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Catalytic Behavior of Pt/SbO_x for Selective Oxidation of i-C_4H_{10} and i-C_4H_8 in Stationary and Nonstationary Conditions

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It was found that Pt/SbO_x catalysts were active for the selective oxidation of i-C_4H_{10} and i-C_4H_8 to methacrolein (MAL) at 773 K. The SbO_x itself was inactive for the selective oxidation of i-C_4H_{10}, while i-C_4H_8 was converted to MAL on the SbO_x. Small amounts of Pt (0.2–0.72 wt%) supported on the SbO_x promoted the i-C_4H_{10} oxidation with good selectivity to MAL (typically 50–60%) and MAL + i-C_4H_8 (80–90%). The selective oxidation of i-C_4H_8 to MAL was also markedly enhanced by Pt. The performance of Pt/SbO_x catalysts for the i-C_4H_{10} selective oxidation may be attributed to combinative catalysis of Pt particles modified with SbO_y ($y < x$) and Sb_6O_{13} produced under the oxidation conditions. © 1997 Academic Press

INTRODUCTION

The functionalization of alkanes using gas phase oxygen is one of the most interesting processes to produce basic chemicals (1). Although catalysts for selective oxidation of alkenes have long been studied to establish and improve industrial processes, the development of selective oxidation catalysts for alkanes is still a challenging subject to be solved. Only the V–P–O catalyst for *n*-butane oxidation to maleic acid anhydride has been commercially successful (2). Catalysts for alkene oxidation cannot naturally be applied to alkane oxidation because of the difficulty of activation of alkanes compared with the corresponding alkenes. Increasing demand for efficient utilization of alkane feedstocks has warmed up both fundamental and applied researches on selective oxidation catalysts and catalysis.

There have been two major trends in the development of catalysts for selective oxidation of alkanes. One is the use of scheelite type oxides, where thermal dehydrogenation of propane in the gas phase occurs first, and the propene produced is converted to acrolein on the catalysts (3). The other is the use of rutile-type catalysts containing Sb oxide: some multicomponent oxides of this type have been known as catalysts for selective oxidation of alkenes.

Highly selective hydrocarbon oxidation reactions have been reported for Sb oxide alone (4), and therefore it has been an important element in selective oxidation catalysts, such as V–Sb–O, Ga–Sb–O, Sn–Sb–O, Fe–Sb–O, and U–Sb–O (5–10). For some of these catalysts, the Sb oxide phase has been regarded to be responsible for selective transformation of hydrocarbon molecules, which is promoted by the surrounding oxides (10–14).

Sb oxides have also been shown to be oxygen donors: α-Sb_2O_4 dissociates O_2 to supply the produced oxygen atoms to another oxide phase in mixed oxide catalysts, where the spillover oxygen is involved in selective oxidation reactions (15–17).

We have reported that a Pt–Sn bimetallic ensemble catalyst, which was prepared by reaction of $Sn(CH_3)_4$ with Pt particles supported on SiO_2, followed by H_2 reduction, was effective for the conversion of hydrocarbons (propene, isobutene, and isobutane) to the corresponding unsaturated nitriles with high selectivity of 70% (17, 18). In the bimetallic Pt–Sn ensemble catalyst, Pt acts as dehydrogenation site for hydrocarbons such as propene, isobutene, and isobutane to form the allyl intermediates and Sn acts as an oxygen acceptor from NO to form SnO_x and atomic N. The SnO_x stabilizes the allyl intermediates which react with atomic N to produce the unsaturated nitriles. Monometallic Pt catalysts show no significant activity for nitrile synthesis (18, 19).

The results on the Pt–Sn/SiO_2 catalyst promoted us to prepare new Pt-base bimetallic catalysts for selective oxidation of alkanes. Second metal additives (X) which have different oxygen affinities (metal–oxygen bond energies) were combined with Pt particles supported on SiO_2 by using the metal alkyls, followed by reduction with H_2 at 673 K. Performance of the resulting Pt–X/SiO_2 catalysts was examined for propane ammoxidation in a closed circulating system (20). The initial reaction rates are shown in Fig. 1. However, the rate of ammoxidation of propane on Pt–X/SiO_2 at 573 K rapidly decreased with reaction time. Therefore, the results in Fig. 1 were only used as a measure for screening selective oxidation catalysts. The additive

