Partial Oxidation of Methane over M-Sb-Te-O (M = Transition Metal) Catalysts

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The catalytic partial oxidation of methane has received a great deal of attention for the utilization of natural gas during the last 20 years. The degree of CH_4 oxidation required depends on the process.[1,2] In the catalytic combustion of CH_4 the objective is full oxidation to CO_2. For chemicals productions the end products are CH_3OH, $HCHO$, and $HCOOH$, in the formation of syngas the target is CO, while in the oxidative coupling the desired products are C_2H_4 and C_2H_6. Oxidative coupling of methane has been recognized as a promising route for the direct conversion of methane to ethane or ethylene. In general, metal oxides show catalytic activity for the oxidative coupling of methane. Adsorbed oxygen and lattice oxygen ions on the surface of metal oxides play an important role on the activation of methane. Although the catalytic reaction mechanisms for the oxidative coupling of methane vary with the metal oxide catalysts, it is generally accepted that methyl radicals are produced *via* the dehydrogenation of methane on the surface of metal oxide catalyst and the resulting methyl radicals are coupled to ethane on the surface or in the gas phase.

A variety of solid materials have been examined as catalysts for the oxidative coupling of methane to identify suitable catalysts which can give high yield of C_2-hydrocarbons in the reaction. However, few Te-containing metal oxides have been tested as catalysts for the reaction until now. In recent years, it has been reported that metal tellurides show excellent catalytic performance in the ammoxidation and oxidation of hydrocarbons.[3-5] We reported in the previous papers that the oxygen-pretreated $LiSbTe_2$ and $Ni_3Sb_2Te_6$ catalysts showed catalytic activity and C_2-selectivity in the partial oxidation of methane.[6,7] In this work, we prepared various metal tellurides such as $Cr_3Sb_2Te_6$, $Mn_3Sb_2Te_6$, $Fe_3Sb_2Te_6$, $Co_3Sb_2Te_6$, and $Ni_3Sb_2Te_6$ and examined them as catalysts for the partial oxidation of methane in the temperature range of 670 to 730 at atmospheric pressure.

Experimental Section

$M_3Sb_2Te_6$ (M = Cr, Mn, Fe, Co, Ni) compounds were prepared by using a rapid precipitation metathesis reaction between the Zintl material K_3SbTe_3 and the transition-metal salt in solution, as described by Jung *et al.*[8,9] The ternary

Zintl phase K_3SbTe_3 prepared from a direct combination of the elements is described as a polar metallic solid in which the bonding gives rise to a substantial amount of ionic bonding character. Therefore, K_3SbTe_3 is soluble in water by the reaction: $K_3SbTe_3(s) \rightarrow 3K^+ + SbTe_3^{3-}$, and the Zintl solution allows subsequent metathesis reaction with transition-metal salt to form amorphous material due to the transfer of electrons from the $SbTe_3^{3-}$ anion to the metal cation according to the reaction: $3M^{2-} + 2SbTe_3^{3-} \rightarrow M_3(SbTe_3)_2(s)$.[10] A stoichiometric quantity of K_3SbTe_3 aqueous solution was added slowly while stirring the transition-metal salt solution. A precipitate was formed immediately. It was then separated by solution filtration, washed with deionized water and acetone, and dried in a vacuum oven. Sample manipulations were performed under an oxygen free dry box.

The catalytic reactions were performed in a conventional gas-flow reactor operated at atmospheric pressure. The reactor was made of quartz tubing with 0.45 cm inner diameter and 20 cm length. The powdered catalyst was held between two silica wool plugs in the middle of the reactor. The amount of catalyst loaded into the reactor was 200 mg. The reactor was kept in a vertical tubular furnace and a K-type thermocouple sealed with an alumina tube was contacted with the outside wall of the reactor next to the catalyst bed. Both reaction mixtures containing $CH_4/O_2/He$ and $CH_4/O_2/H_2O(g)/He$ were employed for the partial oxidation of methane. The feed flow rates at ambient conditions were $CH_4/O_2/He$ = 6/1/13 cm^3/min and $CH_4/O_2/H_2O(g)/He$ = 6/1/8/5 cm^3/min. Flow rates of gases were controlled by a needle valve and a electronic mass flow controller. The purity of gaseous oxygen, methane, and helium was greater than 99.99%. Steam was produced from deionized water pumped into the reactor by a syringe injection pump. The lines from the exit of the syringe up to the inlet of the reactor were heated at 150 °C. A cold trap was placed at the reactor exit to remove water vapor from the gaseous mixture. Gaseous reactants and products were analyzed by an on-line gas chromatography equipped with a thermal conductivity detector and a flame ionization detector. Gas compositions were calculated using an external standard gas mixture. $M_3Sb_2Te_6$ compounds were treated in a flow of gaseous oxygen (10 cm^3/min) at 600 °C for 1 h before each activity measurement. After the O_2-treatment of catalyst, the reactor was cooled to room temperature, helium gas was passed to

