

Direct Formation of Ketones and Secondary Alcohols from Carbon Monoxide, Hydrogen and Water over Cerium Oxide Catalysts

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The CO-H₂ reaction in the presence of H₂O formed ketones and secondary alcohols over cerium oxide catalysts at around 653 K.

The CO-H₂ reaction can produce oxygenates such as C₂-oxygenates,¹ mixed higher alcohols,² isobutyl alcohol³ and 2-methylpropanal⁴ in addition to methanol. These oxygenates have the carbon-oxygen bond at the terminal position of the carbon chain. The formation of these compounds could be explained by the insertion of CO into metal-surface species bonds followed by the hydrogenation. Thus, the formation of ketones and secondary alcohols from CO and H₂ as the primary products has not been reported. In this paper we report the first example of the direct formation of ketones and secondary alcohols from the CO-H₂ reaction over cerium oxide catalysts.

The catalysts were prepared according to the previous paper.⁵ The reaction was carried out using a conventional flow system with a quartz reactor of 12 mm outer diameter under atmospheric pressure. The catalyst (1.0 g) was treated with a mixture of CO, H₂ and N₂ (1 : 1 : 0.5) at 673 K for more than 4 h and then cooled to a given temperature. The production of ketones and secondary alcohols was carried out by the continued addition of H₂O vapour to the reaction gas. The reaction reached the steady state 8 h after the H₂O addition. Water vapour was introduced by passing the reaction gas at 50 ml min⁻¹ through water at room temperature, where the molar concentration of H₂O was between 4 and 8%. The products were identified by GC-MS and determined by GC equipped with an Adsorb P-1 column.

Table 1 shows the product formation rates in the CO-H₂ reaction in the presence of H₂O over cerium oxide catalysts at 653 K. Under the same reaction conditions ZrO₂ catalysts formed only CO₂ and H₂ by the water gas shift reaction of CO. However, CeO₂ catalysts produce hydrocarbons, alcohols and ketones along with a large amount of CO₂ by the water gas shift reaction. Hydrocarbons are distributed from C₁ to C₅

unselectively. Isobutene selectivity in C₄ hydrocarbons was about 50%, which is fairly low in comparison with the value of more than 90% in the CO-H₂ reaction.⁶ Table 2 shows the distribution of ketones. Only trace amounts of ketones higher

Table 1 Product formation rates in the CO-H₂ reaction in the presence of H₂O over cerium oxide catalysts at 653 K^a

Catalyst (atomic ratio)	Surface area/ m ² g ⁻¹	Formation rates/μmol h ⁻¹ (g cat) ^{-1b}		
		Hydrocarbons	Alcohols	Ketones
CeO ₂ (100)	27	6.5	1.9	2.5
Y ₂ O ₃ -CeO ₂ (10 : 100)	63	8.1	2.9	2.7
La ₂ O ₃ -CeO ₂ (5 : 100)	79	4.0	4.1	2.7
Cs ₂ O-CeO ₂ (5 : 100)	86	10.1	2.9	2.3
MgO-CeO ₂ (5 : 100)	68	9.5	1.2	2.6
CaO-CeO ₂ (5 : 100)	54	5.6	5.2	3.9

^a Catalyst: 1.0 g, flow rate: 50 ml min⁻¹ (CO : H₂ : N₂ = 20 : 20 : 10).

^b Based on carbon.

Table 2 Selectivity in ketones

Catalyst	Selectivity (%)		
	Acetone	Butan-2-one	3-Methylbutan-2-one
CeO ₂	30	35	35
Y ₂ O ₃ -CeO ₂	24	29	47
La ₂ O ₃ -CeO ₂	41	32	27
Cs ₂ O-CeO ₂	26	32	42
MgO-CeO ₂	28	40	32
CaO-CeO ₂	36	29	35

Table 3 Alcohol formation rates in the CO-H₂ reaction in the presence of H₂O over cerium oxide catalysts at 583 and 653 K

Catalyst	T/K	Water content (%)	CO conv. (%)	Formation rate/ $\mu\text{mol h}^{-1} (\text{g cat})^{-1}$ ^b						
				MeOH	EtOH	1-PrOH	2-PrOH	2-Me-1-PrOH	2-BuOH	CO ₂
CeO ₂	583	4.0	0.2	23	1.3	0.7	0.2	1.0	—	80
	653	3.0	0.8	1.0	—	—	0.8	—	0.1	670
Y ₂ O ₃ -CeO ₂	583	2.8	0.3	28	1.6	0.8	0.6	1.9	0.2	110
	653	2.5	2.5	2.2	—	—	0.9	0.4	0.2	690
La ₂ O ₃ -CeO ₂	583	^a	0.3	47	1.9	0.9	0.3	2.2	0.1	80
	653	4.7	1.1	3.0	—	—	0.8	0.2	0.1	510
Cs ₂ O-CeO ₂	583	3.8	0.5	29	1.0	0.5	0.3	1.3	—	190
	653	2.1	1.8	1.6	—	—	1.1	0.2	0.2	870
MgO-CeO ₂	583	7.9	0.6	12	1.1	0.3	0.7	0.1	0.2	170
	653	1.2	2.1	0.5	—	—	0.6	—	0.1	990
CaO-CeO ₂	583	9.3	0.3	49	3.8	1.0	0.4	2.7	0.1	110
	653	5.6	1.3	4.2	—	—	0.8	0.1	0.1	610

^a Not measured. ^b Based on carbon.

than C₆ were formed. Aldehydes, in particular 2-methylpropanal, which is a main product from CO and H₂ over CeO₂ at 523 K, were not detected.⁴ The addition of CO₂ instead of H₂O only led to the retardation of the CO-H₂ reaction. Thus, the addition of H₂O resulted in the retardation of branched-chain C₄ product formation.

Table 3 shows water concentration, CO conversion and the formation rates of alcohols and CO₂ at 583 and 653 K.

The lowering of the reaction temperature to 583 K led to a much lower yield of CO₂, higher yield of alcohols, and almost no formation of hydrocarbons and ketones. Alcohols formed at 583 K consist mainly of methanol and contain terminal alcohols such as ethanol, propan-1-ol, and 2-methylpropan-1-ol, which are not formed in the reaction at 653 K. The reaction at 673 K resulted in an increase in production of CO₂ and hydrocarbons and the severe retardation of the formation of oxygenates. These results indicate that the presence of H₂O and a reaction temperature of around 653 K are essential for the formation of ketones and secondary alcohols.

The distributions of the alcohols, propan-2-ol and butan-2-ol, and the ketones, acetone, butan-2-one and 3-methylbutan-2-one, and the relatively good effect of alkali and alkaline-earth oxide additives seems to suggest that carbon bond propagation occurs by an aldol condensation type reaction. However, the formation of propan-2-ol and acetone may indicate a mechanism other than the aldol condensation type reaction, because the reaction of methanol and ethanol forms propan-1-ol but not propan-2-ol.⁷ The X-ray diffraction measurement of the catalysts showed only broad fluorite

structure pattern due to cerium oxide, indicating a good dispersion of additives. One of the effects of additives may be to keep the higher surface area by the high dispersion.

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