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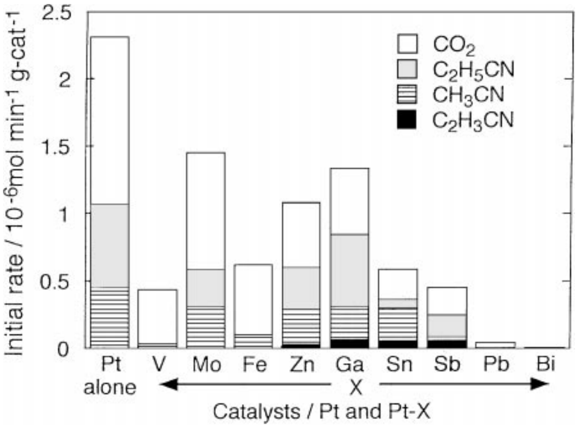


FIG. 1. Initial rates (C-base mol min^{-1} g-cat^{-1}) for propane ammoxidation reaction on Pt–X/SiO$_2$ catalysts at 573 K; Pt, 1.0 wt%, X/Pt = 1 (atomic ratio).

effects in Fig. 1 are categorized to (i) suppression of the formation of C_2H_5CN and CH_3CN more than that of total oxidation to CO_2 (V, Mo, and Fe), (ii) suppression of combustion and synthesis of unsaturated nitrile (acrylonitrile) (Zn, Ga, Sn, and Sb), and (iii) inhibition of propane oxidation (Pb and Bi). Among the second-category elements, Sb promoted the unsaturated nitrile synthesis and suppressed the undesired C–C bond breaking.

Thus we chose a combination of Pt and Sb and prepared supported Pt/SbO$_x$ catalysts instead of the Pt–Sb/SiO$_2$, because the state of Sb atoms under the oxidation reaction conditions is not metallic but oxidic. To simplify the catalytic system and reaction, we have investigated the selective oxidation catalysis by the Pt/SbO$_x$ catalyst for the conversion of i-C_4H_{10} to methacrolein (MAL). We have also studied the oxidation properties of the Pt/SbO$_x$ catalyst for i-C_4H_8 which is an intermediate for the reaction from i-C_4H_{10} to MAL.

In the Pt/SbO$_x$ system, activation of i-C_4H_{10} to form the dehydrogenated species may occur on the Pt surface, and oxygen addition (C–O bond formation) may take place on the SbO$_x$ surface. In addition to the cooperative reaction processes, the metal–metal oxide junction may promote the reactivity of lattice oxygen of the metal oxide (21–23). Reversely, the Pt surface may be modified by reduced Sb oxides depending on the surface and ambient atmosphere. These expected Pt–SbO$_x$ interactions are predicted to generate favorable catalysis for the selective oxidation of i-C_4H_{10} to MAL.

EXPERIMENTAL

Catalyst Preparation

SbO$_x$ was prepared by hydrolysis of $SbCl_5$ with an aqueous ammonia solution, followed by drying at 373 K and calcination at 773 K. Pt was supported on the SbO$_x$ by an impregnation method using an acetone solution of Pt(acac)$_2$, followed by drying at 323 K and calcination at 773 K. Averaged Pt particle sizes were estimated to be 3.7–5.5 nm for 0.3–1.0 wt% Pt samples by TEM. BET surface areas were 50–60 m^2 g^{-1} for all the samples examined. For comparison, Pd/SbO$_x$ and Rh/SbO$_x$ were also prepared by using Pd(acac)$_2$ and Rh(acac)$_3$, respectively. Ir/SbO$_x$ was obtained by using H_2IrCl_6 as precursor. Supporting Ag and Cu on SbO$_x$ was accomplished by using an aqueous solution of $AgNO_3$ and an acetone solution of Cu(acac)$_2$, respectively. All the precursors were purchased from Soekawa Chemical Co.

Catalytic Reactions

Performance of the catalysts was examined in a fixed-bed flow reactor system equipped with two gas chromatographs. Two sets of experiments were performed; steady-state reaction and temperature-programmed (increasing and decreasing rates, 1.7 K min^{-1}) reaction. The steady-state kinetic data were measured over a few several-hour periods after the first 1-h reaction for each constant reaction temperature.

Reactant gas feeds were controlled by digital mass flow controllers (KOFLOC Model 3510), which had been calibrated for He, O_2, i-C_4H_8, and i-C_4H_{10} flows. Temperature-programmed operation was carried out by a digital programmed thermocontroller, and catalyst temperature was monitored by an Al–Cr thermocouple attached to a reactor tube made from Pyrex glass. Gas flow lines were made by stainless-steel tubes and Teflon tubes, except for the quartz-made reactor tube.

