

Synthesis of acetic acid from methanol alone by homogeneous metal complex catalyst. Part 4¹. In-situ formation of catalyst species and halogen effect in the $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}-\text{SnX}_2$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) composite system

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Abstract

Highly selective formation of methyl acetate has been found possible from methanol alone using the catalyst generated in situ from $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and SnCl_2 as well as SnX_2 ($\text{X} = \text{F}, \text{Br}, \text{I}$). The reaction did not occur in the absence of SnCl_2 added and the optimum $[\text{Sn}]/[\text{Ru}]$ ratio appeared at about 16. The halogen effect showed the order of $\text{SnF}_2 > \text{SnCl}_2 > \text{SnBr}_2 > \text{SnI}_2$, which indicates the importance of cationic character of Ru(II) center to facilitate its electrophilic interaction with β -hydrogen of Ru–OCH₃ intermediate in the rate-limiting dehydrogenation step. © 1998 Elsevier Science B.V.

Keywords: Acetic acid; Methanol; Methyl acetate; Ruthenium complex; Tin(II) ligand

1. Introduction

We have previously reported that Ru(II)–Sn(II) cluster complexes can catalyze the unprecedented reaction, where acetic acid (and/or methyl acetate due to fast esterification) is formed in a single step with methanol used as the sole source both in the homogeneous solution [1–6] and in the heterogeneous gas–solid phase [6,7]. Compared with the Monsanto pro-

cess which produces acetic acid by the carbonylation of methanol with Rh catalyst and an iodide promoter, this reaction seems of interest because acetic acid is obtainable from methanol alone by use of less expensive metals (Ru and Sn) without a corrosive iodide promoter.

Since the halide salts of group VIII metals are known to form coordination compounds with halide salts of Sn(II) [8], we attempted here the acetic acid formation using the catalyst generated in situ from the most common salts, $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and SnCl_2 as well as SnX_2 ($\text{X} = \text{F}, \text{Br}, \text{I}$). Despite the simplicity of catalyst preparation, the catalytic activity (per ruthenium) was found to be considerably high.

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¹ For Part 3 see Ref. [5].

2. Experimental

2.1. Reagents

All chemicals and solvents were of reagent grade. Methanol was dried over CaH_2 and then Na, and distilled under an argon atmosphere before use. Acetonitrile was dried over CaH_2 and distilled in the same manner. SnI_2 was recrystallized from CHCl_3 . Other reagents were used without further purification.

2.2. Preparation of catalyst solutions

All manipulations were carried out under an argon atmosphere using standard vacuum-manifold and Schlenk techniques. Typically, a calculated amount of SnCl_2 was added to a deaerated mixed solvent of methanol (15 ml) and acetonitrile (15 ml). Stirring for 30 min gives a homogeneous solution, to which an appropriate amount of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ was dissolved. Similar procedures were adopted for SnX_2 ($\text{X} = \text{F}, \text{Br}, \text{I}$), but a longer time of stirring (60 min) was necessary for SnF_2 and SnI_2 .

2.3. Catalytic reactions

Catalytic reactions were carried out with a solution volume of 0.56 ml in a Pyrex glass ampule (3.5 ml volume), which was sealed under vacuum with the solution frozen by liquid nitrogen. The products were identified with GC-MS (Hitachi M-7200, PEG 20 M capillary column, 50 m) and analyzed quantitatively with GC (PEG 6000 column). In order to examine the stoichiometry between dehydrogenated products and dihydrogen, the reactions were performed at refluxing temperature (68°C) under a dinitrogen atmosphere (1 atm), where the reactor was equipped with a refluxing condenser to which the gas burette with a mercury seal [9] was attached. After the reaction was ceased, a part of the gas in the reactor was withdrawn with a syringe through a rubber septum at the

top of the condenser and was analyzed with GC (active carbon and Porapak T columns). For the sake of higher precision for analyzing CO and CO_2 , a methane convertor was used with a flame-ionization detector. The formed amounts of gaseous products were calculated on the basis of the composition and the total volume of gas phase.

^{119}Sn -NMR spectra were recorded on a Jeol JNM-FX60Q spectrometer, operating at 22.30 MHz at 25°C . Chemical shifts are quoted relative to $\text{Sn}(\text{CH}_3)_4$ as an external standard.

