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Selective Catalytic Hydrosilylation of Ethylene. Preparation of Ethyltrimethoxysilane by H_2O Promoted $RuCl_3 \cdot 3H_2O$ Catalyst

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Abstract—The work describes an efficient one-step solvent-free synthesis of ethyltrimethoxysilane through hydrosilylation reaction catalyzed by $RuCl_3 \cdot 3H_2O–H_2O$. The procedure involves time point and dose of adding additive water. Excellent yields, short reaction times, and easy reaction handling under solvent-free and mild conditions are the most important advantages of the present protocol. A possible reaction mechanism was discussed by empirical method.

Keywords: ethyltrimethoxysilane, hydrosilylation reaction, $RuCl_3 \cdot 3H_2O–H_2O$ catalyst, reaction mechanism

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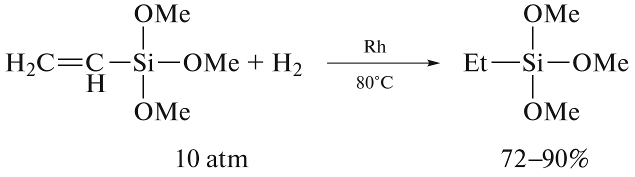
INTRODUCTION

Ethyltrimethoxysilane (ETMS) belongs to an important class of organic silicon chemical reagents, which are widely used in the field of hydrophobic surface treatment and it is an important intermediate for the preparation of silicone rubber, silicone resin and silane coupling agent. Besides, these compounds also play an important role in the preparation of dielectric and insulating materials.

The first synthesis of ETMS was reported by Marciniec in 1993 [1]. The yield of target product ETMS was only 20%. Later, other synthesis methods were reported (Table 1, entries 2–8). Among these various methods, hydrogenation of vinyl trimethoxysilane (VTMS) may be the most effective method (Table 1, entry 5). However, the reaction is carried out under the pressure of hydrogen at 10 atm, and benzene is used as the reaction solvent, which is not conducive to industrial production. The harsh reaction conditions and toxic solvent benzene prevented its application in industrial processes. Therefore, it is of great significance to find out a solvent-free preparation method with mild reaction conditions.

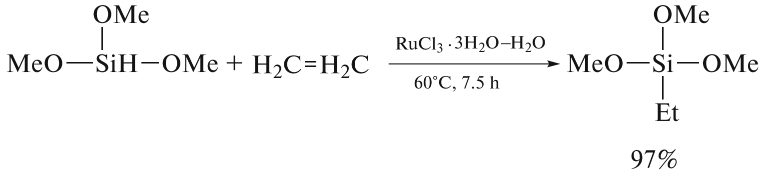
In 2010, we reported a very simple and effective method for the synthesis of ETMS by hydrosilylation reaction of ethylene and trimethoxysilane [6]. In this reaction, $RuCl_3 \cdot 3H_2O$ doped with iodine was screened as the catalytic system and exhibited higher catalytic activity and selectivity. Comparing with Mieczynska's method [5] (Scheme 1), this catalytic system showed some advantages due to low 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.



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

To overcome such shortages, here we report a new method for the synthesis of ETMS (Scheme 2) without iodine as the promoter. This method was found while optimizing the preparation process of ETMS in our earlier study. A slight difference in the catalytic activity and selectivity between anhydrous ruthenium trichloride and ruthenium trichloride hydrate was observed. We speculated that the difference might be caused by the crystalline water in ruthenium trichloride hydrate molecule. In order to find out the truth, we did the following research.

Abbreviations: ETMS, ethyltrimethoxysilane; TMS, trimethoxysilane; VTMS, vinyl trimethoxysilane.



$$\mathrm{MeO{-}\overset{OMe}{SiH}{-}OMe} + \mathrm{H_2C{=}H_2C} \xrightarrow[60^\circ\mathrm{C},\ 7.5\ \mathrm{h}]{\mathrm{RuCl_3\cdot 3H_2O{-}H_2O}} \mathrm{MeO{-}\underset{Et}{\overset{OMe}{Si}}{-}OMe}$$

97%

Scheme 2. Synthesis of ethyltrimethoxysilane by Ru-catalyzed hydrosilylation reaction.