The reaction products were analyzed by two gas chromatographs (Shimadzu GC-9A and GC-8Ait), using columns of Unibeads C at 423 K for O_2 and CO_2, Gaskuropack 54 at 423 K for C_3 products, i-C_4H_{10} and MAL, and VZ-10 at 343 K for i-C_4H_{10} and i-C_4H_8.

The O_2 conversion, MAL yield, i-C_4H_8 yield, CO_2 yield, C_3 (mainly C_3H_6) yield, MAL selectivity, and i-C_4H_8 selectivity are defined as

$$O_2 \text{ conversion } (\%) = \frac{\text{moles of } O_2 \text{ consumed}}{\text{moles of } O_2 \text{ in feed}} \times 100$$

$$\text{MAL yield } (\%) = \frac{\text{moles of MAL produced}}{\text{moles of i-}C_4H_{10} \text{ in feed}} \times 100$$

$$\text{i-}C_4H_8 \text{ yield } (\%) = \frac{\text{moles of i-}C_4H_8 \text{ produced}}{\text{moles of i-}C_4H_{10} \text{ in feed}} \times 100$$

$$CO_2 \text{ yield } (\%) = \frac{\text{moles of } CO_2 \text{ produced} \times 0.25}{\text{moles of i-}C_4H_{10} \text{ in feed}} \times 100$$

$$C_3 \text{ yield } (\%) = \frac{\text{moles of } C_3 \text{ produced} \times 0.75}{\text{moles of i-}C_4H_{10} \text{ in feed}} \times 100$$

$$\text{MAL selectivity (\%)} = \frac{\text{moles of MAL produced}}{\text{moles of i-}C_4H_{10}\text{ consumed}} \times 100$$

$$\text{i-}C_4H_8\text{ selectivity (\%)} = \frac{\text{moles of i-}C_4H_8\text{ produced}}{\text{moles of i-}C_4H_{10}\text{ consumed}} \times 100.$$

RESULTS

Promotion Effect of Pt on the Sb Oxide Catalysis for i-C_4H_{10} Oxidation

Figure 2 shows the dependence of Pt loading in Pt/SbO_x catalysts on the O_2 conversion, MAL yield, MAL selectivity, and MAL + i-C_4H_8 selectivity in the i-C_4H_{10} selective oxidation at 773 K under steady-state conditions. SbO_x alone (Pt free) was inactive for the oxidation of i-C_4H_{10} at 773 K, whereas small amounts of Pt supported on SbO_x promoted the selective oxidation of i-C_4H_{10}. The O_2 conversion increased with an increase of Pt loading. MAL and i-C_4H_8 were produced in high selectivities of 87.1 and 89.6% (MAL + i-C_4H_8) when the Pt loadings were 0.2 and 0.35 wt%, respectively. The maximum MAL yield was achieved on the catalyst with a Pt loading of 0.5 wt%, where the selectivity to MAL was 56.6% (Table 1). The MAL selectivity also showed a maximum on the 0.5 wt% Pt/SbO_x catalyst as shown in Fig. 2. The product yields and selectivities in i-C_4H_{10} oxidation on Pt/SbO_x at 773 K are summarized in Table 1.

We also examined the additive effect of other metals on the SbO_x catalysis for the i-C_4H_{10} oxidation reaction. Only Pt and Ir oxidized i-C_4H_{10}, while Rh and Pd were much less active and readily deactivated, and oxidation reaction did not proceed on Ag/SbO_x and Cu/SbO_x, as shown in Table 2. Pt showed the highest activity among the examined metals and was the sole metal which could produce MAL. Ir/SbO_x showed merely total oxidation to CO_2 (Table 2).

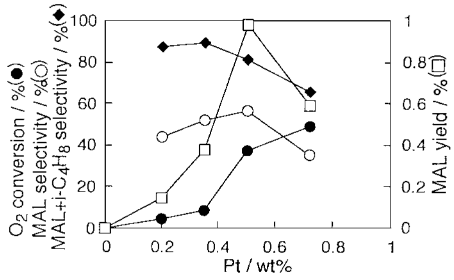


FIG. 2. The dependence of O_2 conversion (●), MAL selectivity (○), MAL + i-C_4H_8 selectivity (◆), and MAL yield (□) for i-C_4H_{10} oxidation at 773 K on Pt loading in Pt/SbO_x. Catalyst, 0.3 g; total flow rate, 2400 ml h^{-1}; i-C_4H_{10}, 20%, O_2, 4%, balanced with He.

