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Short communication

Ru/12SrO–7Al_2O_3 (S12A7) catalyst prepared by physical mixing with Ru $(PPh_3)_3Cl_2$ for steam reforming of toluene

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Steam reforming of toluene as a model of aromatics was performed over various Ru/12SrO–7Al_2O_3 (S12A7) catalysts, and the effects of Ru precursor, calcination and pre-treatment conditions on the catalytic activity and durability of Ru/S12A7catalysts were investigated. The catalytic activity of prepared Ru/S12A7 catalysts exhibited higher than that of a commercial Ru/Al_2O_3 (RA), despite low Ru loading. The catalysts prepared by the physical mixing of Ru $(PPh_3)_3Cl_2$ and S12A7 (PPH) had higher catalytic activities than the catalysts prepared by the impregnation with $RuCl_3$ nH_2O (CL). It is interesting that the N_2 pre-treated PPH and CL catalysts especially had higher catalytic activities than the H_2 pre-treated PPH and CL catalysts. In their catalysts, there was a linear relationship between the catalytic activity and the Ru dispersion estimated by CO chemisorption. The catalytic activity of the N_2 pre-treated PPH catalyst has little decreased with time on stream, whereas the catalytic activities of the N_2 pre-treated CL catalyst and H_2 pre-treated PPH catalyst gradually decreased with time on stream.

1. Introduction

Catalytic steam reforming of hydrocarbons is an important route for hydrogen production for fuel cell systems. Liquid fuels such as kerosene are one of the promising hydrogen sources for fuel cell systems because of its high energy density and low cost [1,2]. However, there is serious catalyst deactivation due to the carbon deposition on the catalyst surface because kerosene mainly contains alkanes with carbon number of above 10, and aromatic hydrocarbons. In particular, typical nickel based catalysts are well known to suffer from the carbon deposition during the reaction [3]. Although an increase in the amount of steam suppresses the coking, a high steam to carbon ratio (S/C ratio) causes large energy consumption for vaporization of water. Therefore, the developments of catalysts that have superior catalytic activity and durability for steam reforming of liquid fuels under low S/C conditions have been demanded. In order to achieve the high catalytic activity and durability, how to activate the water over the catalyst surface to promote the oxidation of hydrocarbon reactants and the deposited carbons is an important factor. Recently, Sekine et al. have focused on a redox property of perovskite oxide supports to promote the oxidation of adsorbed CH_x species on the catalyst surface, and reported that Ni/$LaAlO_3$ and Ni/$La_{0.9}Sr_{0.2}AlO_{3-\delta}$ catalysts showed excellent catalytic activity for steam reforming of toluene [4,5]. On the other hand, 12CaO–7Al_2O_3 (C12A7) is known to have the nanocage that can incorporate active oxygen ions (O^-, O^{2-}, and O_2^{2-}). Yang et al. have reported that Ni/C12A7 exhibited higher catalytic activity and lower coke formation rate in partial oxidation of methane [6]. Li et al. have reported that Ni/C12A7 showed excellent performance for steam reforming of biomass tar [7]. Recently, the authors have reported that the 12SrO–7Al_2O_3 (S12A7) catalysts exhibited superior catalytic activities for steam reforming of dodecane and toluene compared to a commercial Ru/Al_2O_3 catalyst because the active oxygen species in S12A7 contribute to the acceleration of oxidation of CHx species on Ru metals [8]. However, the Ru/S12A7 catalyst suffered from gradual deactivation with time on stream.

In the present study, in order to improve the catalytic activity and durability of Ru/S12A7 catalysts for steam reforming of toluene, the effects of Ru precursor, the Ru-supporting method, and the calcination and pre-treatment conditions on the catalytic performances of Ru/S12A7 catalysts were investigated.

2. Experimental

2.1. Catalyst preparation

S12A7 support materials were prepared as follows. Strontium hydroxide (Kojundo Chemical Laboratory) was used as a strontium precursor, aluminum hydroxide (Wako Pure Chemical Industries) or γ-alumina (Strem Chemicals) was used as an aluminum precursor. Both precursors were wet-blended with ethanol in a glove box under nitrogen atmosphere. The Sr/Al (S/A) atomic ratio was 0.874 (slightly Sr rich amount) [9]. After mixing until ethanol completely evaporated, the mixture was calcined at various conditions. The calcination conditions employed were as follows: calcination temperature: 873 K, ramping rate of temperature: 200 K h^{-1}, partial pressure for H_2O of the stream

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(p_{H2O}): 1.9 kPa [9,10], cooling rate of temperature: 1500 K h^{-1} [9,10]. The Sr/Al (S/A) atomic ratio was 0.874 (slightly Sr rich amount).

