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Vapor-Phase Carbonylation of Methanol over Tin-on-Active Carbon Catalysts

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It was found that a number of metals or metal oxides showed catalytic activities for the vapor-phase carbonylation of methanol in the presence of methyl iodide (CH_3I) promoter under the conditions of 250 °C and 10 atm (1 atm=1.01325×10^5 Pa), when they were supported on active carbon. Particularly, tin and lead showed high activities. The catalytic activity of the metallic tin increased with the process time over 5 h while that of the unreduced tin catalyst increased for more than 10 h to reach the same level. The catalytic performances of the tin on active carbon were similar to those of the nickel on active carbon which have been already reported.[1-3] It was suggested that the active species of the tin catalyst was some kind of metal compounds which was highly dispersed on active carbon and was able to be incorporated in the redox cycle.

It has been well-known that the carbonylation of methanol is catalyzed by metal carbonyl complexes of cobalt,[4] rhodium,[5] nickel,[6] and iridium,[7] dissolved in the liquid media, in the presence of iodide promoter. However, in the liquid phase, it has never been reported that metal species other than group VIII metals show the catalytic activity for the carbonylation of methanol.

We have already reported[1-3] that nickel and other group VIII metals supported on active carbon (AC) show high catalytic activities and selectivities for the vapor phase carbonylation of methanol. We have also reported that the activities of group VIII metals supported on AC can be ordered by the affinity between metal and halide ion, which exhibits a clear volcano shape with a peak at rhodium.[8] We have already reported in the letters that metal species such as Mo,[9] Sn,[10] and Pb[11] show catalytic activity for the title reaction, when they were supported on AC.

Experimental

Catalyst precursors were prepared by impregnating a commercially available active carbon (AC; Takeda Pharmaceutical Inc., Shirasagi C, specific surface area 1200 $m^2 g^{-1}$, particle size 20—40 mesh) with metal chloride or acetate from their aqueous solutions by the dry-up method. They were reduced in a hydrogen stream, at 400 °C, for 3 h, before the reaction. Also, silica gel (Fuji Davison ID, S.A. 270 $m^2 g^{-1}$) and γ-Al_2O_3 (Tokai konetsu,TKS 99651,S.A. 170 $m^2 g^{-1}$) were used for the tin catalyst. A flow type reaction apparatus with a fixed catalyst bed was employed under the pressurized conditions. The reactor was made of stainless-steel tube with an inner diameter of 8 mm. Methanol was mixed with CH_3I and was introduced to the reactor by a micro-feeder. The reaction mixture from the reactor was sampled by a heated gas sampler and was analyzed with a gas chromatograph. The temperature-programmed reaction (TPR) of chemisorbed CO on Sn/AC was done. The XPS analysis of catalysts were conducted before and after the reaction using Shimazu ESCA-850.

Results and Discussion

1. Catalytic Activity of Metal-on-Active Carbon.

Figure 1 shows the carbonylation activities of a variety of metal species other than group VIII metal, which we are plotted as a function of their first ionization potential. Among the metal species listed, tin, lead, copper, manganese, and molybdenum show high activities. The relation between the activity and the ionization potential represents a volcano shape which has a peak at tin. The reason why the catalytic activity are classified with respect to their ionization potential, should be attributed to the redox cycle of metal cation, which has been postulated for Rh-catalyzed[5] or Ni/AC catalyzed[8] carbonylation reaction. This subject will be discussed later.

In the present study, the characteristic features of the tin-on-AC catalyst, which exhibits the highest activity among the metals tested, were clarified in more detail.