EXPERIMENTAL

Apparatus and Reagents

Ruthenium(III) trichloride hydrates, ruthenium(III) trichloride, ruthenium(III) tribromide and ruthenium(III) triiodide were obtained from Aldrich (USA) and were used without further purification. Trimethoxysilane (TMS) was an industrial grade material with mass fraction higher than 0.99, which was purchased from commercial sources. Ethylene was a chemical reagent grade with purity higher than 99.99%, obtained from Hangzhou Southeast Gases Co., Ltd. (China). Both TMS and ethylene gas were used directly without further purification.

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 (0.32 mm × 30 m) and a~~n~~ 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, then it was raised to 100°C at a heating rate of 20°C/min, subsequently it was further raised to 220°C at a heating rate of 30°C/min; (2) vaporization chamber 220°C; (3) sample chamber 220°C.

Preparation of Ethyltrimethoxysilane

The hydrosilylation reaction was performed in a 2 L cylindrical round-bottomed autoclave (Weihai automatically-controlled reaction kettle Co. Ltd., China) equipped with plug-in intake manifold and a pusher-type propeller driven by magnetic force, a snake-type water-cooled condenser and a vertical thermometer. Before each experiment, gas-tightness examination was conducted at a 0.5 MPa of nitrogen. After the nitrogen had been completely discharged, the autoclave was firstly heated to above 100°C under the protection of a nitrogen flow and dried for about 1 h to ensure that was free from moisture. After cooling to room temperature, the requisite amounts of TMS and catalyst were fed into the autoclave, 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 pressure of 0.35 MPa was continuously fed into the autoclave through the inserted gas pipeline. The pressure inside the autoclave remained steady. After the ethylene-feeding valve was closed, the reaction was stopped. After cooling to room temperature, the product was recovered and analyzed. Synthesis yield, selectivity and conversion data were calculated based on the GC analysis results.

Table 1. Synthesis methods for ethyltrimethoxysilane (ETMS)

Entry	Raw material		Catalyst	Promoter/ Solvent	T, °C	Yield$_{\mathrm{ETMS}}$, %
1	$CH_2CHSi(OMe)_3$ [1]	$HSi(OEt)_3$	$C_{10}H_{14}NiO_4$	–*	–	20.0
2	$HSi(OMe)_3$ [2]	$CH_2{=}CH_2$, 55 kPa	$PtCl_2(NH_3)_4$	–	150	5.0
3	$HSi(OMe)_3$ [3]	$CH_2{=}CH_2$	$PtSi(CH{=}CH_2)_3OSi(CH{=}CH_2)_3$	–	60–70	72.0
4	$HSi(OMe)_3$ [4]	$CH_2{=}CH_2$	H_2PtCl_6, $C_{12}H_{18}OSi_2$	Me_2CHOH	40–50	78.8
5	$CH_2CHSi(OMe)_3$ [5]	H_2, 10 atm	$PPh_3RhOSiMe_3(CH_2)_4(CH{=}CH)_2$	–/benzene	80	90.0
6	$CH_2CHSi(OMe)_3$ [5]	H_2, 10 atm	$(C_6H_{12})_3PRhOSiMe_3(CH_2)_4(CH{=}CH)_2$	–/benzene	80	82.0
7	$CH_2CHSi(OMe)_3$ [5]	H_2, 10 atm	$Rh_2O_2Si_2Me_6(CH_2)_8(CH{=}CH)_4$	–/benzene	80	72.0
8	$HSi(OMe)_3$ [6]	$CH_2{=}CH_2$, 0.3 MPa	$RuCl_3\cdot 3H_2O$	I_2	80–100	>90%

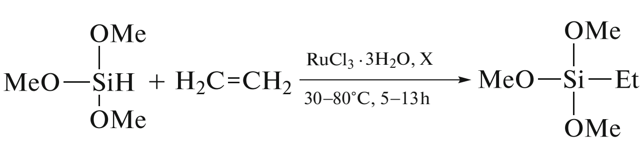
* Not indicated in the literature.

