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### The Catalytic Reactions of CO and H<sub>2</sub>O over New Amorphous Ternary Metal Chalcogens

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The water gas shift reaction, the reaction of water vapor and carbon monoxide to produce carbon dioxide and hydrogen, has been studied by many investigators for the past several years because of its industrial importance. The water gas shift reaction can be used to increase the hydrogen content of synthesis gas with various H<sub>2</sub>/CO ratios appropriate to the production of methane, methanol, higher hydrocarbons or alcohols,<sup>1,2</sup> which is believed to be the most important use of the reaction. Metal oxide systems such as Cr<sub>2</sub>O<sub>3</sub>/Fe<sub>3</sub>O<sub>4</sub>, Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>, CoO/Al<sub>2</sub>O<sub>3</sub>, and MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> are known as good catalysts for the reaction. The purpose of this work is to proceed with studies of synthesis, physical characterization, and catalytic activities of novel ternary metal chalcogens prepared by using the Zintl phase as a precursor. As reported in the previous papers,<sup>3,4</sup> ternary metal chalcogens prepared from a simple metathesis reaction between a Zintl phase materials and a divalent transition metal halide have an amorphous structure because of the rapid precipitation of the intermetallic products. No results have been reported for the catalytic activity of Zintl phase compounds so far. In this work, we prepared three amorphous ternary metal chalcogens such as Ni<sub>3</sub>(SbTe<sub>3</sub>)<sub>2</sub>, Cr<sub>3</sub>(SbTe<sub>3</sub>)<sub>2</sub>, and Mn<sub>3</sub>(SbTe<sub>3</sub>)<sub>2</sub>, and examined their catalytic activities for the water gas shift reaction in a single-pass flow reactor, in which appreciable catalytic activities of the amorphous chalcogens were observed. This paper reports on the catalytic activity of amorphous ternary metal chalcogens for the first time.

### Experimental

Preparation and sample manipulations were performed under an argon-filled glovebox containing less than 1 ppm of oxygen. The ternary Zintl material K<sub>3</sub>SbTe<sub>3</sub> was prepared as described previously.<sup>5,6</sup> M<sub>3</sub>(SbTe<sub>3</sub>)<sub>2</sub> (M=Ni, Cr, Mn) compounds were prepared by the reaction of an aqueous solution of K<sub>3</sub>SbTe<sub>3</sub> and MCl<sub>2</sub>. A stoichiometric quantity of K<sub>3</sub>SbTe<sub>3</sub> solution (50 mL, 0.03 M) was added slowly while stirring the metal chloride solution (20 mL, 0.05 M). A precipitate was immediately formed, which was then separated by solution filtration, washed with deionized water and acetone, and dried overnight under vacuum. To investigate the electrical properties of the compounds, the electrical conductivity was measured on pressed pellets over the temperature range 30-300 K using a van der Pauw four-probe method.<sup>7</sup> The current was supplied by a Keithley model 224 programmable current source and voltage drop across the sample was measured using a Keithley model 181 digital nanovoltmeter. Catalytic activity of the specimens was tested in a conventional single-pass flow reactor operated at atmospheric pressure. The reactor was made of alumina tubing with 1.2 cm o.d. and 30 cm length. The catalyst was held in the middle of the reactor and the section beyond the catalyst bed in the reactor was filled with alumina beads to reduce the free space. The purity of carbon monoxide was greater than 99.99% and water vapor was produced from deionized water pumped into the reactor by a Union syringe injection pump; the lines from the exit of the syringe up to the inlet of the reactor were heated at 200 °C. The range of reaction temperature explored was 600-800 °C and the major products were CO<sub>2</sub>, H<sub>2</sub>, and O<sub>2</sub>. Blank runs were performed over inert alumina beads in the absence of catalyst and approximately 2% conversion of CO to CO<sub>2</sub> was obtained in the reaction temperature range. Gas analyses were performed by on-line gas chromatography using a thermal conductivity detector and a mass spectrometer detector, and gas compositions were calculated using external standard mixtures prepared by KSRI. A cold trap was placed at the reactor exit to remove water vapor from the gaseous mixture. Following conditions were used to compare the activity of the catalysts: atmospheric pressure, a 0.3 g sample loading of catalyst, P<sub>CO</sub>=0.19 atm, P<sub>H<sub>2</sub>O</sub>=0.81 atm, a feed flow rate at ambient conditions of 23.2 mL/min. The conversion of carbon monoxide to carbon dioxide was typically compared after 3 hrs time-on-stream. No appreciable decrease in catalytic activity were observed over extended period of 48 hrs. The details of equipments are described in the previous paper.<sup>8</sup>

