

Catalytic properties of high surface area titanium nitride materials

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Abstract

Titanium nitride materials with specific surface areas up to $200 \text{ m}^2 \text{ g}^{-1}$ are tested in hydrogen transfer reactions. The TiN nanoparticles are obtained using pyrolysis reactions of donor-stabilized titanium halide precursors in ammonia atmosphere at high temperatures (973–1273 K). The particles catalyze the reduction of alkynes to alkenes with complex hydrides such as NaAlH_4 in solution. Titanium nitride nanoparticles significantly accelerate the reduction of diphenylethyne (DPE) to stilbene. A high selectivity for *Z*-stilbene is observed for the TiN-catalyzed reaction whereas in the uncatalyzed reaction *E*-stilbene is the predominant product. The reduction of DPE to *E:Z*-stilbene is used as a test reaction to study the catalytic properties of the materials with respect to the specific surface area of the nanoparticles. The highest activity and selectivity is observed for catalysts synthesized at 973 K. Filtration tests and recycling of the catalysts indicate that the reaction mechanism is heterogeneous and not homogeneous. NMR spectra of the intermediates formed in the course of the reduction are consistent with the presence of hydroalumination intermediates.

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1. Introduction

In recent years, there has been considerable interest in the development of transition metal nitrides for catalytic applications. They have a high sintering and poisoning resistance and a variety of applications in hydrogenation, hydrogenolysis, dehydrogenation, ammonia synthesis, and Fischer–Tropsch synthesis have been explored [1]. Tungsten and molybdenum nitride have been studied most frequently. They are generally considered to have similar catalytic properties as platinum metals due to similarities in the electronic structure. Several studies have also focused on vanadium, niobium, and chromium nitride for catalytic applications [2,3]. Silicon nitride has been developed for solid base applications [4–7], boron nitride as a support [8] and even rhenium nitride was active in hydrodenitrogenation reactions [9].

For titanium group nitrides, to our knowledge, catalytic applications have not been reported. Only in combination

with iron, titanium nitride has been studied for ammonia synthesis [10]. Recently, we have developed a new synthesis route to high surface area titanium nitride materials with specific surface areas exceeding $200 \text{ m}^2 \text{ g}^{-1}$ [11]. Surprisingly, we found that ultrafine TiN powders catalyze the decomposition of complex aluminum hydrides after mixing via ball milling at temperatures of about 393 K in the solid state [12,13]. These results motivated us to further investigate the activation of complex hydrides for hydrogen transfer reactions in solution. We have therefore studied the reaction of diphenylethyne with NaAlH_4 in aprotic solvents using ultrafine titanium nitride as a solid, highly dispersed activator. In this reaction titanium nitride can be used to enhance the reaction rate but interestingly, also the selectivity is significantly affected. In the following we describe the performance of ultrafine titanium nitride materials prepared from various precursors with specific surface areas ranging from 100 to $200 \text{ m}^2 \text{ g}^{-1}$. The conditions and kinetics of the reaction are analyzed and optimized and a mechanism for the reaction is proposed.

The DPE reduction is used as a test reaction to characterize the materials and optimize the preparation conditions

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of the catalyst. Since hydroaluminations can also be used for the synthesis of carboxylic acids, deuterated products, or vinyl halides via quenching with CO₂, D₂O, or Br₂ [14], the method is also a valuable organic synthesis tool. However, as compared with molecular catalysts like Cp₂TiCl₂ that are known to catalyze hydroaluminations [14], the titanium nitride materials described here are solid catalysts and can be separated by centrifugation. Moreover, they can be re-used several times which is an advantage as compared to molecular catalysts.

2. Experimental

2.1. General remarks

All operations were performed using a glove box (Argon, O₂ < 1 ppm, H₂O < 1 ppm) or a vacuum line and dry solvents.