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remove oxygen gas remaining in the reactor, then the reactor temperature was ramped to the desired value using a programmable temperature controller and finally a reaction mixture was fed over the catalyst. The catalytic reactions were carried out in the temperature range from 670 to 730 °C. The conversion of methane was calculated from the amounts of products generated and the methane introduced in the feed stream. The selectivities were calculated on the basis of the conversion of methane to each product and the yield was obtained from the methane conversion and the selectivity to each product. The methane conversion and product selectivities were typically compared after 1 h time-on-stream. Thermogravimetry (TG) and X-ray powder diffraction (XRD) analyses were performed for the catalysts.

Results and Discussion

Oxygen-treated $M_3Sb_2Te_6$ compounds showed catalytic activity for the partial oxidation of methane. Because amorphous $M_3Sb_2Te_6$ compounds were treated in a flow of gaseous oxygen at 600 °C prior to the reaction, the catalysts are substantially mixed oxides, representing as M-Sb-Te-O. When the reaction mixtures containing $CH_4/O_2/He$ and $CH_4/O_2/H_2O/He$ were fed over the catalysts in the temperature range of 670 to 730 °C, the major products were CO, CO_2, C_2H_4, C_2H_6, and C_3 hydrocarbons. Table 1 shows the methane conversion and product selectivities of several catalysts when the reaction mixture $CH_4/O_2/He$ was fed in the temperature range of 670-730 °C at atmospheric pressure. Among the catalysts tested, both the Cr-Sb-Te-O and Fe-Sb-Te-O revealed negligible C_2-selectivities and methane conversions ($\leq 2\%$) for the reaction. The C_2-selectivity declined with increasing temperature while the methane conversion increased with increasing temperature. The Ni-Sb-Te-O catalyst showed the best C_2-yield of 5.9% with a C_2-selectivity of 40% at 730 °C. The Co-Sb-Te-O catalyst showed C_2-selectivities of 50-68% with C_2-yields of 3.7-4.8% in the temperature range of 670 to 730 °C.

When steam was added into the reaction mixture $CH_4/O_2/$ He, C_2-selectivity and methane conversion were significantly

Table 1. Methane conversion and product selectivities of oxygen-treated $M_3Sb_2Te_6$ catalysts for the partial oxidation of methane

| Catalyst | T (°C) | Product Selectivity (%) | | | | | Methane Conversion (%) |
		CO	CO_2	C_2H_4	C_2H_6	C_3	
$Mn_3Sb_2Te_6$	670	42.5	25.3	16.3	15.5	0.4	7.9
	700	33.6	40.2	16.9	8.6	0.7	14.4
	730	31.1	41.0	17.8	7.7	2.4	16.2
$Co_3Sb_2Te_6$	670	18.2	12.4	44.8	22.8	1.8	5.5
	700	16.7	23.1	39.3	18.4	2.5	8.4
	730	15.3	28.8	34.1	16.7	5.1	9.5
$Ni_3Sb_2Te_6$	670	17.9	15.1	39.2	27.8	0	7.2
	700	15.4	31.6	36.0	14.9	2.1	11.1
	730	13.0	45.0	30.5	9.5	2.0	14.7

Catalyst weight: 200 mg, reaction feed: $CH_4/O_2/He=6/1/13$ cm³/min.

