Rh-catalyzed syngas conversion to ethanol: Studies on the promoting effect of FeO$_x$

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ABSTRACT

Rhodium catalysts loaded on silica modified by various transition metal oxides were investigated for the conversion of syngas to ethanol. Iron oxide was found to be an efficient promoter for ethanol formation. The increase in iron content up to 5 wt% significantly increased CO conversion and ethanol selectivity. The preparation method used for introducing FeO$_x$ was found to affect both the conversion and the selectivity significantly. The catalyst prepared by the impregnation of a FeO$_x$–SiO$_2$ composite, which was synthesized by a sol–gel technique preliminarily, with Rh(NO$_3$)$_3$ aqueous solution provided better ethanol formation activity than those prepared by co-impregnation and co-sol–gel methods. An ethanol selectivity of 42% was achieved at CO conversion of 12% over a 5 wt% Rh/(5 wt% FeO$_x$–SiO$_2$) catalyst prepared by this method. Larger interfaces between Rh and FeO$_x$ species were proposed to be a crucial factor for obtaining higher ethanol selectivity. The co-existence of Rh^{3+} with Rh^0 and the size of Rh particles also played key roles in ethanol formation.

1. Introduction

Catalytic transformations of syngas (H$_2$ + CO), which can be produced from non-petroleum carbon resources including natural gas, coal, and biomass, into clean fuels and valuable chemicals have attracted much attention in recent years because of the global demand for the decrease in the dependence on petroleum [1,2]. Ethanol is one of the attractive target products in syngas transformations, because it can be used as a fuel or fuel additive and a potential source of hydrogen for fuel cells, and it can also serve as a feedstock for the production of a variety of chemicals and polymers [3,4]. Many catalysts, particularly Rh-, Co-, Cu- and Mo-based catalysts, have been reported to be capable of catalyzing the conversion of syngas to ethanol [3,4]. However, these catalysts still suffer from lower productivity. Relatively high ethanol selectivity (40–50%) can only be achieved at low CO conversions (typically <10%). It is worthy mentioning that Tsubaki and co-workers [5,6] have developed an intriguing method for ethanol synthesis from dimethyl ether and syngas using the combined zeolite (e.g., H-ZSM-5) and metal (e.g., Cu/ZnO) catalysts.

Among the catalysts reported to date for the direct conversion of syngas to ethanol, supported Rh shows the most promising ethanol

formation activity [3,4,7–14]. However, the main products over the supported single Rh catalysts are typically hydrocarbons (particularly methane) [3,4]. The presence of a promoter (e.g., transition metal oxide such as MnO$_x$, VO$_x$, or FeO$_x$) or the combination of several promoters is required for obtaining higher ethanol selectivity [7–14]. The understanding of the functioning mechanism of the promoter will certainly be helpful for the rational design of efficient catalysts for ethanol synthesis. A few studies have demonstrated that the location of promoter (or the contact between promoter and Rh) is quite important for obtaining better catalytic performances [8,15,16]. Thus far, many of the reported studies have employed co-impregnation or sequential impregnation for introducing the transition metal promoters [7–14]. However, these methods cannot ensure the high dispersion of promoters on support and the contact between Rh and transition metal oxide promoters.

The sol–gel technique is known to be capable of producing catalysts with homogeneously distributed supported species [17]. Recently, we prepared transition metal oxide-containing SiO$_2$ composites using the sol–gel technique and investigated the catalytic performances of Rh catalysts supported on these composite oxides with highly dispersed transition metal oxide promoters for syngas conversions. Herein, we report the catalytic behaviors and the structural features of these catalysts with finely dispersed promoters. The effect of catalyst preparation methods is also discussed to gain insights into the active sites.

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2. Experimental

2.1. Catalyst preparation

Transition metal oxide (MO_x)–SiO_2 composites (denoted as MO_x–SiO_2 hereafter) were prepared by the sol–gel technique [17]. Typically, tetraethyl orthosilicate (TEOS) and the precursor of transition metal oxide (metal nitrates except for NH_4VO_3 used for VO_x-modified SiO_2) were dissolved in the mixture of water and ethylene glycol, and a homogeneous sol was obtained. The sol was then heated at 343 K for 16 h to form a homogenous gel. After being dried at 383 K in air for 12 h, the gel was calcined at 623 K for 6 h in air. The supported Rh catalysts were prepared by incipient wetness impregnation method using $Rh(NO_3)_3$ as the precursor of Rh. After being dried at 383 K for 12 h in air, the supported catalyst was calcined at 623 K in air for 6 h and finally reduced by H_2 at 573 K for 2 h. The catalyst prepared by this procedure was denoted as $Rh/(MO_x$–$SiO_2)$.

Co-impregnation and co-sol–gel methods were also employed for the preparation of FeO_x-promoted Rh catalysts supported on SiO_2. For the co-impregnation method, the powdery SiO_2, which was prepared preliminarily by the sol–gel technique described above, was added into the mixed aqueous solution containing $Rh(NO_3)_3$ and $Fe(NO_3)_3$, followed by drying at 383 K for 12 h, calcination at 623 K for 6 h, and H_2 reduction at 573 K for 2 h. For the co-sol–gel method, TEOS, $Rh(NO_3)_3$, and $Fe(NO_3)_3$ were dissolved in the mixture of water and ethylene glycol, and the mixture underwent heating at 343 K to form a homogenous gel. After being dried at 383 K in air for 12 h, the sample was calcined at 623 K for 6 h in air, followed by H_2 reduction at 573 K for 2 h. The catalysts prepared by the co-impregnation and co-sol–gel methods were denoted as $(Rh–FeO_x)/SiO_2$ and $Rh–FeO_x$–SiO_2, respectively.