3. Results

3.1. RuCl_3 - SnCl_2 composite catalyst

A representative time-course of methyl acetate formation is shown in Fig. 1. The turnover number is calculated from the amount of product (mol) divided by the amount of charged ruthenium (mol). As is seen in Fig. 1, methyl acetate is formed without an induction period and the formation of other dehydrogenated products (formaldehyde, methylal and methyl

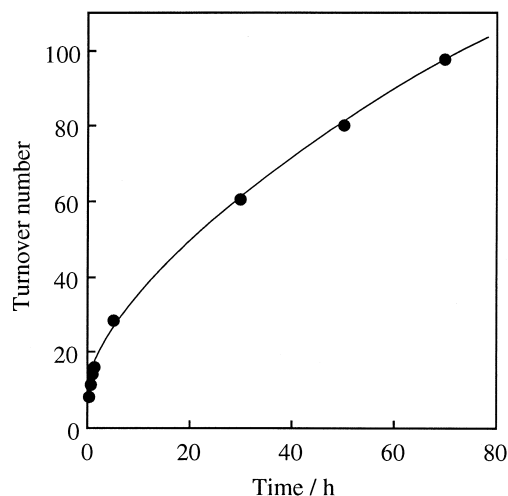
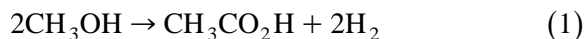


Fig. 1. Time-course of methyl acetate formation for the $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ - SnCl_2 composite catalyst. $[\text{Ru}] = 50 \text{ mM}$, $[\text{Sn}]/[\text{Ru}] = 16$, $\text{MeOH}:\text{MeCN} = 1:1$ (v/v), reaction temperature 140°C .

formate) was negligible. Thus, the selectivity of methyl acetate formation is quite high.

In the gas phase, any products other than H_2 (CO , CO_2 , CH_4) were not detected and the stoichiometry between methyl acetate and H_2 (1:2 mole ratio) was satisfactory. For instance, formation of 1.19×10^{-2} mmol of H_2 was observed with a 4.0% deviation from the expected value (1.24×10^{-2} mmol), when 6.22×10^{-3} mmol of methyl acetate was formed ($[\text{Ru}] = 50$ mM, $[\text{Sn}]/[\text{Ru}] = 16$, 68°C , 24 h). Hence, it is certain that acetic acid (methyl acetate) is produced through the dehydrogenation of methanol as shown in Eq. (1)



3.2. Dependence of the rate of methyl acetate formation on the $[\text{Sn}]/[\text{Ru}]$ ratio

Fig. 2 shows the dependence of the initial rate of methyl acetate formation on the $[\text{Sn}]/[\text{Ru}]$ ratio, where the total concentration of ruthenium was kept constant (50 mM). The initial rates were determined from the initial

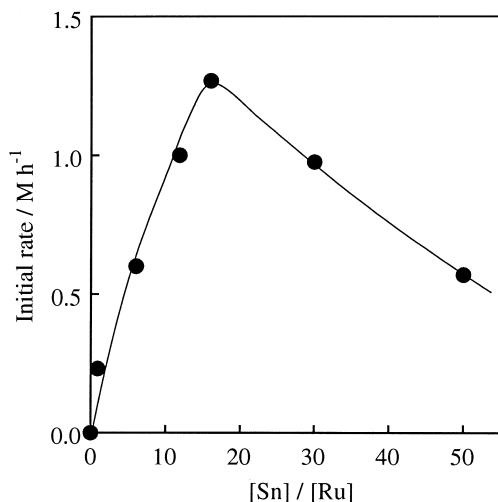


Fig. 2. Dependence of the initial rate on the $[\text{Sn}]/[\text{Ru}]$ ratio for the $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}-\text{SnCl}_2$ composite catalyst. $[\text{Ru}] = 50$ mM, $\text{MeOH}:\text{MeCN} = 1:1$ (v/v), reaction temperature 140°C .

