

Notes

NO Adsorption on Transition Metal-Containing Cellulose Acetate Film and Its Reduction by CO and H₂

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Received November 22, 1993

There have been extensive researches on the reduction of NO because of its importance in pollution control. The most widely used systems have been the reduction of NO by CO on inorganic oxide-supported transition metal catalysts and a number of studies have focused on the formation and reactivity of surface intermediates during the reaction. In the related typical reaction, NCO surface species is usually observed to be formed as an intermediate and the main products are found to be N₂O and N₂ as well as CO₂.¹⁻⁵

However, similar reaction chemistry using polymer-immobilized catalysts has not, to the best of our knowledge, been extensively investigated although the reactivities of transition metals and their peculiar catalytic properties in organic polymer matrices have been a subject of particular interest in recent years.⁶⁻⁹ We report here the results of an infrared study of the behavior of NO on transition metal-containing cellulose acetate and its catalytic reduction by CO and H₂.

Ruthenium (RuCl₃·3H₂O), rhodium (RhCl[P(C₆H₅)₃]₃) or palladium (Pd(O₂CCH₃)₂, Aldrich) metal-containing cellulose acetate (Aldrich) films used in this study were prepared by using cosolvent as previously reported¹⁰⁻¹³ and their metal complex concentrations were controlled to 5-40 wt%. These films, of which thickness is about 10-20 μm, were thermally stable below 150°C. The gas reactions were carried out in 250 ml glass flasks, connected to vacuum line without circulation. The gas adsorption on the metal-containing films and the reaction processes including gas phase product analyses were investigated by IR spectroscopy (Hitachi 260-10) and gas chromatography (Shimazu GC-R14). We used Helium as a carrier gas and 6 ft. copper column, containing molecular sieve 5 Å¹⁰⁻¹³.

According to the previous study in our laboratory, the incorporated transition metals into the neutral cellulose acetate (CA) were found to interact with the relatively soft part of the polymer; as evidenced by IR spectroscopic study, they are believed to at least partially coordinate to the electron rich oxygen atoms of acyl group of CA¹⁰⁻¹³. Also, the transition metals in CA were found to be active toward CO, H₂, O₂, and C₂H₄ under relatively mild conditions and in the cases of Rh¹⁰ and Pd¹² contained in CA, metal particles of ca 10-60 Å size in diameter were observed to be formed in the CA by reduction with H₂ (600 torr, 100°C).

Table 1 summarizes the observed transition metal carbon-

Table 1. Transition metal carbonyls and hydride formed in CA

Films	$\nu(\text{CO})$ or $\nu(\text{M-H}) \text{ cm}^{-1}$	Remarks	Ref.
[CA*+Ru ^a] film			13
carbonyls	2150 2086, 2010 2050, 1990 1960	physically absorbed CO CA-Ru(III)(CO) ₂ , cis CA-Ru(II)(CO) ₂ , cis CA-Ru(II)(CO)	
hydride	1960	CA-Ru monohydride (very stable in air)	
[CA+Rh ^b] film			10
carbonyls	2086, 2010 1990 2035	CA-Rh(I)(CO) ₂ , cis CA-Rh(I)(CO) CA-Rh(O)CO	
hydride	1990	CA-Rh monohydride (unstable in air)	
[CA+Pd ^c] film			12
carbonyls	2060 1945	CA-Pd(O)-CO, linear CA-Pd ₂ (O)-CO, bridged	
hydride	1915	CA-Pd monohydride (unstable in air)	

*CA: cellulose acetate, metal complex contents of films; 10 wt% each, ^a RuCl₃·3H₂O, ^b RhCl[P(C₆H₅)₃]₃, ^c Pd acetate (Pd(O₂CCH₃)₂).

yls and hydrides formed in CA films.

When 10 wt% Ru metal-containing CA films¹³, after dried in vacuum at 150°C for 12 h, were treated with NO gas (50 torr, Matheson) at room temperature, its infrared spectrum showed a strong band at 1882 cm⁻¹, which can be easily assigned to CA-Ru(II)NO⁺(linear) by comparing it to the known Ru-nitrosyl species and considering its oxidated state¹⁴⁻¹⁵. This band was quite stable in air and its intensity reduced about 30% after reaction with H₂ (600 torr) at 140°C for 12 days. When this film was exposed to CO (600 torr, Matheson) at 130°C, there was no CA-Ru(NO)(CO), nor CA-RuNCO species except the appearance of bands due to $\nu(\text{CO})$ as listed in Table 1 and the slight decrease of the band intensity at 1882 cm⁻¹. As expected, no reduction of NO by CO was observed. But when the gas mixture of NO (20 torr) and H₂ (50 torr, Matheson) was reacted with the films at 130°C for several days, small amount of N₂O gas was found to be produced without NH₃ formation in gas product.

