

ON THE REACTIONS OF SURFACE ISOCYANATE OVER PLATINUM CATALYST

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Abstract: The reactions of isocyanate on $\text{Pt}/\text{Al}_2\text{O}_3$ were investigated by infrared spectroscopy combined with mass spectrometry. Its stability was found to be very sensitive to the conditions under which the isocyanate was formed. It decreased with the surface concentration of chemisorbed oxygen and with the Pt content of the catalyst. The number of isocyanate species in many cases greatly exceeded the number of surface Pt atoms, indicating that a significant proportion of the isocyanate is located on the carrier. The reactivity order of the gases depended on the temperature. In the presence of water at 200–400°C the hydrolysis of surface isocyanate into ammonia was almost complete.

INTRODUCTION

Recent infrared studies revealed the formation of a surface complex during the reaction of NO and CO over supported noble metals /1,2/. On $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst two intense bands were observed, at 2267 cm^{-1} and 2148 cm^{-1} . The first band was assigned to covalently-bonded isocyanate, $-\text{NCO}$, the second one to anionic isocyanate $[\text{NCO}]^-$. Our subsequent work disclosed more details on the formation of isocyanate complex on $\text{Pt}/\text{Al}_2\text{O}_3$, and attempts were made to evaluate the roles of the Pt dispersity and of different carriers on the chemistry of surface isocyanate over Pt /3,4/.

In the present paper we deal with the reactivity of surface isocyanate over $\text{Pt}/\text{Al}_2\text{O}_3$. Attention is paid to determination of the surface concentration of the isocyanate species and its relation to the number of surface Pt atoms.

EXPERIMENTAL

Catalysts were obtained by impregnation of a Degussa P110 Cl alumina with H_2PtCl_6 . The homogenized suspension was dried for 16 hr at 100°C, and then 30x10 mm coherent, self-supporting tablets (10 mg/cm^2), satisfactorily transparent to infrared light, were prepared. The dispersity of the supported Pt was determined by O_2 - H_2 titration /5/. The solid sample was treated in situ as follows: /i/ oxidation for 30 min with 100 Torr O_2 at 400°C; /ii/ evacuation for 15 min at 400°C; /iii/ reduction for 30 min with 100 Torr H_2 at 400°C.

A greaseless vacuum infrared cell was combined with an MS 10 mass spectrometer. Details of the spectrophotometer and the cell have been described elsewhere /3/. Isocyanate surface complexes were produced in most cases in the following way: 45 Torr of a gas mixture of NO (5%), CO (10%) and N_2 (85%) was admitted to the pre-treated $\text{Pt}/\text{Al}_2\text{O}_3$ at the reaction temperature. After a certain time (see later) the gas pressure was reduced to 10^{-1} Torr, and the catalyst sample was moved to the cold part of the cell. In agreement with the former results /2,3/, below 300°C a band appeared at 2267 cm^{-1} ($-\text{NCO}/$ and another one at 2080 cm^{-1} (linearly-bonded CO). At higher temperatures a medium intense band, or only a shoulder, was also observed at 2140 cm^{-1} ($[\text{NCO}]^-$).

RESULTS

The decomposition of isocyanate complexes was first investigated in the infrared cell in the range 200–500°C under constant evacuation. It was found that the stability of surface isocyanate on $\text{Pt}/\text{Al}_2\text{O}_3$ depends sensitively on the conditions under which it was formed. Isocyanate produced at higher temperature is more stable than that formed at lower temperature. Treating the sample containing isocyanate with CO at 300°C or using a reaction mixture of higher CO content also increased the stability of this surface species. On the other hand, on an oxidized surface it decomposed faster. In the case of the complex formed at 320°C for 10 min, a slight decrease in the intensity of the band at 2267 cm^{-1} was detectable first around 250°C. The intensity of

this band gradually decreased with time and with increase of the temperature (Fig. 1). While at the beginning the band at 2140 cm^{-1} was very weak, or hardly detectable, with the progress of the heat treatment of the sample it came into the foreground. This band was much more resistant to the heat treatment; its intensity decreased only above 400°C .

