of (a) CO, (b) CO_2, (c) H_2, and (d) H_2O selectivities for oxidative dehydrogenation of ethane over Pt-, Pt–Sn-, and Pt–Cu-coated α-Al_2O_3 monoliths (the same experiment as in fig. 1).

amount of Sn (Sn/Pt = 1/1) enhanced the selectivity significantly and the further addition led to a slight increase in the selectivity.

Pt–Cu (Cu/Pt = 1/1) showed comparable results to Pt–Sn, as described above. However, Pt–Cu (Cu/Pt = 3/1) could not be ignited in the mixture of C_2H_6 and O_2. A NH_3/O_2 mixture was used for ignition, but the catalyst extinguished upon exchange of NH_3 for C_2H_6.

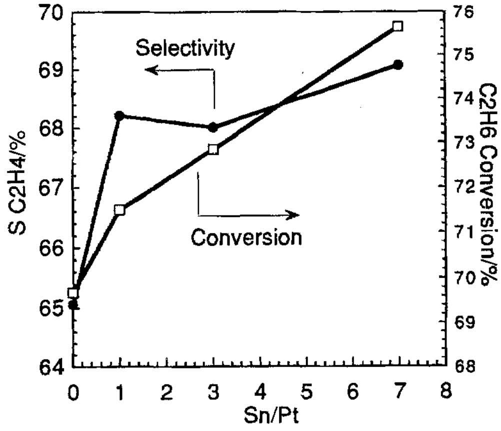

Fig. 3. Effect of the Sn/Pt ratio on C_2H_6 conversion and C_2H_4 selectivity for oxidative dehydrogenation of ethane over Pt–Sn monolith catalysts (Pt loadings are all 2 wt%). C_2H_6/O_2 = 1.9; total flow rate = 5 slpm at 25°C feed; 30% N_2 diluent.

A sample of 5 wt% Pt was nearly identical to 2 wt% Pt, although the C_2H_6 conversion was 1% lower with 5 wt% loading. The addition of Sn to 5 wt% Pt also enhanced both the conversion and C_2H_4 selectivity. The 5 wt% Pt–Sn (Sn/Pt = 1/1) exhibited comparable results (1% higher conversion and 1% lower selectivity) to 2 wt% Pt–Sn (Sn/Pt = 1/1). This fact confirms that Sn acts as a promoter for ethane oxidation, regardless of Pt loadings. 5 wt% Pt–Cu (Cu/Pt = 1/1) did not work autothermally just as the 2 wt% Pt–Cu (Cu/Pt = 3/1).

3.1.4. Preheat

Fig. 4 shows the effect of preheat on the conversion, selectivity, and yield over Pt–Sn (Sn/Pt = 7/1) catalyst at C_2H_6/O_2 = 1.9. Preheat of reaction gases up to 400°C increased the conversion from 77 to 89% and decreased the selectivity from 69 to 65%, which led to an increase in yield from 53 to 58%.

3.2. n-butane

Oxidative dehydrogenation of *n*-butane was examined over Pt, Pt–Sn (Sn/Pt = 3/1), and Pt–Cu (Cu/Pt = 1/1). Both Pt–Sn and Pt–Cu showed much higher

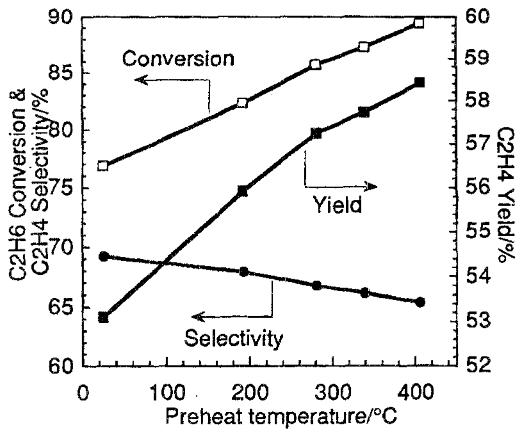

Fig. 4. Effect of preheat of reaction gases on C_2H_6 conversion, C_2H_4 selectivity, and C_2H_4 yield for oxidative dehydrogenation of ethane over Pt–Sn monolith catalysts (Pt = 2 wt%, Sn/Pt = 7). C_2H_6/O_2 = 1.9; total flow rate = 5 slpm; 30% N_2 diluent.

