

Selective Catalytic Oxydehydrogenation of Methane to Z-But-2-ene on Cobalt Ferrite

Cvetana Besoukhanova,^a Elly Uzunova^b and Veneta Nenova^a

^a University of Sofia 'St.Kl.Ochridski', Faculty of Chemistry, James Bourchier Str. 1, Sofia 1126, Bulgaria

^b Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Acad. G. Bontchev Str., bl.11, Sofia 1113, Bulgaria

Oxidative oligomerisation of methane proceeds over unpromoted cobalt ferrite catalyst with high yield of Z-but-2-ene.

A great number of catalysts for converting methane to higher hydrocarbons have been tested in recent years and a classification has been proposed.^{1,2} The following main groups are most representative (i) IA ions in IIA oxides; (ii) lanthanide oxides; (iii) IA carbonates on basic oxides; (iv) IA and basic mixed oxides; (v) modified transition metal oxides; (vi) post transition metal oxides, and (vii) monophasic oxides. The synthesis of longer chain hydrocarbons from methane is a thermodynamically favourable process, either *via* alkane-alkene coupling, or oxidative dehydrogenation reaction.^{3,4} Oxidative dehydrogenation reactions are thermodynamically more feasible than the dehydrogenation-oligomerisation reactions between 400 and 1500 K.¹ However, in the presence of oxygen, CO_x can predominate. A selective catalyst is, therefore, used to avoid total oxidation but this unfortunately reduces activity. Generally, reaction products are limited to C₂, but oxygenates may also be formed.⁵ Methane partial oxidation to hydrocarbons (up to C₃) has been performed with alkali-promoted vanadium-alkaline mixed-oxide catalysts⁶ (yield of C₂₊ 7–8%) at 1073 K. At 873 K, 90% selectivity to hydrocarbons with up to 11% C₃–C₄ has been achieved on a CaNiK oxide catalyst.⁷

Mixed oxides such as cobalt ferrite, and other transition metal ferrites, are known catalysts for dehydrogenation of olefins and other unsaturated hydrocarbons.⁸ Here, we describe the potential use of cobalt ferrite in the oxidative dehydrogenation of methane with high selectivity to C₄.

High-dispersity cobalt ferrite (mean particle diameter 0.6–0.9 nm) was obtained by thermal decomposition at 675 K of a pyroaurite-like hydroxidecarbonate precursor.⁹ Surface characterization of the catalyst was made by ESCA (electron spectroscopy for chemical applications) on an ESCALAB MkII spectrometer with Mg-K α radiation (1253.67 eV). A significant excess of surface oxygen was found, even when the calcination temperature was 875 K. The Co/Fe ratio (0.55) was close to the stoichiometric, but the O/(Co + Fe) ratio (2.34) was far above that expected on the base of the formulae of spinel (1.33) or sesquioxides (1.5). The O 1s peak (E_B = 530.0 eV) in the X-ray photoelectron spectrum is symmetric in

shape, indicating a single type of oxygen species on the surface.

The positions of iron and cobalt were deduced from the Mössbauer spectrum, recorded in constant acceleration mode at room temp. with a ⁵⁷Co/Cr matrix as a source. The spinel is partly inverse, and the bulk cation distribution of the sample synthesized at 875 K may be written as [Co_{0.2}Fe_{0.8}]_{tetra}–[Co_{0.8}Fe_{1.2}]_{octa}O₄.

Catalytic measurements were performed in a fixed-bed flow reactor at 1.0133 kPa with 1 g catalyst samples. Before the experiments the catalyst was pretreated at 675 K in an air flow for 2 h and then flushed with Ar for 0.5 h. A methane–air feed was employed with O₂/CH₄ ratio 0.2 at gas hourly space velocity (GHSV) 3.6 × 10³ h^{–1}. Reaction products were analysed on-line by gas chromatography ('Cvet' apparatus, equipped with a 2 m Porapak Q column) and IR spectra (Perkin-Elmer 983 G spectrometer, gas-phase sample), after 30 min on-stream (TOS) at each temperature.

A high yield of Z-but-2-ene was obtained at 675–1050 K, while C₂ production was relatively low, see Table 1. As conversion and CO₂ formation remain almost constant with temperature, the increase in C₄ selectivity at high temperature

Table 1 Catalytic activity of cobalt ferrite in methane oxidative oligomerization

T/K	Methane conversion (%)	Yield (%)		
		C ₂	Z-but-2-ene	Activity ^a
673	24.0	—	6.28	4.52
773	27.0	—	9.39	5.09
823	26.9	—	7.90	5.07
873	25.8	—	8.30	4.86
923	27.4	0.05	10.19	5.16
973	27.2	0.11	9.49	5.13
1023	27.7	0.11	9.89	5.22
1048	28.8	0.09	11.20	5.43

^a mol methane converted per mol catalyst per hour.