TABLE 1

Product Yields and Selectivities on the Pt/SbO_x Catalysts with Different Pt Loadings in the Catalytic i-C_4H_{10} Oxidation Reaction at 773 K

	Products yield/%				Selectivity/%	
Pt/wt%	MAL	i-C_4H_8	CO_2	C_3	MAL	i-C_4H_8
0.0	0.0	0.0	0.0	0.0	—	—
0.2	0.15	0.15	0.0	0.04	43.8	43.3
0.35	0.38	0.27	0.02	0.06	52.1	37.5
0.5	0.98	0.43	0.24	0.08	56.6	24.9
0.72	0.59	0.51	0.52	0.06	35.1	30.4

Note. Catalyst, 0.3 g; total flow rate, 2400 ml h^{-1}; i-C_4H_{10}, 20%; O_2, 4% and balanced with He. C_3 was mainly C_3H_6.

The promotion effect of Pt in Fig. 2 and Table 1 may be compared with the dehydrogenation activity to form i-C_4H_8 as shown in Fig. 3. The i-C_4H_8 yields using Pd/SbO_x and Rh/SbO_x were almost negligible (Fig. 3). The rates of the formations of MAL and i-C_4H_8 on the Pt/SbO_x catalyst at 773 K were of nearly first order with respect to i-C_4H_{10} partial pressure (pressure range, 18–50 kPa) and were independent of O_2 pressure (pressure range, 4–20 kPa); $r_{\text{MAL}} = kP_{\text{i-}C_4H_{10}}$ and $r_{\text{i-}C_4H_8} = k'P_{\text{i-}C_4H_{10}}$, where r_{MAL} and $r_{\text{i-}C_4H_8}$ stand for the rates of the formations of MAL and i-C_4H_8, respectively, and $P_{\text{i-}C_4H_{10}}$ is the partial pressure of i-C_4H_{10}. From the reaction kinetics, the rate-determining step for the MAL synthesis is likely to be C–H bond breaking of i-C_4H_{10}. The i-C_4H_8 yield in the i-C_4H_{10} oxidation reaction increased as Pt loading increased, which suggests that Pt works as the dehydrogenation site during the i-C_4H_{10} oxidation.

Promotion Effect of Pt on SbO_x Catalysis of i-C_4H_8 Oxidation

The preceding result that Pt promoted selective i-C_4H_{10} oxidation with high selectivity to MAL may be relevant to the dehydrogenation of i-C_4H_{10} to i-C_4H_8 which occurs on the Pt surface. To examine the promoter effect of Pt in the further oxidation step of i-C_4H_8 to MAL, i-C_4H_8 oxidation under temperature-programmed reaction conditions was studied on Pt/SbO_x, and performances of Pd/SbO_x, Rh/SbO_x, and SbO_x were also determined for comparison.

TABLE 2

Promoter Effect of Metal Additives on the SbO_x Catalysis for i-C_4H_{10} Oxidation Reaction at 773 K

Metal (wt%)	Pt (0.5)	Pd (0.3)	Rh (0.3)	Ir (0.5)	Cu (0.2)	Ag (0.2)
O_2 conversion/%	37.5	1.1	2.0	23.3	0.0	0.0
MAL selectivity/%	56.6	0.0	0.0	0.0	—	—

Note. Catalyst, 0.3 g; total flow rate, 2400 ml h^{-1}; i-C_4H_{10}; 20%, O_2, 4% and balanced with He.

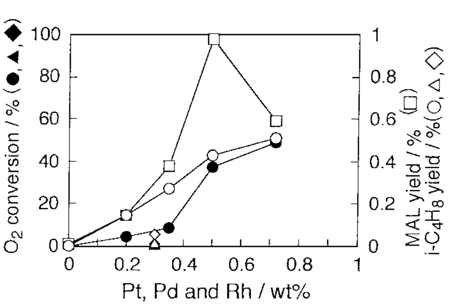


FIG. 3. The MAL yield (□) on Pt/SbO$_x$, the i-C_4H_8 yields on Pt/SbO$_x$ (○), Pd/SbO$_x$ (△) and Rh/SbO$_x$ (◇), and the O_2 conversions on Pt/SbO$_x$ (●), Pd/SbO$_x$ (▲), and Rh/SbO$_x$ (◆) in the i-C_4H_{10} oxidation at 773 K, as a function of metal loading. Catalyst, 0.3 g; total flow rate, 2400 ml h^{-1}; i-C_4H_{10}, 20%, O_2, 4%, balanced with He.