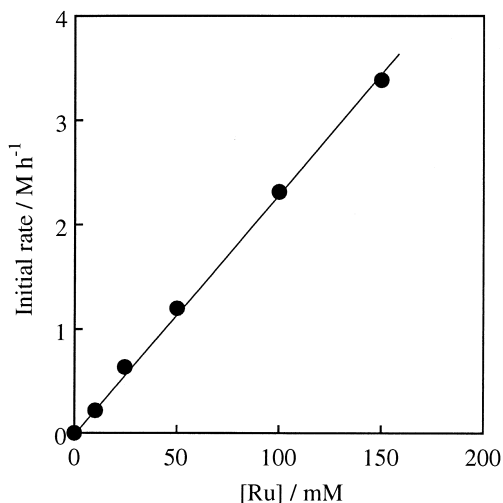


Fig. 3. Initial rate of methyl acetate formation plotted as a function of catalyst concentration for the $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}-\text{SnCl}_2$ composite catalyst. $[\text{Sn}]/[\text{Ru}] = 16$, $\text{MeOH}:\text{MeCN} = 1:1$ (v/v), reaction temperature 140°C .

linear slopes of the time versus conversion curves (typically 0–1 h). It is obvious from Fig. 2 that the addition of SnCl_2 is indispensable for the methyl acetate formation, and that an optimum value appears at about $[\text{Sn}]/[\text{Ru}] = 16$.

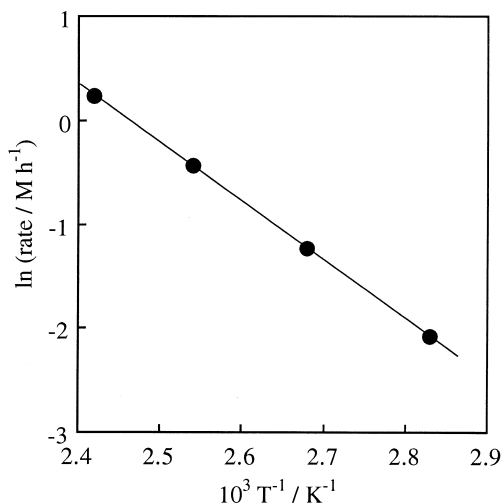


Fig. 4. Temperature dependence of the initial rate of methyl acetate formation for the $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}-\text{SnCl}_2$ composite catalyst. $[\text{Ru}] = 50$ mM, $[\text{Sn}]/[\text{Ru}] = 16$, $\text{MeOH}:\text{MeCN} = 1:1$ (v/v).

Table 1
Initial rate for the $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}-\text{SnX}_2$ ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$) composite catalyst^a

	SnX_2			
	SnF_2	SnCl_2	SnBr_2	SnI_2
Initial rate (Mh^{-1})	0.198	0.179	0.125	0.096

^a[Ru] = 25 mM, [Sn]/[Ru] = 1, reaction temperature 140°C.

3.3. Dependence of the rate of methyl acetate formation on the concentration of catalyst

Fig. 3 gives the dependence of the initial rate of methyl acetate formation on the concentration of catalyst, where the charged amount of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ was varied (10–150 mM) with a fixed ratio of [Sn]/[Ru] = 16. An almost linear relationship suggests that the composition of catalyst species does not change appreciably under the condition of constant [Sn]/[Ru] ratio.

3.4. Temperature dependence

Temperature dependence of the initial rate of methyl acetate formation was examined in the range from 80 to 140°C. A linear Arrhenius plot (Fig. 4, $E_a = 47.3 \text{ kJ mol}^{-1}$) suggests the virtual invariance of catalyst composition in this temperature range.

3.5. Comparison among SnX_2 ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$)

Because of the low solubility of SnF_2 and SnI_2 in the methanol/acetonitrile mixed solvent, reactions were carried out with [Sn] = 25 mM and [Sn]/[Ru] = 1. Results listed in Table 1 indicate the activity order of $\text{SnF}_2 > \text{SnCl}_2 >$

$\text{SnBr}_2 > \text{SnI}_2$. When the activation energies were compared (100–140°C), the same trend was observed as the halogen effect (Table 2).

