[5] W. Feitknecht, Chem. and Ind. *5*, (9) 1, 102 (1959); W. Feitknecht, Helv. Chim. Acta *32*, (7) No. 205, 2, 294 (1949).
[6] U. R. Evans und D. E. Davies, J. Chem. Soc. London *2*, 607 (1951).
[7] R. Fresenius, Handbuch der analyt. Chemie III, S. 155, Springer Verlag Berlin 1949.
[8] C. F. Baes und R. E. Mesmer, The Hydrolysis of Cations. John Wiley and Sons, New York, London, Sydney, Toronto 1979.
[9] H. Falkenhagen, Theorie der Elektrolyte, S. Hirzel Verlag, Leipzig 1971.
[10] W. Nernst, Z. Phys. Chem. *4*, 372 (1889).
[11] I. M. Kolthoff und Kameda Tohru, J. Am. Chem. Soc. *53*, 832 (1931).
[12] P. Schindler, H. Althaus und W. Feitknecht, Helv. Chim. Acta *47* (4), No. 108, 982 (1964).

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The Formation of Isocyanates on Noble Metals and Supported Noble Metal Catalysts

F. Schüth and E. Wicke

Institut für Physikalische Chemie der Universität Münster, Schloßplatz 4, D-4400 Münster

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The formation of support-NCO and noble metal-NCO groups on oxide supported noble metal catalysts and high area evaporated metal films during the NO/CO reaction was studied by FTIR spectroscopy. With SiO_2 and Al_2O_3 as supports the results reported in the literature were essentially reproduced. With TiO_2 and ZrO_2 absorption bands in the region between 2000 and 2100 cm^{-1} were detected, which had not been described before. On evaporated metals NCO-groups could be detected in situ. They are located at 2185 cm^{-1} for Pd and at 2170 cm^{-1} for Pt. Based on kinetic measurements the spillover of NCO-groups from the noble metal to the support is proposed as a mechanism for support-NCO formation. For this spillover a connection between support and noble metal is necessary, which is formed during hydrogen treatment at elevated temperatures. This connecting species could be a noble metal/support intermetallic phase, as Pd_3Ti resp. Pt_3Ti.

1. Introduction

In investigations of the NO/CO reaction on supported noble metal catalysts by IR-spectroscopy, absorption bands in the region between 2000 and 2300 cm^{-1} occur that can not be attributed to adsorbed NO or CO. These bands were first detected by Unland [1–3] in the early seventies, and later on extensively studied by Solymosi and his group [4–7]. Unland and Solymosi identified these bands as isocyanate-bands.

Since this discovery great effort has been made to clarify the location of the isocyanates on the catalyst. At first it was assumed that isocyanates were adsorbed on the catalytically active metal [3, 5], but later on strong evidence for support-isocyanate species was found [8,9]. Especially the large differences in the frequencies of isocyanate absorption bands on noble metal catalysts with different supports led to this interpretation (Pt/TiO_2 2210 cm^{-1}, Pt/MgO 2241 cm^{-1}, Pt/Al_2O_3 2272 cm^{-1}, Pt/SiO_2 2318 cm^{-1} [9]).

Nevertheless, an isocyanate species was supposed to exist also on the surface of the metal, playing an important role in different reactions as synthesis of NH_4OCN or urea on Pt [10] or automotive exhaust control. For the latter case isocyanates may lead to undesired byproducts as ammonia [3, 6]. Moreover, it is reported that automotive exhaust control catalysts become deactivated by isocyanates [11, 12]. Niiyama [12] states that the deactivation of the catalyst is a mere blocking effect, whereas Lorimer and Bell [11] attribute the deactivation mainly to an electronic influence of support-isocyanate on the properties of the Pt. Crucial in this discussions is the question whether isocyanate-groups are present also on the metal during reaction. Evidence for metal-NCO was found only in the case of Pt [7]; in that work, however, spectra were not recorded in situ but only after cooling the catalyst down to room temperature after treatment with a reaction gas mixture at elevated temperatures.

The mechanism of isocyanate formation is not clear, too. There are two possibilities in principle: Spillover of N-atoms to the support and reaction with CO to isocyanate on the support, or formation of isocyanate on the metal with subsequent NCO-spillover [9].

In this work it will be shown that under reaction conditions isocyanate is not only located on the support but also on the metal, and that support-isocyanate is most probably formed by spillover of metal-isocyanate to the support via "alloy-bridges".

2. Experimental

2.1. Materials

All catalyst samples were prepared by a wet impregnation technique from metal nitrate solutions with pH 1 and subsequent freeze drying. About 35 mg of the catalyst powder were then pressed to a thin disk of 20 mm diameter and about 0.1 mm thickness. The preparation was completed by drying of these disks at 363 K in flowing N_2 for 2 h, calcination at 573 K in flowing N_2 for 12 h, and reduction at 723 K in flowing H_2 for 8 h. Catalysts were prepared with a nominal metal loading of 1 wt%. Very finely powdered oxides of high surface area were used as supports, i.e. Aerosil 200, Titania P25, Alumina C and a zirconia sample which is not commercially available*). Gases were supplied by Sauerstoffwerke Westfalen AG. CO 99.97 and N_2 99.998 were purified over molec-

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*) We are greatly indepted to Degussa AG for making available to us all those support materials.

ular sieves, NO was of 99.7 purity and could not be purified by a molecular sieve due to decomposition on such materials. It was therefore used without further purification. The main impurities, however, N_2O and N_2, do not influence the measurements.