In a typical catalytic run, 0.0069 g (26.4 mmol) $RuCl_3 \cdot 3H_2O$, and 344.0 g (2.819 mol) TMS were added into the dried autoclave mentioned above (Table 2, entry 13). The mixture was stirred at a rate of 200 rpm. When the reaction temperature was raised to 40°C, ethylene at a pressure of 0.35 MPa was fed into the autoclave. When the ethylene pressure in the kettle reached 0.35 MPa, the inlet valve was closed. When the pressure in the kettle dropped to 0.05 MPa, gaseous ethylene was discharged from the high-pressure reactor and 0.0264 g (2.9 mmol) of H_2O was added through the feeding port. After that, the feeding port was sealed. The reaction process continued and the ethylene gas at a constant pressure of 0.35 MPa was continuously fed into the autoclave. The reaction mixture of 0.5 μL was sampled periodically and analyzed by GC. As the ETMS concentration did not increased after 8.5 h, 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 based on the GC analysis and the results were 98 and 98%, respectively.

RESULTS ADN DISCUSSION

Influence of Water on Hydrosilylation Reaction

In order to investigate the influence of water on the hydrosilylation of ethylene in more detail, we designed the reaction in the presence of $RuCl_3 \cdot 3H_2O/H_2O$, $RuCl_3 \cdot 3H_2O$ and $RuCl_3$, respectively (Table 2, entries 1–3). When free water was used (Table 2, entry 1), the reaction occurred effectively and quickly, and 98% yield of ETMS in 13 h was obtained. However, when no free water or $RuCl_3$, $RuCl_3 \cdot 3H_2O$ was added, the reaction rate was very slow, and only 60 or 65% yield of ETMS, respectively (Table 2, entries 3 and 2) was obtained within the same period. The results showed that water as a promoter played an important role in speeding up the reaction and it could greatly increase the reaction yield when it existed in a free state. Various factors affecting the selectivity and yield of the target product were examined and presented in Table 2 (Scheme 3).



$$\mathrm{MeO{-}\overset{OMe}{\underset{OMe}{Si}}H} + \mathrm{H_2C{=}CH_2} \xrightarrow[30\text{–}80^\circ\mathrm{C},\ 5\text{–}13\,\mathrm{h}]{\mathrm{RuCl_3 \cdot 3H_2O,\ X}} \mathrm{MeO{-}\overset{OMe}{\underset{OMe}{Si}}{-}Et}$$

Scheme 3. Synthesis of ethyltrimethoxysilane by Ru-X-catalyzed hydrosilylation reaction.

Influence of Catalyst on Hydrosilylation Reaction

The influence of catalysts on the hydrosilylation of ethylene was examined and the results are summarized in Fig. 1 (Table 2, entries 2–5). As is seen from the figure, $RuCl_3 \cdot 3H_2O$ exhibited the best effect among these four catalysts in the absence of additives. It is advisable that $RuCl_3 \cdot 3H_2O$ should be selected as the primary catalyst, since this kind of catalyst has the advantages of low cost and high catalytic activity and can effectively catalyze the hydrosilylation reaction of ethylene with trimethoxysilane if suitable promoters are used.

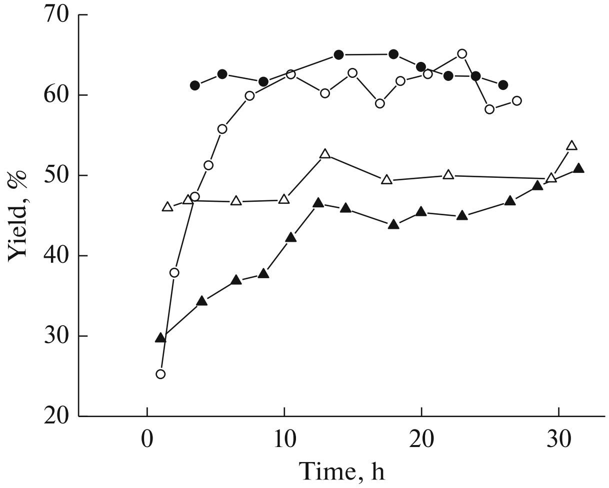


Fig. 1. Influence of catalyst on yield of ETMS: ● $RuCl_3 \cdot 3H_2O$ (entry 2), ○ $RuCl_3$ (entry 3), ▲ $RuBr_3$ (entry 4), △ RuI_3 (entry 5).