Table 2. Methane conversion and product selectivities of oxygen-treated $M_3Sb_2Te_6$ catalysts in the reaction mixture containing $CH_4/O_2/H_2O(g)/He$

| Catalyst | T (°C) | Product Selectivity (%) | | | | | Methane Conversion (%) |
		CO	CO_2	C_2H_4	C_2H_6	C_3	
$Cr_3Sb_2Te_6$	670	34.1	0	35.3	25.1	5.3	3.3
	700	30.5	1.3	45.9	20.1	2.2	7.9
	730	29.7	3.0	51.3	13.7	2.3	9.2
$Mn_3Sb_2Te_6$	670	25.6	0	40.2	31.2	3.0	7.0
	700	28.6	0	42.3	24.2	4.9	10.9
	730	32.1	1.9	42.8	15.7	7.5	13.6
$Fe_3Sb_2Te_6$	670	-	-	-	-	-	<1
	700	20.4	18.5	25.8	35.1	0.2	1.5
	730	18.3	26.8	35.2	18.4	1.3	2.6
$Co_3Sb_2Te_6$	670	18.5	0	41.0	35.5	5.6	6.7
	700	18.4	0.9	46.4	28.7	5.6	10.1
	730	15.4	2.3	56.7	17.1	8.5	13.5
$Ni_3Sb_2Te_6$	670	38.7	7.5	28.1	24.4	1.3	7.7
	700	30.6	9.3	35.5	23.1	1.5	12.1
	730	20.9	15.8	43.1	18.4	1.8	13.8

Catalyst weight: 200 mg, reaction feed: $CH_4/O_2/H_2O(g)/He = 6/1/8/5$ cm³/min.

increased. Table 2 gives the methane conversion and product selectivities of the catalysts when the reaction mixture $CH_4/O_2/H_2O(g)/He$ was fed in the temperature range of 670 to 730 °C. The Co-Sb-Te-O catalyst showed the C_2-selectivity of 73.8% (56.7% to ethylene and 17.1% to ethane) with a methane conversion of 13.5% at 730 °C, which is rather appreciable. Although the Cr-Sb-Te-O catalyst showed poor activity and negligible C_2-selectivity in the reaction feed of $CH_4/O_2/He$, in the presence of water vapor it showed a good C_2-selectivity of 65% with a C_2-yield of 6% at 730 °C. It is noted that the formation of CO_2 over the Cr-Sb-Te-O, Mn-Sb-Te-O, and Co-Sb-Te-O catalysts is negligible in the presence of steam.

Thermogravimetry analysis was performed for amorphous $Cr_3Sb_2Te_6$, $Fe_3Sb_2Te_6$, $Co_3Sb_2Te_6$, and $Ni_3Sb_2Te_6$ compounds at a heating rate of 10 °C/min in the temperature range of 25-1000 °C in a flow of $O_2(20\%)/Ar$ mixture and the results are shown in Figure 1. Weight gains occur in the temperature range of 150-750 °C, which means that a lot of gaseous oxygen is chemisorbed on the catalyst surface, leading to an oxidation of catalyst. In general, metal tellurides are readily oxygenated in the presence of gaseous oxygen and the present result is in agreement with those by other investigators.[6,11,12] The cause of the weight decrease above 750 °C is mainly the vaporization of tellurium. As shown in Figure 1, the weight uptake of $Fe_3Sb_2Te_6$ begins from 150 °C, while those of the other samples occur above 200 °C. The weight uptake of $Cr_3Sb_2Te_6$ was much less than those of the other samples. Both the O_2-treated $Fe_3Sb_2Te_6$ and $Cr_3Sb_2Te_6$ catalysts showed poor activities for the partial oxidation of methane, which enables us to consider that the catalytic activity and C_2-selectivity is closely related with the extent of oxygenation of $M_3Sb_2Te_6$ by the O_2-treatment.
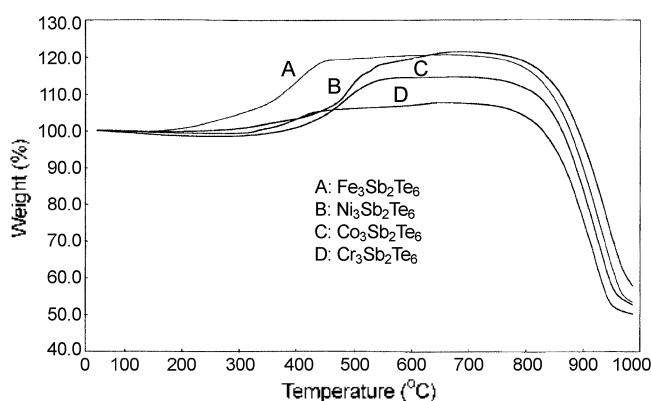
Notes

Bull. Korean Chem. Soc. **2004**, Vol. 25, No. 4   575

Figure 1. TG curves of several $M_3Sb_2Te_6$ in a flow of $O_2(20\%)/Ar$ gas mixture.