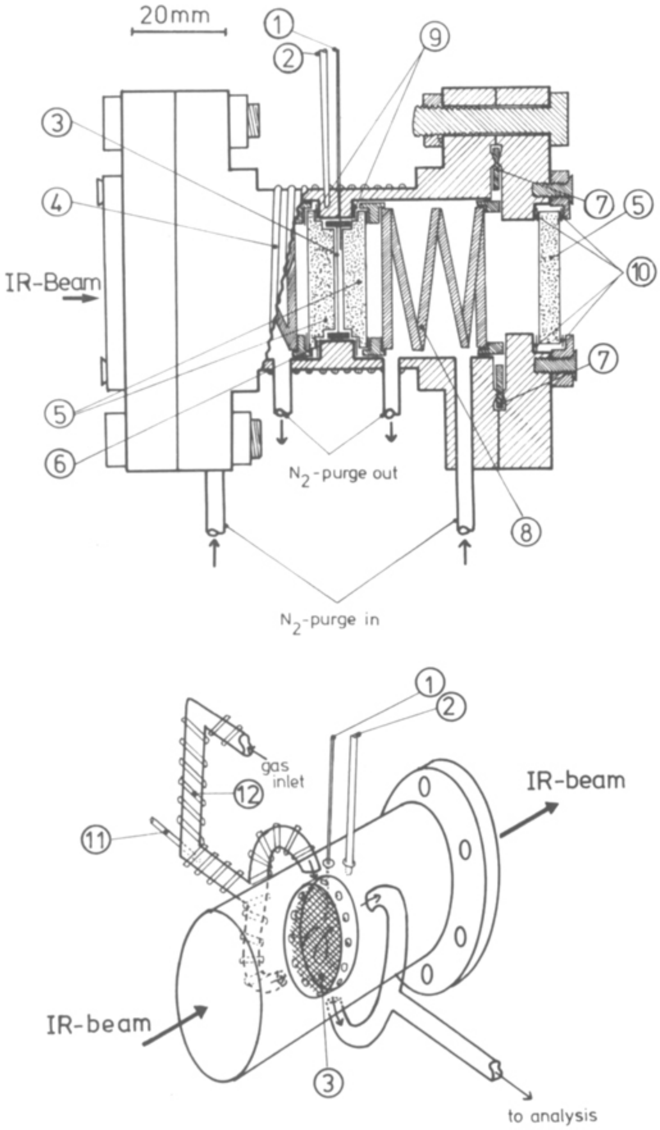

Fig. 1
IR cell reactor. a: schematic, b: gas flow scheme (purge tubings omitted here). ① 0.5 mm steel mantled thermocouple (catalyst temperature), ② 1.0 mm steel mantled thermocouple (reactor temperature control), ③ catalyst disk, ④ steel mantled heating conductor, ⑤ CaF_2-windows, ⑥ catalyst holder, ⑦ copper gaskets, ⑧ automotive valve springs, ⑨ graphite gaskets, ⑩ PTFE gaskets, ⑪ 1.0 mm steel mantled thermocouple (preheating control), ⑫ preheating

2.2. Methods

2.2.1. IR Measurements

The experiments were performed in a stainless steel infrared cell as shown in Fig. 1. The most important features of this reactor are the very thin layer of reaction gas mixture in the IR-beam (about 1 mm pathlength) and the possibility to heat it up to 800 K. This could not be achieved with PTFE as gasket material but only with graphite. Since graphite can not be pressed to absolute gas-tightness by the CaF_2-windows, the cell was made up of two compartments: The reaction chamber and a purge chamber, separated by the CaF_2-windows which were pressed against the graphite gaskets by an automotive valve spring. The sealing between reaction chamber and purge chamber is not absolutely gas-tight. So the outer (purge) chamber was purged with a 20 ml/s flow of N_2 to carry out traces of the reaction gases that would otherwise accumulate in the path of the IR-beam. The purge chamber was sealed against the atmosphere by a gas-tight flange with copper gaskets and PTFE-gaskets for the outer CaF_2-windows (PTFE could be used in this part of the cell because only the center part is heated).

The cell was heated in the center region by a metal mantled heating conductor that was controlled by a PID unit. The control thermocouple was welded into the reactor wall very near to the internal surface. Controlling via the gas phase temperature was also possible but never used, because the reactor originally was designed for the study of nonisothermal oscillations of the NO/CO reaction. The reactor temperature could be kept constant within ± 0.1 K.

Gases were supplied via thermal mass flow controllers and a mixing chamber. Spectra were taken with a Nicolet 5 SXB-E FTIR spectrometer which allowed kinetic measurements with a maximum time resolution of 1 s. Spectra presented in this paper are always ratiod against the spectra of the catalyst in a N_2-atmosphere, i.e. without absorption of reaction components, as background.

