Reaction of Carbon Monoxide and Hydrogen on Rare Earth Metal Oxide Catalysts

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Isobutane, 2-methylprop-1-ene, and aromatic compounds are formed from CO–H_2 on rare earth metal oxides (La_2O_3 and Dy_2O_3) under severe conditions (*P* 400 bar and *T* 410—475 °C).

The preparation of branched compounds from CO–H_2 using ThO_2 or ThO_2–Al_2O_3 catalysts was reported by Ziesecke in 1949.[1,2] We report on the use of rare earth metal oxides and palladium promoted catalysts for this reaction under high pressure and high temperature conditions (*P* 400 bar and *T* 410—475 °C). Table 1 shows that some of the products, especially the iso-C_4 and aromatic hydrocarbons, are formed in proportions that are different from those in a Schulz–Flory distribution. This must occur by a different mechanism to a normal chain-growing process.[3]

In CO–H_2 reactions on the rare earth metal oxides used methanol (or dimethyl ether) and hydrocarbons were produced with a good selectivity for C_4 products and preference for iso-C_4 compounds. A liquid organic fraction ($>C_5$) which contained aromatic molecules especially substituted benzenes (xylenes, trimethyl-, and hexamethyl-benzene), naphthalenes (dimethyl- and isopropyl-naphthalene), and anthracene was also formed.

The nature of the products and their distribution suggest a 'Mobil Process'[4,5] type two-step mechanism for the synthesis

Table 1. The reaction of CO–H_2 on La_2O_3, Dy_2O_3 and palladium-supported catalysts.[a]

	Conversion (%)			Selectivity for RH (%)						
Catalyst	RH	MeOMe + MeOH	CO_2	C_1	C_2	C_3	C_4	C_5	$>C_5$	Ratio iso-$C_4/\Sigma C_4$ (%)
La_2O_3	8.3	2.9	12.7	14.5	6.7	8.5	30.9	4.0	9.6	81.1
Dy_2O_3	9.0	4.0	13.4	13.0	4.1	6.3	24.6	4.7	16.0	84.5
Pd–La_2O_3	13.7	8.0	15.5	36.7	3.3	4.5	16.3	2.4	—	73.6
Pd–Dy_2O_3	18.4	0.1	15.5	56.4	8.1	9.5	21.9	3.8	—	61.7
Pd–$SiO_2 \cdot Al_2O_3$	9.8	—	9.4	31.5	19.6	24.1	15.7	8.3	—	36.4

[a] *T* 475 °C, *P* 400 bar, $H_2/CO = 1$, gas space velocity = 2 l (g cat)$^{-1}$. The oxides (La_2O_3 and Dy_2O_3) were prepared by calcination (12 h at 550 °C) of the hydroxides obtained by precipitation from solutions of commercial nitrates (Rhône–Poulenc) with NH_4OH at pH 8. $SiO_2 \cdot Al_2O_3$ is an industrial support (Rhône–Poulenc H.D.H., 75% Al_2O_3, 25% SiO_2). The Pd supported catalysts were prepared by impregnation (ref. 7). Reactions were carried out in a stainless steel reaction vessel (ref. 7) adapted to high pressure conditions. The products were analysed by g.l.c. (ref. 5). The C_4 fraction analysis was carried out as follows, FID 'Intersmat IGC 15' equipment; column containing picric acid on 'Vulcan', length 4 m, diameter 3.2 mm, at room temp.; helium as carrier gas.

of iso-C_4 compounds whereby MeOH is formed first and then transformed into the hydrocarbons. This sequence is strongly supported by the three observations, (a) that an injection of MeOH (or MeOMe) under the same reaction conditions gave nearly the same hydrocarbon distribution as in the direct synthesis; (b) that an increase in the gas flow (a reduction in the contact time) enhances the production of methanol, the probable primary product; and (c) that under high pressure conditions the formation of MeOH is possible on La_2O_3 and Dy_2O_3. These observations agree with those of Trambouze.[6]

Promoters which favour methanol formation increase the yield of C_4 compounds. Palladium–rare rarth metal oxide catalysts[7] show good methanol formation and adequate stability at temperatures >400 °C. On these surfaces there is an increase in the total conversion but an unfavourable higher formation of methane. The proportion of branched C_4 species is maintained at a high level but is reduced in comparison with La_2O_3 and Dy_2O_3. Also there are no C_5 products formed. The palladium seems to introduce secondary reactions, *i.e.* methanation by decomposition of methanol or rapid hydrogeneration of intermediates which compete with the chain-growth process.

Received, 10th March 1983; Com. 318

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