2. Operational Factors Controlling Catalyst Performances. Figure 2 shows the effect of reaction temperature on the yield of carbonylation products on tin,

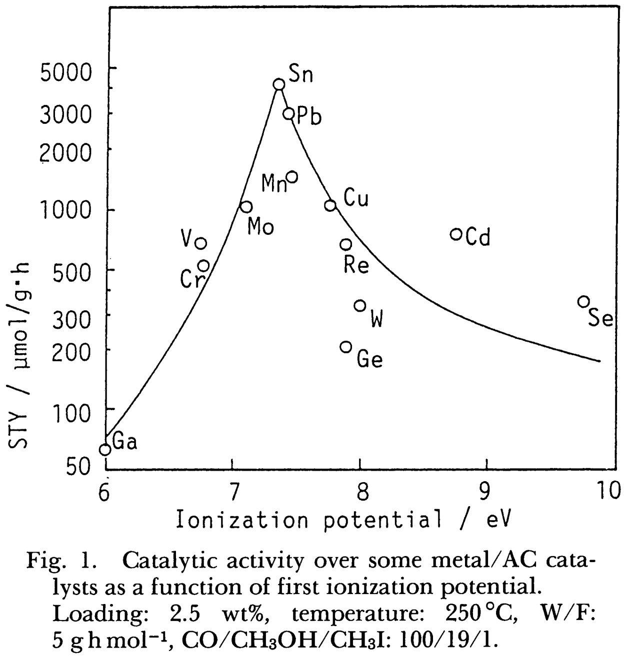

Fig. 1. Catalytic activity over some metal/AC catalysts as a function of first ionization potential. Loading: 2.5 wt%, temperature: 250 °C, W/F: 5 g h mol^{-1}, $CO/CH_3OH/CH_3I$: 100/19/1.

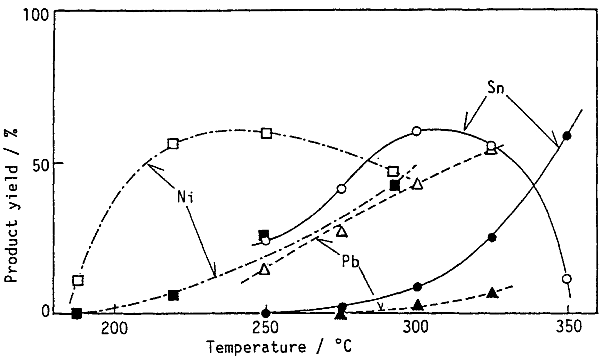

Fig. 2. Effect of reaction temperature about some metal/AC catalysts.
Loading: 2.5 wt%, pressure: 11 atm, W/F: 5 g h mol^{-1}, $CO/CH_3OH/CH_3I$: 100/19/1.
○: AcOMe (Sn/AC), ●: AcOH (Sn/AC), △: AcOMe (Pb/AC), ▲: AcOH (Pb/AC), □: AcOMe (Ni/AC), ■: AcOH (Ni/AC).

Table 1. Carbonylation of CH_3OH with Supported Tin Catalyst

Catalyst	Yield/%			
	AcOMe	AcOH	CH_4	DME
Sn/AC	25.1	0.6	0.2	3.1
Sn/SiO_2[a]	0	0	0.1	0.5
Sn/Al_2O_3[b]	0	0	0.7	86.3

Loading: 2.5 wt%, temperature: 250 °C, pressure: 11 atm, W/F: 5 g h mol^{-1}. a) ID, S.A.: 270 $m^2 g^{-1}$. b) TKS99651 , S.A. : 170 $m^2 g^{-1}$.

lead and nickel supported on active carbon. The yields of aimed products, methyl acetate and acetic acid, increased with increasing reaction temperature, for all catalysts. The yield of methyl acetate was higher than that of acetic acid for all metals at lower temperature. The yield of acetic acid exceeded that of methyl acetate at 300 °C for the Ni/AC catalyst, while the point was 340 °C on the Sn/AC catalyst and methyl acetate was the major product over all temperature range tested on the Pb/AC. These differences can be explained by the successive reaction mechanism (the primary product is methyl acetate and acetic acid is formed successively from methyl acetate).[1] The catalyst of higher activity has the crossing point at lower temperature.

