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# Hydrosilylation reaction of ethylene with triethoxysilane catalyzed by ruthenium halides and promoted by cuprous halides



Ling Liu<sup>a,b</sup>, Xiaonian Li<sup>a,\*</sup>, Hong Dong<sup>b</sup>, Chuan Wu<sup>b,\*\*</sup>

<sup>a</sup> College of Chemical Engineering and Materials Science, Zhejiang University of Technology, Hangzhou 310032, PR China
<sup>b</sup> Key Laboratory of Organosilicon Chemistry and Material Technology, Ministry of Education, Hangzhou Normal University, Hangzhou 310012, PR China

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## ABSTRACT

The hydrosilylation reaction of ethylene with triethoxysilane catalyzed by ruthenium halides and promoted by cuprous halides, iodine or ferrous chloride tetrahydrates was conducted at temperatures ranging from 30 to 80 °C under a mild pressure of ethylene gas. Ruthenium chloride trihydrates and cuprous chloride are proved to be the best catalyst and promoter for this reaction. With the addition of  $6.8 \times 10^{-5}$  mol ruthenium chloride trihydrates per mole of triethoxysilane together with over 3 times of cuprous chloride per mole of ruthenium chloride trihydrates, the reaction can conduct rapidly at temperatures ranging from 40 to 60 °C under a pressure of ethylene gas lower than 0.35 MPa with over 96% vield of ethyltriethoxysilane within 6 h.

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# 1. Introduction

Ethyltriethoxysilane (ETES, CAS RN: 78-07-9) is really an important organic silicon chemical in the silicone industry, and it has been widely used in many fields such as functional materials, silane coupling agents, and modifying agents for zeolite nanoparticle-supported catalysts with good stability and high selectivity. Besides, ETES also plays an important role in the fabrication of organosilicon polymers due to its three hydrolyzable oxyethyl groups.

The first synthesis of ETES was reported by Mikaya in 1985 (Scheme 1) [1]. The reaction was run in a gas phase and analyzed on-line through a column connected to the mass spectrometer. So the output of product is limited. Later, other synthesis methods were reported (see Table 1). Among these various methods lined, hydrosilylation of ethylene may be the most effective method (Entry 3, Table 1). However, the expensive platinum complexes bis [1,3-bis( $\eta^2$ -ethenyl)-1,1,3,3-tetramethyldisiloxane)][ $\mu$ -( $\eta^2$ : $\eta^2$ -1,3-die thenyl-1,1,3,3-tetramethyldisiloxane)]di-(9Cl) was employed in the catalytic hydrosilylation process. It is well-known that the cost of platinum and its complexes blocked their application in industrial

processes. Therefore, it is of great significance to find out a platinum substitute with lower price and higher catalytic activity. In 2010, we reported a very simple and effective method for synthesis of ethyltrimethoxysilane through the hydrosilylation reaction between ethylene and trimethoxysilane [7]. In this reaction, RuCl<sub>3</sub>·3H<sub>2</sub>O doped with iodine was screened as the catalytic system and it exhibited higher catalytic activity and selectivity. Besides, we also applied this catalytic system to the hydrosilylation reaction between ethylene and triethoxysilane. Comparing with Chernyshev's method [3] (Scheme 2), this catalytic system showed some advantages due to its cheaper cost and excellent catalytic activity and selectivity even under mild reaction conditions. However, the catalytic system mentioned above is still disadvantageous because iodine is liable to sublimate and thus may pollute the environment.

To overcome such shortages, here we reported a new method for synthesis of ETES (Scheme 3) without the addition of iodine as the promoter.

### 2. Experimental

# 2.1. Materials

Ruthenium (III) trichloride hydrate was obtained from Aldrich Chemical Co. Inc. (USA). Anhydrous ruthenium (III) trichloride and ruthenium (III) triiodide were obtained from Alfa Aesar Chemical Co., Ltd. Cuprous chloride, cuprous bromide, cuprous iodide, iodine

<sup>\*</sup> Corresponding author. Tel.: +86 571 88320002; fax: +86 571 88320667.

<sup>\*\*</sup> Corresponding author. Tel.: +86 571 28867861; fax: +86 571 28865135. E-mail addresses: nanyangliuling@163.com (L. Liu), xnli@zjut.edu.cn (X. Li),

donghong@hznu.edu.cn (H. Dong), chaunwu@yahoo.com (C. Wu).

