Ethanol synthesis from carbon dioxide on TiO_2-supported $[Rh_{10}Se]$ catalyst

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Supported $[Rh_{10}Se]$ catalyst on TiO_2 converted carbon dioxide into ethanol faster (60×10^{-3} mol h^{-1} g cat^{-1}) and more selectively ($\approx 83\%$) than other supported Rh clusters or $[Rh_{10}Se]$ on other inorganic oxides, presumably due to the effects of interstitial Se and the interface of the $[Rh_{10}Se]$ cluster and TiO_2.

Recent environmental conditions require the development of effective catalysts for the reduction of NO_x, CO_2, SO_x, benzene, *etc.* Compared to conventional rhodium catalysts known to produce methane (and other hydrocarbons) from $CO_2 + H_2$,[1] we have concentrated on rhodium-based catalysts which convert CO_2 into ethanol. Some examples of oxygenate syntheses (methanol, acetaldehyde, *etc.*) from $CO + H_2$ over Rh catalysts are known, but their activities are very low (3.5×10^{-5}–2.3×10^{-2} min^{-1}, ≈ 673 K).[2–4] There are some reports of ethanol synthesis from CO_2/H_2, but here also activities and selectivities were low.[5] In this study, we report on an efficient synthesis of ethanol from CO_2/H_2 over supported $[Rh_{10}Se]$ clusters prepared from $[Rh_{10}Se(CO)_{22}]^{2-}$.[6,7] The promoter effect of interstitial Se (inside the $[Rh_{10}]$ framework) for ethanol synthesis was considered.

$[N(PPh_3)_2]_2[Rh_{10}Se(CO)_{22}]$ **1**, $[PhCH_2NMe_3]_2[Rh_6C(CO)_{15}]$ **2** and $Rh_6(CO)_{16}$ **3** were supported on inorganic oxides by reaction at 290 K (2 h) in purified THF in Ar atmosphere, with subsequent removal of THF. TiO_2 (Aerosil P25), Al_2O_3 (Aerosil alon C) and SiO_2 (Fuji Silysia silica gel no. 952) were treated at 573 K for 2 h under vacuum prior to use as supports. MgO was prepared from $Mg(OH)_2$ (99.99%) by treatment at 773 K for 2 h in vacuum. The loadings of Rh were fixed to 1.3 mass% Rh for TiO_2 and Al_2O_3, 2.8 mass% for SiO_2, and 1.6 mass% for MgO. The supported $[Rh_{10}Se]$, $[Rh_6C]$ and $[Rh_6]$ clusters prepared from **1**, **2** and **3** are denoted $[Rh_{10}Se]$/oxide, $[Rh_6C]$/oxide and $[Rh_6]$/oxide, respectively. The incipient supported clusters were totally decarbonylated (checked by GC) by heating in vacuum at 593–813 K. TiO_2 was impregnated with $Rh(NO_3)_3$ in aqueous solution, followed by treatments in air (1 h), then in H_2 (1 h) at 523 K (Rh/TiO_2). CO_2 hydrogenation was carried out under 47 kPa of $CO_2 + H_2$ ($CO_2 : H_2 = 1:2$) in the temperature range 523–723 K ($T_{react.}$) in a closed circulating system (dead volume 210 cm^3). The reaction products were analysed by a gas chromatograph using a column of Unibeads C for CH_4, Porapak Q for CO_2 and hydrocarbons and dioctyl sebacate for ethanol at 353 K.

Depending on the nature of supporting oxide, the supported $[Rh_{10}Se]$ clusters exhibited a sharp variation in the activity and selectivity of CO_2 hydrogenation. After pretreatment in vacuum (total decarbonylation) at 623–653 K, the $[Rh_{10}Se]/TiO_2$ produced ethanol (3.7×10^{-3} mol h^{-1} g_{cat}^{-1}) (and some methane) (Table 1 entry b); however, no ethanol was produced on $[Rh_{10}Se]$ supported on Al_2O_3, MgO or SiO_2 (Table 1, entries h–j). The $[Rh_{10}Se]/SiO_2$ system showed no activity.