### Results and Discussion

It has been known that amorphous materials are often vastly different from those of their crystalline counterparts in the physical properties and find use in a variety of applications such as ionic conductor, photosensor, electronic switching material, and catalyst.<sup>9</sup> Most amorphous solids are prepared by rapid thermal quenching, pyrolytic, or sputtering techniques. Also, chemical methods involving rapid precipitation produce noncrystalline solids in certain types of mate-

**Table 1.** Catalytic activity of various  $M_3(SbTe_3)_2$  catalysts for the water gas shift reaction

Catalyst	Temperature (°C)	Conversion of CO to CO <sub>2</sub> (%) <sup>a</sup>	Rate constant ( $k_{app}$ ) <sup>b</sup> (mL/g min.)
Cr <sub>3</sub> (SbTe <sub>3</sub> ) <sub>2</sub>	750	72.0	18.7
Mn <sub>3</sub> (SbTe <sub>3</sub> ) <sub>2</sub>	800	28.0	4.8
Ni <sub>3</sub> (SbTe <sub>3</sub> ) <sub>2</sub>	800	65.9	15.8

Catalyst weight = 0.3 g,  $P_{H_2O}/P_{CO} = 4.26$ . <sup>a</sup> $\ln(1-X) = -k(W/F)$ , X = conversion of CO to CO<sub>2</sub>, W = catalyst weight, F = flow rate, based on a pseudo first-order reaction in CO.

rials.<sup>10</sup> The ternary metal chalcogens can be obtained from a simple metathesis reaction between a Zintl phase material and a divalent transition metal halide. The Zintl phase  $K_3SbTe_3$ , which was recently synthesized from a direct combination of the elements,<sup>3</sup> has a substantial amount of ionic character, which may be sufficient to allow the solvation of salt-like ions in some polar solvents such as DMSO, ethylenediamine, and H<sub>2</sub>O. The Zintl ion,  $SbTe_3^{3-}$ , is quite reactive and the Zintl solution allows subsequent metathesis reaction with transition metal salts to produce amorphous intermetallic materials due to the transfer of electrons from the  $SbTe_3^{3-}$  anion to the metal cation according to the reaction:  $3M^{2+} + 2SbTe_3^{3-} \rightarrow M_3(SbTe_3)_2(s)$ . In this work, three amorphous ternary metal chalcogen compounds such as Cr<sub>3</sub>(SbTe<sub>3</sub>)<sub>2</sub>, Mn<sub>3</sub>(SbTe<sub>3</sub>)<sub>2</sub>, and Ni<sub>3</sub>(SbTe<sub>3</sub>)<sub>2</sub> have been synthesized to examine their catalytic activities for the water gas shift reaction. The three amorphous materials showed catalytic activities in the reaction and the catalytic activity varies with a transition element M in  $M_3(SbTe_3)_2$ . Among the catalysts tested, Cr<sub>3</sub>(SbTe<sub>3</sub>)<sub>2</sub> catalyst showed the best CO conversion of 72.0% to CO<sub>2</sub> at 750 °C and the CO conversion decreased in the sequence Cr<sub>3</sub>(SbTe<sub>3</sub>)<sub>2</sub> > Ni<sub>3</sub>(SbTe<sub>3</sub>)<sub>2</sub> > Mn<sub>3</sub>(SbTe<sub>3</sub>)<sub>2</sub> as listed in Table 1. The rate constant  $k$  in Table 1, being based on a pseudo-first-order reaction in carbon monoxide, was calculated for the rate of carbon monoxide conversion as a measure of activity; as a first approximation any effect of water was neglected due to its large surplus. Figure 1 shows variations of CO conversion to CO<sub>2</sub> with temperature over the three catalysts, in which the CO conversion increases with temperature in the range of 600 to 800 °C. Figure 2 shows the comparative rates of H<sub>2</sub> production over the three catalysts. As listed in Table 2, apparent activation energies obtained from the plot are found to be 15.2, 18.7, and 14.4 kcal/mol for Cr<sub>3</sub>(SbTe<sub>3</sub>)<sub>2</sub>, Mn<sub>3</sub>(SbTe<sub>3</sub>)<sub>2</sub>, and Ni<sub>3</sub>(SbTe<sub>3</sub>)<sub>2</sub>, respectively. The value for Ni<sub>3</sub>(SbTe<sub>3</sub>)<sub>2</sub>, 14.4 kcal/mol, is somewhat lower than 18.7 kcal/mol for 5% Ni/Al<sub>2</sub>O<sub>3</sub> catalyst.<sup>11</sup>