The infrared cell was part of an open flow system. In a typical experiment a gas flow of 10 ml/s was adjusted, composed of the appropriate reaction gases – NO, CO or both – and N_2 as balance. Spectra were taken always at reaction temperature (usually between 600 and 700 K). During preadsorption experiments the catalysts were exposed for a certain time to gas flows containing NO resp. CO in N_2, then the other component was added to the gas flow in the appropriate concentration. Conversions of NO and CO were always below 10% over the whole regime of reaction conditions investigated in this study.

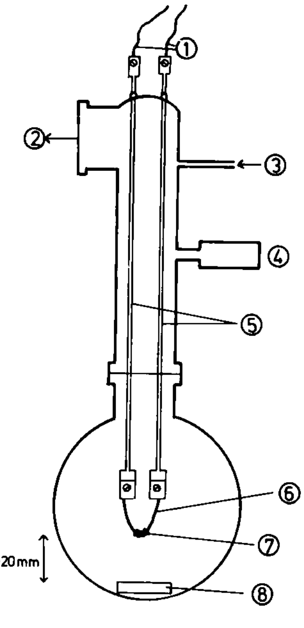

Fig. 2
Evaporation bulb. ① current supply, ② to mercury diffusion pump, ③ gas inlet, ④ pressure gauge, ⑤ 2.0 mm tungsten rods, ⑥ 0.4 mm tungsten wire, ⑦ 0.05 mm Pd- or Pt-wire, ⑧ substrate (CaF_2 single crystal)

2.2.2. Evaporation Technique

Evaporated metal films on CaF_2 single crystals were produced by a modification of the method described by Garland [13] (Fig. 2). The evaporation was done in a glass flask that could be evacuated to 10^{-2} Pa by a mercury diffusion pump. The metal was evaporated from a tungsten wire of 0.4 mm diameter around which a wire of the appropiate metal of about 30 mm length and 0.05 diameter was wound. Before evaporation the filament was degassed by heating the W-wire up to nearly the melting point of the metal to be evaporated. The evaporation itself was done by turning on a voltage of

20 V (yielding a current of about 15 A) for 1–2 s. In the case of Pd one flash was sufficient to evaporate an appropriate amount of the metal. For Pt several flashes were necessary. Due to alloy formation between tungsten and the noble metal the filament became very brittle and sometimes broke. In those cases it was replaced and degassed between subsequent flashes. During the evaporation an Ar-pressure of 200 Pa was maintained.

By this technique soot-like metal films with a sufficiently high surface area for investigation of adsorbates with IR-spectroscopy could be produced on the front plane of the CaF_2 single crystals.

Usually a metal loading of about 0.05 mg/cm^2 was achieved which reduced the transmittance of the crystals to 10–50%. By SIMS-analysis of those evaporated films no tungsten contamination could be found on the samples.

2.2.3. Treatment with Atomic Hydrogen

For some experiments the TiO_2 powder was treated with atomic hydrogen. Two methods of producing this species were applied: First thermal dissociation of H_2 on a tungsten wire under Knudsen conditions, and second dissociation of H_2 by UV-radiation from a Quartz-lamp under various pressures.

Table 1
Absorption bands in the Isocyanate region on different catalysts[1]

Catalyst	Band positions (cm^{-1}) this work	Band positions (cm^{-1}) literature
Pd/TiO_2	2207 vs, 2060 s, 2015 m	2210 s [9]
Pd/Al_2O_3	2268 vs, 2225 w	2272 s, 2138 w [9] 2264 s [3]
Pd/ZrO_2	2294 s, 2204 vs, 2046 vs	–
Pd/SiO_2	2298 w[2,3]	–
Pt/SiO_2	2294 s[3]	2318 s [9] 2304 vs [8] 2280 s [11] no bands [15]
Pt/Al_2O_3	2264 s, 2230 w	2267 s [3] 2260 vs [8]

[1] Band positions are not sensitive to temperature or gas phase concentrations. Therefore different conditions are not mentioned.

[2] Developed very slowly; reaction time 5 h at 583 K.

[3] Not present on all samples.

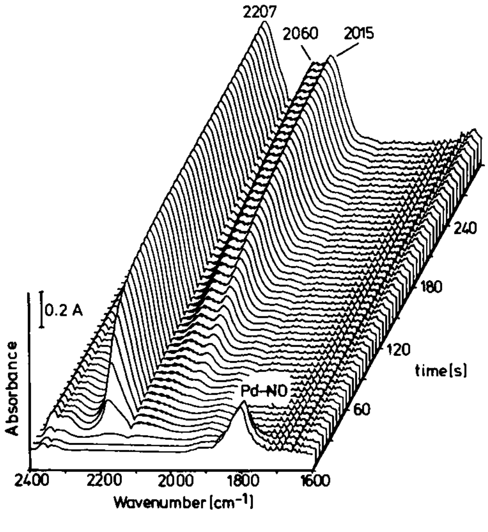

Fig. 3
Development of bands between 2300 and 2000 cm^{-1} on Pd/TiO_2. T = 553 K, 1% NO preadsorbed, after second spectrum 10% CO added

3. Results and Discussion

3.1. Isocyanates on the Support Surface

In our experiments with Pd or Pt as catalytically active metal on various supports (SiO_2, Al_2O_3, TiO_2 and ZrO_2) we could essentially reproduce results from literature (Table 1) with two exceptions:

On TiO_2 supported catalysts not only the band at 2207 cm^{-1}, described already by other groups, could be found but also two bands at about 2015 cm^{-1} and 2060 cm^{-1}. As indicated in Fig. 3, these bands develop slower from preadsorbed NO after addition of CO than the 2207 cm^{-1} absorption. Growing of the low frequency bands starts, when the 2207 cm^{-1}-band has nearly reached its maximum intensity.

