

## Light Olefin Synthesis from Carbon Dioxide by Hydrogenation over $\text{Fe}_3(\text{CO})_{12}$ Supported on ZSM-5 Zeolite Catalyst

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An  $\text{Fe}_3(\text{CO})_{12}$  catalyst supported on zeolite ZSM-5, prepared by a 'multiple-reflux-impregnation' method, exhibits high catalytic activity for hydrogenation of carbon dioxide and gives a high selectivity for light olefins, with a selectivity for ethene of >90 mol%.

Hydrogenation is an important route for utilization of carbon dioxide as a carbon resource,<sup>1</sup> and many catalysts have been developed for hydrogenation of carbon dioxide to produce methane, methanol and liquefied petroleum gas or gasoline.<sup>2</sup> The direct synthesis of light olefins from carbon dioxide by hydrogenation is a challenging subject. We now report the successful application of an  $\text{Fe}_3(\text{CO})_{12}$  catalyst supported on zeolite ZSM-5 for the hydrogenation of  $\text{CO}_2$  to produce light olefins, with a particularly high selectivity for ethene production.

This catalyst was prepared by a 'multiple-reflux-impregnation' method which was developed in our laboratory; *i.e.*  $\text{Fe}_3(\text{CO})_{12}$  was supported on ZSM-5 (Si/Al = 40) zeolite by a combination of multiple reflux and impregnation,<sup>†</sup> and then the iron-containing ZSM-5 zeolite was separated from organic solvent by filtration in the absence of air and finally dried *in vacuo* by temperature-programmed heating to 200 °C. In order to compare this catalyst with other iron catalysts supported on ZSM-5,  $\text{Fe}(\text{CO})_5$  and  $\text{Fe}(\text{NO}_3)_3$  supported catalysts were also prepared by chemical vapour deposition and conventional impregnation, respectively. For evaluation, the supported iron catalyst (0.5 g) was placed in a flow micro-reactor and reduced at 200 °C with hydrogen for an hour, and then argon was passed through the reactor under the same conditions for another hour. Catalytic hydrogenation was carried out with a mixture of Ar,  $\text{H}_2$  and  $\text{CO}_2$  (91:6:3) under atmospheric pressure. The reaction temperature was increased at *ca.* 2 °C  $\text{min}^{-1}$  to 260 °C. The product stream and feed gas were analysed on line by gas chromatography using a flame ionization detector (FID) and a thermal conductivity detector (TCD), respectively.

Table 1 presents typical results for the activity and selectivity of zeolite-supported iron catalysts for  $\text{CO}_2$  hydrogenation. Under the conditions used, with the reactants carbon dioxide and hydrogen being diluted with argon, the  $\text{Fe}_3(\text{CO})_{12}$ /ZSM-5 catalyst exhibits high activity for  $\text{CO}_2$  hydrogenation and excellent selectivity for ethene synthesis. The hydrocarbon product consists mainly of ethene, with small amounts of propene and methane; traces of carbon monoxide, ethane, propane and  $\text{C}_4+$  hydrocarbons were detected, but not quantitatively determined by gas chromatography under the conditions we used. A high  $\text{H}_2$ : $\text{CO}_2$  ratio enhances the activity for  $\text{CO}_2$  hydrogenation and a high selectivity for ethene synthesis is maintained. In comparison, the  $\text{Fe}(\text{CO})_5$ /ZSM-5 catalyst obtained by chemical vapour deposition shows some activity for

ethene production accompanied by a smaller but comparable amount of methane, but the conversion is low. The  $\text{Fe}(\text{NO}_3)_3$ /ZSM-5 catalyst obtained by conventional impregnation shows a completely different product distribution with almost 100% selectivity for methane production, and with very low conversion of  $\text{CO}_2$ .

The activity and selectivity of the  $\text{Fe}_3(\text{CO})_{12}$ /ZSM-5 catalyst for  $\text{CO}_2$  hydrogenation as a function of reaction temperature are presented in Fig 1. The reaction temperature has a marked effect on product distribution in  $\text{CO}_2$  hydrogenation. At low temperatures (<220 °C), the conversion of  $\text{CO}_2$  is less than 10 mol%, and significant amounts of methane are formed. The formation of ethene takes place effectively at a temperature of *ca.* 240–280 °C, leading to a selectivity for ethene as high as 82 mol%. At higher temperatures, the activity and selectivity for ethene of the  $\text{Fe}_3(\text{CO})_{12}$ /ZSM-5 catalyst drop sharply, and more methane and propene are formed. Thus the optimum

