

Activation of Flue Gas Nitrogen Oxides  
by Transition Metal Complexes

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Introduction

Sulfur and nitrogen oxides are major flue gas pollutants released by coal-fired electric power plants. In the atmosphere these oxides are converted to sulfuric and nitric acids, which contribute to the acid rain problem [1]. Most of the nitrogen oxides (90%-95%) present in coal-derived flue gas exist as the relatively inert and water-insoluble nitric oxide (NO), thus presenting a difficult removal problem.

Nitric oxide reacts with oxygen to form the more reactive nitrogen dioxide:



The equilibrium constant is about 400 at a typical flue gas temperature of 200°C (e.g., after the air preheater). However, the rate law

$$-\frac{d[\text{NO}]}{dt} = k[\text{NO}]^2[\text{O}_2]; \quad k(197^\circ\text{C}) = 3,340 \text{ M}^{-2}\text{sec}^{-1}$$

predicts very slow conversion to NO<sub>2</sub> under normal flue gas conditions (500 ppm NO and 4% O<sub>2</sub>). About 2.5 hours would be required for 50% conversion of the NO to NO<sub>2</sub> [2]. Catalysis would be necessary to increase the rate of this oxidation reaction. Gaseous nitric oxide attacks a wide variety of transition metal complexes to produce nitrosyl compounds [3-5]. Thus transition metal complexes are candidate systems for control of nitrogen oxides via sorption, as well as candidate systems for catalysis of NO transformations.

A practical strategy for nitrogen oxides removal might utilize a solid support that has been impregnated with an active transition metal complex. Some supported transition metals are expected to remove NO<sub>x</sub> by sorption, with regeneration of the sorbent being a necessary property. Others catalyze NO oxidation to the more soluble NO<sub>2</sub> and N<sub>2</sub>O<sub>5</sub>, which has been demonstrated for certain transition metal species [6]. These activated nitrogen oxides can be more efficiently removed along with SO<sub>2</sub> in conventional scrubbing or spray-drying processes, in which an aqueous slurry of sorbent, such as hydrated lime, is injected into the hot flue gas [7,8].

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We present here preliminary studies intended to establish basic homogeneous chemistry of transition metal complexes with nitrogen oxides. The transition metals considered in this work are volatile carbonyl complexes. This work is the first step in the development of supported metal species for enhanced nitrogen oxides removal.

#### Experimental Methods

Reaction mixtures are prepared on a standard glass vacuum manifold. A mercury manometer measures the pressure of each gaseous component of the sample ( $\pm 1$  torr). The reactions take place inside Pyrex reaction cells with KBr or  $\text{CaF}_2$  windows. The cells are mountable inside a Digilab FTS-20C FTIR instrument that records the IR spectra of reacting mixtures. In photochemical experiments, a Hanovia 901B0011 200-watt mercury arc lamp irradiates the sample for periods of 15 or 30 seconds.

Metal carbonyls are obtained from Strem Chemicals and transferred to Pyrex vacuum cells inside a dry nitrogen-purged glove bag. Gases ( $\text{NO}$ ,  $\text{NO}_2$ , and  $\text{O}_2$ ) are used as received from Scott Specialty Gases. Small amounts ( $< 5$  torr) of certain gases are taken from previously made dilution mixtures of each gas in nitrogen.

#### Results and Discussion

Irradiation of a mixture of 0.3 torr  $\text{Fe}(\text{CO})_5$  and 20 torr  $\text{NO}$  produces new infrared bands in the carbonyl-stretching region (2092 and 2049  $\text{cm}^{-1}$ ) and in the nitrosyl-stretching region (1822 and 1787  $\text{cm}^{-1}$ ). The new IR spectrum (see Table 1) agrees with published  $\text{Fe}(\text{CO})_2(\text{NO})_2$  spectra after taking solvent shifts into account [9-11].