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Scheme 1. Synthesis of ethyltriethoxysilane by Rh-catalyzed hydrogenation reaction.

and ferrous chloride tetrahydrate were obtained from Hangzhou Bond Easy Chemical Co. Ltd. Triethoxysilane was industrial grade material with mass fraction higher than 0.99, which was purchased from commercial sources. High purity ethylene gas with mass fraction higher than 99.99% was obtained from Hangzhou Southeast Gases Co., Ltd. (China). All the chemicals were used directly without further purification.

#### 2.2. Sample analysis

The structure of each component in hydrosilylation product was qualitatively characterized on a GC–MS TRANCE DSQ (Thermo Finnigan, USA) and their contents were determined by means of a SP6890 gas chromatograph (Shandong Lunan Ruihong Chemical Instrument, China) equipped with an Agilent HP-5 column ( $\Phi$ 0.32 mm × 30 m) and an FID detector. The chromatography conditions used were as follows: (1) the initial column temperature was set to 60 °C and held for 2 min at this temperature, after then, it was raised to 100 °C at a heating rate of 20 °C min<sup>-1</sup>, subsequently it was further raised to 200 °C at a heating rate of 30 °C min<sup>-1</sup>; (2) vaporization chamber = 200 °C; (3) sample chamber = 200 °C.

#### 2.3. Hydrosilylation reaction

All experiments were performed in a 2 L cylindrical, roundbottomed autoclave (Weihai automatically-controlled reaction kettle Co. Ltd., China) equipped with an inserted gas feeding pipe, a pusher-type propeller driven by magnetic force, a snake-type water-cooled condenser and a vertical thermometer. Before each experiment, the autoclave was firstly heated to above 100 °C under the protection of a dried nitrogen flow and dried for about 0.5 h to ensure that it was free from moisture. After cooling to room temperature, the requisite amounts of triethoxysilane and catalyst as well as promoters were fed into the autoclave and gas-tightness examination was subsequently conducted with 0.5 MPa nitrogen gas. When the nitrogen gas had been completely discharged, the rate of the stirrer was set to a certain value and the mixture was stirred for half an hour. Meanwhile, the temperature was raised to a certain value. Subsequently, ethylene gas at a constant pressure of 0.35 MPa was continuously fed into the autoclave through the inserted gas pipe line, and this moment was marked as the

Table 1
Synthesis methods for ethyltriethoxysilane.

synthesis methods for ethyltriethoxysilane.										
Entry	Raw material		Catalyst	Promoter	RT <sup>d</sup> (°C)	Product	Yield <sub>ETES</sub> (%)			
1 <sup>a</sup> 2 <sup>b</sup>	$C_2H_3Si(OEt)_3$ [1] HSi(OEt)_2 [2]	$H_2$	$RhCl(PPh_3)_3$ $Ru_2(CO)_{12}$	56592-21-3 —	60—160 25—80	ETES <sup>e</sup> CHa <del>_</del> CHSi(OFt)a FTFS	_			
3 <sup>c</sup>	$HSi(OEt)_3$ [2] $HSi(OEt)_3$ [3]	$CH_2 = CH_2$ $CH_2 = CH_2$	11057-89-9(Pt)	_	15-70	ETES	>91			
4	HSi(OEt) <sub>3</sub> [4]	$CH_2 = CH_2$	H <sub>2</sub> PtCl <sub>6</sub>	30110-75-9 Me <sub>2</sub> CHOH	25-65	ETES	90			
5	Si(OEt) <sub>4</sub> [5]	-	NaH	_	275	ETES	6			
6	Si(OEt) <sub>4</sub> [6]	_	NaH	KF	400	ETES	_			

<sup>a</sup> The reaction was run in a gas phase, on line, in a column connected to the mass spectrometer.

<sup>b</sup> The solvent was benzene.

<sup>c</sup> The reaction result showed that the Pt (0) catalysts are considerably more active in ethylene hydrosilylation than Pt (II) catalysts.

<sup>d</sup> The abbreviation of reaction temperature.