The reaction and preheating conditions were varied for the $[Rh_{10}Se]/TiO_2$ catalyst. According to the increase of $T_{react.}$ from 523 to 723 K, the rate of ethanol synthesis increased to 6.0×10^{-3} mol h^{-1} g_{cat}^{-1}, but the selectivity decreased from 83 to 51% (Table 1, entries a–c). The preheating temperature ($T_{evac.}$) was also varied in the range 523–813 K. In the CO_2/H_2 reaction at 623 K, the ethanol synthesis rate at $T_{evac.} = 813$ K was 57% of that at $T_{evac.} = 623$ K (Table 1, entries b, f), and the rate at $T_{evac.} = 523$ K was only 26% of that at $T_{evac.} = 623$ K. Use of a trap (193 K) in the closed circulating system (Table 1, entry d) led to a decrease in synthesis rate to 38% compared to the case without a trap (Table 1, entry b) probably due to a poisoning effect of the product. Ethanol formation was also checked by mass spectrometry for the $[Rh_{10}Se]/TiO_2$ system: peaks of EtOH (*m/z* 31, 45, 27) and CH_4 (*m/z* 16, 15) grew as the reaction proceeded, while peaks at *m/z* 44 (CO_2) and 2 (H_2) diminished gradually. From $CO + H_2$ (36 kPa), $[Rh_{10}Se]/TiO_2$ produced methane (3.1×10^{-4} mol $h^{-1} g_{cat}^{-1}$) besides CO_2 and C_2H_6 at 623 K. The total activity (4.6×10^{-4} mol h^{-1} g_{cat}^{-1}) was lower than for CO_2 hydrogenation under the same conditions (5.1×10^{-3} mol h^{-1} g_{cat}^{-1}, Table 1, entry b). It is interesting that a strong hydrogen isotope effect was observed for ethanol synthesis ($r_{CO_2 + D_2}/r_{CO_2 + H_2} \approx 0.2$–$0.3$). As (almost) no isotope effect was detected for CH_4 production, the activated reaction process of CO_2 with CH_x(a), probably at the interface between $[Rh_{10}Se]$ and TiO_2, may be a cause for the selective ethanol synthesis. The causes of selective reaction of adsorbed species from CO_2 with CH_x(a) (EtOH formation), rather than with H(a) (CH_4 formation) over $[Rh_{10}Se]/TiO_2$ is under investigation by FTIR studies.

Next we studied other Rh clusters (or salts) for their catalytic activity supported on TiO_2. The Rh cluster containing interstitial carbon $[Rh_6C]$ on TiO_2 produced ethanol (0.4×10^{-3} mol $h^{-1} g_{cat}^{-1}$, Table 2, entry b); only 11% that of $[Rh_{10}Se]/TiO_2$ ($T_{evac.} = 623$ K), and the selectivity was also lower (10%, Table 2, entry b). The $[Rh_6]/TiO_2$ and conventional Rh/TiO_2 from $Rh(NO_3)_3$ produced only methane (Table 2, entries c, d). The presence of an interstitial atom (Se or C) in the Rh cluster framework may be of importance in ethanol synthesis.

We measured the Rh K-edge EXAFS spectra for the catalysts (KEK-PF, Tsukuba, proposal no. 95G226). For $[Rh_{10}Se]/TiO_2$, the coordination number (*N*) of the Rh–Rh bonds was found to

Table 1 The reaction rates of CO_2 hydrogenation over $[Rh_{10}Se]$ clusters supported on TiO_2, Al_2O_3, MgO and SiO_2[a]

				Initial rate/10^{-3} mol h^{-1} g_{cat}^{-1}		
Entry	Support	$T_{evac.}$/K	$T_{react.}$/K	EtOH	CH_4	EtOH select./%
a	TiO_2	623	523	1.9	0.4	83
b[b]		623	623	3.7	1.4	71
c		623	723	6.0	5.8	51
d[c]		623	623	1.4	1.9	42
e		813	523	0.9	0.4	71
f		813	623	2.1	1.4	59
g		813	723	4.7	5.9	42
h	Al_2O_3	653	623	0	0.15	0
i	MgO	623	623	0	0.039	0
j	SiO_2	623	623	0	0	0

[a] Cluster catalysts were evacuated at the temperature indicated then in H_2 at 623 K before catalysis. [b] The corresponding carbon dioxide consumption was 9.0×10^{-3} mol h^{-1} g_{cat}^{-1}. [c] Using a dry ice–acetone (193 K) trap.