Addition of nitrogen dioxide to  $\text{Fe}(\text{CO})_5$  results in the loss of all iron carbonyl spectral features and the appearance of free CO (see Table 2). The reaction produces an orange film on the bottom of the cell, whose IR spectrum was recorded after depositing this coating on a KBr plate. This solid exhibits a weak band in the terminal CO-stretch region (1910  $\text{cm}^{-1}$ ) and a strong band at 1805  $\text{cm}^{-1}$ , which is probably due to a bridging carbonyl. Infrared bands are also observed at 1485, 1355, 1315, and 1220  $\text{cm}^{-1}$ . The highest frequency absorbance may be a bridging nitrosyl, while the others are probably coordinated  $\text{NO}_2$  or nitrite ( $\text{NO}_2^-$ ) groups [5]. The formation of a solid containing bridging ligands indicates that iron clustering results from reaction with  $\text{NO}_2$ . Free CO is generated as this ligand is eliminated between clustering metal centers.

A sequence of chemical changes, which are followed by FTIR, occurs upon addition of 16 torr of oxygen to a mixture of 0.3 torr  $\text{Fe}(\text{CO})_5$  and 25 torr  $\text{NO}$ . Five minutes after mixing, the  $\text{Fe}(\text{CO})_5$  concentration is reduced by 72%, free carbon monoxide appears, and a small amount of  $\text{Fe}(\text{CO})_2(\text{NO})_2$  is observed. Eight minutes following mixing, iron pentacarbonyl is gone, while the  $\text{Fe}(\text{CO})_2(\text{NO})_2$  concentration is halved. Nitrogen dioxide is not observed until eleven minutes after mixing, when all of the iron carbonyls have left the gas phase (see Figure 1). (We observe that binary samples of  $\text{NO} + \text{O}_2$  begin producing  $\text{NO}_2$  immediately upon mixing; see Figure 2.) An orange film results, such as in the reaction of  $\text{Fe}(\text{CO})_5 + \text{NO}_2$ . Our interpretation is that the initial  $\text{NO}_2$  formed by  $\text{NO}$  oxidation reacts with the iron carbonyls

to produce iron clusters, and only after this reaction is complete does free  $\text{NO}_2$  appear.

The next set of experiments involves dicobalt octacarbonyl. Upon addition of  $\text{NO}$ ,  $\text{Co}_2(\text{CO})_8$  is quickly converted to  $\text{Co}(\text{CO})_3\text{NO}$ , as determined by FTIR (see Table 1) [9-12]. No irradiation is necessary to initiate this reaction. Pure  $\text{Co}(\text{CO})_3\text{NO}$ , produced by the introduction of  $\text{NO}$  into a cell containing a crystal of  $\text{Co}_2(\text{CO})_8$ , exhibits no reactivity toward oxygen. Upon addition of  $\text{NO}_2$ , both  $\text{Co}_2(\text{CO})_8$  and  $\text{Co}(\text{CO})_3\text{NO}$  leave the gas phase, and free carbon monoxide is produced. We believe that cobalt clustering results from the interaction with  $\text{NO}_2$ , much as with  $\text{Fe}(\text{CO})_5$  (see above).

### Summary and Conclusions

The metal carbonyls studied take up nitric oxide homogeneously in the gas phase. Iron requires UV light for reaction with  $\text{NO}$ , but the same result is expected with the application of heat. The metal carbonyls also react with nitrogen dioxide but in this case produce polynuclear metal species. Oxygen does not attack the carbonyl or nitrosyl complexes.

The results indicate high potential for  $\text{NO}_x$  removal from stack gases by sorption onto supported metal carbonyl complexes. The solid form allows ease in separation from the flue gas. Regeneration of the sorbent might be achieved by treating with  $\text{CO}$  to liberate  $\text{NO}_x$  by displacement or by heating to decompose and drive off  $\text{NO}_x$ .