<sup>e</sup> The abbreviation of ethyltriethoxysilane; "\_\_\_", not mentioned in the literature.

beginning of hydrosilylation. The course of each reaction was monitored by quantitative GC utilizing the procedure above mentioned. At specified time intervals, 0.5  $\mu$ L of the reaction mixtures were sampled via syringe. When the concentration of ETES was not increased any more, the reaction was stopped. After cooling to room temperature, the product was recovered and analyzed. The synthetic yield, selectivity, and conversion data were calculated on the basis of GC analysis results.

In a typical catalytic run, 0.0417 g (159.5  $\mu$ mol) RuCl<sub>3</sub>·3H<sub>2</sub>O, 0.1442 g (1449.2  $\mu$ mol) CuCl and 382.2 g (2.330 mol) triethoxysilane [HSi(OEt)<sub>3</sub>] were added into the dried autoclave mentioned above (Entry 16 in Table 2). The mixture was stirred at a rate of 300 rpm. When the reaction temperature was raised to 50 °C, ethylene gas at a constant pressure of 0.35 MPa was continuously fed into the autoclave. After then, 0.5  $\mu$ L of the reaction mixtures were sampled periodically and analyzed by GC. After 6 h, since the concentration of ETES was not increased any more, the reaction was stopped. The final reaction products were collected, weighed, and analyzed by GC after cooling to room temperature. The obtained yield and selectivity were determined on the basis of the GC analysis with results of 97% and 97%, respectively.

#### 3. Results and discussions

#### 3.1. Effect of iodine on hydrosilylation reaction

In order to investigate the influence of iodine on the hydrosilylation of ethylene in more detail, we designed the reaction in the presence of RuCl<sub>3</sub>·3H<sub>2</sub>O/I<sub>2</sub>, RuCl<sub>3</sub>·3H<sub>2</sub>O and Rul<sub>3</sub>, respectively (Entries 1–3, Table 2). When molecular iodine was used (Entry 1, Table 2), the reaction was conducted effectively and quickly, and 93% yield of ETES in 16 h was obtained. However, when no iodine or Rul<sub>3</sub> was added, the reaction rate was very slow, and only 24% or 6% yield of ETES, respectively (Entries 2 and 3, Table 2) was obtained within the same period. The results showed that iodine as promoter played an important role in speeding up the reaction and it could greatly increase the reaction yield when it is existed in a form of molecular state.

Various factors affected on the selectivity and yield of the objective product were examined and presented in Table 2 (Scheme 4).



Scheme 2. Synthesis of ethyltriethoxysilane by Pt-catalyzed hydrosilylation reaction.

# 3.2. Kind of catalyst

The influence of catalysts on the hydrosilylation of ethylene was examined and the results were shown in Fig. 1 (Entries 1–4, Table 2). It could be observed from these results that RuCl<sub>3</sub> exhibited the best effect among these three catalysts in the absence of additives and RuCl<sub>3</sub>·3H<sub>2</sub>O was inferior to it. Considering the price and the catalytic activities, it is advisable that RuCl<sub>3</sub>·3H<sub>2</sub>O should be selected as the primary catalyst since this kind of catalyst has the cost advantage and can effectively catalyze the hydrosilylation reaction of ethylene with triethoxysilane when suitable promoter is used.

### 3.3. Effect of promoter on the hydrosilylation reaction

To investigate the influence of promoters on hydrosilylation of ethylene with triethoxysilane, I<sub>2</sub>, CuCl, CuBr, CuI and FeCl<sub>2</sub> $\cdot$ 4H<sub>2</sub>O were

added as promoters separately in each reaction in the same level while keeping the ratio between ruthenium and the promoter as well as other operating parameters constant. The obtained results were shown in Table 2 (Entries 5-10) and Fig. 2. It could be observed that when CuCl and CuBr were used, the yield of ETES could reach 97% and 96% after reacted at 50 °C for 10 h, which were much higher than that obtained when I<sub>2</sub> was used as the promoter. When CuI was used, the yield of ETES was 79%, which was much close to the result obtained when  $I_2$  was used as the promoter. It is possible that cuprous ion play an important role in the hydrosilvlation when CuCl. CuBr or CuI is added as promoter. The effects of cuprous ion can be affected by different halide ion and halide ion itself has no direct impact on the hydrosilylation of ethylene with triethoxysilane. Although FeCl<sub>2</sub>·4H<sub>2</sub>O could help to increase the yield of ETES, however, its influence on the catalytic activity was not evident since the yield of ETES was only increased by 8% relative to no promoter used (Entry 5, Table 2).