The nature of these bands is not quite clear. Unland [3] identifies species with frequencies about 100 cm^{-1} lower than the main –NCO-bands as negatively charged –NCO-adsorbates. But there is also the possibility that these bands are products of a partial decomposition of –NCO-groups to surface cyanides and/or isocyanides.

Adsorption of HCN (prepared from KCN p.a. and 98% H_2SO_4 with subsequent drying over a molecular sieve filter) at 523 K on TiO_2 yielded four bands in the region between 2000 and 2200 cm^{-1} (2019 cm^{-1}, very weak; 2058 cm^{-1}, very weak; 2120 cm^{-1}, weak; 2200 cm^{-1}, medium). The bands around 2015 and 2060 cm^{-1} are much weaker than the bands produced by reaction of NO and CO on Pd/TiO_2, but different adsorption sites for –NC or –CN might be accessible by decomposition of –NCO than by simple HCN-adsorption.

It should be pointed out, however, that we can not give a definite proof of the nature of the appropriate species. There are too many adsorbates possible with frequencies in the region of interest as to allow adjoining a certain structure to a certain absorption band only on chemical reasoning [14]. To obtain decisive proofs isotope labelling experiments would be necessary.

Bands in the 2000–2100 cm^{-1} region were also observed on ZrO_2, but not with SiO_2 or Al_2O_3 as support (Table 1). This suggests that these species are formed by a process which can occur on oxides of the fourth transition metal group only.

The other difference to previous results of other authors is the behaviour of catalysts with SiO_2 as support. Formation of isocyanates absorbing around 2300 cm^{-1} could be detected on some of our catalyst samples only, whereas on catalysts from other charges no isocyanates could be found under reaction conditions. This observation is in agreement with work of Wolf and Regalbuto [15], who did not find isocyanates during NO/CO reaction on SiO_2-supported noble metal catalysts in an extended number of experiments over a large range of parameters. The ability of SiO_2-supported catalysts to form support-isocyanates seems to be very sensitive to the preparation conditions. The band position, too, seems to be sensitive to the preparation, since only for SiO_2 as support large differences occur in the band positions reported by different authors (Table 1). A possible explanation for this behaviour will be given below.

3.2. Isocyanates on the Metal Surface

The observable bands on supported catalysts described above originate all together from isocyanate groups adsorbed on the support. Whether isocyanates are present also on the noble metal surface during reaction is not yet quite clear. There are only the results of Raskó and Solymosi [7], who detected —NCO-species at room temperature after exposition of a Pt-sample (prepared by spraying of a methanolic metal solution onto a NaCl crystal with subsequent drying and reduction) to a NO/CO mixture at 473 K. But to our knowledge no in situ observation of isocyanates on unsupported metals during NO/CO reaction at elevated temperatures has been reported so far.

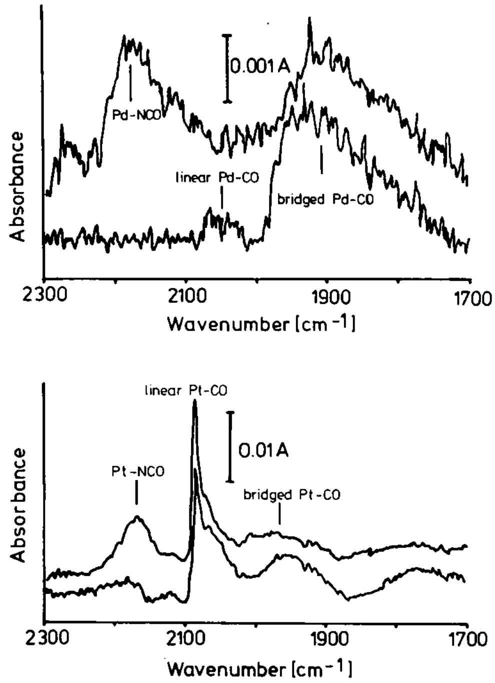

Fig. 4
Isocyanates on evaporated metal films. a: Spectra of Pd at 543 K, lower spectrum 1% CO, above 1% CO + 0.3% NO. CO gas-phase absorption bands are subtracted. b: Spectra of Pt at 493 K, lower spectrum 1% CO, above 1% CO + 0.7% NO

We were able to detect isocyanates on pure metal surfaces evaporated by the method described above. Figs. 4a and b show the spectra of CO alone and of a mixture of CO and NO on Pd at 543 K resp. Pt at 493 K. On Pd the —NCO band is located at about 2185 cm^{-1}, whereas on Pt this band is found at 2170 cm^{-1}. The measurements on such samples are very delicate, since the signal intensities are just above the noise level of the spectrometer, but the results for Pt are well in accordance with the room temperature measurement of Rasko and Solymosi, who found an —NCO absorption band on Pt at 2180 cm^{-1}.