Ru/S12A7 catalysts were prepared by physical mixing with Ru $(PPh_3)_3Cl_2$ (PPH) and a conventional impregnation with $RuCl_3$ nH_2O (CL). In the preparation of PPH catalysts, Ru $(PPh_3)_3Cl_2$ (Wako Pure Chemical Industries) and S12A7 powders were mixed by an agate mortar for 0.5 h, the mixture then were calcined at 873 K for 1 h in a stream of N_2, then pelletized and crushed (0.5–1.0 mm φ). CL catalysts were prepared as follows. An ethanol solution of ruthenium chloride n-hydrate (Wako Pure Chemical Industries) was added to the S12A7 powder. The mixture was evaporated on a water bath at 373 K, and the resultant material was dried for 15 h at 373 K, then finally calcined in a stream of air at 873 K for 1 h, then pelletized and crushed (0.5–1.0 mm φ) [8]. The loading of ruthenium was 1.0 wt.%. A commercial Ru (2.0 wt.%)/Al_2O_3 (RA) catalyst was employed as a reference catalyst.

2.2. Activity test

Steam reforming of toluene was performed at atmospheric pressure using a conventional fixed bed flow reactor. The catalyst was placed in a reaction tube (8 mm φ i.d.) made of quartz glass, and was then pretreated in an N_2 or H_2 stream (100 $cm^3{}_{\text{-SATP}}$ min^{-1}) at 873 K for 1 h. H_2O was supplied using a micro feeder and was then introduced via a vaporizer to the reactor. Following the supply of steam, toluene was supplied via a vaporizer to the reactor using a plunger pump. Nitrogen was used as a carrier gas. Liquid products and unreacted liquid reactants were trapped by an ice water bath located downstream of the reactor, and the gas and liquid compositions were analyzed using gas chromatographs with a thermal conductivity detector (TCD) and a flame ionization detector (FID), respectively. The flow rate of gas products was measured using a soap bubble flow meter or a wet gas meter. The reaction conditions for steam reforming of toluene were a reaction temperature 873 K, a S/C molar ratio of 2.0, a time factor (W/F) of 7 g $hmol^{-1}$.

2.3. Catalyst characterization

X-ray diffraction (XRD; RINT2000, Rigaku) analysis of used catalysts was carried out using Cu Kα radiation. The Brunauer–Emmett–Teller (BET) surface area of the newly-prepared, pre-treated, and used catalysts was determined by N_2 adsorption at 77 K using a flow absorption apparatus (Flow Sorb II 2300, Micromeritics). The composition of the flow gas was N_2:He = 30:70. The catalyst was degassed at 473 K for 15 min prior to the measurement.

The amount of chemisorbed CO on the pre-treated catalysts was estimated by a pulse adsorption method. The ruthenium dispersion (D_{Ru}) of the catalysts was calculated from the amount of chemisorbed CO, where D_{Ru} was defined as:

$$D_{Ru} = \left\{V_{CO} f_{CO/Ru}/0.0224\right\}/\{L_{Ru}/M_{Ru}\}, \tag{1}$$

Table 1
Catalytic properties and activity of Ru (1.0 wt.%)/S12A7 catalysts.

Ru precursor	Calcination atmosphere	Pre-treatment atmosphere	Ru dispersion (%)[a]	Toluene conversion (%)[b]	TOF (s^{-1})[b]
$Ru(PPh_3)_3Cl_2$	N_2	N_2	5.7	80.1	5.7
		H_2	4.0	61.9	6.3
$RuCl_3$ nH_2O	N_2	N_2	1.4	42.1	12.2
		H_2	0.3	21.3	28.8
	Air	H_2	0.5	15.2	12.3
Commercial Ru (2.0 wt.%)/Al_2O_3		H_2	2.0	11.8	1.2

[a] After pre-treatment, CO/Ru = 0.5.
[b] Time on stream: 0.5 h.

