Liquid-phase Synthesis of Olefins from Methanol with Cobalt Catalysts

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Olefins, mainly ethene, propene, and butenes, are obtained from the reaction of methanol with a cobalt slurry.

Cobalt catalysts are used for the synthesis of hydrocarbons from CO and H_2 (Fischer–Tropsch synthesis). This condensation of carbon monoxide can be directed towards the production of n-paraffins with a supported catalyst or n-olefins with a slurry of cobalt in a high-boiling solvent.[1] Obviously, olefins are the precursors of n-paraffins and the selectivity for olefin

Table 1. Products from methanol and synthesis gas with the cobalt catalyst after 2 h.

	% Conversion	Product composition, %								
		CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	C_4H_{10}	C_4H_8	C_5H_{12}	$>C_5$
CH_3OH	90	23	11	1.6	8	33.5	3	7.5	3	3
$CO–H_2$ (1 : 2)	100	20	13	3	6	26	3	14	—	8

vs. paraffin formation is related to the adsorption ability of the supported catalyst which permits the reduction of the unsaturated hydrocarbons. These olefins could in turn be formed from oxygenated species such as alcohols (or their surface equivalent), and we now report our results obtained from the reaction of methanol. This compound is the equivalent of synthesis gas, as far as the $CO : H_2$ ratio is concerned, and moreover it can be an alternative starting material for the synthesis of substitutes for petroleum derivatives.

We used a cobalt slurry as the catalyst, obtained by the reduction of cobalt(II) acetylacetonate [$Co(acac)_2$] with triethylaluminium[1] in *o*-terphenyl. In a typical experiment, cobalt (2.92 g) in 50 ml of solvent was stored at 190 °C under N_2 (1 atm) in order to check that hydrocarbons were not produced by decomposition of the aromatic solvent. Pulses (100 μl) of liquid methanol were then introduced into the reaction vessel, and the disappearance of methanol and the analysis of the hydrocarbon products were followed by gas chromatography. As soon as all the alcohol had been consumed the reaction vessel was evacuated, and another pulse was introduced in order to check the stability of the catalyst, which can also be tested for its activity for synthesis gas conversion. Table 1 shows the results for a standard pulse, together with the results for a run with synthesis gas ($CO : H_2$, 1 : 2; 240 ml).

In the reactions with methanol, it appears that propene is the major constituent of the olefinic fraction and that ethene is present in small proportions as in the experiments with synthesis gas. The selectivities for formation of C_1, C_2 *etc.* . . . are roughly the same as those obtained with synthesis gas except for the ratio of C_4H_8 to C_3H_6 so methanol could be used as a substitute for synthesis gas in this reaction. These results, together with the recently reported[2] observation of C–O heterolysis to produce carbenes, illustrate the proposal that in heterogeneous catalysis surface carbenes could arise from alkoxide intermediates.

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References

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