Figure 3 shows how the operating pressure affects the catalyst performances. The yields of methyl acetate and dimethyl ether increased with increasing operation pressure while those of methane and acetic acid were almost constant over the pressure region tested. The selectivity to carbonylation products was kept almost constant at 80%. Since the Sn/AC catalyst shows the positive reaction orders with respect to CO and CH_3OH, as well as the Ni/AC catalyst (Table 2), the rate of reaction should be increased with the increase in the reaction pressure, because of the increase in the partial pressures of CO and CH_3OH.

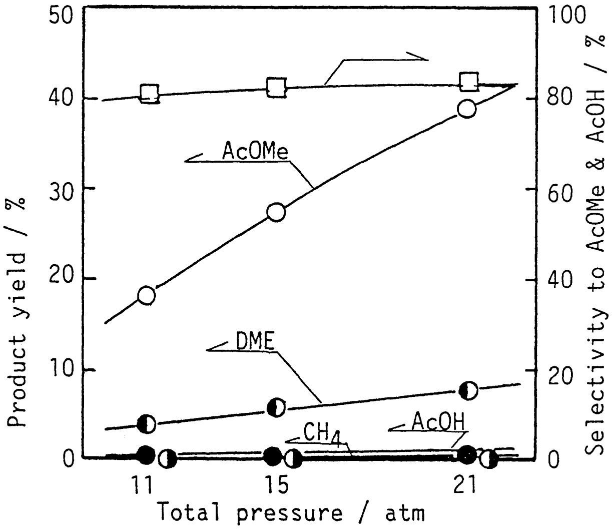

Fig. 3. Effect of reaction total pressure.
Catalyst: Sn/AC (2.5 wt%), temperature: 250 °C, W/F: 5 g h mol^{-1}, $CO/CH_3OH/CH_3I$: 100/19/1.

3. Catalytic Features of Sn/AC Catalyst. 3-a. Effect of Supports. Table 1 shows the effect of supports on the catalytic activity of tin. The activity of tin for the carbonylation appeared only when it was supported on active carbon (AC) giving the methyl acetate yield of 25.1% and the acetic acid (AcOH) yield of 0.6% at 250 °C and 11 atm. This products distribution is almost the same as that of nickel on AC (Ni/AC). When supported on SiO_2 or Al_2O_3, tin exhibited no carbonylation activity, quite similarly to that of nickel.[11] The appearance of the carbonylation activity of tin only AC is most presumably attributed to the same carrier effects of AC which was suggested for the Ni/AC catalyst.[1]

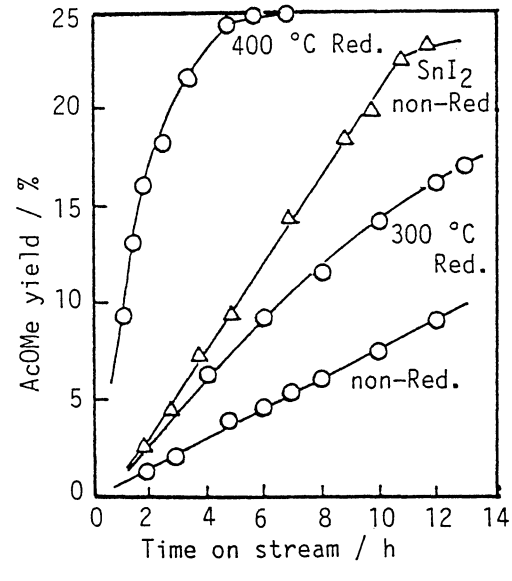

Fig. 4. Activity change with process time. (the effct of reduction) Catalyst: Sn/AC (2.5 wt%), temperature: 250 °C, W/F: 5 g h mol^{-1}, $CO/CH_3OH/CH_3I$: 100/19/1.