Influence of Catalyst Concentration and Promoter to Catalyst Molar Ratio on Hydrosilylation Reaction

When $RuCl_3 \cdot 3H_2O$ was used as a catalyst and H_2O was used as a promoter for ethylene hydrosilylation with trimethoxysilane, the influence of catalyst content on the ETMS yield was investigated, the molar ratio of H_2O to $RuCl_3 \cdot 3H_2O$ and other conditions being constant. The results are shown in Table 2 (entries 6–9) and graphically in Fig. 2. It could be found that with the decrease of catalyst content, the reaction rate decreased rapidly. For example, when the ruthenium content decreased from 1.2×10^{-4} to 3.3×10^{-5} mol per mole of TMS, the yield of ETMS decreased from 98 to 80% after 12 h at 40°C. However, when the molar ratio of water to ruthenium increased to 33.6, the ETMS yield increased to 98%. As is seen from Fig. 2, under the condition of relatively high catalyst concentration, the amount of water has no obvious effect on the yield of the target product ETMS. However, when the catalyst concentration is low, the amount of water has a significant effect on the yield of the target product ETMS. At the same reaction time, the increase of the ETMS yield is obvious, when the molar ratio of water to ruthenium is 33.6 and ruthenium content is 3.3×10^{-5} mol per mole of TMS. Obviously, the reaction rate was greatly affected by the

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

Entry	Catalyst	Promoter	[Ru]/[HSi(OMe)$_3$]	[Promoter]/[Ru]	T, °C	Time, h	P_{C2H4}, MPa	Selectivity, %	Yield, %
1	$RuCl_3 \cdot 3H_2O$	H_2O	1.1×10^{-4}	3.0	40	13	0.35	98	98
2	$RuCl_3 \cdot 3H_2O$	–	1.1×10^{-4}	–	40	13	0.35	90	65
3	$RuCl_3$	–	1.1×10^{-4}	–	40	13	0.35	93	60
4	$RuBr_3$	–	1.1×10^{-4}	–	40	13	0.35	92	46
5	RuI_3	–	1.1×10^{-4}	–	40	13	0.35	95	53
6	$RuCl_3 \cdot 3H_2O$	H_2O	1.2×10^{-4}	3.5	40	12	0.35	98	98
7	$RuCl_3$	H_2O	1.2×10^{-4}	8.4	40	12	0.35	97	98
8	$RuCl_3 \cdot 3H_2O$	H_2O	3.3×10^{-5}	3.5	40	12	0.35	97	80
9	$RuCl_3 \cdot 3H_2O$	H_2O	3.3×10^{-5}	33.6	40	12	0.35	97	98
10	$RuCl_3 \cdot 3H_2O$	H_2O	1.2×10^{-4}	5.5	40	8.5	0.35	94	96
11	$RuCl_3 \cdot 3H_2O$	H_2O	6.0×10^{-5}	11.0	40	8.5	0.35	97	59
12	$RuCl_3 \cdot 3H_2O$	H_2O	6.0×10^{-5}	18.5	40	8.5	0.35	98	79
13	$RuCl_3 \cdot 3H_2O$	H_2O	3.0×10^{-5}	37.0	40	8.5	0.35	97	91
14	$RuCl_3 \cdot 3H_2O$	H_2O	9.4×10^{-6}	110.7	40	8.5	0.35	98	98
15	$RuCl_3 \cdot 3H_2O$	H_2O	3.2×10^{-6}	182.6	40	8.5	0.35	97	59
16	$RuCl_3 \cdot 3H_2O$	H_2O	9.4×10^{-6}	110.7	30	5	0.35	99	22
17	$RuCl_3 \cdot 3H_2O$	H_2O	9.4×10^{-6}	110.7	40	5	0.35	98	93
18	$RuCl_3 \cdot 3H_2O$	H_2O	9.4×10^{-6}	110.7	50	5	0.35	98	92
19	$RuCl_3 \cdot 3H_2O$	H_2O	9.4×10^{-6}	110.7	60	5	0.35	97	93
20	$RuCl_3 \cdot 3H_2O$	H_2O	9.4×10^{-6}	110.7	80	5	0.35	97	61
21	$RuCl_3 \cdot 3H_2O$	H_2O	9.4×10^{-6}	110.7	40	9	0.1	93	92
22	$RuCl_3 \cdot 3H_2O$	H_2O	9.4×10^{-6}	110.7	40	9	0.2	96	90
23	$RuCl_3 \cdot 3H_2O$	H_2O	9.4×10^{-6}	110.7	40	9	0.3	94	93
24	$RuCl_3 \cdot 3H_2O$	H_2O	9.4×10^{-6}	110.7	40	9	0.35	96	96
25	$RuCl_3$	–	9.4×10^{-6}	–	60	7.5	0.35	96	35
26	$RuCl_3 \cdot 3H_2O$	–	9.4×10^{-6}	–	60	7.5	0.35	96	45
27	$RuCl_3 \cdot 3H_2O$	H_2O	9.4×10^{-6}	110.7	60	7.5	0.35	97	97
28	$RuCl_3 \cdot 3H_2O$	CH_3OH	9.4×10^{-6}	110.7	60	7.5	0.35	97	93
29	$RuCl_3 \cdot 3H_2O$	C_2H_5OH	9.4×10^{-6}	110.7	60	7.5	0.35	97	91
30	$RuCl_3 \cdot 3H_2O$	C_3H_7OH	9.4×10^{-6}	110.7	60	7.5	0.35	98	74