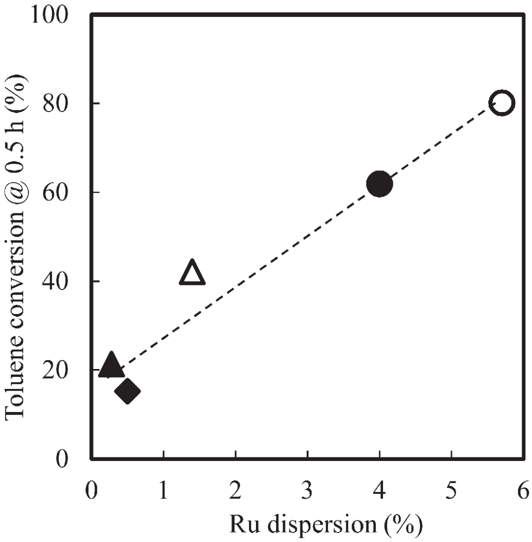

Fig. 1. Relationship between catalytic acitivity and Ru dispersion of Ru/S12A7 catalysts; ○: $Ru(PPh_3)_3Cl_2$, N_2 calcination, N_2 pre-treatment; ●: $Ru(PPh_3)_3Cl_2$, N_2 calcination, H_2 pre-treatment; △: $RuCl_3$ nH_2O, N_2 calcination, N_2 pre-treatment; ▲: $RuCl_3$ nH_2O, N_2 calcination, H_2 pre-treatment; ◆: $RuCl_3$ nH_2O, Air calcination, H_2 pre-treatment.

where V_{CO} ($m^3{}_{\text{-STP}}$ $g^{-1}_{\text{-cat}}$) is the amount of chemisorbed CO on the catalyst, L_{CO} (−) is the Ru content in the catalyst, $f_{CO/Ru}$ (= 0.5) is the stoichiometric factor for CO chemisorption on Ru, and M_{Ru} (= 101.07 g mol^{-1}) is the molar mass of Ru.

Turn over frequency (TOF) for steam reforming of toluene was defined as follows:

$$TOF = \frac{F \times X}{\dfrac{V_{CO}}{0.0224 f_{CO/Ru}} \times W_{Cat}}. \tag{2}$$

where F (mol s^{-1}) is the toluene molar flow rate, X (−) is the toluene conversion at 0.5 h, and $W_{Cat.}$ (g) is the catalyst weight.

3. Results and discussion

The catalytic activity, Ru dispersion, and TOFs of various Ru/S12A7 catalysts were listed in Table 1. The toluene conversion of Ru/S12A7 catalysts was higher than that of the RA catalyst, despite low Ru loading.

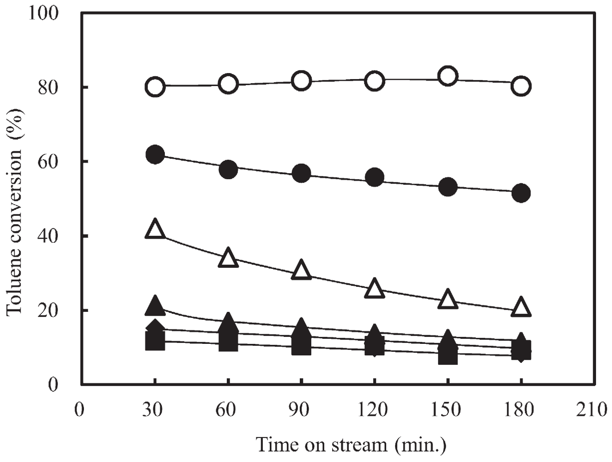

Fig. 2. Time dependency of catalytic activity of various Ru/S12A7 catalysts; ○: $Ru(PPh_3)_3Cl_2$, N_2 calcination, N_2 pre-treatment; ●: $Ru(PPh_3)_3Cl_2$, N_2 calcination, H_2 pre-treatment; △: $RuCl_3$ nH_2O, N_2 calcination, N_2 pre-treatment; ▲: $RuCl_3$ nH_2O, N_2 calcination, H_2 pre-treatment; ◆: $RuCl_3$ nH_2O, Air calcination, H_2 pre-treatment; ■: commercial Ru/Al_2O_3.