counts/s

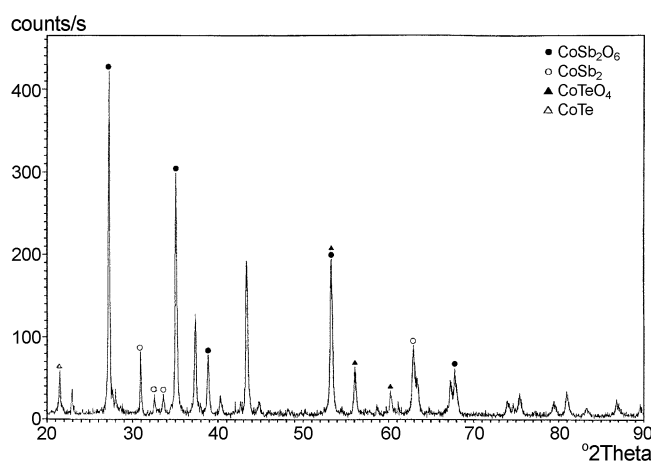**Figure 2.** X-ray diffraction pattern of the oxygen-treated $Co_3Sb_2Te_6$ catalyst.

Figure 3. X-ray diffraction pattern of the oxygen-treated $Ni_3Sb_2Te_6$ catalyst.

In the oxidative coupling of methane over metal oxide catalysts, methyl radicals must be primarily produced by the abstraction of a hydrogen atom from methane which is chemisorbed on active oxygen ions on the catalyst surface. Many investigators have reported that active oxygen species such as O^-, O_2^-, and O_2^{2-} can be generated on oxygen vacancy or basic sites in metal oxide catalysts[13-15] and the stability of active oxygen species formed on the catalyst surface depends on the basicity of metal oxide and the existence of suitable sites.[1] As listed in Tables 1 and 2, the oxygen-treated $M_3Sb_2Te_6$ catalysts were active for the reactions, implying active oxygen ions to be formed on the catalysts. XRD results of the catalysts showed that amorphous $M_3Sb_2Te_6$ compounds were decomposed and oxidized to form oxides during the oxygen treatment, indicating the catalysts to be mixed oxides. Figure 2 presents the X-ray diffraction pattern of the O_2-treated $Co_3Sb_2Te_6$ catalyst which was active for the reaction, in which the presence of $CoSb_2O_6$, $CoSb_2$, $CoTeO_3$, and $CoTe$ phases is observed. Among the phases identified, $CoSb_2O_6$ and $CoTeO_3$ oxides are considered to be active components for the oxidative coupling of methane.

Figure 3 presents the XRD result for the O_2-treated $Ni_3Sb_2Te_6$ catalyst, showing the presence of NiO, $NiSb_2O_6$,
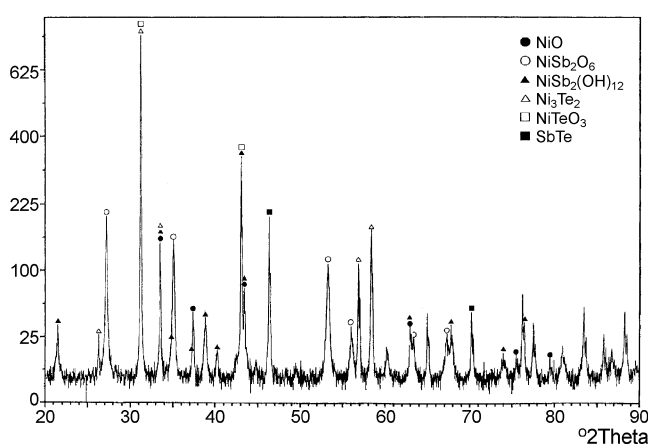
and $NiTeO_3$ phases. We measured methane conversions and selectivities of NiO, Sb_2O_3, TeO_2, and $NiSb_2O_6$ catalysts for the partial oxidation of methane under the reaction conditions. At 700 °C, both NiO and TeO_2 catalysts did not produce ethylene and ethane. Sb_2O_3 catalyst showed a C_2 selectivity of 30% at a methane conversion of 5%, and $NiSb_2O_6$ catalyst showed a C_2 selectivity of 51% at a methane conversion of 8%. We could not measure the catalytic activity of $NiTeO_3$. We tried to prepare $NiTeO_3$ pahse from both the oxidation of Ni-Te mixture at 600 °C and the direct solid-state reaction between NiO and TeO_2 at 700 °C, but various nickel-tellurium oxide phases such as $NiTe_2O_5$, $Ni_2Te_3O_8$, and $NiTeO_3$ were produced and thus, the synthesis and activity of monophase $NiTeO_3$ catalyst remain to be further studied. The nickel-tellurium oxide mixture exhibited a methane conversion of 4% with a C_2 selectivity of 23% for the reaction at 700 °C. The results indicate that these catalysts are less active and selective than the O_2-pretreated $Ni_3Sb_2Te_6$ catalyst.