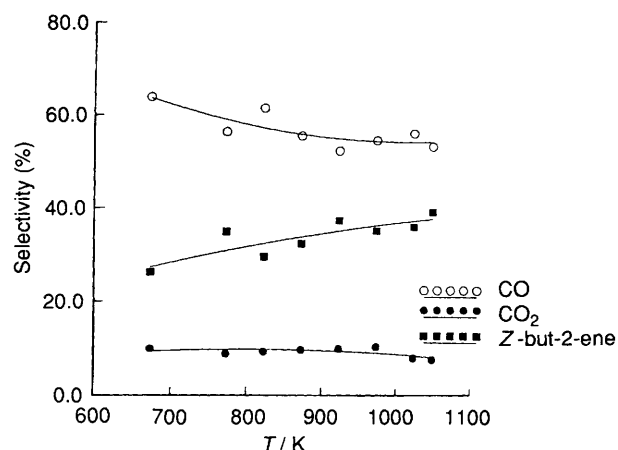
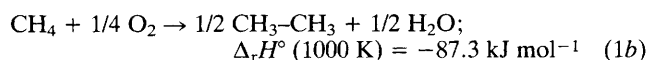
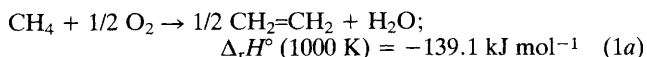


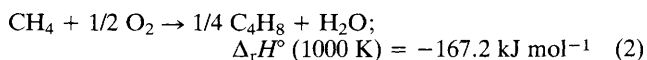
Fig. 1 Selectivity in the oxidative dehydrogenation of methane. (Ethene is <1%.)

is related mainly to the smaller amount of CO produced. In the temperature range, far more CO, than CO₂ was obtained, Fig. 1. No other butenes, C₃, or higher hydrocarbons were detected. Ethene was not present among the products below 920 K.

Ethene and ethane are produced by the methane oxidative coupling reactions shown in eqns. (1a) and (1b).



The reaction of C₄ formation may be written as eqn. (2).



All the reactions are exothermic; production of ethene is related to lower values of the change in standard free energy, than that of ethane for the temperature range, Fig. 2. $\Delta_{1a}G^\circ(T)$ and $\Delta_{2b}G^\circ(T)$ intersect, so that below 850 K, butenes should prevail, while at higher temperature ethene is the thermodynamically favoured product, if total oxidation is avoided. (Thermodynamic data are taken from ref. 10.) Even at 1050 K, however, we find below 1% ethene in the products. These results indicate, that ethene and ethane are intermediates only and eventually participate in further reactions to yield Z-but-2-ene. Thermodynamic equilibrium ratio for the various butenes, produced by reaction (2) at 1000 K is Z-but-2-ene : E-but-2-ene : but-1-ene = 1 : 1.09 : 1.02. If a gas-phase C₂ radical reaction is assumed to occur, a significant amount of E-but-2-ene would be present among the reaction products. The absence of other butenes and C₃, compared with the small amount of ethene leads to the hypothesis that dimerisation of C₂ products takes place on the catalyst surface. Adsorbed C₂ species, obtained from the oxidative coupling of methane, can react further to Z-but-2-ene, and a Langmuir-Hinshelwood mechanism would be valid.

When ethene was passed over the catalyst at 675 K at the same space velocity as the methane-air mixture, the yield of Z-but-2-ene was close to that in the methane oligomerisation, although ethene conversion in the absence of oxygen was lower, Table 2. Oxygen does not participate in the ethene dimerisation reaction: $2 \text{CH}_2=\text{CH}_2 \rightarrow \text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$. But again some CO_x was produced, indicating that oxygen from the catalyst is consumed. In that case, activity decreases with time on-stream. Only surface oxygen is responsible for

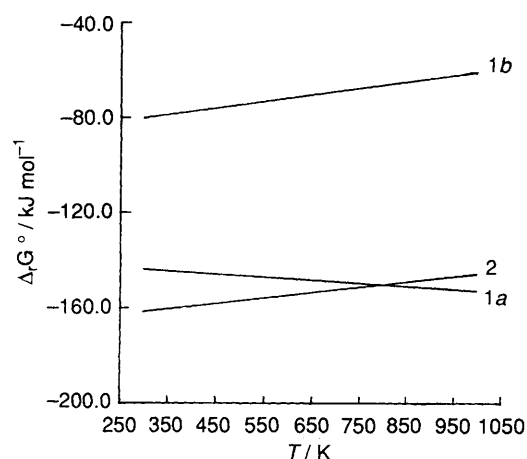


Fig. 2 Gibbs free energy as a function of temperature for processes of methane oxydehydrogenation to ethene 1a, ethane 1b and Z-but-2-ene 2. ($\Delta_r G^\circ$ for but-1-ene and E-but-2-ene formation from methane are very close to 2.)

Table 2 Catalytic activity of cobalt ferrite in ethene dimerization

TOS/min	Ethene conversion (%)	Yield (%)		
		CO	CO ₂	Z-but-2-ene
15	8.8	2.9	0.6	5.3
30	6.8	3.2	0.6	3.0

the production of CO_x, as no changes in the X-ray diffraction patterns nor in the Mössbauer spectra of the spent catalyst were registered. The high stereoselectivity of the reactions of ethene dimerisation and methane oligomerisation leads to the assumption, that in both cases recombination of adsorbed C₂ species predominates.

Changes in the catalyst bulk composition were not detected after ethene dimerisation, nor in the oxidative oligomerisation of methane.

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