2.2. Catalyst synthesis and characterization

TiCl₄ (9.0 g, 47.5 mmol, Aldrich, 99.9%) was diluted with pentane to a 6% solution. The ligand L (THF, 142.5 mmol, in pentane; 2,2'-bipyridine, 49.8 mmol, in toluene) was added slowly to the TiCl₄ solution. For L = NH₃ gaseous ammonia (UHP, Messer) was dosed to the solution. The precipitate was filtered out, dried in vacuum ($p < 10^{-4}$ mbar) and filled in a ceramic boat. The boat was placed in a horizontal quartz tube ammonia flow reactor (60 ml min⁻¹) and heated with a rate of 5 K min⁻¹ to the final temperature (typically 973 K) and annealed at that temperature for 1 h to give a black ultrafine powder.

BET surface areas were measured using a micromeritics 2000 instrument. X-ray powder diffraction (XRD) patterns were recorded on a STOE diffractometer equipped with a position sensitive detector and a germanium primary beam monochromator in the transmission mode using Cu K α 1 radiation (1.54051 Å). For the XRD measurements the dried powders were filled into 0.5 mm capillaries and sealed under argon. A detailed description of the materials properties is reported in [11].

2.3. Catalytic tests

The catalytic test reactions were carried out at 328 K in the liquid phase using THF as the solvent. NaAlH₄ (Chemetall) was purified by re-crystallization in THF. A suspension of high surface area titanium nitride (0.1 mmol) was prepared by stirring with NaAlH₄ (1.8 mmol) in THF at 328 K. Dry diphenylethyne (1.0 mmol, Merck, >98%) was added at 328 K. The product composition was determined using GC–MS (internal standard: hexadecane). Prior to analysis the solutions were hydrolyzed at 293 K in order to separate excess NaAlH₄ and subsequently dried with Na₂SO₄.

3. Results and discussion

3.1. Catalyst preparation and characteristics

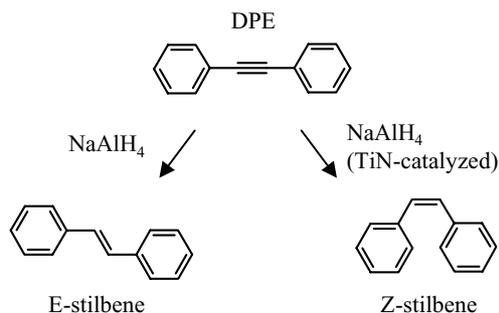
We have used a ligand-assisted ammonolysis for the preparation of high surface area titanium nitride-based materials [11]. In this reaction, TiCl₄ complexes are used as precursors. They are converted at high temperature (973–1273 K) into titanium nitride. The heat treatment is carried out in an anhydrous ammonia atmosphere.



In this reaction, L is a donor ligand such as NH₃, an amine, a bipyridine, or an ether. In the course of the reaction, the donor ligand as well as chlorine is gradually replaced by nitrogen. The role of the donor ligand is to lower the sublimation temperature of the titanium precursor and thus increase the ceramic yield. For pyrolysis temperatures of 973 K or higher, the peaks of crystalline TiN are detected in the XRD patterns and the chlorine content is typically below 1%. In addition, high surface area titanium nitride synthesized using organic donor ligands contains carbon impurities (up to 5%) due to incomplete removal of the organic ligand. The carbon-containing impurities are structurally related to carbon deposits observed in coked catalysts [11]. TEM studies and peak shape analyses of Bragg reflections show that the ultrafine powders consist of very small titanium nitride particles (7–20 nm diameter). Typically, the powders have specific surface areas ranging from 100 to 200 m² g⁻¹, depending on the precursor and heat treatment used. Thus, the precursor chemistry is used to direct the formation of the TiN nanoparticles and control size and morphology [11]. Since particle size and morphology affect the performance of solid catalysts, the test reaction described here allows to study relations between texture and catalytic properties.