Several investigators have recently reported that M-Sb-O such as $NiSbO_x$, $GaSbO_x$, $VSbO_x$, $MoSbO_x$, $FeSbO_x$, and $ReSb_2O_x$ showed appreciable activities for the ammoxidation of hydrocarbons.[16-20] In the M-Sb-O catalysts for the ammoxidation of hydrocarbons, hydrocarbon molecules are activated by metal antimonate and antimony is considered to facilitate the abstraction of hydrogen from hydrocarbon molecules. The results give an feasibility that M-Sb-O (M = transition metal) phases act as active components in the partial oxidation of methane. In the previous paper, we showed that $NiSb_2O_6$ catalyst was active and selective for the oxidative coupling of methane. On the other hand, Te-containing compounds are also active catalysts for the ammoxidation of propane.[4] MoVNbTeO catalyst was found to show excellent catalytic performance for the selective ammoxidation and oxidation of propane to acrylonitrile and acrylic acid, in which MTe_xO_3 (M = Mo, V, Nb) with a hexagonal bronze structure is an active component for the reactions.[4,5] In the previous paper,[7] we suggested from the XRD and XPS results of the Ni-Sb-Te-O catalyst that $NiTeO_3$ containing some higher valent Ni ions was a selec-
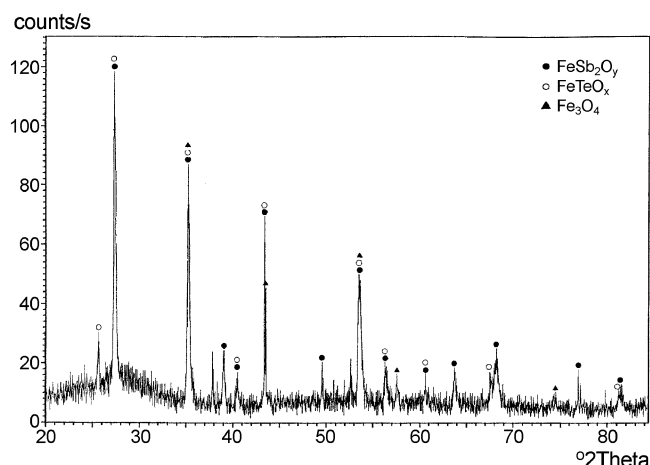
counts/s

Figure 4. X-ray diffraction pattern of the oxygen-treated $Fe_3Sb_2Te_6$ catalyst.

tive phase in the oxidative coupling of methane. The results support that M-Te-O phases formed on the catalyst surface can act as active components for the partial oxidation of methane. Although the respective roles of the two phases are not yet fully understood, it is believed that their coexistence is needed to obtain effective catalyst for the reaction.

Figure 4 presents the X-ray diffraction pattern of O_2-treated $Fe_3Sb_2Te_6$ catalyst which showed poor activity for the partial oxidation of methane. The XRD pattern exhibits the presence of magnetite (Fe_3O_4), $Fe_2Te_3O_6$, and $FeSb_2O_y$ ($4 \leq y \leq 7$) phases. In the reaction feed of $CH_4/O_2/He$ over Fe-Sb-Te-O catalyst, the major product was CO_2. Magnetite catalyst is known to be active for the water-gas shift reaction ($CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$), but inactive for the oxidative coupling of methane. Poor activity of Fe-Sb-Te-O catalyst in the partial oxidation of methane is believed to be due to the presence of magnetite phase on the catalyst surface.

As given in Table 2, the C_2-selectivity and methane conversion were markedly increased when steam was added to the reaction mixture $CH_4/O_2/He$. A comparison between the results given in Tables 1 and 2 indicates that the production of carbon oxides markedly decreases in the presence of steam, which implies that steam inhibits the formation of

carbon oxides. The role of steam on the catalytic reaction seems to be related to the formation of a stable concentration of hydroxyl species on the surface instead of the oxygen species which are more likely to produce carbon oxides. The need for the presence of steam requires further research to be understood and studies on the detailed reaction mechanism over the present specimens are currently in progress.

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