C_4H_{10} conversion (by ~16%) than Pt as a function of feed composition (fig. 5a). On the three catalysts, the selectivities to C_2H_4 and COx decreased and selectivity to C_3H_6 increased with increasing C_4H_{10}/O_2 ratio. The C_4H_8 selectivity was only 3–5% and increased slightly with increasing C_4H_{10}/O_2 ratio. The C_2H_4 selectivity from n-C_4H_{10} was much higher on Pt–Sn and Pt–Cu than on Pt, while the C_3H_6 selectivity was much lower on Pt–Sn and Pt–Cu than on Pt.

However, considerable cracking is predicted in this reaction. With increasing flow rate (decreasing contact time), the C_3H_6 selectivity increased while both C_2H_4 and CH_4 selectivities decreased over Pt-monoliths [17]. This suggests that the mechanism involves cracking of propylene. Therefore, it would be appropriate to compare the selectivities as a function of the conversion rather than as a function of C_4H_{10}/O_2 ratio. As shown in fig. 5b, Pt–Sn and Pt–Cu exhibited higher selectivities to olefins and acetylene than Pt at higher conversion. Correspondingly, COx selectivity was lower on Pt–Sn and Pt–Cu than on Pt. These results are consistent with the fact that Pt–Sn and Pt–Cu exhibited higher C_2H_4 selectivities than Pt for oxidation of ethane.

3.3. Isobutane

Oxidation of isobutane was similar to n-butane. Both Pt–Sn (Sn/Pt = 3/1) and Pt–Cu (Cu/Pt = 1/1)

