

The Reaction of Diazomethane with Co-adsorbed Carbon Monoxide on an Iron Surface: the Formation of Carbon–Carbon Bonds

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X-Ray photoelectron spectroscopic evidence is reported for C–C bond formation during the interaction of chemisorbed carbon monoxide with diazomethane on a polycrystalline iron surface.

The mechanism by which carbon–carbon bonds are formed during carbon monoxide hydrogenation remains a matter of considerable controversy. Proposals that have received some experimental support involve polymerisation of C_1 surface fragments,¹ in particular methylenecarbene (formed by CO dissociation and hydrogenation), and the role of oxygenated species, *e.g.* hydroxycarbene and acyl, has also been considered. Brady and Pettit² reported a study of the reaction of CH_2N_2 with H_2 and with $CO-H_2$ over a range of catalysts and concluded that the results supported involvement of a surface methylenecarbene intermediate in carbon–carbon bond formation during CO hydrogenation. However, as has been indicated by Henrici-Olivé and Olivé³ these results cannot be used as evidence to preclude a mechanism in which oxygenated surface species are dominant. Recently Bock *et al.*⁴ have suggested that their photoelectron spectroscopic studies using dimethylcarbene dimerisation add further support to the conclusions of Brady and Pettit.² However, the products observed in their study can be explained solely in terms of thermal reactions of the carbenes. In addition it should be noted that the Ni catalyst chosen by Bock *et al.* would not be particularly active for carbon–carbon bond formation during CO hydrogenation and only the expected thermal products were reported. We have recently shown⁵ that such products cannot be used as specific evidence to support the involvement of the surface as a catalyst in the reactions. Hence the results of Bock⁴ in addition to those of Brady and Pettit³ cannot be viewed as conclusive evidence supporting the proposed

carbene mechanism. Additionally, the possible involvement of CO in carbon–carbon bond formation has recently been demonstrated in a homogeneous system⁶ in which CO insertion into a metal–alkyl bond was shown to be a useful model for the CO hydrogenation reaction. To date, however, there has been no evidence reported for the direct interaction of oxygenated and non-oxygenated intermediates to form carbon–carbon bonds using an active catalyst surface. We now

Table 1. Surface coverages, atom cm^{-2} (± 0.2) $\times 10^{15}$.

Surface condition ^a	C 	O 	O ^b C 	CH ₂ N ₂ 	CH ₂ /\	N 	C=O ^b
1	0.1	0.3	—	—	—	—	—
2	0.1	0.3	1.8C 1.9O	—	—	—	—
3	0.1	0.3	—	0.5C 1.0N	8.0	—	—
4	0.1	0.3	1.9C 1.9O	0.5C 1.2N	—	—	—
5	0.1	0.4	—	1.6C 1.4N	8.4	—	2.8C 3.0O

^a Refer to Scheme 1. ^b Schematic representations of what are referred to as “strongly” and “weakly” adsorbed CO in the text.

Table 2. A comparison of O, C, and N relative surface coverages when warming up the iron surface, atom cm⁻² (± 0.2) $\times 10^{15}$.

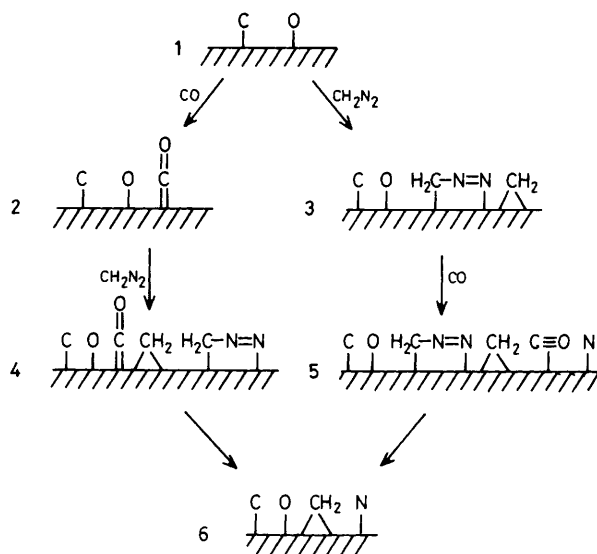
T/K	Scheme 1 route 1 → 2 → 4 → 6 (pre-adsorbed CO)			Scheme 1 route 1 → 3 → 5 → 6 (pre-adsorbed CH ₂ N ₂)		
	O(1s): 532.2 eV	C(1s): 285.5 eV	N(1s): 397.8 eV	O(1s): 533.2 eV	C(1s): 285.5 eV	N(1s): 397.8 eV
ca. 203	0.6	2.4	0.0	0.2	3.6	0.4
293	0.0	1.1	0.2	0.1	2.4	0.9
Decrease in surface coverage	0.6	1.3	-0.2 ^a	0.1	1.2	-0.5 ^a

^a Coverages of nitride actually increase in these temperature ranges owing to surface segregation, and this is more marked for pre-adsorbed CH₂N₂ experiments.

present X-ray photoelectron spectroscopic (X p.e.s.) evidence for the reaction of adsorbed carbon monoxide with co-adsorbed methylene on an iron surface to form C₂ species.