Scheme 3. Synthesis of ethyltriethoxysilane by Ru-catalyzed hydrosilylation reaction.

Table 2
Effect of catalysts, promoters and reaction temperature and time on hydrosilylation of ethylene with triethoxysilane.

Entry	Catalyst	Promoter	[Ru]/[HSi(OEt) <sub>3</sub> ]	[Promoter]/[Ru]	Temperature/°C	Time/h	р <sub>С2Н4</sub> /МРа	Selectivity	Yield/%
1	RuCl <sub>3</sub> ·3H <sub>2</sub> O	I <sub>2</sub>	$3.0 \times 10^{-5}$	1.2	50	16	0.35	97	93
2	RuCl <sub>3</sub> ·3H <sub>2</sub> O	-	$7.1 \times 10^{-5}$	-	50	16	0.35	87	24
3	RuI <sub>3</sub>	-	$3.0 \times 10^{-5}$	-	50	16	0.35	49	6
4	RuCl <sub>3</sub>	_	$3.0  imes 10^{-5}$	_	50	16	0.35	95	33
5	RuCl <sub>3</sub> ·3H <sub>2</sub> O	_	$7.1 \times 10^{-5}$	8.3	50	10	0.35	84	19
6	RuCl <sub>3</sub> ·3H <sub>2</sub> O	I <sub>2</sub>	$7.1 \times 10^{-5}$	8.3	50	10	0.35	95	83
7	$RuCl_3 \cdot 3H_2O$	CuCl	$7.1 \times 10^{-5}$	8.3	50	10	0.35	98	97
8	$RuCl_3 \cdot 3H_2O$	CuBr	$7.1 \times 10^{-5}$	8.3	50	10	0.35	97	96
9	RuCl <sub>3</sub> ·3H <sub>2</sub> O	CuI	$7.1 \times 10^{-5}$	8.3	50	10	0.35	96	79
10	RuCl <sub>3</sub> ·3H <sub>2</sub> O	FeCl <sub>2</sub> ·4H <sub>2</sub> O	$7.1 \times 10^{-5}$	8.3	50	10	0.35	91	27
11	$RuCl_3 \cdot 3H_2O$	CuCl	$7.9 imes10^{-6}$	10.0	50	7	0.35	94	7
12	$RuCl_3 \cdot 3H_2O$	CuCl	$2.3  imes 10^{-5}$	10.0	50	7	0.35	97	29
13	$RuCl_3 \cdot 3H_2O$	CuCl	$3.7  imes 10^{-5}$	10.0	50	7	0.35	98	68
14	$RuCl_3 \cdot 3H_2O$	CuCl	$6.8 \times 10^{-5}$	10.0	50	7	0.35	97	97
15	$RuCl_3 \cdot 3H_2O$	CuCl	$1.4  imes 10^{-4}$	10.0	50	7	0.35	98	98
16	$RuCl_3 \cdot 3H_2O$	CuCl	$6.8 \times 10^{-5}$	10.0	50	6	0.35	97	97
17	$RuCl_3 \cdot 3H_2O$	CuCl	$6.8 \times 10^{-5}$	6.0	50	6	0.35	97	96
18	$RuCl_3 \cdot 3H_2O$	CuCl	$6.8 \times 10^{-5}$	3.0	50	6	0.35	98	97
19	$RuCl_3 \cdot 3H_2O$	CuCl	$6.8 \times 10^{-5}$	1.5	50	6	0.35	97	85
20	$RuCl_3 \cdot 3H_2O$	CuCl	$6.8 \times 10^{-5}$	0.8	50	6	0.35	97	74
21	$RuCl_3 \cdot 3H_2O$	CuCl	$6.8 \times 10^{-5}$	9.0	30	6	0.35	96	14
22	$RuCl_3 \cdot 3H_2O$	CuCl	$6.8 \times 10^{-5}$	9.0	40	6	0.35	97	79
23	$RuCl_3 \cdot 3H_2O$	CuCl	$6.8 \times 10^{-5}$	9.0	50	6	0.35	97	97
24	$RuCl_3 \cdot 3H_2O$	CuCl	$6.8 \times 10^{-5}$	9.0	60	6	0.35	97	96
25	$RuCl_3 \cdot 3H_2O$	CuCl	$6.8 \times 10^{-5}$	9.0	70	6	0.35	96	63
26	$RuCl_3 \cdot 3H_2O$	CuCl	$6.8 \times 10^{-5}$	9.0	80	6	0.35	95	52
27	$RuCl_3 \cdot 3H_2O$	CuCl	$6.8 \times 10^{-5}$	3.3	50	9	0.35	90	78
28	$RuCl_3 \cdot 3H_2O$	CuCl	$6.8 \times 10^{-5}$	3.3	50	9	0.30	90	71
29	$RuCl_3 \cdot 3H_2O$	CuCl	$6.8 \times 10^{-5}$	3.3	50	9	0.20	89	64