It has been known that the catalytic activities of metal oxides are related to their nonstoichiometric composition and electronic properties. To investigate whether there exists a relation between the electrical property and catalytic activity of the amorphous chalcogens or not, we measured the electrical conductivity of the specimens as a function of temperature in the range of 30 to 300 K. From the conductivity data, it was found that the Ni<sub>3</sub>(SbTe<sub>3</sub>)<sub>2</sub> exhibits a metallic behaviour with a electrical conductivity of  $\sigma = 1.98 \times 10^3$  (ohm cm)<sup>-1</sup> at 298 K, while both the Cr<sub>3</sub>(SbTe<sub>3</sub>)<sub>2</sub> and Mn<sub>3</sub>(SbTe<sub>3</sub>)<sub>2</sub>

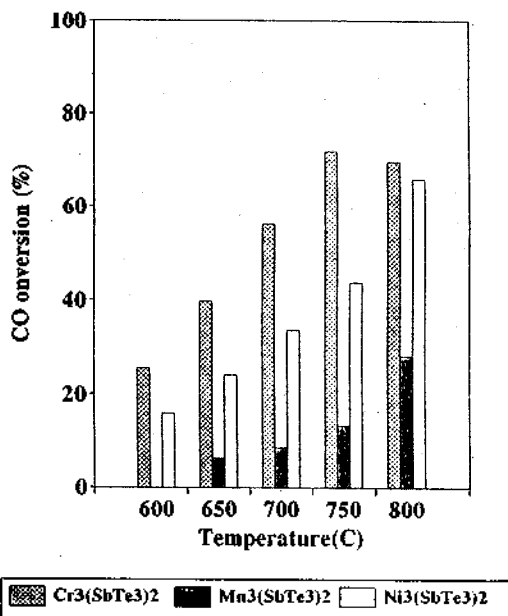
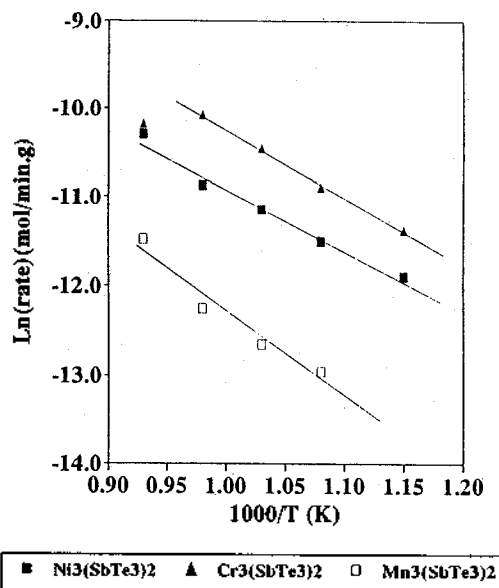
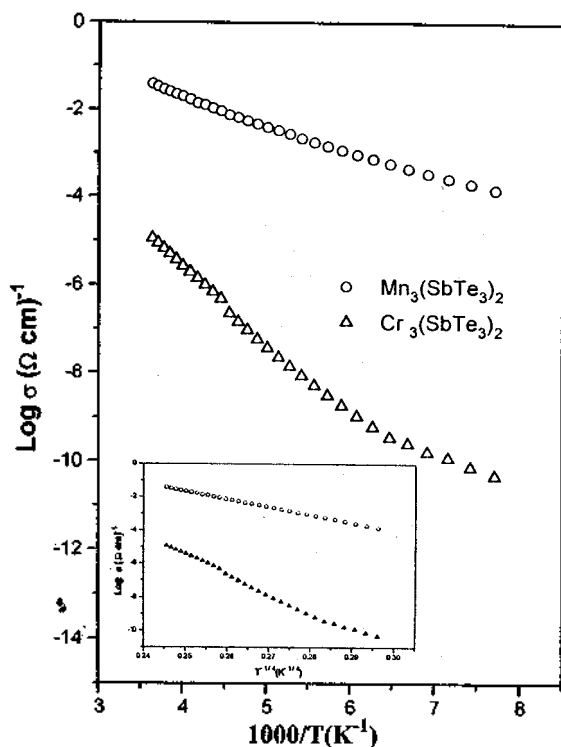
**Figure 1.** Variations of the conversion of CO to CO<sub>2</sub> with temperature over various  $M_3(SbTe_3)_2$  catalysts.**Figure 2.** Arrhenius plots for the H<sub>2</sub> production over various  $M_3(SbTe_3)_2$  catalysts.