molar ratio of water to ruthenium, the catalyst concentration being low.

Based on the above results, the effects of catalyst concentration and water–ruthenium molar ratio on the yield of target products were studied in detail. The results are summarized in Table 2 (entries 10–15) and graphically shown in Fig. 3. The results show that the reaction time is greatly shortened when the molar ratio of ruthenium to water is increased in a certain catalyst concentration range (1.2×10^{-4}–9.4×10^{-6} mol per mole of TMS). The yield of ETMS in the target product increases first and then decreases with increasing molar ratio of ruthenium to water. When ruthenium content was 3.2×10^{-6} mol per mole of TMS, even if the molar ratio of water to ruthenium increased to 182.6, the yield of the target product ETMS decreased significantly. Even if the reaction time is prolonged, the yield of the target product increases only slightly. The above results indicate that the lowest concentration of ruthenium that can effectively catalyze the hydrosilylation of ethylene with trimethoxysilane was

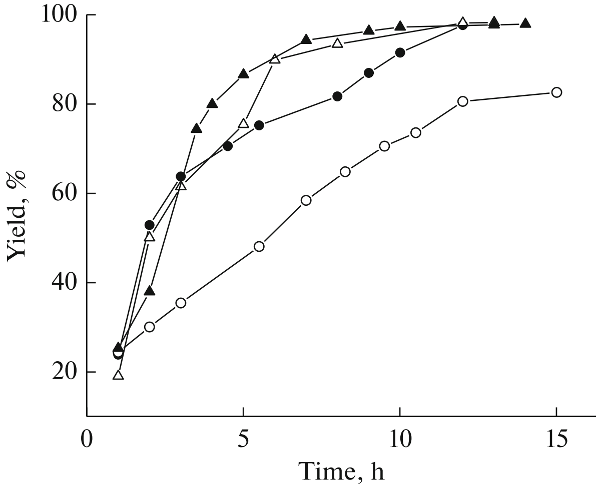


Fig. 2. Influence of catalyst contents and molar ratio of promoter/catalyst on yield of ETMS. Catalyst contents: ● 1.1×10^{-4}, ▲ 1.1×10^{-4}, ○ 3.3×10^{-5}, △ 3.3×10^{-5}. The molar ratio of H_2O to ruthenium: ● 3.5 : 1, ▲ 8.4 : 1, ○ 3.5 : 1, △ 33.6 : 1. The catalyst concentration indicated was the molar ratio of ruthenium to trimethoxysilane.