In the case of i-C_4H_8 oxidation, SbO$_x$ without any promoter was active and all three metals, Pt, Pd, and Rh, enhanced the SbO$_x$ reactivity for the synthesis of MAL (Figs. 4 and 5). Among the three metals, Pt was the best promoter. Pt increased the MAL yield at 773 K to five times what it was on SbO$_x$, while the increase in the yield by Pd and Rh additions was less than two times.

Figure 4 shows O_2 conversion, the MAL yield, and the MAL selectivity plotted against reaction temperature. At temperatures below 623 K, the complete oxidation to CO_2 preferentially proceeded on Pt/SbO$_x$, and the selectivity to MAL was less than 20%. At 650 K the oxygen conversion decreased from 76 to 12% and the selectivity to MAL increased from 11 to 65%.

Above 673 K, the MAL yield and selectivity increased with temperature and the selectivity reached 90% at 773 K. The high selectivity of 90% was also observed on SbO$_x$ at 773 K, but the activity of SbO$_x$ was much lower than that of Pt/SbO$_x$. SbO$_x$ was active only above 723 K as shown in Fig. 4.

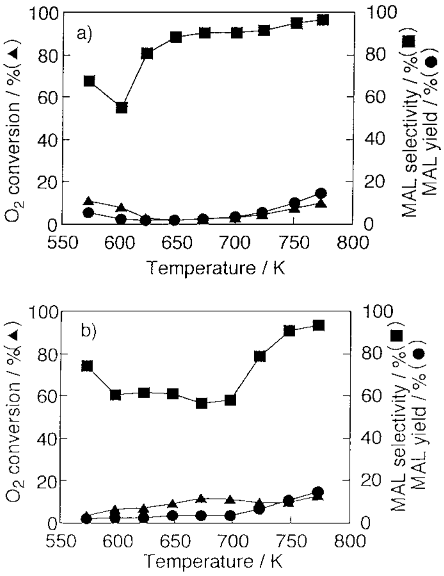


FIG. 5. The O_2 conversion, MAL yield, and MAL selectivity in i-C_4H_8 oxidation reaction on (a) Pd/SbO$_x$ (0.3 wt%) and (b) Rh/SbO$_x$ (0.3 wt%) as a function of reaction temperature. The reaction condition and symbols are the same as those in Fig. 4.

The performance of the temperature-programmed catalytic reaction for i-C_4H_8 oxidation showed an irreversible behavior with respect to reaction temperature as shown in Fig. 6. The data were recorded while increasing the temperature to 773 K under flowing reaction gases and then while decreasing temperature from 773 K. The O_2 conversion, the MAL yield and the MAL selectivity while decreasing temperature were plotted against the temperature in Fig. 6. Once the high selectivity was attained, the selectivity of more than 90% was kept in the temperature-decreasing process.

The profile observed in the temperature-programmed reaction of i-C_4H_8 oxidation in Fig. 4 was also observed for the i-C_4H_{10} oxidation in Fig. 7, where the O_2 conversion steeply decreased at 650 K, followed by the selective MAL formation.

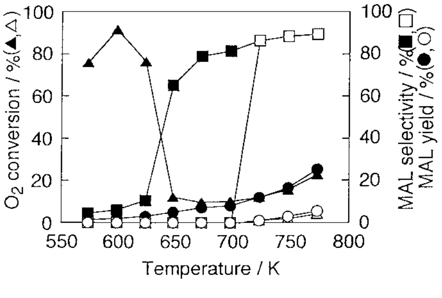


FIG. 4. The promoter effect of Pt (0.5 wt%) in i-C_4H_8 oxidation; (●, ▲, ■) Pt/SbO$_x$; (○, △, □) SbO$_x$; catalyst, 0.3 g; total flow rate, 2400 ml h^{-1}; i-C_4H_8, 1.7%; O_2, 4%, balanced with He. The data were recorded under the temperature-programmed reaction condition (1.7 K min^{-1}). Circle, triangle, and square denote MAL yield, O_2 conversion, and MAL selectivity, respectively.