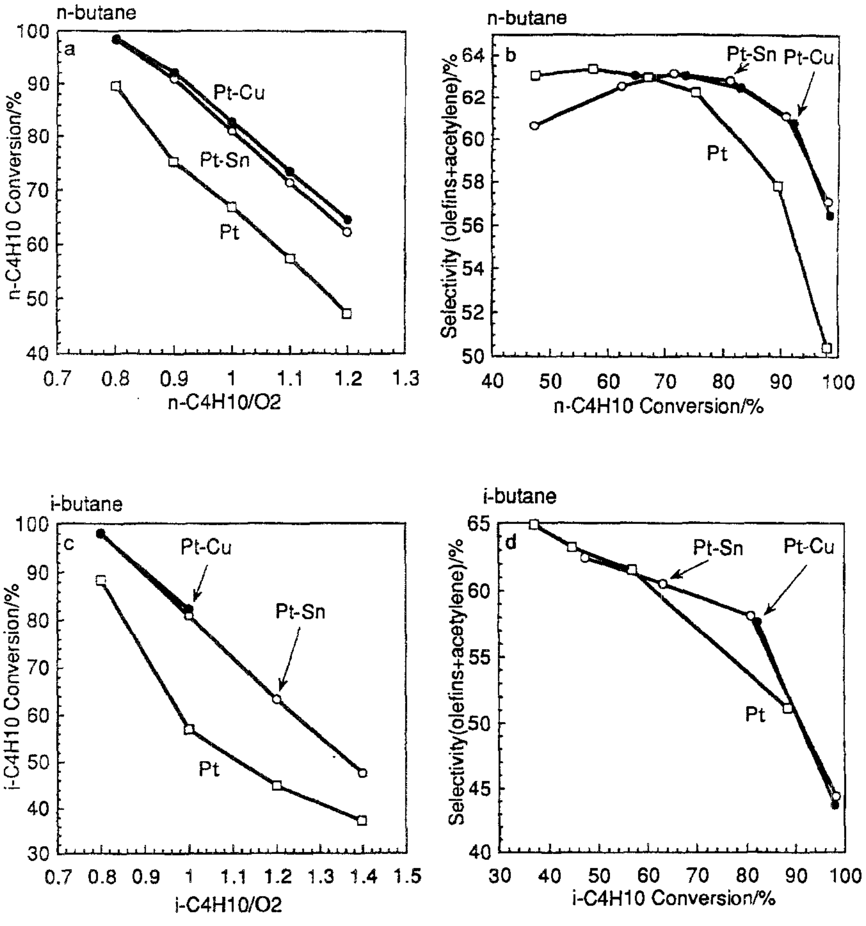

Fig. 5. Conversion of (a) n-butane and (c) isobutane for oxidative dehydrogenation of n-butane and isobutane over Pt, Pt–Sn (Sn/Pt = 3), and Pt–Cu (Cu/Pt = 1) monolith catalysts as a function of the fuel/O_2 ratio. Correlation between conversion and sum of the selectivities to olefins and acetylene for oxidation of (b) n-butane and (d) isobutane. Total flow rate = 5 slpm at 25°C feed; 50% N_2 diluent.

showed much higher conversion (by 15–25%) than Pt (fig. 5c). With i-C_4H_{10} the dominant olefins are i-C_4H_8 (~30%) and C_3H_6 (~30%) as previously observed by Huff and Schmidt [26] for Pt monoliths. On all the three catalysts, selectivities to C_2H_4 decreased and selectivities to C_3H_6 and i-C_4H_8 increased with increasing C_4H_{10}/O_2 ratio. As a function of conversion, Pt–Sn and Pt–Cu exhibited higher selectivities to olefins and acetylene than Pt at high conversion (fig. 5d).

3.4. Characterization

3.4.1. XRD

X-ray diffraction patterns were determined for Pt and Pt–Sn (Sn/Pt = 1/1 and 7/1) catalysts after reaction. On Pt catalyst, only peaks of Pt metal were observed except for that of the α-Al_2O_3 support. On the other hand, only PtSn and Pt_3Sn peaks were observed for Pt–Sn catalysts and there were no Pt metal peaks. The PtSn/Pt_3Sn ratio was higher for Pt–Sn (Sn/Pt = 7/1) than for Pt–Sn (Sn/Pt = 1/1). These results clearly indicate that Pt exists in the forms of only Pt_3Sn and PtSn alloys on the support for Pt–Sn catalyst.

3.4.2 XPS

For XPS measurement of Pt–Sn (Sn/Pt = 1/1), two Sn $3d_{5/2}$ peaks were observed and both can be assigned to Sn^0 (lower BE) and $Sn^{2,4+}$ (higher BE), respectively, according to literature [18]. The peak intensity of Sn^0 was three times larger than that of $Sn^{2,4+}$, indicating that all SnOx was formed by air oxidation after the catalyst was removed from the reactor. These results support the XRD result that Pt exists in the forms of Pt_3Sn and PtSn alloys on the support. Pt 4f peak could not be analyzed because it overlapped with Al 2p.

4. Discussion

4.1. Active sites

The addition of Sn or Cu to Pt-monoliths enhanced alkane conversion and olefin selectivities and suppressed COx formation for the oxidative dehydrogenation reactions. Since Pt exists in the forms of only PtSn and Pt_3Sn alloys on Pt–Sn catalyst, it is presumed that PtSn and Pt_3Sn alloys are the active sites and are more selective to C_2H_4 formation than Pt. Perhaps PtSn has better performance than Pt_3Sn, because both C_2H_6 conversion and C_2H_4 selectivity increased with an increase in PtSn/Pt_3Sn ratio (Pt–Sn (Sn/Pt = 7/1)>Pt–Sn (Sn/Pt = 1/1)).

Pt–Sn catalysts are predicted to be durable at reaction conditions (⩾900°C), because melting points of Pt_3Sn and PtSn alloys are ~ 1300°C. Experimentally, no deactivation or volatilization of the catalysts were observed for at least several hours of operation at ⩾900°C.