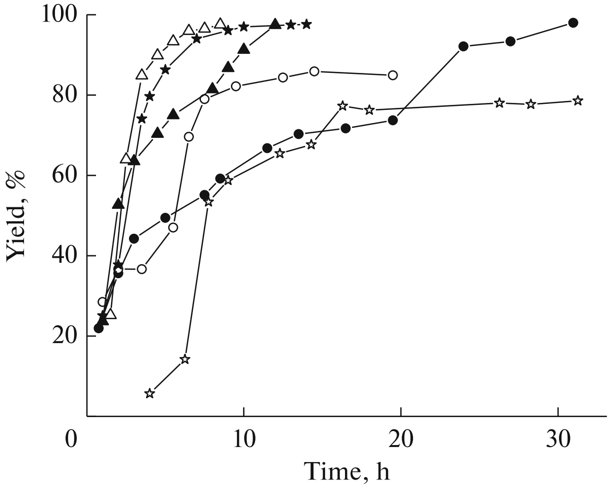


Fig. 3. Influence of catalyst contents and molar ratio of promoter/catalyst on yield of ETMS. Catalyst contents: ★ 1.2×10^{-4}, ● 6.0×10^{-5}, ○ 6.0×10^{-5}, ▲ 3.0×10^{-5}, △ 9.4×10^{-6}, ☆ 3.2×10^{-6}. The molar ratio of H_2O to ruthenium: ★ 5.5 : 1, ● 11.0 : 1, ○ 18.5 : 1, ▲ 37.0 : 1, △ 110.7 : 1, ☆ 182.6 : 1. The catalyst concentration indicated was the molar ratio of ruthenium to trimethoxysilane.

9.4×10^{-6} mol per mole of TMC, and the maximum H_2O/Ru molar ratio was determined to be 110.7. It also can be seen from Fig. 3 that with the extension of the reaction time, the yield of ETMS increased gradually in a certain interval of catalyst concentrations (1.2×10^{-4}–9.4×10^{-6} mol per mole of TMS). Even though the molar ratio $H_2O/RuCl_3 \cdot 3H_2O$ decreased to 11.0, the hydrosilylation reaction could still be carried out almost completely, thus indicating that the reaction rate was greatly affected by the amount of H_2O. Nevertheless, the reaction equilibrium was not affected.

Influence of Temperature on Hydrosilylation Reaction

The influence of reaction temperature on hydrosilylation reaction was also investigated and five reactions were conducted at temperatures ranging from 30 to 80°C. The results are listed in Table 2 (entries 16–20) and graphically shown in Fig. 4. These results indicated that the influence of reaction temperature on the ETMS yield was very complicated. When the reaction was conducted at 30°C, the reaction rate was very low and the ETMS yield was no more than 25% after 5 h. With increasing reaction temperature, the reaction rate increased rapidly and a yield of 93% could be obtained when the reaction was conducted at 40°C for 5 h. However, as the temperature increased further, the yield of ETMS decreased gradually. It was well-known that TMS was highly reactive and was liable to be transformed into tetramethoxysilane (Scheme 4) under mild conditions in the presence of weak acids or weak bases, or even simply under elevated temperature conditions [7–9]. Therefore, the optimum reaction temperature range for hydrosilylation reaction of ethylene with trimethoxysilane was between 40–60°C since the reaction could be rapidly conducted in this range and at the same time, the disproportionation reaction of trimethoxysilane was not significant.

$$4\mathrm{HSi(OMe)_3} \rightarrow \mathrm{SiH_4}\uparrow + 3\mathrm{Si(OMe)_4}$$

Scheme 4. Disproportionation of trimethoxysilane.