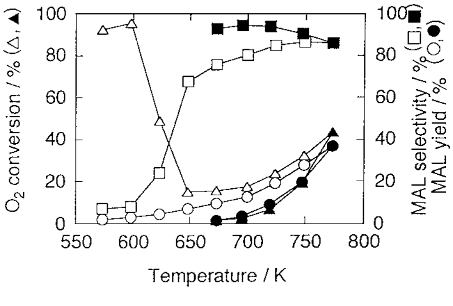


FIG. 6. Hysteresis profiles in the catalytic performance of Pt/SbO$_x$ (1.0 wt%) for i-C_4H_8 oxidation. Catalyst, 0.3 g; total flow rate, 2400 ml h^{-1}; i-C_4H_8, 1.7%; O_2, 4%, balanced with He. (○, △, □) Under increasing temperature (1.7 K min^{-1}); (●, ▲, ■) under decreasing temperature (−1.7 K min^{-1}).

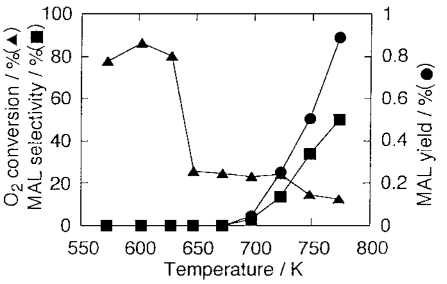


FIG. 7. The catalytic performance of Pt/SbO_x (0.5 wt%) in i-C_4H_{10} oxidation reaction under temperature-programmed conditions (1.7 K min^{-1}). Catalyst, 0.3 g; total flow rate, 2400 ml h^{-1}; i-C_4H_{10}, 20%; O_2, 4%, balanced with He.

Dependences of the MAL yield at 773 K and the activation energy for i-C_4H_8 oxidation were plotted against Pt loading in Fig. 8. The activation energies were measured for the samples which were once pretreated at 773 K under the reaction condition (1.7% i-$C_4H_8 + 4\%$ O_2, balanced by He). By the treatment at 773 K, intrinsic change in the performance of the samples became negligible and the steady-state kinetic data for estimation of the activation energies were measured in the temperature range 673–773 K. The activation energy drastically decreased by the addition of Pt, and MAL yield at 773 K reached seven times (Pt 1.0 wt%) that of SbO_x alone. The MAL yields and the activation energies in Fig. 8 did not change so much in the range of Pt loading 0.3–1.0 wt%, which is contrasted to the optimum activity at 0.5 wt% Pt for i-C_4H_{10} oxidation in Figs. 2 and 3.

Oxidation Activity Control by Reductive Condition

XAFS and XRD revealed that Pt was supported on SbO_x in the form of metallic Pt particles, and the temperature-programmed reaction profiles suggested that the Pt surface was modified by reduced Sb oxide during the catalytic reaction (24, 25). This surface modification may originate from the reduction of the SbO_x support by i-C_4H_{10} and i-C_4H_8. Though Pt modification by Sb seemed to be important for the selective oxidation by Pt/SbO_x catalysts, reduction conditions which were too severe harmed the selective oxidation to MAL. The selective oxidation activity of Pt/SbO_x was suppressed by H_2 reduction treatment. When the i-C_4H_8 oxidation was performed with high i-C_4H_8 concentration (20%), the selectivity to MAL decreased with time-on-stream as shown in Fig. 9. According to the characterization results on SbO_x, α-Sb_2O_4 was identified after the i-C_4H_8- rich reaction, while only Sb_6O_{13} was observed under the catalytic i-C_4H_{10} oxidation (20% i-C_4H_{10}) and low i-C_4H_8 concentration oxidation (1.7% i-C_4H_8) reaction conditions (24, 25).

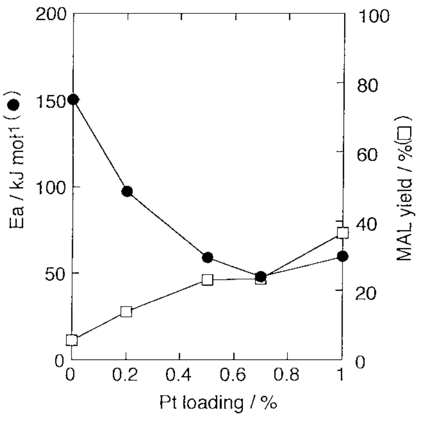


FIG. 8. The dependence of the activation energy (673–773 K) and the MAL yield at 773 K in i-C_4H_8 oxidation on Pt loading in Pt/SbO_x catalysts. Catalyst, 0.3 g; total flow rate, 2400 ml h^{-1}; i-C_4H_8, 1.7%; O_2, 4%, balanced with He.