3-b. Effect of H_2 Reduction on the Activation of Sn/AC Catalyst. Figure 4 shows the effect of pre-reduction of the Sn/AC catalyst by hydrogen on the change in the catalytic activity as a function of process time. In the case of the unreduced tin catalyst (made of tin acetate), the yield of methyl acetate increased slowly with the reaction time. As the temperature of pre-reduction was increased, the rate of catalyst activation increased. When the catalyst was reduced by hydrogen at 400 °C, the yield of methyl acetate increased quickly and leveled off at about 5 h. Similar phenomenon was also observed for the Pb/AC catalyst.[11] Supported tin acetate was decomposed to tin oxide during the heating step and it was reduced to metallic tin upon hydrogen reduction at 400 °C (Fig. 6). The data in Fig. 4 shows that metallic tin is quickly converted to active species and that the slow activation of the unreduced catalyst should be attributed to the slow reduction of the catalyst during the carbonylation reaction. The SnI_2/AC was activated rather quickly in spite of no pre-treatment. In all cases which were examined, the yields of methane and dimethyl ether were almost constant over the process period.

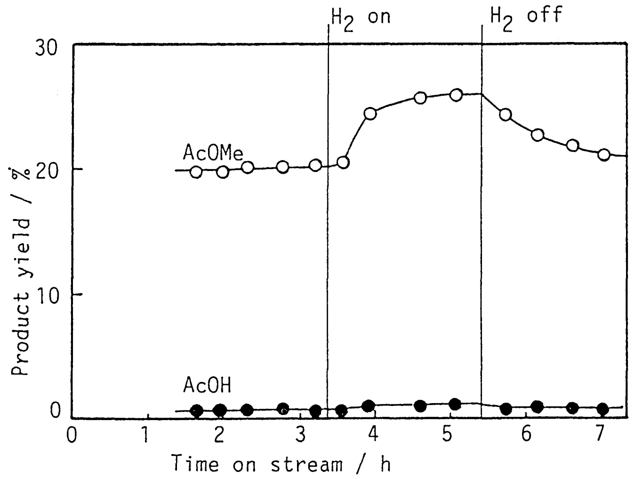

Fig. 5. Effect of H_2 addition.
Catalyst: Sn/AC (2.5 wt%), temperature: 250 °C, W/F: 5 g h mol^{-1}, $CO/CH_3OH/CH_3I/H_2$: 100/19/1/19.

3-c. Effect of Added H_2 on the Catalytic Activity. Figure 5 shows the effect of added hydrogen gas in the feed. The yields of carbonylation products rose after 30 minutes from the hydrogen addition and reached a constant level after 1 h. After 1 hour from the stop of hydrogen addition, the yield returned to the level under the hydrogen free condition. The reason of the promotional effect of hydrogen should be similar to that on the Ni/AC catalyst,[12] which will be discussed, later.

3-d. Physical and Chemical State of Tin on Active Carbon. Figure 6 shows XRD pattern of the Sn/AC catalysts, before and after the reaction. In case of the unreduced catalyst, no clear peak was observed before and after the reaction, the weak peaks assigned to tin acetate and tin oxide were observed. In case of the

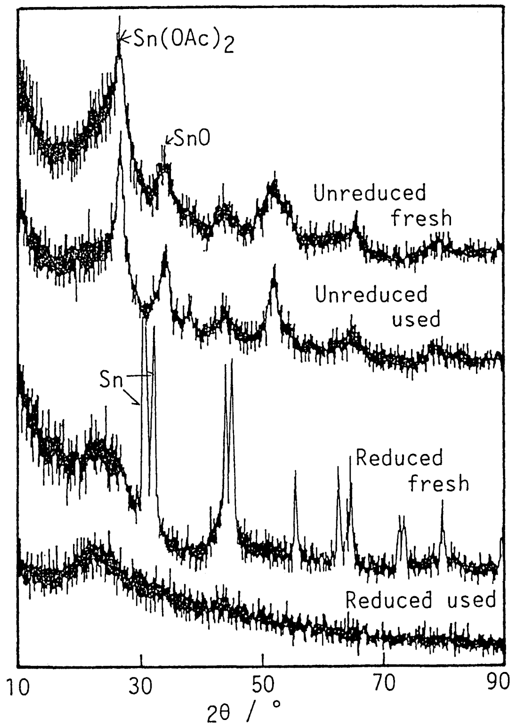

Fig. 6. XRD pattern of Sn/AC catalysts.