Table 2 The reaction rates of CO_2 hydrogenation at 623 K over several Rh clusters (or salts) supported on TiO_2

			Initial rate/10^{-3} mol h^{-1} g_{cat}^{-1}			
Entry	Cluster	$T_{evac.}$/K	EtOH	CH_4	Other hydro-carbons[a]	EtOH select./%
a	$[Rh_{10}Se(CO)_{22}]^{2-}$	623	3.7	1.4	0	71
b	$[Rh_6C(CO)_{15}]^{2-}$	673	0.4	1.2	2.4	10
c	$Rh_6(CO)_{16}$	593	0	6.2	0	0
d[b]	$Rh(NO_3)_3$	—	0	1.8	0	0

[a] Ethene and ethane. [b] In O_2/H_2 at 523 K prior to catalysis.

be 4.8 when preheated at 523 K; the same value as in the $[Rh_{10}Se(CO)_{22}]^{2-}$ crystal (bicapped square-antiprismatic).[6,7] The Se : Rh ratio did not change upon supporting and heating of the catalyst, based on the edge jump for Se K-edge XANES; hence, we believe that the cluster framework unit $[Rh_{10}Se]$ remained intact. Examples of supported clusters of Ru, Rh, Re or Os attached through metal (M)–surface oxygen $[O_{(S)}]$ bonds (2.00–2.24 Å) have been reported.[8] The present $[Rh_{10}Se]$ cluster is attached with $r_{Rh-O(s)}$ 2.07–2.18 Å in accord with the above. By raising $T_{evac.}$ to 623 K, N_{Rh-Rh} decreased from 4.8 to 4.0 whereas $N_{Rh-O(s)}$ increased from 1.2 ($T_{evac.}$ = 523 K) to 1.5 (623 K). One explanation of these changes of N is if one triangular face of $[Rh_{10}Se]$ is attached to the TiO_2 surface at $T_{evac.}$ = 523 K, and if upon heating to 623 K $[Rh_{10}Se]$ is transformed from a bicapped square-antiprismatic geometry to a realtively flat shape by cleavage of Rh–Rh bonds of the triangular face and by additional formation of $Rh-O_{(s)}$ bonds. By raising $T_{evac.}$ further to 673–813 K, N_{Rh-Rh} further decreased as did the synthesis rate (Table 1). Hence, the $[Rh_{10}Se]$ catalyst with N_{Rh-Rh} = 4.0 seems to have the optimum ('fried egg') structure for catalysis. N_{Rh-Rh} values were smaller (2.7–3.3) for $[Rh_{10}Se]/Al_2O_3$, $[Rh_{10}Se]/MgO$ or $[Rh_{10}Se]/SiO_2$ at $T_{evac.}$ = 623–653 K compared to those for $[Rh_{10}Se]/TiO_2$ (4.0–4.8). N_{Rh-Rh} values for $[Rh_6C]/TiO_2$, $[Rh_6]/TiO_2$ and Rh/TiO_2 were 7–10, indicating the formation of aggregated Rh particles.

Besides Rh K-edge EXAFS, corresponding results were obtained for supported $[Rh_{10}Se]$ samples by Se K-edge EXAFS (r_{Se-Rh} = 2.42 ± 0.01 Å) and XANES (spectra similar to Rh_3Se_8 alloy[9]), supporting the 'fried egg' structure of $[Rh_{10}Se]$.

Three controlling factors are thus proposed for preferential ethanol synthesis, (*i*) the structural effect of a 'fried-egg' $[Rh_{10}Se]$ framework, (*ii*) the electronic effect of interstitial Se (oxidation state −2 by XPS and XANES), and (*iii*) the support effect of TiO_2.

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