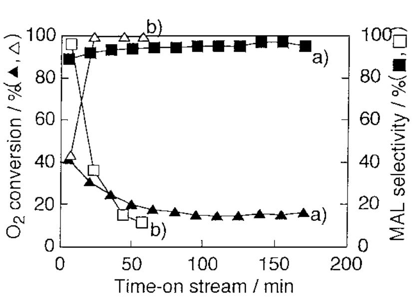


FIG. 9. Reaction profiles for i-C_4H_8 oxidation on Pt/SbO_x (0.5 wt%) at 773 K. Catalyst, 0.3 g; total flow rate, 2400 ml h^{-1}. (a) (▲, ■) i-C_4H_8 4%, O_2, 4%, balanced with He. (b) (△, □) i-C_4H_8 20%, O_2, 4%, balanced with He. Triangle and square denote O_2 conversion and MAL selectivity, respectively.

DISCUSSION

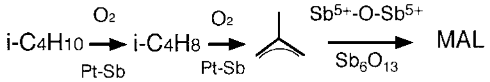
The formation of both MAL and i-C_4H_8 in the i-C_4H_{10} oxidation reaction on Pt/SbO_x possessed the same kinetics that were of nearly first order with respect to i-C_4H_{10} pressure and zero order with respect to O_2 pressure. Selective oxidation reactions of alkanes on mixed-oxide catalysts often show similar reaction kinetics, where dehydrogenation from alkanes is suggested to be the rate-determining step for the overall reaction (26). The i-C_4H_{10} selective oxidation on Pt/SbO_x may also proceed by the successive steps, i-$C_4H_{10} \rightarrow$ i-$C_4H_8 \rightarrow$ i-C_4H_7 (methallyl) $\rightarrow$ MAL, as generally accepted (27, 28).

The addition of Pt to SbO_x promoted the dehydrogenation of i-C_4H_{10} to i-C_4H_8 (Table 1 and Fig. 3). Simultaneously, Pt increased the complete oxidation of i-C_4H_{10} to CO_2 as shown in Table 1. Thus, there existed an optimum Pt loading in Pt/SbO_x for the MAL yield from i-C_4H_{10} as shown in Figs. 2 and 3. It was found that the Pt/SbO_x catalyst with 0.5 wt% Pt produced MAL most selectively (56.6% for MAL; 81.4% for MAL + i-C_4H_8 in Table 1).

Similarly Pd, Rh, and Ir were expected to work as promoters for the i-C_4H_{10}-selective oxidation. However, Pt was the only metal that can promote the selective oxidation of i-C_4H_{10} to MAL as shown in Table 2. Rh in Rh/SbO$_x$ was transformed to the oxide under the catalytic reaction conditions, which would be the reason why Rh did not promote the dehydrogenation of i-C_4H_{10} (24, 25). The difference between Pt and Pd in the promoter effect is not clear at present, but the subtle difference of the two metals may be attributed to different modification of the metal surface by Sb. Ag/SbO$_x$ was also tested as it has been reported that Ag worked as a good dopant for Bi–V–O scheelite-type oxides for propane ammoxidation to acrylonitrile (3). Table 2 shows no promotion effect of Ag for the i-C_4H_{10} selective oxidation on SbO$_x$. In addition, Cu/SbO$_x$ was investigated in relation to the effect and role of the Cu–SbO$_x$ junction due to the band-bending effect between metal and oxide (21). The Cu/SbO$_x$ system was inactive for the selective oxidation (Table 2).

Propene oxidation has been reported to take place on Sb oxide (Sb_6O_{13}) (10, 11). In the i-C_4H_{10} oxidation the i-C_4H_8 intermediate should be further oxidized to MAL on the SbO$_x$ surface in Pt/SbO$_x$. It is to be noted that Pt also promoted the selective oxidation of i-C_4H_8 to MAL, and the selectivity to MAL was as high as 90%, as shown in Fig. 4. The addition of a small amount (0.5 wt%) of Pt to SbO$_x$ increased the MAL yield from i-C_4H_8 to five times of what it was on SbO$_x$ alone, while retaining the high selectivity of the SbO$_x$ itself (Fig. 4). The yield to MAL was increased seven times for 1.0 wt% Pt. Further, the activation energy drastically decreased from 150 kJ mol^{-1} for SbO$_x$ to 60 kJ mol^{-1} for Pt (0.5 wt%)/SbO$_x$ (Fig. 8). As mentioned above, the formation of MAL from i-C_4H_8 occurs through methallyl intermediate (i-C_4H_7) (27, 28). These results indicate that the dehydrogenation of i-C_4H_8 to i-C_4H_7 preferentially proceeds on the Pt surface and the methallyl species may migrate to the SbO$_x$ surface on which MAL is produced. The complete oxidation of i-C_4H_8 to CO_2 preferentially occurred in the low temperature range below 623 K, while above 650 K CO_2 formation was remarkably suppressed and MAL selectivity dramatically increased as shown in Fig. 4. This phenomenon was irreversible as shown in Fig. 6. Once an active phase at the Pt/SbO$_x$ catalyst surface was formed under the reaction conditions, typically at 773 K, the high selectivity to MAL is maintained when the temperature is lowered.