Our strategy was to produce a polycrystalline iron surface by Ar⁺ bombardment containing traces of surface oxide and carbide (known¹ to be present during the synthesis reaction) and to co-adsorb diazomethane and carbon monoxide at 103 K. The order in which this was done proved to be crucial in controlling the subsequent thermally induced reactions as the surface was allowed to warm to room temperature, these being monitored using X p.e.s. We prepared diazomethane using a modification of the published method⁷ such that the pure solid, originally at 80 K contained in a Pyrex tube, could be vapourised *via* an all metal bakeable manifold and leak valve into the ultra-high vacuum chamber (Vacuum Generators 'Solar 300' with 'CLAM' X p.e.s. and Auger facilities: base pressure 4×10^{-10} mbar). Final purification of the diazomethane was achieved by two or three freeze-pump-thaw cycles. For successful adsorptions of diazomethane (when the parent ion signal at *m/z* 42, CH₂N₂⁺, was observed by the mass spectrometer attached to the vacuum chamber) it was necessary to dose the gas manifold with several samples of diazomethane prior to adsorption. Our assignments of the spectra obtained are depicted in Scheme 1 and Table 2 and include surface coverage data determined⁸ from photoelectron peak areas, after appropriate corrections using an electron escape depth for Fe(2p) photoelectrons of 10.3 Å. Binding energies were calibrated with respect to the Fe(2p_{3/2}) signal,⁹ taken as 707.4 ± 0.3 eV. † Attempts to detect product species directly with a residual gas analyser during desorption experiments were unsuccessful owing to massive adsorption on the sample holder and cooling device at low temperatures.

When the iron surface at 103 K was exposed to diazomethane (1×10^{-6} mbar; 7 min), a strong C(1s) signal appeared at 285.5 eV and this was accompanied by an N(1s) signal at 400.0 eV which we assign to molecularly adsorbed CH₂N₂ and CH₂(ads.) [the C(1s) signals of which we are unable to resolve]. Bridging CH₂(ads.) has been identified by electron energy loss spectroscopy¹⁰ on iron surfaces under very similar reaction conditions to those reported here and by X p.e.s.¹¹ The N(1s) signal at 397.8 eV we attribute to adsorbed nitride, this being formed by the (partial) decomposition of molecularly adsorbed diazomethane.¹² Post-adsorption of CO(g) (1×10^{-6} mbar; 15 min) leads to the appearance of C(1s) and O(1s) features at 289.1 and 533.2 eV respectively, with a C/O ratio of 0.93. We assign these latter features to 'weakly adsorbed' molecular CO; this is supported by the high C(1s) and O(1s) binding energies when compared to 'strongly adsorbed' CO. The large coverage of surface methylene



Scheme 1. All sample temperatures 103 K, except for stage 6 (293 K).

groups effectively blocks the reactive sites for CO adsorption, and the CO is quickly lost as the surface is allowed to warm up. Warming up also leads to the loss and decomposition of molecularly adsorbed diazomethane, the N(1s) signal at 400.0 eV declining in favour of the 397.8 eV nitride peak, and the CH₂(ads.) signal at 284.5 eV declining, with a concomitant growth of a new C(1s) feature at 283.0 eV which we assign to surface carbide. Tables 1 and 2 list surface species observed and their coverages, and, together with Scheme 1, show that the final surface at 293 K is composed of oxide, carbide, methylene, and nitride, with a methylene coverage of some 1.0×10^{15} atom cm⁻². The coverages for CH₂N₂ (ads.) and CH₂(ads.) have been apportioned using the intensities of the 400.0 eV N(1s) signals; we believe the rather high coverages observed (e.g. condition 2 in Scheme 1) are due to a disordered iron surface which, in our current apparatus, could not be thermally annealed prior to low temperature adsorptions.

X p.e.s. measurements resulting from the pre-adsorption of carbon monoxide (1×10^{-6} mbar; 8 min) on polycrystalline iron at 103 K yield O(1s) and C(1s) signals, at binding energies of 532.2 and 285.8 eV respectively, with a C/O ratio of 0.96 which are assigned to 'strongly adsorbed' molecular¹⁰ CO. Post-adsorption of diazomethane (1×10^{-6} mbar; 8 min) in this case leads to a *singlet* N(1s) peak at 400.0 eV and an intense C(1s) peak (methylene plus molecularly adsorbed CH₂N₂) at 285.5 eV. Significantly, as the iron surface is

† Throughout this paper; 1 eV = 1.60×10^{-19} J

allowed to warm, the adsorbed CO is retained at higher temperatures compared to the post-adsorbed CO case [as shown by the O(1s) signal]. Moreover, a surface nitride species does not appear until the diazomethane eventually starts to decompose (213–293 K), yielding a methylene surface coverage at 293 K of 0.4×10^{15} atom cm^{-2} . It is particularly noteworthy that the *pre*-adsorbed CO experiments lead to much larger changes in the O(1s) and C(1s) regions as the sample is allowed to warm up, compared to the *post*-adsorbed CO experiments. The corresponding surface coverages for each case have been tabulated in Table 2 for the *ca.* 203 to 293 K temperature changes. It is clear that the extent of loss of C and O in this temperature range can be correlated with a C/O atomic ratio ≈ 2 for *pre*-adsorbed CO, whereas the C/O ratio for *post*-adsorbed CO surfaces is greater than 10. Since 'strongly adsorbed' CO is potentially much more reactive (and would, if left to warm to room temperature, dissociate¹³) it is proposed that the desorbing species, 'C₂H_xO', is formed by the thermally induced reaction of CH₂(ads.) with CO(ads.). We thus have evidence for the formation of C–C bonds as an initial step in the interaction of adsorbed carbon monoxide and methylene on iron surfaces, confirming both these intermediates to be important in the CO hydrogenation reaction. We are currently extending these studies to other metal surfaces of catalytic importance.

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