Fig. 4 gives the spectra of NO/CO on evaporated metals at the highest temperature where a metal-NCO band was observable on the appropriate metal. The problem with evaporated films of high surface area is their strong loss in transmittance and surface area when heated well above 500 K. So the spectrum for Pd, recorded at 543 K shows large scatter. Spectra taken at lower temperatures were of better quality, as can be seen on Fig. 4b for Pt. In the case of Pt we raised the temperature up to 573 K, but under that conditions the scatter was larger than the intensity of the isocyanate band to be expected, thus we could not detect Pt—NCO-groups at that temperature.

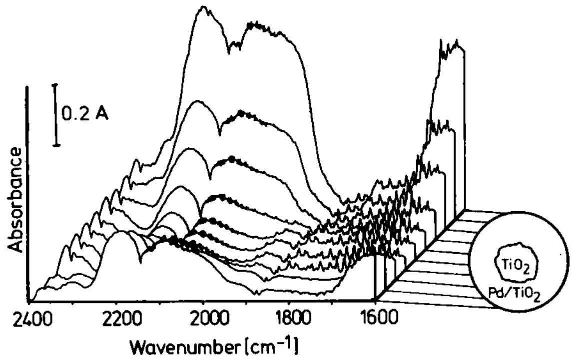

Fig. 5
Spatially resolved spectra of a catalyst disk consisting of TiO_2 in the center and Pd/TiO_2 in the annulus. The lines from the spectra to the drawing of the catalyst indicate the focus of the IR-beam. $T = 553$ K, 2% NO, 9% CO. Spectra are base line corrected

3.3. Mechanism of Spillover

As a mechanism for support-NCO formation a spillover of —NCO or —N from the metal to the support has been assumed [9]. A further possibility might be HNCO formation by reaction of NCO on the noble metal with traces of H_2 or H_2O from impurities and subsequent gas phase transport of HNCO to the support. In order to test this possibility, a catalyst disk was prepared, made of TiO_2 in the center and of Pd/TiO_2 around it as shown in Fig. 5. The catalyst disk was then exposed to reaction conditions (T = 553 K, 2% NO, 9% CO) and the IR-cell moved through the IR-beam from top to bottom. Every two mm a spectrum was recorded. During this procedure the IR beam was shielded to yield only a spot of about 2—3 mm diameter at the catalyst wafer for better spatial resolution. As Fig. 5 shows, isocyanates are found only in the Pd-loaded regions of the catalyst. The absorption bands are broad and not very well resolved. This is due to the fact that the IR intensity is strongly reduced by the shielding and that a small residue of the radiation only is transmitted in the spectral region of the absorption bands. This experiment showed, that support-NCO is neither formed directly on the support without Pd nor via gas phase transport of HNCO, but only by spillover of —N or —NCO from the catalytically active metal to the support material.

The spillover of the whole isocyanate group could be excluded — in favour of the spillover of N-atoms —, if the formation of support-NCO were faster than that of the metal-NCO. We therefore performed time resolved IR-studies with evaporated films on the one hand and TiO_2-supported catalysts on the other.

Figs. 6a and b show the development of the integral absorption intensity versus time in the isocyanate region on evaporated Pd resp. Pt after admission of NO to the CO/N_2 flow, to which the catalysts had been exposed before (the time resolution in the case of Pt is better because the Pt films can be produced in a better quality than the Pd films). The experiment shows that the isocyanate band develops very fast to its full intensity on the pure metal, i.e. in less than 5 to 10 s.

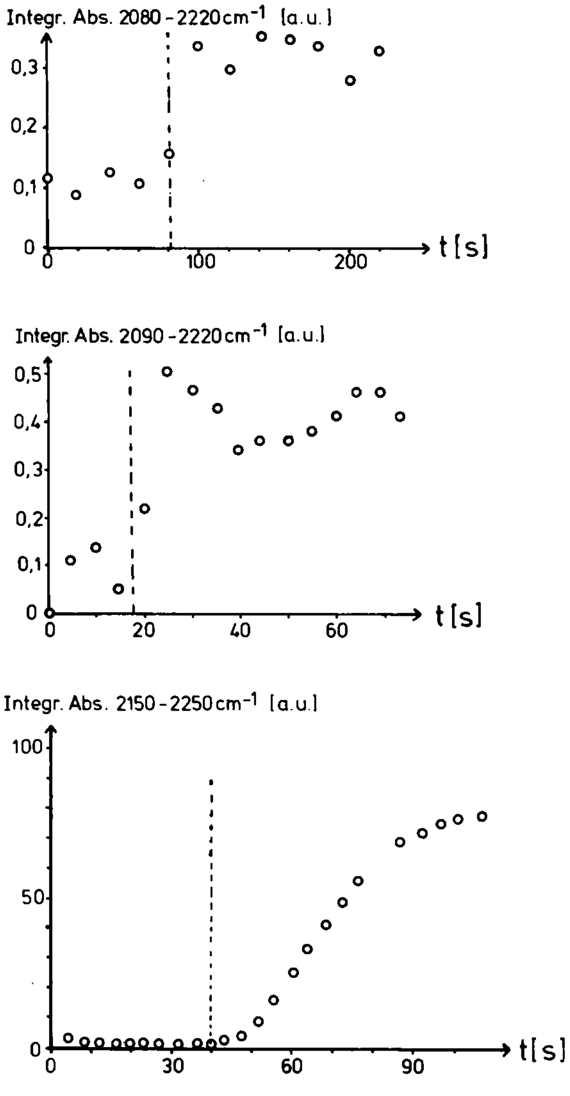

Fig. 6
Growing with time of the isocyanate bands on different samples with preadsorbed CO. First, 1% CO only in the gas-phase, then, at the dotted line addition of 0.7% NO. a: evaporated Pd, T = 478 K. b: evaporated Pt, T = 493 K. c: Pd/TiO$_2$, T = 548 K