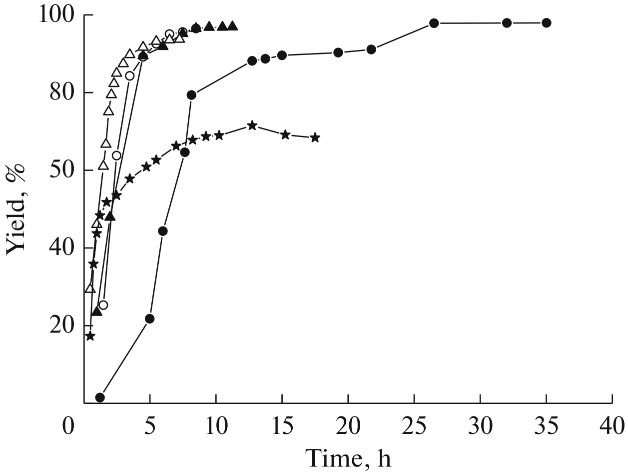


Fig. 4. Influence of reaction temperature on yield of ETMS, °C: ● 30, ○ 40, ▲ 50, △ 60, ★ 80. The concentration of ruthenium was 9.4×10^{-6} mol per mole of trimethoxysilane and the molar ratio of H_2O to $RuCl_3 \cdot 3H_2O$ was 110.7 for each reaction (Table 2, entries 16–20).

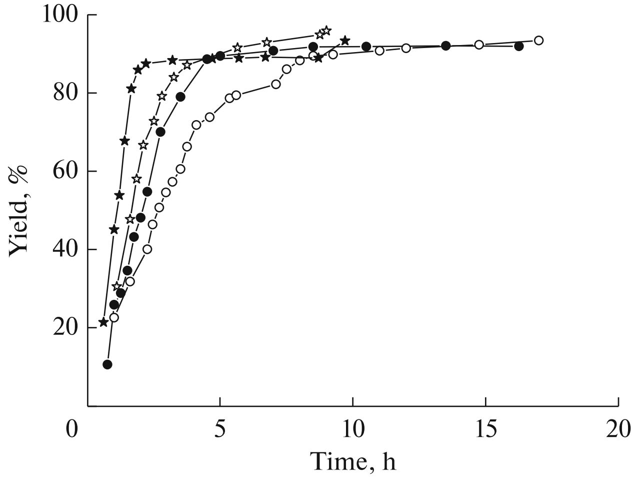


Fig. 5. Influence of ethylene pressure on yield of ETMS, MPa: ● 0.1, ○ 0.2, ★ 0.3, ☆ 0.35. The concentration of ruthenium was 9.4 × 10^{-6} mol per mole of trimethoxysilane and the molar ratio of H_2O to $RuCl_3 \cdot 3H_2O$ was 110.7 for each reaction (Table 2, entries 19–22).

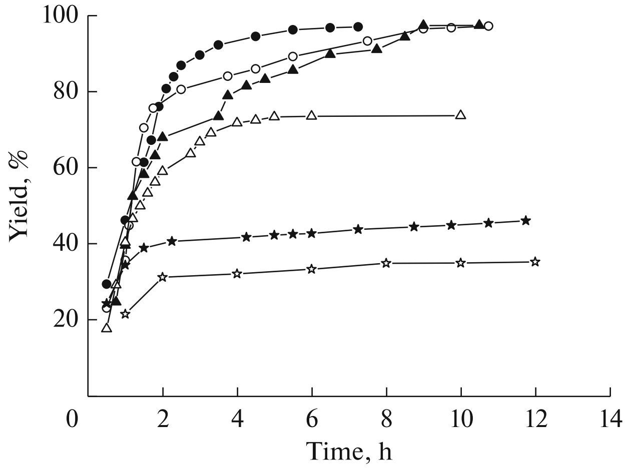


Fig. 6. Influence of promoters on yield of ETMS: ☆ anhydrous ruthenium trichloride as catalyst, ★ no promoter, ● H_2O, ○ CH_3OH, ▲ C_2H_5OH, △ C_3H_7OH.

Influence of Ethylene Pressure on Hydrosilylation Reaction

The influence of ethylene pressure on the yield of ETMS was also investigated. Therefore, four hydrosilylation reactions of ethylene with TMS were carried out under ethylene pressure of 0.10, 0.20, 0.30 and 0.35 MPa, other parameters being constant (Table 2, entries 21–24) and Fig. 5. As expected, the ETMS yield increased with the increasing ethylene pressure, and the yield reached 96% after 9 h at the ethylene pressure of 0.35 MPa. The hydrosilylation reaction of ethylene with TMS is a typical gas-liquid reaction and the chemical reaction generally occurred 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 ETMS. With increasing the gaseous ethylene pressure, the diffusion rate, the adsorption rate or dissolution rate of ethylene and the surface reaction rate increased. Therefore, the increase of the ethylene pressure was beneficial to improve the yield of ETMS.