Experiments conducted between the time of this writing and the 194th ACS National Meeting will focus on efforts to produce supported transition metal complexes and to conduct fundamental studies involving their testing as  $\text{NO}_x$  sorbents and as catalysts for nitrogen oxide transformations. Support materials will include alumina and titania. Transition metal sources will be metal carbonyls and metal salts, such as the nitrates.

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### Disclaimer

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Table 1. Gas Phase FTIR Spectra of Some Metal Complexes as Measured in this Work.

<u>Compound</u>	<u>Absorbance maxima, cm<sup>-1</sup> (relative intensity)</u>
Fe(CO) <sub>5</sub>	2034(.58), 2014(1.0), 1976(.02)
Fe(CO) <sub>2</sub> (NO) <sub>2</sub>	2092(.34), 2049(.76), 1822(.54), 1787(1.0)
Co <sub>2</sub> (CO) <sub>8</sub>	2075(.64), 2052(1.0), 2037(.69), 2002(.07), 1867(.21), 1825(weak)
Co(CO) <sub>3</sub> NO	2108(.12), 2045(1.0), 2010(.02), 1821(.52)

Table 2. Gas Phase FTIR Spectra of Simple Nitrogen and Carbon Oxides as Measured in this Work.

<u>Compound</u>	<u>Absorbance maxima, cm<sup>-1</sup> (relative intensity)</u>
NO <sub>2</sub>	2920(.07), 2890(.05), 1625(1.0), 1605(.74)
NO	1910(1.0), 1855(.88)
N <sub>2</sub> O	2238(1.0), 2212(.72), 1302(.17), 1275(.14)
CO	2170, 2115
CO <sub>2</sub>	2365(1.0), 2335(.76)

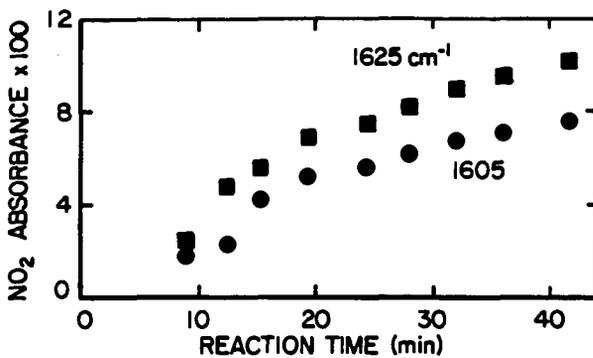


Figure 1. Evolution of  $\text{NO}_2$  in the presence of  $\text{Fe}(\text{CO})_5$  as monitored by FTIR. Initial pressures: 0.18 torr  $\text{Fe}(\text{CO})_5$ , 1.1 torr NO, and 18 torr oxygen. Note: these initial pressures are different from the experiment described in the text, but the overall chemical behavior is the same.

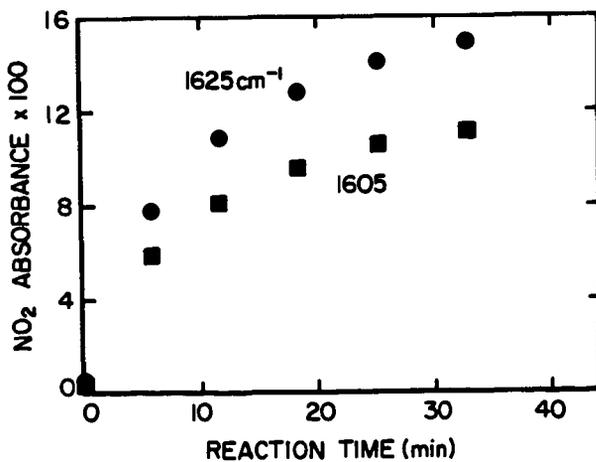


Figure 2. Oxidation of nitric oxide as followed by FTIR. Initial pressures: 1.1 torr NO and 20 torr oxygen.

NO/13,999