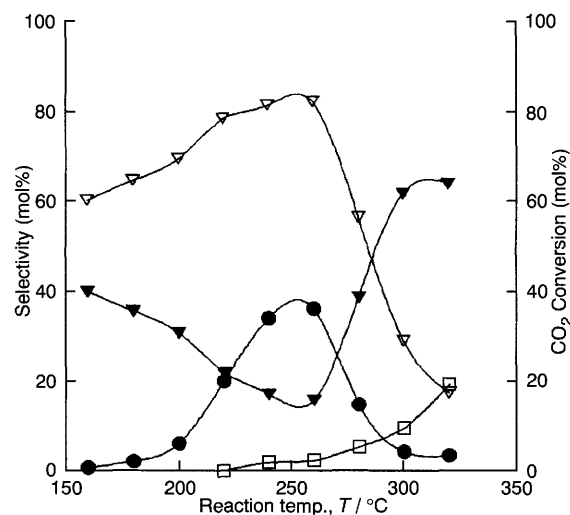


Fig. 1 Activity and selectivity of  $\text{Fe}_3(\text{CO})_{12}$ /ZSM-5 catalyst for  $\text{CO}_2$  hydrogenation as a function of temperature. Conditions:  $P = 1$  atm; space velocity = 1000  $\text{h}^{-1}$ ;  $\text{CO}_2/\text{H}_2/\text{Ar} = 2/6/92$ . ●, conversion of  $\text{CO}_2$ ; selectivity for ▽, ethene; ▼, methane; □ propene.

Table 1 Activity and selectivity of zeolite ZSM-5-supported iron catalysts for  $\text{CO}_2$  hydrogenation<sup>a</sup>

Catalysis	Conv. of $\text{CO}_2$ (mol%)	Selectivity (mol%)						
		CO	$\text{C}_1$	$\text{C}_2=$	$\text{C}_2$	$\text{C}_3=$	$\text{C}_3$	$\text{C}_4+$
$\text{Fe}_3(\text{CO})_{12}$ /ZSM-5 <sup>b</sup>	36.1	— <sup>c</sup>	15.7	82.0	—	2.3	—	—
$\text{Fe}_3(\text{CO})_{12}$ /ZSM-5	18.5	—	7.3	91.7	—	1.0	—	—
$\text{Fe}(\text{CO})_5$ /ZSM-5	0.65	—	45.1	54.1	—	0.8	—	—
$\text{Fe}(\text{NO}_3)_3$ /ZSM-5	0.42	—	100	—	—	—	—	—

<sup>a</sup>  $T = 260$  °C,  $P = 1$  atm, space velocity = 1000  $\text{h}^{-1}$ ,  $\text{CO}_2/\text{H}_2/\text{Ar} = 3/6/91$ . <sup>b</sup>  $\text{CO}_2/\text{H}_2/\text{Ar} = 2/6/92$ . <sup>c</sup> Trace amount, not quantitatively detected by gas chromatography.

temperature range for selective synthesis of ethene is 240–280 °C.

The application of oxide-supported iron carbonyl complex catalysts to the hydrogenation of carbon monoxide is well known (Fischer–Tropsch synthesis),<sup>3,4</sup> as is the deviation of the product distribution from Schulz–Flory statistics,<sup>4</sup> which is due to the formation of a particular metal cluster structure and high dispersion of small metal particles, subsequently produced by decomposition of the clusters, as well as the surface pore structure of the supports. Furthermore, CO<sub>2</sub> hydrogenation to form hydrocarbons is usually considered to be similar to CO hydrogenation to hydrocarbons, the former reaction consisting of two elementary step reactions, *i.e.* a reverse water–gas shift (RWGS) reaction and a Fischer–Tropsch (F–T) reaction.<sup>2,5</sup> Therefore, the present use of the iron carbonyl compound as a precursor for the CO<sub>2</sub> hydrogenation catalyst, whose performance would be expected to be the same as that for CO hydrogenation, leads to a high activity and selectivity for synthesis of low-carbon hydrocarbons as a result of a limitation of the chain growth. However, the high selectivity of the Fe<sub>3</sub>(CO)<sub>12</sub>/ZSM-5 catalyst for ethene synthesis is probably due to the formation of active sites with a specific metal cluster structure, together with a high dispersion of small metal particles and the surface pore structure of the zeolite support.

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## Footnote

† Further details will be published in a Chinese Patent.

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