Scheme 4. Synthesis of ethyltriethoxysilane by Ru–X-catalyzed hydrosilylation reaction.

The above-mentioned experimental results showed that the cocatalytic effect of CuI was weaker than CuBr or CuCl. It could be that the inductive effect of iodine ion was a main factor for causing the weaker co-catalytic effect of CuI, however, the inductive effect of chloride ion and bromide ion was weaker than iodine ion's, so the influence of the inductive effects on co-catalytic effect of CuBr or CuCl was not obvious. In FeCl<sub>2</sub>·4H<sub>2</sub>O, the iron ion with +2 valent state might have a certain degree of reducibility, which was probably the main reason for the co-catalytic effect of FeCl<sub>2</sub>·4H<sub>2</sub>O. However, since the reducing antioxidant power of ferric ion was weaker than cuprous ion, consequently, the co-catalytic effect of FeCl<sub>2</sub>·4H<sub>2</sub>O was inferior to that of CuBr or CuCl.

The above experimental results also indicated that CuCl was the best promoter for RuCl<sub>3</sub>·3H<sub>2</sub>O in the hydrosilylation of ethylene with triethoxysilane. It has ever been reported in previous literature that several kinds of copper compounds including CuCl could exhibit high catalytic activity and regioselectivity for the hydrosilvlation of carbonyl compounds [8-14]. In 2008, Carl Deutsch et al. reported a variety of CuH-catalyzed reactions, including the hydrogenation reaction [15]. The most common and frequently used copper hydride species was the hexamer [(Ph<sub>3</sub>P)CuH]<sub>6</sub> (Scheme 5), the so-called "Stryker's reagent", which was developed by Stryker and co-workers in 2000 [16] and it could substantially improve the chemoselectivity for this reducing agent [17,18]. Later in 2012, Lee [19] also found that a copper complex of a chiral monodentate N-heterocyclic carbene was efficient and highly diastereo- and enantioselective conjugate additions of phenyldimethylsilyl units to acyclic and cyclic dienones and dienoates. Generally, hydrogenation and hydrosilylation of carbonyl groups were catalyzed by transition metals, such as Rh [20,21] and Ru [22,23]. Since triethoxysilane was also a typical reducing agent, therefore, CuH species might be formed when CuCl was added as the promoter in the hydrosilylation reaction of



**Fig. 1.** Effect of catalyst on yield of ETES.  $\blacksquare$ , RuCl<sub>3</sub>·3H<sub>2</sub>O promoted with I<sub>2</sub> (Entry 1);  $\Box$ , RuCl<sub>3</sub>·3H<sub>2</sub>O (Entry 2);  $\checkmark$ , Rul<sub>3</sub> (Entry 3);  $\blacktriangle$ , RuCl<sub>3</sub> (Entry 4).

ethylene with triethoxysilane and thus can greatly improve the catalytic activity and selectivity for this hydrosilylation reaction.

Based on the experimental results observed in this study and the mechanisms for alkene hydrosilylation that had been studied extensively in previous literature [24], a possible mechanism which was compatible with the experimental data obtained was proposed (Scheme 6). According to mechanism presented in Scheme 5, the intermediate H-Ru-Si(OEt)<sub>3</sub> was formed by means of the combination of triethoxysilane [HSi(OEt)<sub>3</sub>] and the active ruthenium species [Ru]. Subsequently, an ethylene complex of H-Ru-Si(OEt)<sub>3</sub> was formed through the coordination between ethylene and ruthenium, and then, ethylene could insert either between hydrogen and ruthenium atom (Path A) through the typical Chalk-Harrod mechanism [25] or between ruthenium and silicon atom (Path B) according to the modified Chalk–Harrod mechanism [26]. Product of the hydrosilylation, namely EtSi(OEt)<sub>3</sub>, could be formed when the active ruthenium species [Ru] was eliminated from the intermediates  $H_{H-X}$  and  $H_{H-Ru}$  intermediates  $H_{H-Ru}$  in the hydrosilvlation reaction.