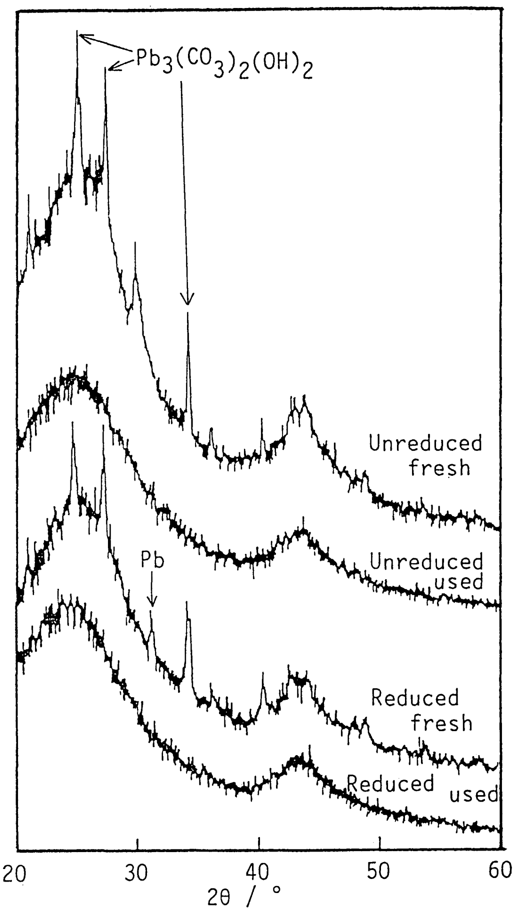

Fig. 7. XRD pattern of Pb/AC catalysts.

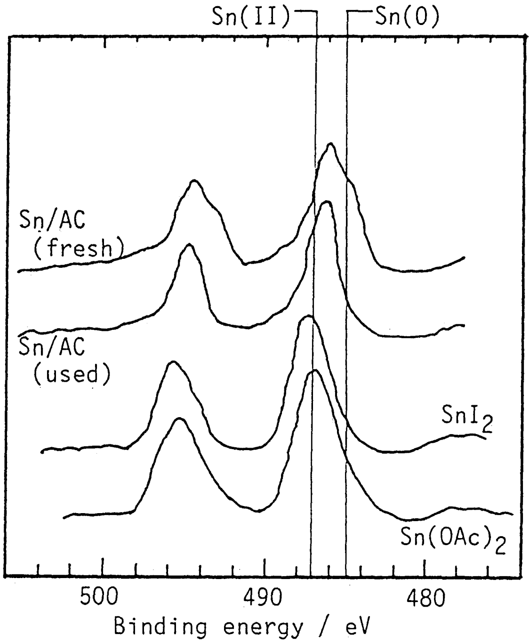

Fig. 8. XPS pattern of Sn/AC catalysts.

reduced catalyst, on the other hand, sharp peaks assigned to tin metal were observed before the reaction, while no peak was observed after the reaction. These facts suggest that tin compounds in the oxidized state and activated tin species are dispersed very finely on active carbon. Similar behaviors were also observed for the Pb/AC catalyst as demonstrated in Fig. 7.

Figure 8 shows the results of XPS analysis of the reduced Sn/AC catalysts before and after the reaction. Before the reaction, the surface of catalyst consists of the mixture of reduced tin and oxidized tin. After the reaction, most of the tin seems to be in the oxidized state. The existence of iodide on the catalyst was also confirmed by the XPS analysis. Thus the main tin species during the reaction can be concluded to tin salts containing iodide ion.

4. Discussions on the Catalysis of Sn/AC for Methanol Carbonylation. 4-a. Redox Cycle of Sn/AC Catalyst. It has been generally accepted that the methanol carbonylation with transition metal complexes, which gives methyl acetate (AcOMe) and acetic acid (AcOH), are based on the redox cycle of metals.[13]

(1) Oxidative addition of CH_3I to the catalyst surface.

(2) Insertion of CO into the methyl-metal bond.

(3) Reductive methanolysis of complex to give the products.