Influence of Promoter on the Hydrosilylation Reaction

In order to clarify the effect of water on the hydrosilylation reaction, the effect of various promoters on hydrosilylation of ethylene with trimethoxysilane was investigated. Water, methanol, ethanol, isopropanol were tested as promoters in each reaction at the same level while keeping the ratio of ruthenium to the promoter as well as other operating parameters constant. The results are listed in Table 2 (entries 25–29) and plotted in Fig. 6. When H_2O and CH_3OH were used, the ETMS yield could reach 97 and 93% after 7.5 h at 60°C. When ethanol or isopropanol were used, the ETMS yields were 91 and 73%, respectively. Thus, these yields were inferior compared to those obtained with H_2O as promoter. It is possible that hydrogen ion play an important role in the hydrosilylation, when H_2O, methanol, ethanol or isopropanol are added as promoters. Activity of hydrogen ion can be affected by different alkoxy group and hydroxyl anion. Alkoxy group and hydroxyl anion have no direct impact on the hydrosilylation of ethylene with trimethoxysilane, but they may affect the rate of hydrosilylation by influencing the rate of hydrogen ion release. Compared with the alkoxy group, the chemical steric hindrance of hydroxyl anion is the smallest. This may be the main reason why the co-catalytic effect of water is better than that of other promoters.

The above experimental results show that water, methanol and ethanol can be used as co-catalysts in the hydrosilylation of ethylene with trimethoxysilane catalyzed by $RuCl_3 \cdot 3H_2O$. It has ever been reported in previous literature that several compounds containing active hydrogen, including water, methanol and ethanol could exhibit high catalytic activity and regioselectivity for the hydrosilylation of unsaturated compounds [10–16]. In 2009, Al Postigo et al. reported on the hydrosilylation of C–C multiple bonds with $(Me_3Si)_3SiH$ in water, and studied the radical initiation step. The hydrosilylation of alkynes in water by $(Me_3Si)_3SiH$ was shown to proceed with the highest *Z*-stereoselectivity, when the reactions are initiated by dioxygen [17]. In 2012, Silbestry et al. reported on the synthesis of water-soluble platinum(0) complexes containing sulfonated N-heterocyclic carbene ligands that can activate the hydrosilylation of some terminal alkynes at room temperature in water [18]. Later in 2016, Pashikanti et al. [19] using catalytic amounts of copper(II) in water, 4-picoline and dimethylphenylsilylpinacol borane, silylated a series of allenoates on the β carbon. The process was conducted at room temperature and in open air, the target product was obtained in excellent yields and high *E*-selectivity. Overall, water can improve the selectivity of hydrosilylation catalyzed by transition metals. The role of clarified water in this process may need further study.

As everyone knows, ruthenium trichloride is a mild Lewis acid, ruthenium metal itself is oxophilic, so it can activate the C–O and H–O bonds of oxygenated compounds. When appropriate amount of water is added to the hydrosilylation system catalyzed by ruthenium trichloride, H–O bonds in water molecules are activated by ruthenium(III) ions. Perhaps the role of water is to stimulate $RuCl_3$ reduction with hydrosiloxane.

CONCLUSIONS

The hydrosilylation reaction of ethylene with trimethoxysilane catalyzed by ruthenium chloride hydrate and promoted by water or alcohols has been investigated. It has been proved that water is a good promoter for ruthenium chloride hydrate catalyzed hydrosilylation of ethylene with trimethoxysilane. The yield of ethyltrimethoxysilane is significantly affected by the concentration of ruthenium chloride hydrate, the molar ratio between water and ruthenium chloride hydrate and the reaction temperature. The effect of ethylene pressure on the yield of ethyltrimethoxysilane is not obvious. With 9.4×10^{-6} ruthenium per mole of trimethoxysilane and over 110 times of water per mole of ruthenium, the hydrosilylation reaction conducted at temperatures ranging from 40 to 60°C for 7.5 h under ethylene pressure of 0.35 MPa can reach an yield higher than 97%.

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CONFLICT OF INTEREST STATEMENT

The authors declare that they have no conflicts of interest.

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