In the case of 10 wt% Rh metal-containing CA films¹⁰ (designated as [CA+Rh] film), three bands at 1660, 1300(sh), 790 cm⁻¹ were appeared in their IR spectra upon treatment with NO (100 torr) at 140°C for 12 h, and disappeared completely in IR spectra at ambient conditions after 24 h. These bands are quite analogous to those of RhCl(NO)(NO₂)[P(C₆H₅)₃]₂¹⁶ which is formed by direct reaction between RhCl[P(C₆H₅)₃] and NO gas. This Rh metal complex had an another band at 1408 cm⁻¹, but in the [CA+Rh] films, this band was superimposed on a strong band at the same region, ari-

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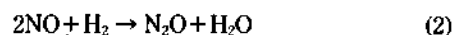
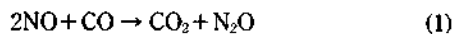
Table 2. Transition metal-nitrosyl and nitro species formed in CA

Films	$\nu(\text{M-NO})$ or $\nu(\text{M-NO}_2)$ cm^{-1}	Remarks
[CA+Ru*]	1882	CA-Ru ²⁺ -NO(linear)
[CA+Rh*]	1660	CA-Rh-NO(bent)
	1300(Sh)	CA-Rh-NO ₂
	790	CA-Rh-NO ₂
[CA+Pd*]	1820(Sh)	CA-Pd-NO(linear)
	1650	CA-Pd-NO(bent)
	1510	CA-Pd ₂ -NO(bridged)
	1300(Sh)	CA-Pd-NO ₂ **
	920	CA-Pd-NO ₂ **
	840	CA-Pd-NO ₂ **
	790	CA-Pd-NO ₂ **

*Metal complex contents: 10 wt%. **Nitro group or chelating nitro group.

sing from the CA polymer. Thus, the band at 1660 cm^{-1} is assigned to Rh-NO⁻(bent)¹⁵⁻¹⁶, and the other bands are believed to come from the coordinated NO₂⁻ species¹⁷. When the mixture of NO (50 torr) and CO (100 torr) gases was reacted in static state at 135°C for 3 days with 0.1 g of [CA+Rh] films, all of the reactants were found to be converted to CO₂ and N₂O, and these products were easily identified by their characteristic infrared adsorption bands (CO₂; 2349 and 667 cm^{-1} , N₂O; 2250 cm^{-1}). The [CA+Rh] films after the reaction showed only trace of weak bands due to Rhodium-carbonyl and Rh-nitrosyl species as listed in Table 1 and Table 2. Surprisingly, there was no metal-isocyanate, nor metal-CN species, arising from NO dissociation^{3,5}. To confirm this result, series of similar reactions were carried out but there were no evidences of such NO dissociation or for the formation of Rh(NO)₂^{18a} and Rh(CO)(NO) species^{18b}. In a separate experiment, we examined other possibility such as CO dissociation¹⁹ on [CA+Rh] films but failed.

When a gas mixture of NO (20 torr) and H₂ (50 torr) are reacted at 140°C for 4 days with 0.1 g of [CA+Rh] films, all of the reactants were completely converted into N₂O and H₂O, and interestingly, there was no evidence for the formation of ammonia which is a typical major product for this type reaction. Also, in the IR spectra of the film after the reaction, only the aforementioned three bands were observed very weak intensity, and these reactions can be represented as below;



During the reaction process, the gas mixture was monitored at regular intervals by taking its gas phase IR spectrum and GC analysis, but there were no other species than those as above (for examples; NH₃ or N₂), indicating that there is no subsequent reaction.

When the 10 wt% Pd metal-containing CA films¹² (designated as [CA+Pd] film) after reduction reaction with H₂ (600 torr) at 120°C were exposed to NO (50 torr) at about 40°C, a band at 1510 cm^{-1} appeared in their IR spectra. On heating to 130°C, several other bands at 1820(sh), 1650, 1510, 1300

(sh), 920, 840, and 790 cm^{-1} were observed. Owing to the relatively few data about palladium-nitrosyl species, it is difficult to make specific assignments for all of these bands. However, the band at 1820 cm^{-1} is believed to arise from linear and the band at 1650 cm^{-1} from bent Pd-nitrosyl species^{17,20-22}. The band at 1510 cm^{-1} may belong to coordinated nitro group as well as the other bands at 1300, 920, and 790 cm^{-1} , but it is reasonable to assume that this band comes from the bridged nitrosyl groups on palladium metal particles (about 30-60 Å size in diameter) formed in CA in comparison to the bridged palladium carbonyl species¹², formed in CA under similar conditions, as listed in Table 1. The other bands below 1500 cm^{-1} are thought to correspond to those of metal nitro or metal chelating nitro groups, reported in many unsupported transition metal cases¹⁷.

