

Branched-chain Alkene Formation from H₂-CO Reaction over Some Metal Oxide Catalysts

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Low molecular weight, branched-chain alkenes were selectively formed from CO-H₂ on metal oxide catalysts of Y, La, Ce, Th, Zr, Hf, and Nb under low-pressure conditions (67 kPa, 673 K).

Hydrocarbons produced from H₂-CO reaction over metal catalysts are mostly linear, while metal oxides such as ThO₂,¹ La₂O₃,² and Dy₂O₃² catalyse the formation of saturated, branched-chain compounds under severe conditions. Recently we found that isobutene is selectively formed by the H₂-CO reaction over ZrO₂ under mild conditions (623 K,

< 880 kPa).³ We report here the highly selective formation of branched-chain alkenes in the C₄ and C₅ hydrocarbons formed from H₂-CO reactions over metal oxide catalysts.

Table 1 shows yields of products and selectivities of branched-chain alkenes in the C₄ and C₅ hydrocarbons formed from the H₂-CO reaction at 673 K over Y₂O₃, La₂O₃, CeO₂,

Table 1. H₂-CO reaction over some metal oxide catalysts.^a

Catalyst	Surface area/m ² g ⁻¹	Yield/μ mol ^b			Isoselectivity/% ^c	
		Hydro-carbon	MeOH + Me ₂ O	CO ₂	iso-C ₄ H ₈	iso-C ₅ H ₁₀
Y ₂ O ₃	57	91	0.21	810	49	88
La ₂ O ₃	14	10	2.8	247	62	98
CeO ₂	29	233	0.00	1050	91	94
ThO ₂	49	148	2.5	648	91	94
ZrO ₂	57	83	0.14	350	88	96
HfO ₂	37	54	0.00	247	98	100
Nb ₂ O ₅	28	1.1	0.01	140	70	84

^a Hydroxides of Y, La, Ce, and Th were prepared with NH₄OH from an aqueous solution of the nitrates. Hydroxides of Zr and Hf were prepared with NH₄OH from an aqueous solution of the oxynitrate and the oxychloride, respectively. Hydrated niobium pentoxide was prepared with NH₄OH from an aqueous solution of potassium niobate. The hydroxides were calcined at 773 K for 3 h. Catalysts (1.5 g) were evacuated at 973 K for 3 h before reactions. Reactions were carried out at 673 K and 67 kPa (H₂/CO = 3) in a gas-circulating glass system. ^b Products were collected at liquid nitrogen temperature for the initial 24 h. ^c Selectivities for the unsaturated, branched-chain components of the total C₄ and C₅ hydrocarbon mixture.

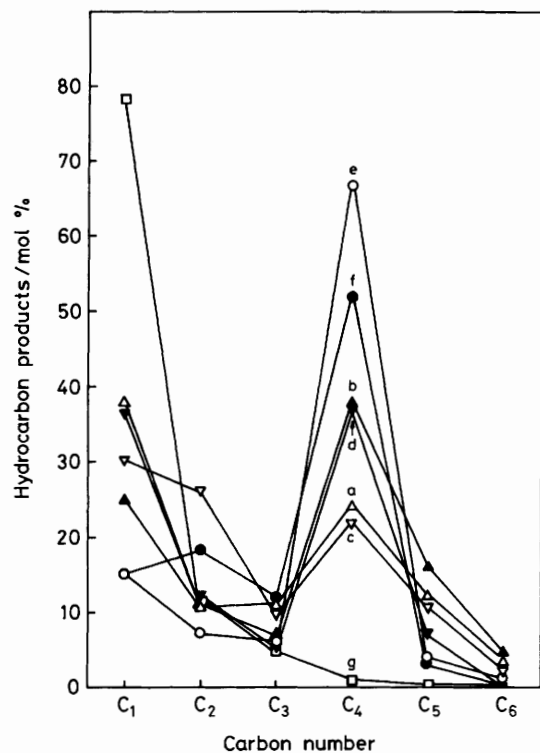


Figure 1. Hydrocarbon product distributions with some metal oxide catalysts. a, Y₂O₃; b, La₂O₃; c, CeO₂; d, ThO₂; e, ZrO₂; f, HfO₂; and g, Nb₂O₅.

ZrO₂, HfO₂, ThO₂, and Nb₂O₅. The carbon-containing products are hydrocarbons, CO₂, and small amounts of methanol and/or dimethyl ether. A Schulz-Flory distribution is not followed for the hydrocarbons except on Nb₂O₅, the deviations being due to the formation of large amounts of C₄ hydrocarbon, as shown in Figure 1. ZrO₂ and HfO₂ catalysts are selective for the formation of C₄ hydrocarbons. Y₂O₃, La₂O₃, CeO₂, and ThO₂ are less selective, although the selectivities for C₄ hydrocarbons are higher than for C₃ and C₅. Detailed analysis of the C₄ and C₅ hydrocarbons shows that selectivities for branched-chain alkenes are very high (Table 1), even for the Nb₂O₅ catalyst which has no preference for C₄ hydrocarbons.

The formation of saturated rather than unsaturated hydrocarbons and the lower selectivity for C₄ hydrocarbon formation reported for isosynthesis^{1,2} may be explained by the use of high-pressure, high-temperature conditions, since a high pressure of H₂ and high temperatures will favour saturated hydrocarbon formation; secondary reactions of the products under a high pressure of CO may result in an increase in the amount of high molecular weight hydrocarbons along with oxygen-containing compounds.^{1,3}

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