Table 2
BET surface area of the Ru (1.0 wt.%)/S12A7 catalysts before and after the reaction.

Ru precursor	Calcination atmosphere	Pretreatment atmosphere	BET surface area ($m^2\ g^{-1}$)			
			Support	After calcination	After pretreatment	After reaction
$Ru(PPh_3)_3Cl_2$	N_2	N_2	5.8	5.4	–	4.6
		H_2			5.5	3.3
$RuCl_3\ nH_2O$	N_2	N_2		3.4	–	2.3
		H_2			3.2	1.5
	Air	H_2		4.3	4.5	2.0
Commercial Ru (2.0 wt.%)/Al_2O_3		H_2	–	6.6	–	4.4

TOFs of Ru/S12A7 catalysts were higher than that of the RA catalyst because the active oxygen species in S12A7 contribute to the acceleration of oxidation of CHx species on Ru metals [8]. Fig. 1 shows the relationship between the catalytic activity and the Ru dispersion. A linear relationship between the catalytic activity and the Ru dispersion estimated by CO chemisorption was observed. The catalytic activity and Ru dispersion of PPH catalysts were higher than those of the CL catalysts. Ru $(PPh_3)_3Cl_2$ fuses at relative lower temperature (432 K) before the decomposition [11]. Therefore, it was inferred that the melted Ru $(PPh_3)_3Cl_2$ could be spontaneously spread over the surface of S12A7 support in the beginning of a calcination step, resulting in the increase in the Ru dispersion. The CL catalyst calcined in the stream of N_2 had slightly higher catalytic activity than that calcined in the stream of air. On the other hand, it is interesting that the N_2 pre-treated PPH and CL catalysts especially had higher catalytic activities and Ru dispersion than the H_2 pre-treated PPH and CL catalysts. Probably, the rapid reduction of Ru precursor in the stream of H_2 promoted the sintering of Ru complexes, resulting in the decrease in Ru dispersion. The mild reduction under inert atmosphere would prevent the sintering of Ru. The results indicate that the physical mixing of Ru $(PPh_3)_3Cl_2$ and S12A7 and the N_2 pretreatment measured before the reaction are effective to enhance the catalytic activity of the Ru/S12A7 catalyst by increasing the Ru dispersion.

Fig. 2 shows the time dependency of catalytic activity of various Ru/S12A7 catalysts. Little deactivation was observed in the N_2 pre-treated PPH catalyst, whereas the catalytic activities of the N_2 pre-treated CL catalyst and H_2 pre-treated PPH catalyst gradually decreased with time on stream. This fact revealed that the N_2 pre-treated PPH catalyst had superior durability for steam reforming of toluene.

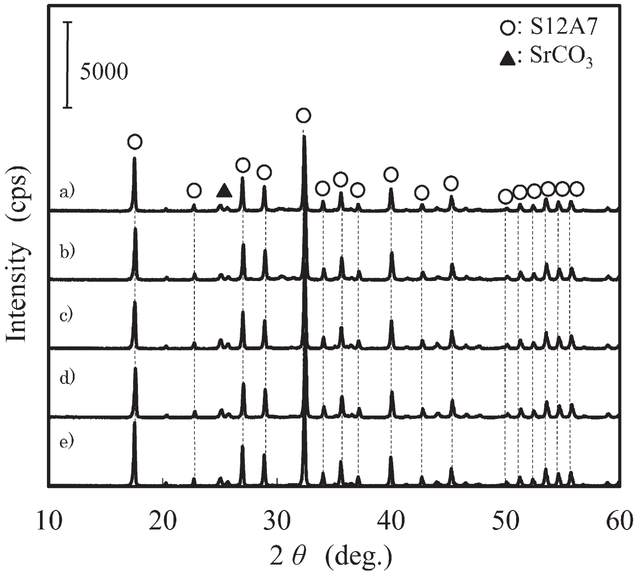

Fig. 3. XRD profiles of Ru/S12A7 catalysts; a) $Ru(PPh_3)_3Cl_2$, N_2 calcination, N_2 pre-treatment; b) $Ru(PPh_3)_3Cl_2$, N_2 calcination, H_2 pre-treatment; c) $RuCl_3\ nH_2O$, N_2 calcination, N_2 pre-treatment; d) $RuCl_3\ nH_2O$, N_2 calcination, H_2 pre-treatment; e) $RuCl_3\ nH_2O$, Air calcination, H_2 pre-treatment.