3.2. Catalytic properties

The activation of NaAlH₄ by titanium nitride for hydrogen storage applications was an accidental discovery and only guided by the fact that titanium nitride catalyzes the decomposition of NaAlH₄ [12,13]. Hereafter, we concluded that it should be possible to use the activation also for a transfer of hydrogen from the complex alanate to an organic substrate. Out of several substrates, diphenylethyne (DPE) was found to be suited to evaluate the catalytic properties of titanium nitride. Whereas the uncatalyzed reduction of carbonyl compounds and nitriles with NaAlH₄ proceeds rather fast, the uncatalyzed reduction of DPE is relatively slow at moderate temperatures (328 K). In addition, only two products are obtained after quenching the solution with water, *Z*- and *E*-stilbene (Scheme 1). This reduction can also be carried out with molecular hydrogen and as such is probably not of any commercial interest. However, it is suited to study the catalytic properties of the ultrafine powders and



Scheme 1. Selectivity differences for the TiN-catalyzed diphenylethyne (DPE) reduction with NaAlH₄ and the uncatalyzed reduction.

serves as a characterization and optimization technique for the titanium nitride nanoparticles in this study.

3.2.1. General observations

Initially, we have compared the reaction of NaAlH₄ and diphenylethyne with and without ultrafine TiN. In general, we have used an excess of NaAlH₄ with respect to the substrate DPE. In the first experiments, a molar TiN:NaAlH₄ ratio of 1:3 was used at 328 K in THF using fresh prepared high surface area titanium nitride. Fig. 1 shows the concentrations of DPE, Z- and E-stilbene for the reaction carried out with (a) and without (b) addition of titanium nitride. The reaction rates are clearly different. For the uncatalyzed

reaction, an exponential decrease of the educt concentration is observed and conversion is complete after 24 h. On the other hand, for the reaction containing TiN nanoparticles the reaction is much faster and approaches 99% conversion after 5 h. For the catalyzed reaction, the rate is lower in the beginning of the reaction as compared with the uncatalyzed reaction (Fig. 1, upper part) which could in principle indicate a depletion of NaAlH₄ in solution due to the adsorption of NaAlH₄ on the outer surface area of the particles. If coordination of NaAlH₄ to the outer surface area would in this way reduce the reaction rate, an increase of catalyst concentration would lead to a decrease in the reaction rate in the beginning of the reaction. However, we did not observe a further decrease in the reaction rate in the beginning of the reaction if the TiN concentration is increased to a ratio of 1.5:1.7 (NaAlH₄:TiN), but an increase of the reaction rate is observed and the DPE concentration is reduced to 50% after 2.5 h reaction time.

In addition, significant selectivity differences were observed for the catalyzed and the uncatalyzed reaction (Fig. 1, lower part). The uncatalyzed reaction (b) gives predominately the thermodynamically more stable E-stilbene and the ratio of E- to Z-stilbene is typically 70:30. However, a complete reversal of the selectivity is observed if TiN nanoparticles are added to the reaction. Under such conditions, Z-stilbene is the predominant product and typically 80% Z-stilbene and only 20% E-stilbene are obtained (a). The comparison of the uncatalyzed (b) and the catalyzed reaction (a) clearly demonstrate the effect of titanium nitride addition. The reaction is significantly accelerated and the product selectivity is reversed.

3.2.2. Heterogeneity tests

Alanate activation effects, similar to those described above, were also observed with molecular catalysts [14]. Typically, the addition of molecular titanium catalysts to alanates results in the formation of a blue-violet solution, often assigned to a hydride formation [15], but only little is known about the nature of the reduced species. The blue color is probably an indication for a colloid formation. The reduction of TiCl₄ with borohydrides for example has been reported to result in the formation of titanium metal colloids [16,17]. Thus, in the case of molecular catalysts it can not be completely ruled out that the colloids are the species that provide active sites for the reaction. On the other hand, for a solid catalyst discussed here, leaching, chemical transformation, or particles dissolving in the course of the reaction could result in the formation of molecular species that act as the catalyst.