The reduction reaction of NO by CO and H₂ using the [CA+Pd] films under the same conditions produced the same products as in Eq. (1) and Eq. (2). No specific intermediate surface species as described, including the metal hypoxynitrite²³, were identified in the films during the reaction, indicating that the NO reduction reaction with [CA+Rh] and [CA+Pd] films as catalysts proceeds in different mechanistic pathway in comparison to those of inorganic oxide-supported transition metal catalysts⁴⁻⁵. Although detailed studies of the reaction mechanism have not been made yet, it is believed that the reaction may include the direct attack of CO or H₂ on the metal-coordinated nitrosyl groups in CA. In addition, it should be mentioned that it is not clear how the CA polymer matrix affects on the such reaction chemistry at this stage.

In conclusion, the reaction chemistry of the Ru, Rh, and Pd-containing cellulose acetate films showed the formation of various metal-carbonyl, -nitrosyl, -nitro, and -hydride species in relatively mild conditions in addition to the catalytic reduction of NO by CO and H₂. The reduction products using [CA+Rh] and [CA+Pd] films as catalyst were N₂O, CO₂ and H₂O. It is noteworthy that no typical surface intermediates in CA films were observed during the reaction.

Acknowledgment. Support of this work by Agency for Defense Development of Korea is gratefully acknowledged.

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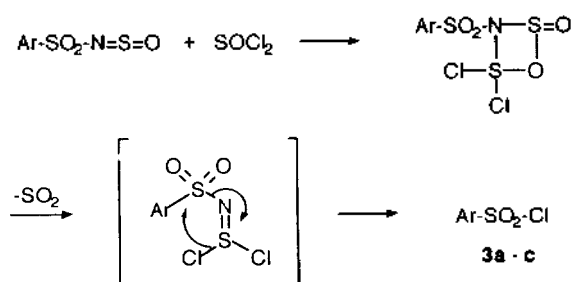
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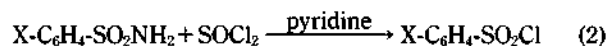
Table 1. Formation of Arenesulfonyl Chloride (**3a-c**) from Arenesulfonamide (**1a-c**) and SOCl₂ (3 equiv) with pyridine (1 equiv)

Substrate	Time (hrs)	Product	Yield ^a
1a	6	3a	48
1b	6	3b	55
1c	6	3c	32

^a Isolated yield.



Scheme 1.



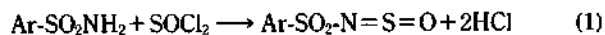
Deaminative Chlorination of Arenesulfonamide with Thionyl Chloride: Formation of Arenesulfonyl Chloride

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Received November 29, 1993

Arenesulfonamide (**1**) is well known to react with thionyl chloride to give corresponding N-sulfinyl compound (**2**), a reactive intermediate,^{1,3} as shown in equation 1.



1

2

The chemistry of N-sulfinyl compound (**2**) has been extensively investigated in connection with synthetic applications such as in the synthesis of pyridine derivatives *via* Diels-Alder reaction,⁴ α -amino acids *via* ene reactions,^{5,6} and derivatives of arylsulfonamides.⁷ We report herein that arenesulfonyl chloride (**3**) is produced from the reaction of arenesulfonamide with more than 2 equivalents of thionyl chloride under refluxing condition in inert solvents (equation 2).

General procedure for the formation of arenesulfonyl chloride using *p*-toluenesulfonamide (**1b**) as a prototype is as follows: **1b** (1 g, 5.8 mmol), pyridine (0.05 mL, 0.62 mmol), thionyl chloride (1.3 mL, 17.8 mmol) were introduced into

a flask containing benzene (20 mL). The reaction mixture was refluxed for 6 hrs, followed by evaporation of benzene and excess of thionyl chloride. Kugelrohr distillation of remaining residue gave **3b**. Yield: 0.61 g (55%) mp. 68-69°C (Ref.⁸ mp. 71°C). The structure of product was identified by comparison of its GC retention time and IR spectra with those of the commercially available authentic sample.

As is shown in Table 1, it can be supposed that the formation of arenesulfonyl chloride (**3a-c**) is a common reaction for arenesulfonamide.

In order to study in more detail, compound **1b** was chosen as a prototype and was reacted with thionyl chloride in various conditions and the results are shown in Table 2. Several points are noteworthy in Table 2. First of all, it can be seen that both thionyl chloride of at least 2 equivalent (entry 9) and refluxing temperature are required for the formation of **3a-c**, which suggests obviously that the reaction of equation 2 might proceed *via* the intermediacy of N-sulfinyl compound. In fact, N-sulfinyl *p*-toluenesulfonamide gave **3b** in reaction with 1 mole of thionyl chloride (entry 14). Though the reaction of equation 2 did not proceed at all without pyridine (entry 4), it gave slowly **3b** both in the presence of large excess of thionyl chloride and under longer period of reflux (entry 8). Also seen in Table 2 is that the reaction of equation 2 proceeded faster in more polar solvent (entry 5-7). This suggests that **3b** would be formed *via* a polar intermediate made between -N=S=O and thionyl chloride.

We then turned to study whether other compounds having an amino group behave similarly as **1a-c**. Among the substrates employed, derivatives of benzamides, Ar-C(O)NH₂, were responsive to give a mixture of benzonitrile (~70%)