Table 2 shows the BET surface area of the Ru/S12A7 catalysts before and after the reaction. Fig. 1 and Table 2 indicate that the decrement of BET surface area corresponds to the decrement of toluene conversion.

Fig. 3 shows the XRD profiles of Ru/S12A7 catalysts after the reaction. In all of the catalysts, the diffraction peaks assigned to S12A7 of used catalysts little changed compared to those of as-prepared catalysts, unrelated to the deactivation behavior of the catalysts. Therefore, the reason why the catalytic activity is decreased with time would be explained by the decrease in the Ru dispersion due to the sintering of catalysts. In addition, Kanda et al. reported that excess phosphorus species over Ru-P/SiO_2 catalyst acted as an anchor of Ru particles [12]. Therefore, it is inferred that the residual phosphorus species over the PPH catalyst prevent the sintering of Ru particles.

The theoretical gas product composition for steam reforming of toluene was obtained using a kinetic equilibrium calculation [13] of the following reactions:

$$C_6H_5CH_3 + 7\ H_2O \rightarrow 7\ CO + 11\ H_2 \tag{1}$$

$$CO + 3H_2 \rightleftarrows CH_4 + H_2O \tag{2}$$

$$CO + H_2O \rightleftarrows CO_2 + H_2 \tag{3}$$

Fig. 4 shows the comparison of the calculated and measured selectivities for carbon contained products over Ru/S12A7 catalysts. The good agreement shown between the calculated and measured CO_2 and CO selectivities indicates that the water gas shift reaction over Ru/S12A7 is close to those at a thermodynamic equilibrium state at 873 K. The experimental CH_4 selectivity for Ru/S12A7 was smaller than the calculated values. This indicates that the methanation reaction was

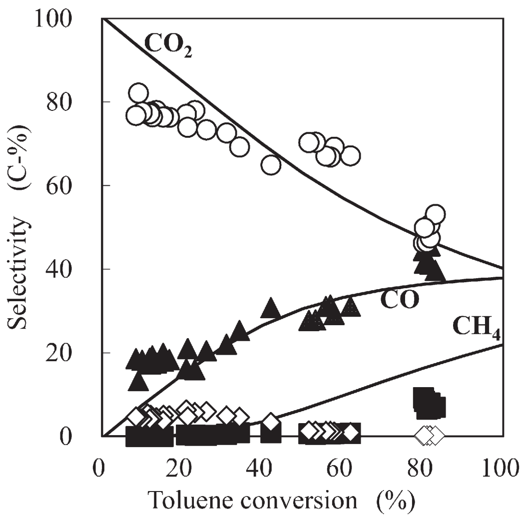

Fig. 4. Comparison of the calculated and measured selectivities for carbon contained products over Ru/S12A7; ○: CO_2, ▲: CO, ■: CH_4, ◇: C_6H_6.

suppressed over Ru/S12A7. The formation of benzene, which formed by hydrogenating dealkylation ($C_6H_5CH_3 + H_2 \rightarrow C_6H_6 + CH_4$), over Ru/S12A7 was a little.

4. Conclusion

In order to improve the catalytic activity and durability of Ru/S12A7 catalysts for steam reforming of toluene, the effects of Ru precursor, the Ru-supporting method, and the calcination and pre-treatment conditions on the catalytic performances of Ru/S12A7 catalysts were investigated. All of the Ru/S12A7 catalysts exhibited higher catalytic activity than the RA catalyst, despite low Ru loading. The physical mixing of Ru $(PPh_3)_3Cl_2$ (PPH) and S12A7, and the N_2 pretreatment before the reaction is effective to enhance the catalytic activity of the Ru/S12A7 catalyst by increasing the Ru dispersion. Furthermore, the catalytic activity of the N_2 pre-treated PPH catalyst has little decreased with time on stream, whereas the catalytic activities of the N_2 pre-treated CL catalyst and H_2 pre-treated PPH catalyst gradually decreased with time on stream. From above facts, it is revealed that the N_2 pre-treated PPH catalyst had superior catalytic activity and durability for steam reforming of toluene.

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