

## Metal Dispersion Effects on CO Hydrogenation over Ru/Graphitized Carbon Black Catalysts

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Ruthenium supported on graphitized carbon black exhibits differences in activity and selectivity for Fischer–Tropsch synthesis when the degree of metal dispersion is changed, even for small dispersions.

In recent studies of the Fischer–Tropsch reaction, much attention has been directed toward the effect of metal dispersion on catalytic behaviour. On alumina and zeolite supported ruthenium catalysts it is reported that the specific activities for methanation and CO consumption decreased with increasing Ru dispersion.<sup>1–3</sup> Moreover, for dispersion below 0.7, the selectivity it is not much affected and only for dispersion above 0.7 were a slight change in the product distribution and a rapid decrease in the alkene:alkane ratio observed. These changes in the selectivity are attributed to changes in the electronic properties of the Ru microcrystallites with size and the occurrence of metal–support interactions. We now relate the results of CO hydrogenation on Ru deposited on a graphitized carbon black, Vulcan 3 graphite (V3G), with different metal dispersions. In this investigation changes in the selectivity (*e.g.* decrease in the alkene:alkane ratio) were observed, even for dispersions below 0.3.

The catalysts were prepared by impregnation of V3G (62 m<sup>2</sup> g<sup>-1</sup>)<sup>4</sup> with RuCl<sub>3</sub>·xH<sub>2</sub>O in acetone solution. These catalysts were reduced by H<sub>2</sub> at 400 °C for 16 h prior to the reaction and chemisorption measurements. This reduction treatment removes all traces of chlorine adsorbed on the metal.<sup>5,6</sup> Thermal analysis studies of the reduction in an H<sub>2</sub> flow were carried out in a Mettler TA-3000 thermobalance. Similar results to those reported by Bossi *et al.*<sup>5</sup> for Ru/SiO<sub>2</sub> catalysts were obtained. The reaction was carried out in a conventional circulating system (CO:H<sub>2</sub> = 1:3, *p*<sub>total</sub> = 101 kPa) under differential conditions in the temperature range 190–250 °C. The products were analysed by gas chromatography. Details of the activity and selectivity calculations can be found elsewhere.<sup>7–9</sup> The procedure used for unsupported Ru preparation has been described by Vannice *et al.*<sup>10</sup>

Typical results are given in Table 1. CO and H<sub>2</sub> chemisorption were measured in a static system (35 ml) at room temperature. The dispersion and metal particle size were calculated from the equilibrium amount of H<sub>2</sub> adsorption by assuming that one hydrogen atom was adsorbed on each Ru atom on the surface. The specific activities, molecules of CH<sub>4</sub> produced (*N*<sub>CH<sub>4</sub></sub>), or molecules of CO transformed (*N*<sub>CO</sub>) per surface atom per second, rapidly decline as the ruthenium particle size decreases. The results presented are in agreement with those of Bell *et al.*<sup>2</sup> This decrease in specific activity over this range is ascribed to a drop in the fraction of sites present on planar surfaces, when the metal particle size decreases.

The results presented in Table 2 indicate that over the range of dispersions studied here, there are important changes in selectivity of the catalysts; the alkene:alkane ratio decreases when the dispersion increases. This type of result is interpreted, for Ru/Al<sub>2</sub>O<sub>3</sub> catalysts with high dispersions, to a metal–support interaction that changes the electronic properties of the Ru particles. Although theoretical<sup>11,12</sup> and infrared<sup>2</sup> studies show that this electronic effect occurs for crystallites smaller than about 2 nm (corresponding to a dispersion of about 0.5), we suggest that with V3G as the support (this graphitic carbon is an electron conductor and could conceivably facilitate the transfer of electrons to or from the metal particles) it is possible that electronic changes are produced for higher metal particles. Moreover, in Table 2, we also observe that the CO:H ratio increases when the Ru particle size decreases. These changes in the CO chemisorption capacity of the catalysts can be interpreted as a result of metal–support interaction of Ru with V3G.<sup>3,13,14</sup>

In conclusion, the selectivity and CO:H chemisorbed ratio changes in the Ru/V3G catalysts suggest that there must be a

**Table 1.** Specific activities of the catalysts in Fischer–Tropsch synthesis.

Catalyst	Ru/Wt%	Dispersion	Particle size <sup>b</sup> <i>d</i> (nm)	Conversion (%)	Specific activity <sup>a</sup> at 210 °C	
					<i>N</i> <sub>CH<sub>4</sub></sub> × 10 <sup>3</sup> (s <sup>-1</sup> )	<i>N</i> <sub>CO</sub> × 10 <sup>3</sup> (s <sup>-1</sup> )
Unsupported Ru	—	—	607	1.5	27.3	17.4
Ru/V3G	11.4	0.12	7.6	4.5	10.0	7.5
Ru/V3G	4.7	0.20	4.6	2.4	9.5	6.9
Ru/V3G	2.0	0.23	3.9	3.5	6.5	5.6

<sup>a</sup> Based on H<sub>2</sub> uptake on fresh sample. <sup>b</sup> Metal particle sizes determined from X-ray diffraction measurements are in agreement with these from H<sub>2</sub>-chemisorption.

**Table 2.** Selectivities of the catalysts at 210 °C in Fischer–Tropsch synthesis.

Catalyst	<i>d</i> (nm)	CO:H <sup>a</sup>	Selectivity <sup>b</sup>	% Product distribution					Alkene:alkane ratio <sup>c</sup>
				C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	
Unsupported Ru	607	0.64	96	84	6	8	2	—	1.63
Ru/V3G	7.6	0.98	98	90	4	4	1	<1	0.66
Ru/V3G	4.6	1.14	99	93	4	2	1	—	0.18
Ru/V3G	3.9	1.22	98	95	3	1	<1	—	0.11

<sup>a</sup> Ratio of CO molecules to H atoms chemisorbed. <sup>b</sup> Selectivity for hydrocarbon production defined by Commereuc *et al.*, ref. 9. <sup>c</sup> For hydrocarbons with 2 and 3 carbon atoms.

specific interaction (electronic or geometric) between a graphitic carbon support on the Ru particles thereon affecting the chemisorbed ratio of CO:H and subsequent selectivities in CO hydrogenation.

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