4.2. Pt–Sn catalysts

There have been many studies of Pt–Sn catalysts for dehydrogenation of alkanes to alkenes and aromatic products, which are performed in a reducing atmosphere (a mixture of alkanes and hydrogen) but not in the presence of O_2 [19–25]. The major advantages of this catalyst seem to be their lower rate of deactivation and higher selectivity to aromatic products.

In this study, we examine the oxidative dehydrogenation of alkanes on Pt–Sn catalysts. However, it is presumed that these reactions also proceed in a strongly reducing atmosphere, because (i) they are conducted in fuel-rich compositions, (ii) oxygen was almost completely consumed, and (iii) considerable H_2 and CO were produced. Taking this into account, the effect of Sn addition in this study is presumably similar to conventional dehydrogenation of alkanes over Pt–Sn catalysts although the oxidative dehydrogenation process operates at much higher temperature and shorter contact time.

4.3. Mechanism

According to the mechanism proposed by Huff and Schmidt [14], ethane dissociates into C_2H_5(ad) and OH(ad) on the surface. Then β-hydrogen elimination produces C_2H_4(ad), which desorbs to form ethylene. On the other hand, α-hydrogen elimination of C_2H_5(ad) gives CH_4 and/or COx.

As shown in fig. 6, higher C_2H_4 selectivity requires either (i) acceleration of the rate of β-elimination relative to α-elimination or (ii) acceleration of the rate of C_2H_4(ad) desorption relative to further reaction on the surface. The latter possibility seems more plausible for the Pt–Sn catalyst. That is, Pt–Sn alloys desorb C_2H_4(ad) more easily than Pt, which gives higher selectivity to C_2H_4. Some arguments favoring this mechanism are (i) the selectivity to C_2H_2 and C_4H_8, which are probably formed from C_2H_4(ad) and are adsorbed more strongly than C_2H_4(ad), was also higher on Pt–Sn than on Pt, and (ii) there was little difference between Pt–Sn and Pt in the formation of CH_4, which is probably produced via α-elimination. Furthermore, the results by Verbeek and Sachtler showed that ethylene adsorbed on PtSn alloy is desorbed at lower temperature in TPD than on Pt_3Sn and that adsorption of ethylene on Pt resulted in autohydrogenation of the ethylene, and therefore it was not desorbed into gas phase as ethylene [25]. This agrees with our results that the C_2H_4 selectivity increased with an increase in PtSn/Pt_3Sn ratio (Pt–Sn (Sn/Pt = 7/1)>Pt–Sn (Sn/Pt = 1/1)).

Pt–Sn catalyst exhibited higher C_2H_6 conversion than Pt, which is in apparent contradiction to the report

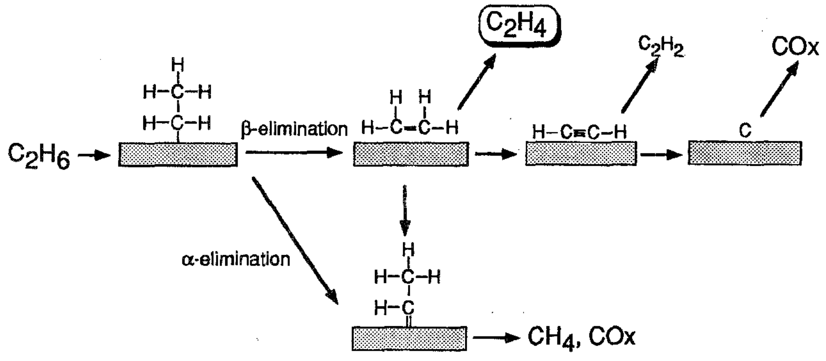

Fig. 6. Sketch of mechanism of oxidative dehydrogenation of ethane to ethylene.