Step (1) is rate determining for the Rh complex catalyst.[5] Also, on the Rh/AC catalyst, the fact that the reaction order with respect to CO is low (0.3) and that of CH_3I is high (0.7) (Table 2), suggests that the adsorption of CH_3I is rather rate-determining. On Ni/AC catalyst, on the other hand, the order with respect to CH_3I is low (0.1) and those of CO and methanol are high (0.1 and 0.5, respectively). Thus, it has been concluded that the oxidative addition of CH_3I (step (1)) is not the rate-determining step, but step (2) or step (3) is rate-determinating on the Ni/AC catalyst.[2]

For the Ni/AC catalyst, the redox cycle consists of the oxidation of Ni^0 to Ni^{2+} by the adsorbed CH_3I (step (1)) and the reduction of Ni^{2+} by methanol or CO (step (2) and (3)). The XPS experiments on the Ni/AC catalyst pointed out that Ni is mostly in the Ni^{2+} state and that active carbon promote the step (3) ($Ni^{2+} \rightarrow Ni^0$).[14]

As described before, the catalytic features of Sn/AC is quite similar to those of Ni/AC as follows;

[1] Carbonylation activity appears only when it is supported on active carbon (Table 1).

[2] The reaction order with respect to CH_3I is low while those with respect to methanol and CO are rather high (Table 2).

[3] Carbonylation activity increases by adding H_2 to feed (Fig. 5). Thus, it is quite probable that the carbonylation reaction on the Sn/AC catalyst proceeds on the catalytic cycle similar to that of the Ni/AC catalyst.

It is well known that metallic tin reacts quickly with CH_3I to form organic tin compound.[15] Rather high average oxidation number of tin after the reaction (1.5), which was determined by XPS (Fig. 8), and the disappearance of metallic tin during the reaction suggests that the chemisorption of CH_3I proceeds in the form of the oxidative addition. The low reaction order with respect to CH_3I also suggests that its adsorption on tin is strong like the case for the Ni/AC catalysts.

If the adsorption of CH_3I to tin is strong, the peculiar promotional effect of active carbon should be attributed to its promotion of the reductive elimination step as is the case of the Ni catalyst.[14] The correlation of catalytic activity to the ionization potential of the catalytically active ingredient, which shows a volcano shape giving a peak at Sn, can be well explained by that the oxidation-reduction character of Sn is best balanced for the redox cycle during methanol carbonylation.

4-b. The Behavior of CO and CH_3I on Sn/AC. Another subject, which should be discussed, is whether the step (2) (insertion of CO into CH_3-Sn bonding) is possible or not. Figure 9 shows the temperature-programmed reaction (TPR) spectra of

Table 2. Reaction Order of Methyl Acetate Formation for Each Metal Active Carbon Catalysts

Catalyst	Reactants		
	CO	CH_3OH	CH_3I
Sn	0.5	0.3	0.0
Ni	0.6	0.5	0.1
Rh	0.3	0.6	0.7

Loading: 2.5 wt%.