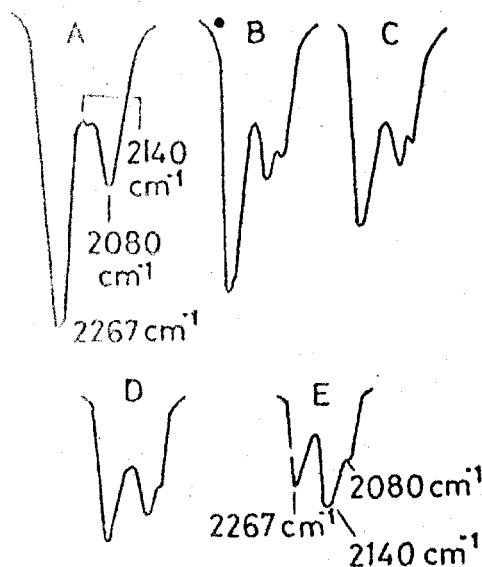


Fig. 1. Change in the infrared spectra of isocyanate on 5% Pt/Al₂O₃ in vacuo as a function of time at 400°C . A) 0 min; B) 5 min; C) 10 min; D) 20 min; E) 30 min.

The stability of surface isocyanate was sensitively influenced by the Pt content of the catalyst (Fig. 2); it decreased with increase of the Pt content, which corresponded to a decrease of the dispersity of the Pt. While the isocyanate on 5% Pt/Al₂O₃ decomposed at 400°C in 30–50 min, on 0.2% Pt/Al₂O₃ surfaces only about 55% of it decomposed during this period, and the reaction ceased before completeness. The decomposition curves of isocyanate can be divided into various parts. At the beginning, the decomposition is very fast, and obeys the first-order equation. This is followed by a slower process, which goes into an extremely slow stage. At lower temperatures the decomposition of isocyanate even ceases before complete decomposition. The duration of the first, fast stage can be shortened by

treating the sample with CO at 300°C .

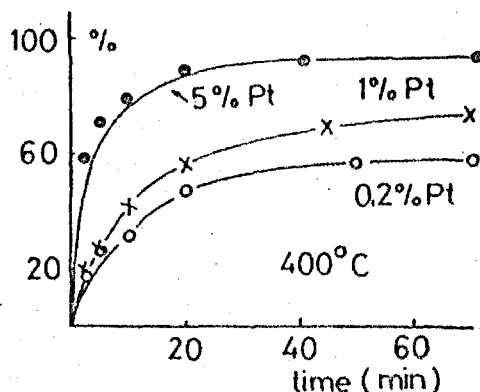


Fig. 2. Decomposition of -NCO complex at 2267 cm^{-1} formed at 400°C .

Simultaneous analysis of the products of surface reactions disclosed more details on the decomposition of isocyanate complexes. In order to decrease the amounts of other adsorbed species, production of the isocyanate complex was carried out at 400°C using a very short, 30–60 sec, reaction time. Before the decomposition, the sample was evacuated at 300°C for 30 min. Control measurement showed that under these conditions the adsorption of CO, CO₂ and particularly NO on Pt/Al₂O₃ was greatly reduced. Results of mass spectrometric analysis are illustrated in Fig. 3. There was a fast initial CO₂ and N₂ evolution. The ratio CO₂/N₂ is approximately 1.2 in this period. After this short stage (3–5 min) the partial pressure of CO₂ did not change and only CO and N₂ were evolved. The ratio CO/N₂ was always larger than 1 during the period. After about 40 min the reaction slowed down; the temperature was therefore raised to 480°C , and the sample was kept at this temperature until N₂ and CO evolution ceased. This almost coincided with the disappearance of the isocyanate band. It should be noted that no CO₂ formation was detected at this temperature. Measurements were repeated with different initial intensities of surface isocyanate (Table I).