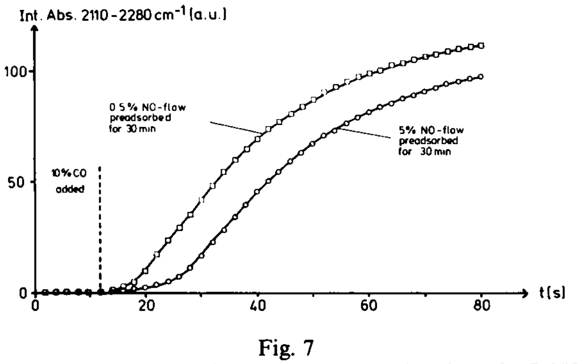

Fig. 7
Development with time of the support-NCO band on the Pd/TiO$_2$ catalyst at 580 K and NO preadsorption under different conditions before CO admission

As shown in Fig. 6c the formation of support-NCO on a Pd/TiO$_2$ catalyst at even higher temperatures takes an appreciably longer time, about 40 s. Accordingly, this experiment can not exclude spillover of the complete NCO-group.

With the Pd/TiO$_2$ supported catalyst we also performed experiments with preadsorption of NO to distinguish between the two mechanisms. To this aim the catalyst was exposed at 580 K for 30 min to a gas flow containing 0.5% NO and, alternatively, 5% NO. Then 10% CO were admixed to the gas flow and the emergence of −NCO (on the support) was followed by IR spectroscopy. Fig. 7 shows the results that are marked by two features: an induction period after the admission of CO that is appreciably longer in the case of the higher NO concentration and subsequently a constant slope, i.e. a constant rate of formation of support-NCO, almost independent of the NO content in the flow (the decreasing slope at longer times is due partly to decomposition of −NCO on the support, but mainly to the fact that the absorption in the center of the band grows to very high values so that the measured absorbance and the NCO concentration are not proportional any longer).

The induction period indicates that the CO-molecules first must remove a chemisorbed species from the metal surface before the formation of −NCO by a LH reaction can begin. This species is obviously a layer of O-atoms formed during the NO pretreatment by NO dissociation [16−18] with subsequent recombination of the N-atoms and desorption as N$_2$, or/and the LH reactions:

$$N_{ad} + NO_{ad} \rightarrow N_2 + O_{ad}$$

$$N_{ad} + NO_{ad} \rightarrow N_2O\,.$$

Because the processes of covering the metal surface with O-atoms from NO continue after CO admission, the induction period extends in time with increasing NO content in the gas phase.

If N-atoms (generated by NO dissociation on the metal and subsequent spillover to the support) were present at the support surface when CO is admitted to the catalyst, such an induction period would not be expected. In this case, −NCO groups on the support could be formed only by an ER mechanism between the −N-atoms at the support and CO from the gas phase, i.e. the −NCO formation would start immediately after the admission of CO. (The Langmuir-Hinshelwood mechanism would not be possible in this case, since CO adsorbs only weakly on TiO$_2$ at room temperature [19] and does almost not adsorb on TiO$_2$ at elevated temperatures higher than 363 K [20].)

There is, however, the possibility that N-atoms on the support can desorb quite readily as N$_2$. In that case support-N formed during the preadsorption time of NO would be completely desorbed before CO is admitted to the gas phase. To examine this possibility, we added CO to the gas phase during still increasing NO chemisorption (indicated by a still growing NO absorption band). Also in this case, however, similar curves to those presented in Fig. 7 were measured, i.e. no immediate slope of the IR absorption in the NCO region was observed.

Accordingly we suggest the spillover of whole the −NCO-group, formed on the metal from chemisorbed N-atoms either by a Langmuir-Hinshelwood reaction with chemisorbed CO, or by an Eley-Rideal mechanism with gas phase CO, as the most probable mechanism for support-NCO formation.

The almost equal slope of the two curves in Fig. 7, i.e. equal rate of NCO accumulation on the support, that establishes after the induction period, suggests that the rate of NCO formation on the metal surface is nearly independent of the NO concentration in the gas phase. This leads to the assumption that the chemisorption sites at edges, corners and other defects at the metal surface, where the NO molecules preferably dissociate [21–23], are saturated with NO in the concentration range applied here in the gas flow. This would mean, that the number of N-atoms produced by NO dissociation would be nearly independent of the NO content in the gas phase, and so would be the fraction of the N-atoms transformed by chemisorbed CO to NCO-groups. With smaller CO admission, i.e. 1% instead of 10%, the rate of NCO formation decreased appreciably, because then a larger fraction of the N-atoms could recombine and desorb as N_2 instead to react with CO to NCO groups.

