

Synthesis of Hydrocarbons from CO and H₂ over Metal Carbide Catalysts†

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Summary Refractory metal carbide catalysts such as TiC, TaC, and Mo₂C catalyse the hydrogenation of carbon monoxide, producing hydrocarbons of higher molecular weight than methane.

THE Fischer-Tropsch synthesis of hydrocarbons is currently an important problem in heterogeneous catalysis and a great deal of research has been conducted into this CO-H₂ reaction catalysed on metal or metal oxide surfaces. In an earlier paper,¹ it was found that the catalytic activity of powdered TaC for hydrogenation of benzene was negligible when the sample was evacuated at temperatures < 1173 K; however, it was highly activated above 1273 K. In addition,² similar experiments were carried out on the hydrogenation of ethylene on a series of metal monocarbides such as TaC, TiC, WC, HfC, and ZrC, to determine whether these refractory materials form a group of new sinter-resistant catalysts. It was confirmed that with TaC and TiC an enhanced activity is observed for an evacuation temperature of 1273 K. With WC, however, the activity is increased rapidly on evacuation above 873 K. We here report that powdered metal carbides such as TaC, TiC, and Mo₂C also exhibit high catalytic activities for the production of various hydrocarbons including ethylene from CO and H₂ mixtures.

The powdered metal carbides (300–350 mesh) (obtained from Materials Research Co.) were > 99% pure, and H₂ (99.999% pure) and CO (99.99%) (both obtained from Takachiho Shoji Co.) were used without further purification. All the measurements were performed in a recirculation reactor in which the products which were condensable at 78 K were continuously removed from the system during the reaction by a liquid nitrogen trap. The products were

analysed by mass spectrometry and g.l.c. Before the measurements, TaC and TiC were catalytically activated by evacuation for 1 h at 1370 K. The presence of hydrogen in this pretreatment did not significantly affect the 'activation temperature,' 1370 K. With Mo₂C, the sample was reduced in hydrogen at 770 K for 2 h. In repeated reactions these carbides were evacuated for 1 h at each activation temperature, since, in subsequent reactions, the catalytic activities were found to decrease to 60–70% of those in the initial reaction and to be restored to their original levels of activity by this evacuation treatment. Mixtures of CO and H₂ gases in mole ratios from 1:1 to 1:10 with 10 Torr (1 Torr = 133.3 Pa) of CO were used as the reactant gases. The reaction temperature was kept constant at 573 K throughout the experiments.

No product was detected when hydrogen gas only was circulated on these catalysts at 573 K, which indicates that hydrogen does not react with the carbon of the carbides. The main products of CO hydrogenation on these catalysts were CH₄, H₂O, CO₂, C₂H₆, and C₂H₄; small amounts of hydrocarbons of higher molecular weight, C₃ to C₈ compounds, were also observed. CH₄ and H₂O were formed in almost equimolar amounts on Mo₂C regardless of the H₂/CO ratio; however their amounts varied on TiC and TaC surfaces. The material balance of the carbon in the reaction mixture was found to be maintained to within 10% if hydrocarbons up to C₃ were taken into consideration; apart from the hydrocarbons, the remainder of the carbon-containing products comprised mainly CO₂.

Several quantities characterizing the catalytic properties of the three metal carbides are compared in Table 1, where a mixture of CO (10 Torr) and H₂ (100 Torr) was allowed to react at 573 K; the initial rate of CO consumption decreases

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TABLE 1. Surface areas and catalytic activities of metal carbides.

	BET surface ^a area /m ² g ⁻¹	Initial rate of CO consumption /molecule s ⁻¹ g ⁻¹	Initial rate of CH ₄ formation /molecule s ⁻¹ g ⁻¹	C _n -selectivity ^b
TiC	0.46	1.9×10^{16}	9.4×10^{15}	0.11
TaC	1.0	1.2×10^{16}	6.8×10^{15}	0.16
Mo ₂ C	0.62	5.6×10^{15}	1.8×10^{15}	0.25

^a BET = Brunauer-Emmett-Teller. ^b (Rate of appearance of carbon in products of C₂ and above, ΣnC_n)/(total rate of consumption of CO).

in the order TiC > TaC > Mo₂C. This trend is identical with that for the rate of CH₄ formation. However, as seen in Table 1, the selectivity for producing C_n ($n \geq 2$) hydrocarbons increases in this order, *i.e.*, the Mo₂C catalyst favours the production of C₂- and C₃-hydrocarbons. The change in the selectivities for production of several hydrocarbons with H₂/CO ratio is shown in Table 2, where only a small amount

An interesting common feature of these metal carbide catalysts is that they can produce C_n ($n \geq 2$) hydrocarbons under conditions of high reaction temperatures and high H₂/CO ratios, which contrasts with Ru or Ni catalysts where the major hydrocarbon product is methane.³ This difference may arise from the structural difference in the active sites between the metal carbide and the pure metal

TABLE 2. %-Distributions of hydrocarbons produced.

H ₂ /CO	Mo ₂ C			TaC			TiC		
	1	3	10	1	3	10	1	3	10
N(CH ₄)/N(CO) ^a	0.11	0.20	0.31	0.29	0.35	0.55	0.21	0.42	0.50
CH ₄ (%) ^b	35.3	52.3	60.3	58.7	65.8	76.9	54.3	60.3	82.3
C ₂ H ₄	52.2	12.2	11.6	9.3	0	0	10.4	0.9	0
C ₂ H ₆	5.3	29.2	22.6	26.8	30.8	20.2	26.2	31.2	15.8
C ₃ H ₆	7.2	3.6	3.3	2.8	0	0	7.0	2.6	0.5
C ₃ H ₈	0	2.7	2.1	2.4	3.4	2.9	2.0	5.0	1.4

^a Ratio of the initial rates of CH₄ formation to CO consumption. ^b $nC_n/\Sigma nC_n$.

of the product comprises hydrocarbons larger than C₃. The selectivities depend on the H₂/CO ratio; an increase of the ratio enhances CH₄ formation and depresses the formation of olefins C₂H₄ and C₃H₆. We also observe that the selectivities of TaC and TiC are similar to each other, whereas the production of olefins, particularly ethylene, is most favourable for Mo₂C. This selectivity for olefin production is a highly desirable property.³

catalysts; in the metal carbides, the positive charge on the metal atom resulting from the electron transfer between the metal and carbon atoms will cause formation of multiple adsorption sites on the metal atoms required for producing hydrocarbons of higher molecular weight.

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