4. Discussion

It is known that Ru(II)–Sn(II) clusters containing one Ru(II) and four to six Sn(II) are formed readily in the solution containing RuCl_3 and SnCl_2 [10]. Actually, ^{119}Sn -NMR spectrum of the reaction solution ([Ru] = 50 mM, [Sn]/[Ru] = 16, after the reaction of 1 h at 140°C) exhibited two peaks at -152.8 and -382.3 ppm, which can be assigned to $[\text{RuCl}(\text{SnCl}_3)_5]^{4-}$ and *trans*- $[\text{RuCl}_2(\text{SnCl}_3)_4]^{4-}$, respectively [10]. Preliminary experiments using these complexes, obtained separately in the form of NEt_4^+ salts [10,11], showed that exclusive formation of methyl acetate was also possible with these complexes as catalysts ([Ru] = 50 mM, $([\text{SnCl}_3^-]_{\text{ligand}} + [\text{SnCl}_2]_{\text{added}})/[\text{Ru}] = 16$, 140°C). This fact indicates that they are active species or catalyst precursors. However, undetected species may also be responsible, because the turnover numbers for 1 h (11.8 and 6.2, respectively) are smaller than that for the composite system (14.1, Fig. 1). Since the maximum number of Sn(II) coordination is six for one Ru(II), the optimum [Sn]/[Ru] ratio appearing around 16 (Fig. 2) suggests that the presence of free SnCl_2 accelerates methyl acetate formation.

It is suggested that the rate-determining step of acetic acid formation is the dehydrogenation of methanol to produce formaldehyde [5]. Since Lewis acid such as SnCl_2 [8] has the ability to eliminate a halide ligand from transition-metal complexes [12], the observed acceleration effect may be ascribed to the generation of vacant site on the catalytic center. In the presence of excess amount of SnCl_2 ([Sn]/[Ru] > 16), however, dissociation equilibrium of Sn(II) ligand would become disadvantageous, leading to the overall retardation of vacant site formation.

Table 2
Activation energy for the $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}-\text{SnX}_2$ ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$) composite catalyst^a

	SnX_2			
	SnF_2	SnCl_2	SnBr_2	SnI_2
E_a (kJ mol^{-1})	68.7	72.2	74.8	78.0

^a[Ru] = 25 mM, [Sn]/[Ru] = 1.

It has been found that dehydrogenation of methanol with a Ru(II)–phosphine complex catalyst is facilitated more by the presence of more electron-withdrawing ligand [13]. Here, electrophilic interaction of an Ru(II) center with β -hydrogen (in the Ru–OCH₃ intermediate) is considered to play an essential role. Tables 1 and 2 clearly show the order of SnF₂ > SnCl₂ > SnBr₂ > SnI₂, which coincides exactly with the electronegativity order of X [3,4]. Thus, the observed trend not only supports the mechanistic view of acetic acid formation, but also gives a clear example for the halogen effect in homogeneous catalysis.

Acknowledgements

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References

- [1] S. Shinoda, T. Yamakawa, *J. Chem. Soc., Chem. Commun.* (1990) 1511.
- [2] T. Yamakawa, M. Hiroi, S. Shinoda, *J. Chem. Soc., Dalton Trans.* (1994) 2265.
- [3] H. Einaga, T. Yamakawa, S. Shinoda, *J. Coord. Chem.* 32 (1994) 117.
- [4] H. Einaga, T. Yamakawa, S. Shinoda, *J. Mol. Catal. A* 97 (1995) 35.
- [5] T. Ohnishi, T. Yamakawa, S. Shinoda, *J. Chem. Soc., Dalton Trans.* (1997) 789.
- [6] S. Shinoda, T. Ohnishi, T. Yamakawa, *Catal. Surv. Jpn.* 1 (1997) 25.
- [7] T. Yamakawa, P.-K. Tsai, S. Shinoda, *Appl. Catal. A* 92 (1992) L1.
- [8] M.S. Holt, W.L. Wilson, J.H. Nelson, *Chem. Rev.* 89 (1989) 11.
- [9] J.A. Lely, *J. Chem. Educ.* 58 (1981) 358.
- [10] H. Moriyama, P.S. Pregosin, Y. Saito, T. Yamakawa, *J. Chem. Soc., Dalton Trans.* (1984) 2329.
- [11] L.J. Farrugia, B.R. James, C.R. Lassigne, E.J. Wells, *Can. J. Chem.* 60 (1982) 1304.
- [12] H. Maeta, T. Hasegawa, K. Suzuki, *Synlett* (1993) 341.
- [13] L.-C. Yang, T. Ishida, T. Yamakawa, S. Shinoda, *J. Mol. Catal. A* 108 (1996) 87.