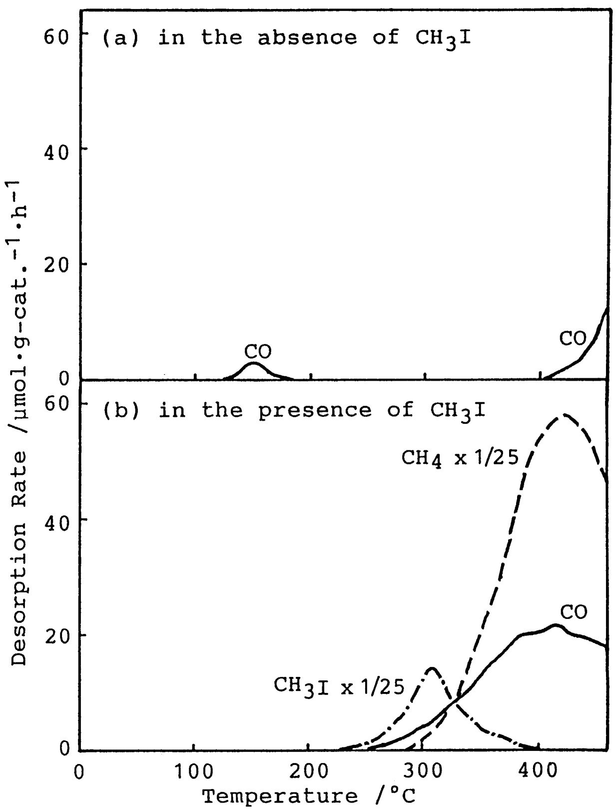

Fig. 9. Temperature-programmed reaction spectra of adsorbed CO. Catalyst: Sn/AC (2.5 wt%), Heating rate: 400 °C h^{-1}, H_2 flow rate: 100 cm^3 g^{-1} min^{-1}. (a) CO adsorbed at 150 °C without the pre-adsorption of CH_3I, (b) CO adsorbed at 150 °C after the pre-adsorption of CH_3I at 250 °C.

adsorbed CO on Sn/AC in H_2 stream. Since the catalyst has been treated with flowing H_2 for 3 h to reduce tin acetate to metallic tin and to decompose surface oxide compounds on AC, the CO desorbed between 100 and 200 °C should be attributed to the adsorbed CO on tin metal, while the CO desorbed at above 400 °C should be attributed to the decomposition of surface oxide remained. From the catalyst with pre-adsorbed CH_3I, no CO was desorbed below 200 °C, but large amount of CH_4 and CH_3I were desorbed above 250 °C which was accompanied by a small CO desorption.

Since little or no CH_3I was adsorbed on active carbon at 250 °C, the desorbed CH_3I and CH_4 should be attributed to adsorbed CH_3I on Sn. Since CH_3I is stable at around 400 °C, CH_4 formation may presumably be attributed to the hydrogenation of dissoatively adsorbed CH_3I.

$$CH_3\text{-}X\text{-}I + H_2 \longrightarrow CH_4 + HI + X.$$

Another point, which should be noticed is that the TPR spectrum of CO is quite similar to that of CH_4, except that its amount is about 1/20 of that of CH_4. Since the adsorption of CO on Sn with pre-adsorbed CH_3I (as demonstrated in Fig. 9(b)), the desorbed CO above 250 °C is most probably attributed to the hydrogenolysis of acyl complex on Sn.

$$CH_3\text{-}CO\text{-}X\text{-}I + H_2 \longrightarrow CH_4 + CO + HI + X.$$

If this assumption is correct, it is further suggested that about 5% of dissociatively adsorbed CH_3I is converted to acyl complex when exposed to CO at 150 °C and that the acyl complex is rather stable to heat and H_2.

The promotional effect of hydrogen on the carbonylation activity is caused by the strong chemisorption of CH_3I to the catalyst surface. The access of methanol or carbon monoxide to the catalyst surface should be suppressed by the adsorbed iodide. However, when hydrogen is added, the catalyst surface is reduced to increase the free sites on which methanol or carbon monoxide is accessible.

The considerations described so far lead us to the concept that the catalysis of the Sn/AC for the carbonylation reaction is composed of (1) the oxidative adsorption of CH_3I to tin (presumably zero valence state), (2) the insertion of CO into Sn-CH_3 bonding to form acyl complex and (3) the carbon catalyzed reductive methanolysis of the complex to form methyl acetate.

Conclusion

(1) A variety of metal species showed the catalytic activity for the vapor phase carbonylation of methanol when they were supported on active carbon, among which tin and lead showed high activities.

(2) The carbonylation activity of tin appeared only when it was supported on active carbon and its activity was promoted by the addition of hydrogen gas in the feed.

(3) The Sn/AC catalyst showed similar characteristic feature in their catalytic performances to the Ni/AC catalyst.

(4) Metallic tin was converted to active species quickly during the reaction.

(5) Redox cycle of Sn^{2+} and Sn^0 has been proposed as the catalysis of Sn/AC for methanol carbonylation in the presence of CH_3I.

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