Mechanism of Formation of Surface Isocyanate During the $SnO_2 \cdot 0 \cdot 55CuO$-catalysed Oxidation of Carbon Monoxide by Nitric Oxide

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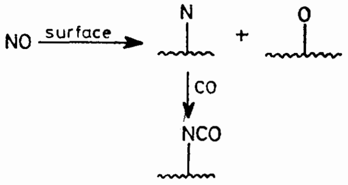
Summary Experiments with ^{18}O-enriched NO and CO in the title reaction at 460—490 K have shown that the oxygen atom of the surface isocyanate is derived from NO and not CO.

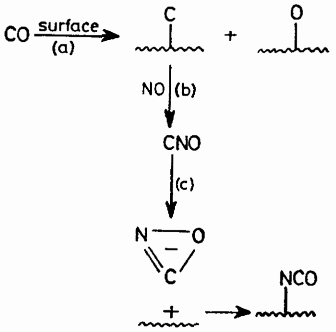
THE formation of a surface isocyanate species (–NCO or NCO^-) during the catalytic oxidation of CO by NO has been observed by i.r. spectroscopy for several different catalyst systems including Ru, Rh, Pd, Ir,[1] and Pt[2] supported on alumina, Ru[3] and CuO[4] supported on silica, and also for unsupported Cu.[5] The $\nu_{as}(NCO)$ band positions for these systems (in the range 2130—2380 cm^{-1}), and also the ^{13}C and ^{15}N isotopic shifts for Pt on alumina[2] ($\Delta^{13}C$, -62 and -52 cm^{-1}; $\Delta^{15}N$, -12 and -18 cm^{-1}) and for Ru on silica[3] ($\Delta^{13}C$, -60 cm^{-1}; $\Delta^{15}N$, -17 cm^{-1}), correlate well with the values reported for surface isocyanate on silica[6] [$\nu_{as}(NCO)$, 2313; $\Delta^{13}C$, -60; $\Delta^{15}N$, -10; and $\Delta^{18}O$, -13 cm^{-1}].

The mechanisms proposed for the Pt–Al_2O_3,[2] CuO–SiO_2,[4] and Cu[5] systems to account for the formation of the surface isocyanate have all involved initial dissociative chemisorption of NO followed by reaction of CO with the chemisorbed nitrogen atom (Scheme 1). Brown and Gonzalez[3] in their mechanistic study of the Ru–SiO_2 system have proposed a more complex reaction scheme between adsorbed CO and NO producing an isocyanate and CO_2. However, whilst these authors have recorded isotopic shifts for ^{13}C and ^{15}N substitution, no attention has been paid to the origin of the oxygen atom of the surface isocyanate, and it is this omission which prompts us briefly to report the results of our studies on the mechanism of surface isocyanate formation during the $SnO_2 \cdot 0{\cdot}55$ CuO catalysis of the CO–NO reaction.



Scheme 1

We have studied this reaction using the disc preparation procedure, apparatus, and i.r. cell already described for our earlier studies on tin(IV) oxide gel.[7] The catalyst came from the same batch which Fuller and Warwick used for their kinetic studies of the oxidation of CO by oxygen[8] and by NO.[9] The oxide discs were pretreated by evacuation and oxygen treatment at 620—630 K. The gas mixture (8·0 kN m^{-2}, 17% NO) was formed by admitting NO and then CO to the cell with the sample at room temperature. The disc was then heated in the gas mixture at 460—490 K for 10 min before cooling and recording the spectrum at ambient beam temperature (*ca.* 380 K). In addition to bands due to surface carbonate, the spectrum also exhibited a sharp, symmetrical, pseudo-antisymmetric stretching vibration at 2189 cm^{-1} attributable to an (isotopically normal) surface isocyanate.† The use of ^{13}CO and ^{15}NO resulted in the expected shifts [$\Delta^{13}C$, -62; $\Delta^{15}N$, -11; and $\Delta(^{13}C + ^{15}N)$, -73 cm^{-1}]. When ^{18}O-enriched CO (60% ^{18}O) was used, the band remained unchanged at 2189 cm^{-1}, still sharp and symmetrical. However, when ^{18}O-enriched NO (40% ^{18}O) was employed, the band maximum was observed to shift to 2184 cm^{-1} and was no longer symmetrical, exhibiting a shoulder on the low energy side. Using usual least-squares curve-fitting techniques, this band envelope was resolved into two component bands at 2189 and 2172 cm^{-1} in an approximately 3:2 ratio of intensities. Thus, the component at 2172 cm^{-1} may be attributed to a surface $-NC^{18}O$ species, and demonstrates that the isocyanate oxygen atom arises from the NO molecule rather than the CO or the oxide surface itself. Separate experiments showed that at 380 K the (isotopically normal) isocyanate is stable to evacuation, and exposure to ^{18}O-enriched oxygen (63% ^{18}O) or ^{18}O-enriched NO produced no asymmetry of the band. At higher temperatures, evacuation or contact with both of these gases results in the destruction of the isocyanate.



Scheme 2

Thus, these data imply that neither of the two mechanisms previously postulated for the formation of isocyanate are operating in the present case. The most likely alternative is a process which involves initial dissociative chemisorption of CO [Scheme 2 (a)] followed by reaction of the adsorbed carbon fragment with NO [Scheme 2 (b)] and a rapid isomerisation of the resultant fulminate to the stable isocyanate structure, probably *via* a cyclic oxaziranyl intermediate [Scheme 2 (c)]. The isomerisation postulated in the final step of the mechanism is known to occur for alkali metal fulminates, as well as for nitrile oxides and for covalent organometallic fulminates on cautious heating.[10]

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† After reaction, NO, N_2O, and CO_2 could be detected in the vapour phase together with CO which was the major component.

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