Considering that adsorption of NO on the Pt/Al₂O₃ surface under the same conditions yielded only 2.5×10^{-8} mole N₂ in the desorbing gases, it can be assumed that almost all the N₂ found during the decomposition of isocyanate resulted from the isocyanate complex. It is also conceivable that during the formation of isocyanate less "N" compounds remain

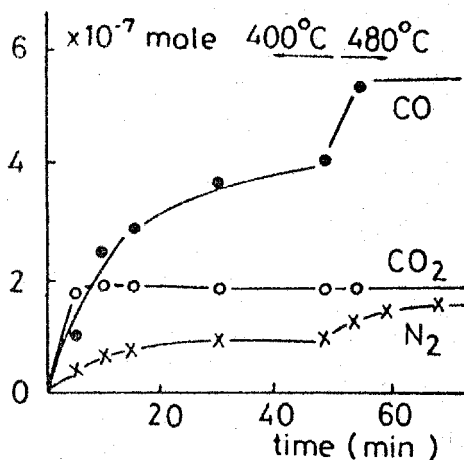


Fig. 3. Evolution of gases during the decomposition of isocyanate complex over 5% Pt/Al₂O₃

adsorbed on the surface, so the above value is certainly too high. In Fig. 4 the amount of N₂ found during the complete decomposition of isocyanate is plotted against the initial intensity of the band at 2267 cm⁻¹. It appears that the amount of N₂ evolved is proportional to the initial intensity of the isocyanate band at 2267 cm⁻¹. From this correlation the apparent extinction coefficient of surface -NCO at 2267 cm⁻¹ was calculated to be 9.3×10^{-18} cm²/molecule.

Considering the dispersity of Pt in the catalyst, 5% Pt/Al₂O₃, and assuming that one NCO group is bonded only to one surface Pt, it resulted that under these conditions from 18 to 82% of the surface Pt atoms should be occupied by NCO groups. By increasing the reaction time of NO + CO, we were able to increase the surface concentration of isocyanate groups. The highest apparent coverage value obtainable on 5% Pt/Al₂O₃ catalyst approached 100% of the surface Pt atoms (Table I).

Similar measurements were made with the catalysts containing 0.2 and 1% Pt. In this case, as mentioned before, complete decomposition of isocyanate complex was difficult to achieve thermally even at 480°C. Therefore, in the last, slow stage of the decomposition isocyanate was oxidized with molecular oxygen; CO₂, NO and N₂ were detected during this oxidation. The quantity of isocyanate was calculated on the basis of nitrogen compounds found (Table I). It appears that the amount of NCO groups in these cases greatly exceeds the number of Pt

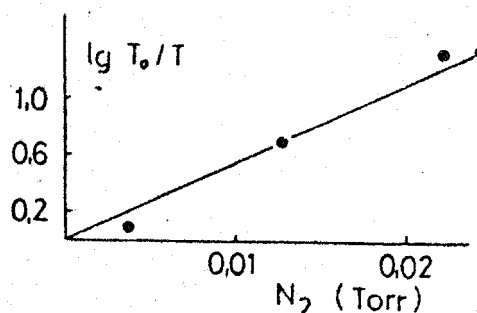


Fig. 4. Initial intensities of the isocyanate band at 2267 cm⁻¹ against the amount of N₂ formed in the complete decomposition

atoms available on the surface.

As regards the reactions of surface isocyanate with different gases, we can refer here only to the main points of the results. The highest reactivity was always observed in the presence of water, the isocyanate bands disappeared in some min after introduction of 2 Torr H₂O into the cell. In the knowledge of the concentration of the isocyanate species and the amount of ammonia formed, it appeared that at 200–400°C isocyanate completely hydrolyzed into ammonia without any replacement reaction. The reactivity order of the other gases depended on the temperature. At 300°C this order was the following: H₂O, O₂, NO, H₂, CO.