exhibit a semiconducting behavior with electrical conductivities of  $1.09 \times 10^{-2}$  and  $2.79 \times 10^{-1}$  (ohm cm)<sup>-1</sup> at 298 K, respectively. Figure 3 shows the log  $\sigma$  values plotted as a function of the reciprocal of absolute temperature for Cr<sub>3</sub>(SbTe<sub>3</sub>)<sub>2</sub> and Mn<sub>3</sub>(SbTe<sub>3</sub>)<sub>2</sub> in the temperature range of 30 to 300 K, in which the electrical conductivity varies with a range of over 5 orders of magnitudes in the temperature range and increases with increasing temperature, indicating the specimens to be semiconductors. From a linear least-squares fit of conductivity data to the relationship,  $\sigma = A \exp(-E_a/kT)$ , in the temperature region 160-300 K, the activation energies for conduction were found to be 0.28 and 0.12 eV for Cr<sub>3</sub>(SbTe<sub>3</sub>)<sub>2</sub> and Mn<sub>3</sub>(SbTe<sub>3</sub>)<sub>2</sub>, respectively. As shown in Figure

**Figure 2.** Apparent activation energies ( $E_{app}$ ) for the production of  $H_2$  in the water gas shift reaction over various  $M_3(SbTe_3)_2$  catalysts

Catalyst	Temperature range (°C)	$E_{app}$ (kcal/mol)
$Cr_3(SbTe_3)_2$	600-750	15.2
$Mn_3(SbTe_3)_2$	650-800	18.7
$Ni_3(SbTe_3)_2$	600-800	14.4

Catalyst weight=0.3 g,  $P_{H_2O}/P_{CO}=4.26$ .



**Figure 3.** Electrical conductivities of  $Cr_3(SbTe_3)_2$  and  $Mn_3(SbTe_3)_2$  as a function of temperature in the range 30-300 K.