This assumption, however, needs to be confirmed by more systematic investigations over a wider range of gas phase concentrations.

3.4. “Bridging” between Noble Metal and Support

Solymosi et al. [9] proposed carbon atoms originating from the dissociation of CO as connection between noble metal and support, via which –NCO spills over to the support. This, however, seems not to be very probable, since there is only little evidence for dissociative adsorption of CO at noble metals. Only Doering [24] found hints for dissociative CO adsorption on evaporated Pt particles with low crystallite size.

In order to find out what type of contact is required between noble metal and support for –NCO transfer, a catalyst, prepared by mechanical mixing of 10 wt% Pd black and 90 wt% TiO_2 powder was investigated. On such a mixture no isocyanates could be found over whole the regime of reaction conditions for which support-NCO on the catalysts prepared by wet impregnation were found (Fig. 8, curve a).

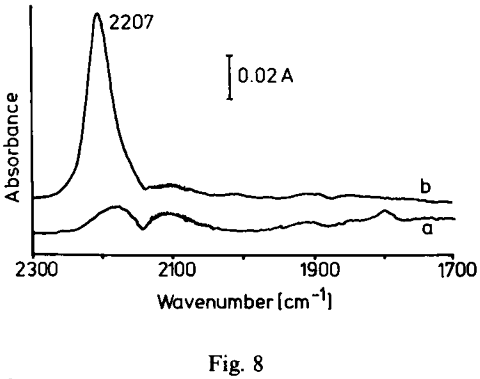

Fig. 8
Spectra of a mechanically mixed Pd-black/TiO_2 catalyst at T = 548 K, 0.7% NO, 2.5%CO. Curve a: fresh catalyst pretreated for 1 h in O_2 at 723 K. Curve b: Same catalyst pretreated for 1 h in H_2 at 723 K

Only after treatment of the mixture with H_2 at 723 K for 3 h isocyanates could be detected under reaction conditions (Fig. 8, curve b) similarly to impregnated catalysts. This behaviour could not be produced by heating the mechanically mixed contact in air or N_2, neither by treating pure TiO_2, with H_2 at 723 K and subsequent mixing with Pd black. On the contrary, a reduction step with Pd and titania in contact is necessary to create a state of the catalyst in which support-NCO can emerge.

There are two possible explanations for this behaviour: 1. Atomic hydrogen formed by dissociative H_2 adsorption on the noble metal creates Ti^{3+}-centers on the titania which act as acceptor sites for the isocyanates, or 2. A new chemical compound is formed at the boundaries of the noble metal crystallites during reduction.

The first hypothesis was checked by treatment of TiO_2 with atomic hydrogen produced either by thermal dissociation of H_2 under Knudsen conditions or by UV dissociation.

TiO_2 treated with thermally dissociated H_2 was completely intransparent to IR radiation and disks pressed from this material showed a metallic shine. The high temperatures near the hot tungsten wire and the presence of atomic hydrogen probably reduced the titania to metallic titanium. By dilution of the hydrogen treated TiO_2 with untreated titania IR transparent disks could be produced. However, under reaction conditions no isocyanates could be detected on this samples, no matter, whether Pd black was added or not.

To avoid the high temperatures involved in the thermal dissociation process, TiO_2 was filled into a quartz bulb and exposed to a hydrogen atmosphere under UV-radiation. This procedure resulted in a slight grey-blue colour of the titania as long as no oxygen contacted the material. After oxygen admission this colour disappeared very quickly. Probably Ti^{3+}-centers were formed, which are, however, not stable against oxygen [25]. The TiO_2 treated in this manner also showed no isocyanates under reaction conditions after mixing with Pd black.

It must be concluded therefore that a chemical compound is formed during reduction at the boundaries of the noble metal crystallites that might be PdTi resp. PtTi or Pd_3Ti resp. Pt_3Ti. Such phases are well known in both systems and might be related to the SMSI effect described for the first time by Tauster et al. [26].

There are at present two different mechanisms to explain the SMSI effect. First the encapsulation of the noble metal crystallites by support suboxides and second the formation of intermetallic phases during reduction in the catalyst preparation.

The catalysts investigated in this study are not yet in the SMSI-state, because CO adsorption is not blocked. However, at the boundaries of the noble metal crystallites alloy “bridges” might be formed as a first stage of SMSI, which facilitate –NCO spillover to the support. The formation of such phases was proven by Beard and Ross [27] in the case of Pt/TiO_2, and by Schulz-Eckloff et al. [28] for Pd/SiO_2. Resasco et al. [29] could deconvolute their XANES data of Rh/TiO_2 catalysts best with Rh plus a contribution from species approximated as Rh_3Ti. This deconvolution was less satisfying, however, at samples reduced at higher temperatures. In these cases TiO_x species might have formed, involving Rh – Ti bonds.