# 3.4. Effect of the initial concentration of catalyst on hydrosilylation reaction

When RuCl<sub>3</sub>·3H<sub>2</sub>O was used as catalyst and CuCl was screened as promoter for hydrosilylation reaction of ethylene with triethoxysilane, the influence of catalyst content on yield of ETES was investigated when holding the ratio between CuCl and RuCl<sub>3</sub>·3H<sub>2</sub>O and other conditions constant. The results were shown in Table 2 (Entries 11–15) and graphically shown in Fig. 3. It could be found that with the increase in catalyst content, the reaction rate increased rapidly. For example, when the ruthenium content was increased from  $7.9 \times 10^{-6}$  to  $6.8 \times 10^{-5}$  mol per mole of triethoxysilane, the yield of ETES increased from 7% to 97% after reacted at 50 °C for 7 h.



**Fig. 2.** Effect of promoters on yield of ETES.  $\blacksquare$ , no promoter;  $\Box$ ,  $l_2$ ;  $\bullet$ , CuCl;  $\blacktriangle$ , CuBr;  $\blacktriangledown$ , Cul;  $\diamond$ , FeCl<sub>2</sub>·4H<sub>2</sub>O.



Scheme 5. Preparation of ligated copper hydrides.

When the catalyst content was further increased to  $1.4 \times 10^{-4}$  mol ruthenium per mole of triethoxysilane, the yield of ETES increased slightly. It could also be observed from Fig. 3 that the yield of ETES increased very slightly, though the reaction time was prolonged. Obviously, the reaction rate was greatly affected by the catalyst content and the lowest concentration of ruthenium that can effectively catalyze the hydrosilylation of ethylene with triethoxysilane was determined to be  $6.8 \times 10^{-5}$  mol per mole of triethoxysilane.

# 3.5. Effect of molar ratio of promoter/catalyst on hydrosilylation reaction

When holding the catalyst concentration at  $6.8 \times 10^{-5}$  mol per mole of triethoxysilane and decreasing the molar ratio between CuCl and ruthenium from 10.0 to 0.8, the yield of ETES decreased from 97% to 74% after a reaction carried out at 50 °C for 6 h as presented in Table 2 (Entries 16–20, Table 2) and graphically shown in Fig. 4. It could be found that when the molar ratio between CuCl and ruthenium was higher than 3.0, the yield of ETES changed



**Scheme 6.** Proposed mechanisms for hydrosilylation of ethylene with trimethoxysilane catalyzed by ruthenium.



**Fig. 3.** Effect of catalyst contents on yield of ETES.  $\blacksquare$ ,  $7.9 \times 10^{-6}$ ;  $\square$ ,  $2.3 \times 10^{-5}$ ;  $\blacktriangle$ ,  $3.7 \times 10^{-5}$ ;  $\blacktriangledown$ ,  $6.8 \times 10^{-5}$ ;  $\bigcirc$ ,  $1.4 \times 10^{-4}$ ; the molar ratio between CuCl and ruthenium was set to 10.0 as shown in Entries 11–15, Table 2 and the catalyst concentration indicated was the molar ratio between ruthenium and triethoxysilane.



**Fig. 4.** Effect of molar ratio between CuCl and RuCl<sub>3</sub>·3H<sub>2</sub>O on yield of ETES.  $\blacksquare$ , 0.8;  $\Box$ , 1.5;  $\blacktriangle$ , 3.0;  $\blacktriangledown$ , 6.0;  $\bigcirc$ , 10.0. The concentration of ruthenium was 6.8 × 10<sup>-5</sup> mol per mole of triethoxysilane and reactions were conducted at 50 °C (Entries 16 to 20 in Table 2).

slightly with the decrease in molar ratio values. However, when values of the molar ratio decreased further, the yield of ETES decreased drastically, which indicated that the reaction rate was greatly affected by the amount of promoter. It also could be observed from Fig. 4 that with the extension of the reaction time, the yield of ETES increased gradually. Even though the molar ratio between CuCl and RuCl<sub>3</sub>·3H<sub>2</sub>O was decreased to 0.8, the hydrosilylation reaction could still be carried out almost completely, which indicated that the reaction rate was greatly affected by the amount of CuCl, nevertheless, the reaction equilibrium was not affected.