3, the plot of  $\log \sigma$  vs.  $1/T^{1/4}$  for  $Cr_3(SbTe_3)_2$  and  $Mn_3(SbTe_3)_2$  shows a straight line, which enables us to consider the variable range hopping conduction in the specimens.<sup>12</sup> A hopping transport mechanism has been observed in mixed valence semiconductors such as the simple 3d oxides, glasses containing 3d ions,<sup>13</sup> and amorphous materials.<sup>14</sup> Since hopping can only occur between ions of dissimilar valence, a hopping conduction in the present chalcogens means that the transition metal ions in  $M_3(SbTe_3)_2$  exist in more than one valence state. Therefore, it can be suggested that in the present chalcogens, an electron migrates from the  $M^{2+}$  to the adjacent  $M^{3+}$  and the  $M^{2+}$  becomes  $M^{3+}$  itself. When the transition metal ions in  $M_3(SbTe_3)_2$  are capable of cycling between at least two oxidation states, the chalcogens are applicable to a redox catalysis as a catalyst, which is believed to be the origin of a catalytic activity of the specimen for the water gas shift reaction. Considering the sequence of catalytic activity and the behavior of electrical conductivity for the present specimens, catalytic activities of the Zintl phase compounds seem to be not directly related to their electrical

properties.

As mentioned above, the catalytic activity largely depends on a transition metal element M in  $M_3(SbTe_3)_2$ , which indicates that transition metal ions in the specimens play an important role on the catalytic reaction. Iwamoto *et al.*<sup>15</sup> investigated catalytic activities of partially metal ion exchanged Y-type zeolites for the water gas shift reaction in the range of 473-773 K, in which the catalytic activity decreased in the sequence  $NiNaY > MnNaY > CrNaY$  at 773 K, being in the reverse sequence of this work. It is interesting to note that the oxidation number of Cr in the Cr ion exchanged Y-type zeolite (CrNaY) is +3, whereas the oxidation number of Cr in the  $Cr_3(SbTe_3)_2$  is +2. For the water gas shift reaction over metal or metal oxide catalysts, two reaction models have been proposed: regenerative mechanism and associative mechanism.<sup>16,17</sup> Recent works have shown that the regenerative mechanism is dominant on the metal oxide catalysts.<sup>16</sup> In the regenerative mechanism, active oxygen species are produced on the surface by the reaction of  $H_2O$  with metal oxide,  $H_2O(ads) \rightleftharpoons H_2(g) + O(ads)$ , and oxygen vacancies in the metal oxide act as an adsorption site for  $H_2O$  molecule.<sup>17</sup> In the present chalcogens, however, the existence of anion vacancies is not expected because the compounds are stoichiometric and noncrystalline materials. Thus, the regenerative mechanism seems to be not dominant on the catalysts. According to thermodynamic data of nickel compounds, the values of  $\Delta G_f^\circ$  of nickel hydroxide and nickel carbonyl are -106.9 kcal/mol and -140.4 kcal/mol,<sup>18</sup> respectively, which implies that the formation of nickel carbonyl is more favorable than the formation of nickel hydroxide. Ollis *et al.*<sup>11</sup> studied the water gas shift reaction over various alumina-supported metal catalysts. They found that carbon monoxide is primarily chemisorbed on metal site to form the M-CO intermediate and the stability of the M-CO is directly related to the catalytic activity and largely depends on a transition metal element in metal/ $Al_2O_3$ . Now, available thermodynamic and spectroscopic data are not enough for the explanation of the catalytic reaction on the present chalcogens because the specimens are new materials. Although the detailed catalytic reaction mechanism remains to be determined, the water gas shift reaction on the chalcogens seems to proceed catalytically according to the associative mechanism as proposed for metal<sup>11</sup> or organometallic catalysts<sup>19,20</sup> rather than the regenerative mechanism for metal oxide catalysts. Studies of *in situ*  $CO_2$ -laser induced photoacoustic spectroscopy and *in situ* FT-IR spectroscopy are currently in progress to investigate the detailed reaction mechanism over the present specimens.