2.2. Catalytic reaction

Catalytic reactions were performed on a fixed-bed reactor operated at 2 MPa. The catalyst loaded in the reactor was pretreated by H_2 at 573 K for 2 h. After the catalyst was cooled down to the reaction temperature (typically 523 K), the syngas with a H_2/CO ratio of 2.0 was introduced into the reactor. Typical reaction conditions were as follows: pressure (P) = 2 MPa, H_2/CO = 2, temperature (T) = 523 K, WHSV = 8000 mL g(cat)$^{-1}$ h^{-1}. The products were analyzed by on-line gas chromatography.

2.3. Catalyst characterization

XRD patterns were collected on a Philips X'Pert Pro Super X-ray diffractometer equipped with X'Celerator and Xe detection systems. Cu K_α radiation (40 kV and 30 mA) was used as the X-ray source. X-ray photoelectron spectra (XPS) were recorded with a Quantum 2000 Scanning ESCA Microprob instrument (Physical Electronics) using Al–K_α radiation. The binding energy was calibrated using C_{1s} photoelectron peak at 284.6 eV as a reference. Transmission electron microscopy (TEM) measurements were performed on a JEM-2100 electron microscope operated at an acceleration voltage of 200 kV. The mean sizes of Rh particles were estimated from TEM micrographs by counting ca. 150–200 particles.

H_2 temperature-programmed reduction (H_2-TPR) was performed using a Micromeritics AutoChem 2920 II instrument. Typically, after the pretreatment of sample loaded in a quartz reactor and cooling to 303 K, a H_2–Ar gas mixture was introduced into the reactor, and the temperature was raised to 1073 K at a rate of 10 K min^{-1}. H_2 consumption was monitored by a thermal conductivity detector. CO chemisorption was carried out with a Micromeritics ASAP 2010 C. After the sample was pretreated by H_2 reduction at 573 K and evacuation, CO chemisorption was performed at 308 K. After the first isotherm (total CO uptake), the sample was evacuated for 10 min, and the second isotherm (reversible CO uptake) was measured. The amount of the chemisorbed CO (irreversible CO uptake) was calculated using the difference between the total and reversible CO uptakes.

3. Results and discussion

3.1. Catalytic behaviors of promoted Rh catalysts supported on SiO_2

3.1.1. Catalytic performances of Rh catalysts loaded on various MO_x–SiO_2 composites

Table 1 shows the catalytic performances of Rh catalysts loaded on various MO_x–SiO_2 (M = transition metal) composites prepared by the sol–gel method. Under our reaction conditions, the 1.0 wt% Rh/SiO_2 exhibited a CO conversion of 0.7% and a CH_4 selectivity of 59%. The selectivities of C_2H_5OH and CH_3OH over this catalyst were 9.5% and 4.9%, respectively. The presence of a transition metal oxide (MO_x) modifier listed in Table 1 increased the conversion of CO and decreased the selectivity of CH_4, which is a highly undesirable by-product. A CO conversion of 93% was obtained over the $Rh/(CoO_x$–$SiO_2)$ catalyst, and this catalyst showed higher selectivities to CO_2 and C_2^+ hydrocarbons. We speculate that the outstandingly high activity of this catalyst is due to the catalytic functions of cobalt, since cobalt is a well-known active catalyst in Fischer–Tropsch (FT) synthesis for the production of linear long-chain hydrocarbons [1,2]. However, this catalyst only provided a quite low selectivity to C_2H_5OH (1.8%). On the other hand, the catalyst containing MnO_x, CrO_x, FeO_x, or VO_x promoter exhibited relatively higher C_2H_5OH selectivity (≥20%). The selectivity of CH_4 became significantly lower over the $Rh/(MnO_x$–$SiO_2)$ and $Rh/(FeO_x$–$SiO_2)$ catalysts. Among the catalysts showing C_2H_5OH

Table 1
Catalytic performances of Rh catalysts loaded on various transition metal oxide-modified SiO_2.[a]

Catalysts[b]	CO conv. (%)	Selectivity (%)					EtOH yield (%)
		CO_2	CH_4	$C2^+$ HC[c]	MeOH	EtOH	
Rh/SiO_2	0.7	0	59	7.1	4.9	9.5	0.1
$Rh/(VO_x$–$SiO_2)$	5.0	0	45	20	3.7	20	1.0
$Rh/(CrO_x$–$SiO_2)$	3.0	0	38	5.1	28	22	0.7
$Rh/(MnO_x$–$SiO_2)$	1.5	4.1	15	6.0	17	39	0.6
$Rh/(FeO_x$–$SiO_2)$	6.3	3.8	21	12	33	21	1.3
$Rh/(CoO_x$–$SiO_2)$	93	21	46	27	1.9	1.8	1.6
$Rh/(ZrO_x$–$SiO_2)$	4.9	1.3	44	17	15	19	0.9
$Rh/(MoO_x$–$SiO_2)$	7.1	4.3	49	22	14	5.6	0.4

[a] Reaction conditions: H_2/CO = 2; WHSV = 8000 mL g(cat)$^{-1}$ h^{-1}; P = 2.0 MPa; T = 523 K.

[b] The loading of Rh was 1.0 wt%; the content of MO_x was 10 wt%.

[c] C_2^+ hydrocarbons.