# 3.6. Effect of reaction temperature on hydrosilylation reaction

The influence of reaction temperature on hydrosilylation reaction was also investigated and six reactions were conducted at temperatures ranging from 30 to 80 °C. The results were listed in Table 2 (Entries 21–26) and graphically shown in Fig. 5. These results indicated that the influence of reaction temperature on the yield of ETES was very complicated. When the reaction was



**Fig. 5.** Effect of reaction temperature on yield of ETES.  $\blacksquare$ , 30 °C;  $\Box$ , 40 °C; ▲, 50 °C;  $\blacktriangledown$ , 60 °C;  $\bigcirc$ , 70 °C; ●, 80 °C. The concentration of ruthenium was 6.8 × 10<sup>-5</sup> mol per mole of triethoxysilane and the molar ratio between CuCl and RuCl<sub>3</sub>·3H<sub>2</sub>O was 9.0 for each reaction (Entries 16 to 20 in Table 2).

 $4\text{HSi}(\text{OC}_2\text{H}_5)_3 \longrightarrow \text{SiH}_4 + 3\text{Si}(\text{OC}_2\text{H}_5)_4$ 



conducted at 30 °C, the reaction rate was very slow and the yield of ETES was no more than 20% even after 12 h. With the reaction temperature increased, the reaction rate increased rapidly and a yield of 97% could be obtained when the reaction was conducted at 50 °C for 6 h. However, with a further increase in temperature, the yield of ETMS decreased gradually. It was well-known that trie-thoxysilane was very reactive and was liable to be transformed into tetraethoxysilane (Scheme 7) under mild conditions in the presence of weak acids or weak bases, or even simply under elevated temperature range for hydrosilylation reaction of ethylene with triethoxysilane was between 40 and 60 °C since the reaction could be rapidly conducted in this range and meanwhile, the disproportionation reaction of triethoxysilane was not significant.

## 3.7. Effect of pressure of ethylene gas on hydrosilylation reaction

The influence of ethylene pressure on the yield of ETES was also investigated. Therefore, three hydrosilylation reactions of ethylene gas with triethoxysilane were conducted under 0.20, 0.30 and 0.35 MPa pressure of ethylene gas while holding other parameters constant (Entries 27 to 29 in Table 2). As expected, the yield of ETES increased with the increase in pressure of ethylene gas and a yield of 78% was achieved after 9 h under 0.35 MPa pressure of ethylene gas. The hydrosilylation reaction of ethylene with triethoxysilane is a typical gas-liquid reaction and the chemical reaction was generally conducted at the phase interface between gas and liquid. The macroscopic reaction rate was mainly influenced by diffusion and adsorption or dissolution of ethylene, surface reaction, desorption and diffusion of ETES. With the increase in pressure of ethylene gas, the diffusion rate, the adsorption rate or dissolution rate of ethylene and the surface reaction rate increased. Therefore, the increase in pressure of ethylene gas was beneficial to improve the yield of ETES.

#### 4. Conclusions

The hydrosilylation reaction of ethylene with triethoxysilane catalyzed by ruthenium chloride hydrate and promoted by cuprous halides or ferrous chloride tetrahydrate has been investigated. It has been proved that cuprous chloride is a good promoter for ruthenium chloride hydrate catalyzed hydrosilylation of ethylene with triethoxysilane. The yield of ethyltriethoxysilane is significantly affected by the concentration of ruthenium chloride hydrate, the molar ratio between cuprous chloride and ruthenium chloride hydrate, the pressure of ethylene gas and the reaction temperature. With  $6.8 \times 10^{-5}$  ruthenium per mole of triethoxysilane and over 3 times of cuprous chloride per mole of ruthenium, the hydrosilylation reaction conducted at temperatures ranging from 40 to 60 °C for 6 h under a pressure of 0.35 MPa ethylene gas can reach a yield higher than 96%.

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# Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.jorganchem.2013. 07.024. These data include MOL files and InChiKeys of the most important compounds described in this article.

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