Selective Synthesis of Ethane from CO and H_2 catalysed by Zeolite-entrapped Ruthenium Carbonyl Clusters

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$Ru_3(CO)_{12}$ supported on NaY zeolite promoted with MeI exhibits selective formation of ethane from CO and H_2.

It has been proposed that metal carbonyl clusters stabilized on a support are potentially valuable as selective Fischer–Tropsch catalysts.[1] Several attempts to utilize ruthenium carbonyl compounds as catalyst precursors for CO hydrogenation have been reported.[2] Zeolites offer the prospect of better preservation of the original $Ru_3(CO)_{12}$ metal cluster character.[3] Reported here are initial studies of a novel zeolite-supported Ru catalyst, prepared from $Ru_3(CO)_{12}$, which hydrogenates CO with selectivity characteristics unlike those previously found for ruthenium catalysts.

Catalysts were prepared by impregnation by $Ru_3(CO)_{12}$

Table 1. Activities and selectivities of Ru catalysts.[a]

Catalyst	Activity /carbon-μmol g-Ru^{-1}s^{-1}	wt% distribution of hydrocarbon produced			
		C_1	C_2	C_3	$\geqslant C_4$
Unactivated	2.1	57	12	21	10
473 K, N_2	5.2	22	17	20	41
473 K, H_2	17.1	9	7	29	55
MeI-promoted[b]	4.7	17	60	11	12

[a] $Ru_3(CO)_{12}$-NaY (2 wt% Ru), 473 K, 5 MPa (H_2/CO = 1), reaction time = 3—5 h. [b] MeI/Ru = 1.6.

Table 2. Effect of addition of CH_2O or MeOH.[a]

Catalyst	Additive	Activity/carbon-μmol g-Ru^{-1}s^{-1}			
		MeOH	EtOH	CH_4	$\geqslant C_2$
Unactivated	None	0.014	0.019	1.2	0.9
	CH_2O[b]	2.5	2.0	1.2	0.3
473 K, N_2	None	0.17	0.14	1.1	4.1
	CH_2O[b]	4.4	2.5	1.1	0.2
	MeOH[b]	—	1.3	0.8	0.9
473 K, H_2	None	0	0	1.5	15.6
	CH_2O[b]	0.11	0	1.5	2.9
MeI-Promoted[c]	None	0	0	0.8	3.9
	CH_2O[b]	0.11	0	4.4	12.3

[a] $Ru_3(CO)_{12}$-NaY (2 wt% Ru), 473 K, 5 MPa (H_2/CO = 1), reaction time = 3—5 h. [b] CH_2O or MeOH/Ru = 30. [c] MeI/Ru = 1.6.

vapour of NaY zeolite previously dried under vacuum at 673 K. This impregnation process took place in a sealed Pyrex cell held at 393 K for 40 h under an argon atmosphere. Thermal activation was caried out at 473 K under a flow of N_2 or H_2 for 18 h. MeI-promoted catalysts were prepared by allowing the unactivated catalyst to adsorb a calculated amount of MeI at room temperature. The hydrogenation of CO was conducted in an autoclave (150 cm^3) at 5 MPa and 473 K using a 1 : 1 molar mixture of H_2 to CO.

The results are shown in Table 1. The catalyst without thermal activation gave hydrocarbons rich in CH_4. Treatment under N_2 or H_2 resulted in an increase in activity associated with an increase in selectivity of hydrocarbons $\geqslant C_4$ and rich in alkanes. Hydrocarbon distribution drastically changed by addition of a catalytic amount of MeI (MeI/Ru molar ratio = 1.6) to the unactivated catalyst; ethane comprised *ca.* 60% of the total products obtained. This is in contrast to a dip usually encountered at C_2 in the distribution curve of the products obtained over Ru catalysts.[2,4] Selective ethane production *via* reductive coupling of MeI has been eliminated since the catalytic behaviour remained practically unchanged in two runs over identical catalysts; this pathway accounts for less than 10% of the ethane produced. Application of the Schulz–Flory equation leads to the conclusion that the maximum selectivity obtainable for C_2 is 30%.[5]

The mechanism of selective ethane formation is unclear at present. One possible pathway involves the initial formation of methanol from synthesis gas, which is known to be homogeneously catalysed by ruthenium carbonyl clusters at pressures as high as 30—300 MPa.[6] Trace amounts of methanol and ethanol were obtained in addition to hydrocarbons over the unactivated $Ru_3(CO)_{12}$–NaY catalyst. The formation of methanol and ethanol was enhanced by thermal activation under N_2 but ceased by hydrogen treatment.

Experiments were performed in which formaldehyde, generally considered intermediate in most metal carbonyl catalysed CO reduction systems, was added as *s*-trioxane with synthesis gas. The pertinent data are shown in Table 2. This addition to the unactivated and N_2-treated catalysts resulted in an increase in the yield of methanol and ethanol. Methanol also underwent homologation to yield ethanol. However, when formaldehyde was added to the MeI-promoted catalyst system, there was a proportional enhancement of methane, ethane, propane, and butane production. This suggests that formaldehyde is viable as a primary reaction intermediate. In the catalyst systems with no MeI added, the addition of formaldehyde suppressed the formation of hydrocarbons $\geqslant C_2$, excluding its involvement in the formation of higher hydrocarbons. This was also the case for the conventional metallic catalysts prepared by ion-exchange using $[Ru(NH_3)_6]Cl_3$.

It is noteworthy that ruthenium carbonyl complexes in the presence of iodide promoter are known to provide a homogeneous catalytic system for the conversion of synthesis gas into ethanol;[7] the iodide promoter is thought to facilitate the formation of methanol and its subsequent homologation process. Thus it may be deduced that in our catalyst system the formation of ethanol-like products is greatly accelerated by the iodide. However, the enhanced acidity of the zeolite by the iodide could bring about the prompt dehydration of an ethanol equivalent, giving ethene, followed by hydrogenation to ethane. Virtual termination of the hydrocarbon products at the two-carbon length is consistent with the absence of alcohols higher than ethanol in the unpromoted systems. This is plausible since ethanol is known to undergo homologation much more slowly than methanol.[8] We propose that it is this which limits hydrocarbon homologues above ethane.

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