The observations of Schulz-Eckloff et al. could possibly explain the somewhat embarrassing results for SiO_2 supports mentioned above: They report that the formation of Pd_3Si phases (detected by electron micro diffraction) is very sensitive to the hydration state of the SiO_2, i.e. the amount of surface hydroxyl groups, and the reduction temperatures. Especially the first point was not controlled in our experiments and is not reported by Solymosi et al., who always found isocyanates on SiO_2. In connection with the well known difficulties in producing SMSI with SiO_2 this might be the explanation, why on some SiO_2 supported catalysts isocyanates were found and on others not. Depending on the pretreatment of the catalysts alloy "bridges" were formed during reduction or could not develop.

It should be noted, though, that also Ti suboxides could be the "bridging species". However, very sophisticated analytical methods will be necessary to distinguish between these possibilities.

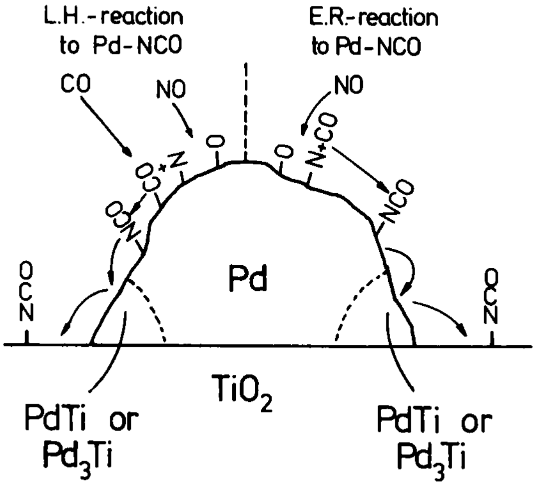

Fig. 9
Model of catalyst and spillover-reaction

3.5. Conclusions

Based on previous work of other authors and on own findings we propose a model for support-isocyanate formation as outlined in Fig. 9: Isocyanates are formed on the noble metal by reaction of N-atoms and CO (most probably by a LH-, but possibly also by an ER-mechanism) and spillover to the support via alloy "bridges".

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References

[1] M. L. Unland, Science *179*, 567 (1972).
[2] M. L. Unland, J. Phys. Chem. *77*, 1952 (1973).
[3] M. L. Unland, J. Catal. *31*, 459 (1973).
[4] F. Solymosi and J. Sárkány, React. Kinet. Catal. Lett. *3*, 297 (1975).
[5] F. Solymosi, J. Sárkány, and A. Schauer, J. Catal. *46*, 297 (1977).
[6] J. Raskó, L. Völgyesi, M. Lanes, and F. Solymosi, Proceedings ICC Berlin III, 671 (1984).
[7] J. Raskó and F. Solymosi, J. Catal. *71*, 219 (1981).
[8] R. A. Dalla Betta and M. Shelef, J. Mol. Catal. *1*, 431 (1975/76).
[9] F. Solymosi, L. Völgyesi, and J. Sárkány, J. Catal. *54*, 336 (1978).
[10] R. J. H. Voorhoeve and L. E. Trimble, J. Catal. *53*, 251 (1978).
[11] D. Lorimer and A. T. Bell, J. Catal. *59*, 223 (1979).
[12] H. Niiyama, M. Tonaka, H. Ida, and E. Echiyaga, Bull. Chem. Soc. Jpn. *49*, 207 (1976).
[13] C. W. Garland, R. C. Lard, and P. F. Troiano, J. Phys. Chem. *69*, 1188 (1965).
[14] B. A. Morrow and I. A. Cody, J. Chem. Soc. Faraday Trans.-I, *71*, 1021 (1975).
[15] E. E. Wolf and J. Regalbuto, private communication.
[16] B. E. Nieuwenhuys, Surf. Sci. *126*, 307 (1983).
[17] P. W. Davies and R. M. Lambert, Surf. Sci. *110*, 227 (1981).
[18] H. Conrad, G. Ertl, J. Küppers, and E. E. Latta, Faraday Disc. Chem. Soc. *58*, 116 (1975).
[19] C. Morterra, G. Ghiotti, E. Garrone, and E. Fisicaro, J. Chem. Soc. Faraday Trans.-I, *76*, 2102 (1980).
[20] M. Primet, J. Bandiera, C. Naccache, and M. V. Mathieu, J. Chim. Phys. *67*, 535 (1970).
[21] H. D. Schmick and H. W. Wassmuth, Surf. Sci. *123*, 471 (1982).
[22] W. F. Banholzer and R. T. Masel, J. Catal. *85*, 127 (1984).
[23] P. W. Davies and R. M. Lambert, Surf. Sci. *110*, 227 (1981).
[24] D. L. Doering, H. Poppa, and J. T. Dickinson, J. Catal. *73*, 104 (1981).
[25] K. H. Stadler and H. P. Boehm, Z. Phys. Chem. Neue Folge *144*, 9 (1985).
[26] S. Tauster, S. Fung, and R. Garten, J. Am. Chem. Soc. *100*, 170 (1978).
[27] B. C. Beard and P. N. Ross, J. Phys. Chem. *90*, 6811 (1986).
[28] R. Lamber, N. Jaeger, and G. Schulz-Eckloff, to be published.
[29] D. E. Resasco, R. S. Weber, S. Sakellson, M. McMillan, and G. L. Haller, J. Phys. Chem. *92*, 189 (1988).

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