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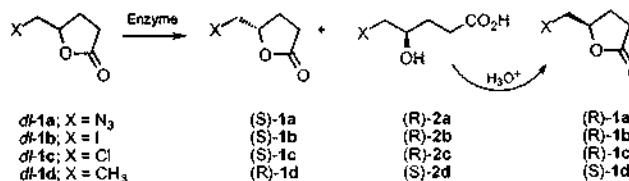
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Another method based on chiral glutamic acid as a chiral pool has also been reported.<sup>5</sup> All of them requires multi-step reaction sequences to elaborate the synthesis of both enantiomers. Due to the usefulness of  $\gamma$ -substituted-methyl- $\gamma$ -butyrolactones, resolution of racemates has been adopted as a method of rapid preparation of both enantiomers. Though the enzymatic hydrolysis<sup>6</sup> of  $\gamma$ -alkyl- $\gamma$ -butyrolactones has been studied to a certain extent, preparation of synthetically more valuable  $\gamma$ -substituted-methyl- $\gamma$ -butyrolactones remains to be investigated.<sup>7,8</sup> We report herein the results and characteristics of the enzyme-mediated resolution of  $\gamma$ -substituted-methyl- $\gamma$ -butyrolactones with azide (**1a**), iodine (**1b**), chlorine (**1c**) and methyl (**1d**) substituents. This appears to be the first example to prepare these lactones by lipase-mediated resolution, though ample examples<sup>9</sup> have been reported for the preparation of other types of  $\gamma$ -lactones *via* lipase-reactions. This study also provides an insight into the effects of the substituents located at four bonds away from the reaction center.

The racemic substrates of  $\gamma$ -chloro- and  $\gamma$ -azidomethyl- $\gamma$ -butyrolactones were prepared by chlorination and azidation of  $\gamma$ -iodomethyl- $\gamma$ -butyrolactone with LiCl and NaN<sub>3</sub> respectively. The resolutions were carried out with several different hydrolytic enzymes such as *Porcine pancreas* lipase (PPL), Lipase Amano AY of *Candida* sp. (AYL), Lipase Amano PS of *Pseudomonas* sp. (PSL) and Pig liver esterase (PLE).



**Scheme 1.**

## Lipase-Catalyzed Preparation of Optically Active $\gamma$ -Substituted-methyl- $\gamma$ -butyrolactones

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Optically active  $\gamma$ -substituted-methyl- $\gamma$ -butyrolactones, especially  $\gamma$ -azido-,  $\gamma$ -iodo- and  $\gamma$ -chloromethyl- $\gamma$ -butyrolactones, are valuable not only as synthons for various types of compounds<sup>1</sup> but as useful chiral auxiliaries.<sup>2</sup> A few methods toward the synthesis of optically active  $\gamma$ -substituted-methyl- $\gamma$ -butyrolactones have been reported, *i.e.*, asymmetric iodolactonization<sup>3</sup> with the aid of a chiral auxiliary and asymmetric reduction of  $\gamma$ -ketobutyric acid followed by lactonization.<sup>4</sup>

At first intensive studies were carried out with  $\gamma$ -azidomethyl- $\gamma$ -butyrolactone (**1a**) as a substrate due to its wide applicability by changing solvent, enzyme, and reaction time. The reaction of azidolactone with PPL proceeded in phosphate buffer (pH 7.2) without significant discrimination of one enantiomer from the other (entries 1 and 2). In the pure organic solvents of hexane reaction proceeded much faster with similar enantioselectivity as in buffer (entry 3). Addition of acetone to phosphate buffer (1/1, v/v) stopped the reaction completely due to possible destruction of the enzyme. Addition of hexane into the phosphate buffer accelerated the PPL-mediated reaction with better enantioselectivity (entries 4-7). With enzymes of AYL or PSL in the mixed media of buffer and hexane (1:3, v/v) resolution was not successful either by retarded reaction rate or by poor selectivity. (entries 8 and 9) The reaction with the esterase enzyme of PLE proceeded faster than with PPL in phosphate buffer (entry 10). But the resolution was poor. The best result was obtained with PPL in the mixed solvent of phosphate buffer and hexane (1:3, v/v) (entries 6 and 7). (S)- and (R)-**1a** from entries 6 and 7 were hydrogenated with Pd C followed by acetylation to afford 5-acetyloxy-2-oxopiperidine (**4**).<sup>5a</sup> Enantioselectivity was re-evaluated with the resolved acetyl peaks of 5-acetyloxy-2-oxopiperidine in the NMR in the presence