that Pt_3Sn and PtSn alloys are less active than Pt for dehydrogenation of *n*-hexane in hydrogen, although benzene selectivity is higher and carbon formation lower with Sn addition [21]. However, oxygen was almost completely consumed for the oxidative dehydrogenation of ethane over both Pt–Sn and Pt, so that the reaction goes to completion in all of these experiments over both Pt–Sn and Pt. Therefore the observed conversion depends on the selectivity, and the higher selectivity to ethylene (stoichiometric $C_2H_6/O_2 = 2.0$) and the lower selectivity to CO (stoichiometric $C_2H_6/O_2 = 1.0$) inevitably cause higher conversion, even though we expect that the alkane adsorption rate is lower on Pt–Sn than on Pt.

For *n*-butane and isobutane oxidation, Pt–Sn and Pt–Cu exhibited higher selectivities to olefins, which can also be explained by this hypothesis. That is, Pt–Sn releases olefins more easily than Pt, causing higher olefins selectivity, leaving more oxygen to produce high alkane conversions.

4.4. Role of homogeneous reactions

Although our results appear to be explained well by a heterogeneous mechanism we cannot exclude that homogeneous reactions can be neglected especially in the longer residence times of the fluidized bed reactor.

However, the following evidence suggests that heterogeneous reactions dominate: (i) the dramatic differences in product distributions on different metals (Pt and Ag (olefins), Rh and Ni (syngas), and Pd (coke)) strongly suggest heterogeneous reactions [14–17], (ii) thermal pyrolysis involves gas phase free radical reactions which should lead to significant production of acetylene, butadiene, and aromatics (up to 10% on a carbon atom basis [1]) while we do not observe significant production of any of these compounds on noble metal catalysts, (iii) the tortuous path and rough surfaces inside the channels of the monolith provide a high surface area to scavenge free radical chain propagators, and (iv) feed mixtures in our experiments are far outside the flammability regime which reduces the possibility of homogeneous oxidation reactions.

4.5. Comparison with fluidized beds

These results for the monoliths are similar to those previously reported by Bharadwaj et al. for the oxidative dehydrogenation of C_1–C_4 alkanes on Pt [17] and Ag [16] in fluidized bed reactors. However, we note here that C_2H_4 yields from C_2H_6 with pure Pt or pure Ag catalysts in the fluidized bed (60–62%) are 2–4% higher than on the promoted Pt–Sn or Pt–Cu monoliths (~58%) and 5–7% higher than on pure Pt monoliths (~55%).

The general trends in selectivities and conversions with variations in process parameters are very similar for both reactors. Both fluidized bed and monolith reactors achieve high rates of mass transfer of reactants to the catalyst surface, the fluidized bed by gases swirling around small particles and the monolith by gases forced at high velocity through the pores. Since the fluidized bed operates close to the turbulent regime, the gas phase in both types of reactors is more or less in plug flow. Also, both fluidized bed and monolith catalysts have low surface areas and are essentially non-porous. This results in almost purely convective flow through the channels of the monolith and around the small particles in the fluidized bed, allowing quick escape of reaction intermediates from the boundary layer.

The main difference between fluidized beds and monoliths is essentially in their heat transfer characteristics. In the fluidized bed, solids circulation efficiently carries heat back upstream to maintain nearly isothermal conditions. A monolith relies exclusively on solid conduction and radiation to carry heat upstream to minimize temperature gradients which have a detrimental effect on the selectivities. This also explains why C_2H_6 oxidation could be sustained on Pt–Au in the fluidized bed and not on the monolith. A fluidized bed, by virtue of its better heat transfer characteristics allows reactions on metals with lower sticking coefficients than Pt to be sustained more easily than on monoliths.

Although contact times under reaction conditions in the fluidized bed (50–200 ms) are significantly higher than on monoliths (5–10 ms) similar product distributions suggest that reaction steps are the same in both reactors. Bharadwaj et al. [17] suggest that in the fluidized bed almost all of the O_2 is consumed close to the distributor region and actual reaction times are much smaller and of the same order of magnitude as on the monoliths (5–10 ms).