DISCUSSION

An interesting result of the present work is that the number of isocyanate species greatly exceeds the number of surface Pt atoms in many cases. From this it can justifiably be concluded that a significant part of the isocyanate should be located on the alumina carrier. This has also been assumed in a very recent paper of Dalla Betta and Sholef /6/. Our investigations on the effect of the carrier additionally revealed that the carrier greatly influenced the formation and also the stability of isocyanate /4/. The bands due to isocyanate appeared at 2210 cm⁻¹ on Pt/TiO₂, 2241 cm⁻¹ on Pt/MgO, 2267 cm⁻¹ on Pt/Al₂O₃ and 2318 cm⁻¹ on Pt/SiO₂. Since isocyanate gave an absorption maximum at 2313 cm⁻¹ on silica /7/ and at 2232 cm⁻¹ on magnesia /8/, it seems very likely that isocyanate species migrated from the Pt onto the support. The high stability of isocyanate on

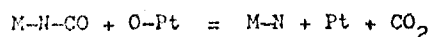
Table I. Some characteristic data for the catalysts and its coverage with isocyanate complex

Pt content (wt %)	Pt dispersion (%)	Initial intensity of (-NCO) band	Amount of N ₂ formed (mole $\times 10^8$)	Coverage of Pt atom with (-NCO) (%)
0.2	34.0	>1.4 ~1.2	7.1 5.5	135.0 104.8
1	25.3	-	-	-
5	9.1	~1.34 0.72 0.082	30.8 15.8 5.7	87.8 45.1 16.3

Pt/SiO₂ is also in harmony with the properties of Si-NCO //.

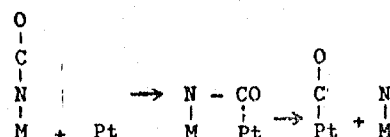
Bearing this conclusion in mind, it is not surprising that the decomposition of isocyanate over Pt/Al₂O₃ consists of different stages. Two factors seem to be important in determining its stability: the surface concentration of chemisorbed oxygen formed in the dissociation of NO, and the Pt content (dispersity) of the catalyst. We propose that the following reactions occur during the decomposition of isocyanate:

/i/ In the first, fast period, when CO₂ is evolved, isocyanate mainly reacted with the chemisorbed oxygen.



(M should be either Pt or Al.) The next step is the recombination of adsorbed N into N₂. This step is much slower than the first one; our measurements indicated that at the beginning of the reaction more CO+CO₂ is evolved than N₂. The N atom is retained on the surface for a while, and its recombination requires more time. The observation that addition of CO on this surface at 350°C, after quick evacuation of gases, increased the intensity of the isocyanate band at 2267 cm⁻¹ seems to prove the presence of adsorbed N atoms.

/ii/ When the chemisorbed O has reacted, the most probable mode of decomposition of -NCO is its dissociation, i.e. rupture of the N-C bond. Comparing the reactivities of isocyanate on different noble metals and on Pt using various supports /4/, we conclude that isocyanate decomposes faster on Pt than on alumina or on silica. It is very likely, however, that in this period the surface Pt promotes the dissociation of isocyanate associated with the carrier. This may occur by an interaction of the CO group with a neighbouring Pt atom:



This step seems to be supported by the observation that in some favourable cases the CO band at 2080 cm⁻¹ transiently increased during the decomposition of isocyanate.

/iii/ When the isocyanate has been decomposed on Pt, and in the neighbourhood of Pt, the stability of the remaining isocyanate is mainly determined by the support. The decomposition may involve the rupture of the N-C bond as above, without the catalytic effect of Pt. This behaviour is exhibited especially at lower temperatures and on catalysts containing less Pt. The complex responsible for the peak at 2140 cm⁻¹ decomposes mainly in that stage.

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