

Effect of structural change of ordered mesopore and Li cation addition upon selective syngas conversion into C₂ oxygenates over Rh/CeO₂ catalysts

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Introduction

Recently, selective formation of C₁ and C₂ oxygenates such as methanol and ethanol from biomass derived synthesis gas (syngas) has attracted great attention since they are becoming key chemicals for energy producing processes to decrease global dependency on petroleum. Since the pioneering work of Mobil research group, various kinds of mesoporous metal oxides such as SiO₂, Al₂O₃, TiO₂ and CeO₂ have been synthesized using organic molecules as structure determining templates. Because of the enlarged of surface area and unique chemical environment inside the pores and controlled porosity, these mesostructured materials attract great attention as catalyst supports.

In the present study, we have chosen two kinds of ordered-mesoporous ceria as support materials to form a unique active site structure with alkali metal cation for the selective formation of C₂ oxygenated compounds in CO-H₂ reaction over supported Rh catalyst at the temperature ranges of 423-493 K and under atmospheric pressures.

Materials and Methods

The ordered mesoporous ceria (MC) was synthesized by using ordered mesoporous silica KIT-6 or SBA-15 as hard templates followed by the removal of silica with LiOH solution and neutralization with HNO₃ (MC(HNO₃)). The addition of Li was achieved during this silica removing process by controlling the amount of surface silica left without neutralization with HNO₃. By these procedures, we could prepare unique thin overlayers of Si-O-Li⁺ inside the CeO₂ mesopores. Precursor salts of RhCl₃·3H₂O were impregnated on these supports by incipient wetness method which was designated as Rh/MC(Li) catalyst. For comparison, amorphous ceria (CE) was prepared without template materials. The catalytic reaction was carried out in a closed gas circulation system with the online gas chromatography (TCD and FID). The catalyst was reduced by 200 Torr of H₂ at 573 K for 5 h before reaction.

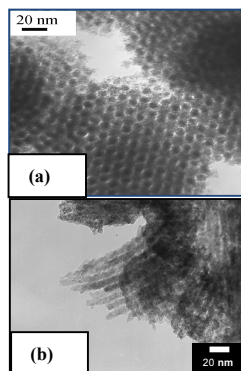


Fig. 1 TEM photos MC formed from (a) KIT-6, and (b) SBA-15 templates

The CO-H₂ reaction was carried out at 423-493 K with 1:2 ratios of CO and H₂ (Total: 150 Torr) employing liquid N₂ cold trap along with the circulation loop to gather primary products.

Results and Discussion

Fig. 1 shows the TEM photo of the MC prepared by using KIT-6 and SBA-15 as hard templates. Three-dimensional ordered arrangement of CeO₂ nanorods in the case of KIT-

6 and one-dimensional cylindrical allays in the case of SBA-15 can be observed clearly, indicating that the replica inherits the symmetry from hard templates. XPS analyses of the in-situ reduced Rh/MC (Li) catalyst showed the presence of approximately 1:1 ratio of Si:Li elements on the surface of reduced Ce³⁺ support. Accordingly, it is reasonable to suppose the formation of unique Rh-Si-OLi structure inside the mesopores of MC.

Table 1 summarizes Rh dispersions estimated from CO adsorption at R.T. as well as the amounts of formed products after 380 min in CO-H₂ reaction at 473 K over various Rh/CeO₂ catalysts. Ordered mesoporous ceria supported catalysts (MC) maintained Rh particle sizes smaller than non-mesoporous ones (CE) even after higher temperature reduction, while the catalytic activity and selectivity are almost the same over both catalysts. On the other hand, LiOH solution treatment significantly suppressed hydrocarbon (H.C.) formation without influencing C₂ oxygenates formation. Consequently the selectivity for C₂ oxygenates is largely enhanced especially in the case of MC catalysts, suggesting the importance of Rh-Si-OLi structure for C₂ oxygenate formation. It is worth noticing that SBA-15 derived catalyst (MC-II) exhibited higher activity and selectivity than KIT-6 derived one (MC-I) for C₂ oxygenates formation.

Table 1. CO-H₂ reaction at 473K for 380 min (Cat=0.2g)

Catalysts	H.C.	MeOH	C2oxy	C2 Selec.	Rh desp. (%)
Rh/CE	86.0	1.7	21.5	19.7	40.4
Rh/CE(Li)	45.4	1.4	25.6	35.1	41.6
Rh/MC-I	70.0	3.0	18.9	20.9	70.0
Rh/MC-I(Li)	12.6	1.0	18.0	56.9	53.2
Rh/MC-II	98.9	7.5	25.6	19.5	62.2
Rh/MC-II(Li)	10.6	0.8	22.9	66.8	27.6

Fig. 2 shows the FT-IR spectra of adsorbed species during CO-H₂ reaction as well as adsorption of EtOH at 473 K over reduced Rh/CE, Rh/MC-I(HNO₃) and Rh/MC-I(Li) catalysts. Over Rh/CE and Rh/MC-I(HNO₃) catalysts, adsorbed species during CO-H₂ reaction were similar each other. Characteristic Rh(a) peak observed at 1671 cm⁻¹ may be assigned to Rh-C=O-Ce³⁺ species at the interface of Rh and CeO₂. Addition of Li cation caused the emergence of a new peak at 1749 cm⁻¹ which may be assigned to Rh-C=O-Li⁺ inside the mesopores of Rh/MC-I(Li). On the other hand, the behavior of EtOH adsorption at 473K was different between Rh/MC-I(HNO₃) and Rh/MC(Li) catalysts. In the former case, acetate peaks were observed at 1540 and 1425 cm⁻¹ with a weak Rh-CO-Ce peak at 1671 cm⁻¹, whereas in the latter case a characteristic 1749 cm⁻¹ peak was observed without the appearance of acetate peaks, which would be the reason why Li modified catalysts showed the higher selectivity of C₂ oxygenate formation.

Significance

Inside ordered mesopores of CeO₂, thin SiO₂ surface layers were formed which could make Li cations dispersed as well as Si-O-Li⁺ over CeO₂. XPS and FT-IR observations revealed the formation of the unique Rh-LiOSi structure, which can stabilize C₂ oxygenated intermediate and can enhance their selectivity in CO-H₂ reaction under mild conditions.

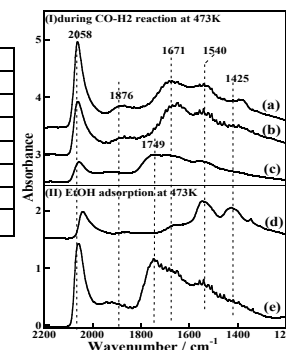


Fig. 2 FT-IR spectra (a)Rh/CE, (b) and (d); Rh/MC-I(HNO₃), (c) and (e); Rh/MC-I(Li).