5. Conclusions

The addition of Sn or Cu to Pt-monoliths enhanced both C_2H_6 conversions and C_2H_4 selectivities significantly for the autothermal oxidative dehydrogenation of ethane to ethylene at contact times of ~ 5 ms, which produced higher C_2H_4 yields. For Pt–Sn, the increase in the ratio of Sn to Pt from 1/1 to 7/1 increased both the conversions and olefin selectivities. XRD and XPS measurements showed that Pt existed in the forms of only PtSn and Pt_3Sn alloys for Pt–Sn catalysts and the PtSn/Pt_3Sn ratio increased with the increase in Sn addition. These results indicate that PtSn and Pt_3Sn alloys are probably the active sites and are more selective to C_2H_4 formation than Pt.

References

[1] L.F. Albright, B.L. Crynes and W.H. Corcoran, eds., *Pyrolysis: Theory and Industrial Practice* (Academic Press, New York, 1983).
[2] J. Le Bars, J.C. Vedrine and A. Auroux, Appl. Catal. A 88 (1992) 179.
[3] E. Morales and J.H. Lunsford, J. Catal. 118 (1989) 255.
[4] A. Erdohelyi and F. Solymosi, J. Catal. 129 (1991) 497.
[5] A. Erdohelyi and F. Solymosi, J. Catal. 123 (1990) 31.
[6] P.M. Michalakos, M.C. Kung, I. Jahan and H.H. Kung, J. Catal. 140 (1993) 226.
[7] R. Burch and E.M. Crabb, Appl. Catal. 97 (1993) 49.
[8] R. Burch and E.M. Crabb, Appl. Catal. A 100 (1993) 111.
[9] K. Seshan, H.M. Swaan, R.H.H. Smits, J.G. van Omens and J.R.H. Ross, in: *New Developments in Selective Oxidation*, eds. G. Centi and F. Trifirò (Elsevier, Amsterdam, 1990) p. 505.
[10] M. Kung, K. Nguyen, D. Patel and H. Kung, in: *Catalysis of Organic Reactions*, ed. D.W. Blackburn (Dekker, New York, 1990) p. 289.
[11] L. Owens and H.H. Kung, J. Catal. 144 (1993) 202.
[12] H. Armendariz, G. Aguilar-Rios, P. Salas, M.A. Valenzuela, I. Schifter, H. Arriola and N. Nava, Appl. Catal. A 92 (1992) 29.
[13] Y. Takita, K. Kurosaki, Y. Mizuhara and T. Ishihara, Chem. Lett. (1993) 335.
[14] M. Huff and L.D. Schmidt, J. Phys. Chem. 97 (1993) 11815.
[15] M. Huff and L.D. Schmidt, J. Catal. 149 (1994) 127.
[16] S.S. Bharadwaj, C. Yokoyama and L.D. Schmidt, Appl. Catal., in press.
[17] S.S. Bharadwaj and L.D. Schmidt, J. Catal. 155 (1995) 403.
[18] C.L. Lau and G.K. Wertheim, J. Vac. Sci. Technol. 15 (1978) 622.
[19] Z. Karpinski and J.K.A. Clarke, J. Chem. Soc. Faraday Trans. II 71 (1975) 893.
[20] A.C. Muller, P.A. Englhard and J.E. Weisang, J. Catal. 56 (1979) 65.
[21] F.M. Dautzenberg, J.N. Helle, P. Biloen and W.M.H. Sachtler, J. Catal. 63 (1980) 119.
[22] R. Burch and L.C. Garla, J. Catal. 71 (1981) 360.
[23] H. Lieske and J. Volter, J. Catal. 90 (1984) 96.
[24] B.A. Sexton, A.E. Hughes and K. Foger, J. Catal. 88 (1984) 466.
[25] H. Verbeek and W.M.H. Sachtler, J. Catal. 42 (1975) 257.
[26] M. Huff and L.D. Schmidt, J. Catal. 155 (1995) 82.