XRD, analytical TEM, and EXAFS reveal that modification of the Pt metallic particles on SbO$_x$ takes place during the selective oxidation reactions of i-C_4H_{10} (20%) and i-C_4H_8 (1.7%) at 773 K, and this modification is caused by SbO$_y$ ($y < x$) (24, 25). The oxidation of i-C_4H_{10} and i-C_4H_8 to CO_2 which readily takes place on unmodified Pt metallic particles is suppressed by the Sb modification, leading to enhancement of the selectivity to MAL. The modification of the Pt particles by Sb is induced by reduction of the Pt/SbO$_x$ catalyst under the reaction conditions. Thus the reaction pathway for the i-C_4H_{10} selective oxidation may be shown in Scheme 1.



SCHEME 1. The reaction pathway of i-C_4H_{10} oxidation on Pt/SbO$_x$ catalysts.

The complete oxidation of i-C_4 hydrocarbons to CO_2 was remarkably reduced by the prereduction of the Pt/SbO$_x$ catalyst with H_2 at 473–623 K, but the deeper reduction spoiled the activity of Pt/SbO$_x$. The selectivity to MAL in the i-C_4H_8 oxidation was deteriorated under the high i-C_4H_8 concentration condition in Fig. 9. In this case, the structural change occurred due to too much loss of lattice oxygen of SbO$_x$ as was determined by XRD: α-Sb_2O_4 was formed under the reductive conditions (24, 25). The Pt/SbO$_x$ sample treated under flowing He at 773 K promoted complete oxidation to CO_2 and no MAL synthesis. Under this treatment α-Sb_2O_4 was observed to be formed. On the other hand, only Sb_6O_{13} was observed when the selective oxidation of i-C_4H_{10} and i-C_4H_8 to MAL was successful (24, 25). The Sb_6O_{13} structure may be responsible for the selective oxidation to MAL (Scheme 1). Pt promotes the selective catalysis of the Sb_6O_{13} under favorable reaction conditions, where Sb-modified Pt particles on the Sb_6O_{13} support are produced, which are active for selective oxidation. Too severe reductive conditions deteriorated the MAL yield as well as the MAL selectivity, and it may be due to the loss of "selective" lattice oxygen supplied from the Sb_6O_{13} surface.

Generally, the sites for hydrocarbon activation and allyl intermediate oxidation in selective oxidation catalysts are different and the sites for reoxidation of the catalysts are separated from these sites, leading to the high selectivities (27). In the Pt/SbO$_x$ catalyst, the Pt metal is a promoter for the selective oxidation catalysis of the SbO$_x$, which is contrasted to typical oxide-supported metal catalysts where metal oxide promotes the supported metal particles. The Pt particles modified by Sb enhance i-C_4H_{10} dehydrogenation to the methallyl intermediate, which moves to the SbO$_x$ surface and reacts with the active lattice oxygen to form MAL. Pt also influences the reactivity of the lattice oxygen of SbO$_x$, which will be reported in a separate paper (24).

CONCLUSIONS

(i) We have found that the Pt/SbO$_x$ catalyst showed good performance for the selective oxidation of i-C_4H_{10} and i-C_4H_8 to MAL with 57 and 90% selectivities, respectively. The selectivities to MAL and i-C_4H_8 in the i-C_4H_{10} oxidation reaction were 80–90%. The reaction of i-C_4H_{10} did not proceed on the SbO$_x$ without Pt.

(ii) SbO_x was selective for the i-C_4H_8 oxidation to MAL. Pt also promoted i-C_4H_8-selective oxidation and MAL production proceeded at much lower temperatures than with only SbO_x.

(iii) A combination of Pt particles modified by Sb and more selective lattice oxygen of SbO_x (Sb_6O_{13}) is proposed to be responsible for the high selectivities to MAL in Pt/SbO_x catalysts.

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