In order to separate homogeneous and heterogeneous contributions, we have used filtering tests [18]. The TiN-catalyzed DPE reduction was carried out to a conversion of 90%. Subsequently, the solid catalyst was separated from the solution by centrifugation (10,000 rpm, 30 min). After separation of the supernatant solution (a) from the solid (b), fresh DPE and NaAlH₄ was added again to (a)

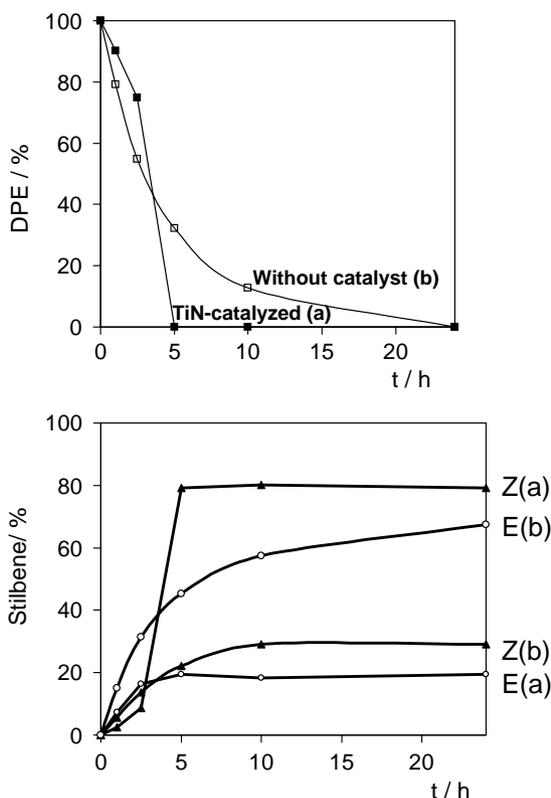


Fig. 1. Kinetics of the DPE reduction (a) with and (b) without ultrafine titanium nitride (concentration of DPE, Z- and E-stilbene in mol%).

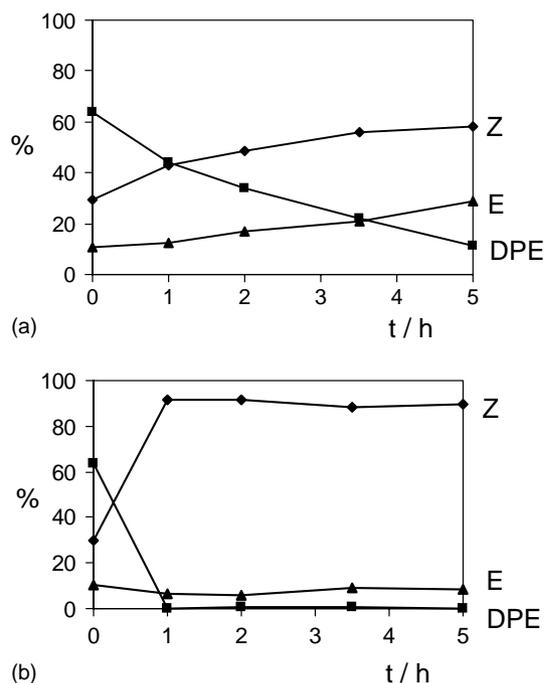


Fig. 2. Heterogeneity test for the TiN-catalyzed reaction. After 5 h, the solid was separated from the solution and DPE and NaAlH_4 were added again. (a) Concentration of DPE, Z- and E-stilbene for the supernatant; (b) for the catalyst particles.

and (b). Fig. 2 shows the concentration of DPE and the products in both experiments: After substrate addition, over the solid catalyst (b) complete conversion is attained after 1 h. On the other hand, the reaction rate in the solution (a), separated shortly before, is much lower and comparable to the rate of the uncatalyzed reaction (Fig. 1, (b)). Over the solid material also the Z:E ratio is high (9:1) whereas in the homogeneous solution reaction the Z:E ratio is decreasing (Fig. 2, a). The latter is due to the predominate formation of E-stilbene favored in the uncatalyzed reaction (above). Comparison of the reaction rate and selectivity in (a) and (b) support the finding that the high Z-selectivity and increased reaction rate after addition of the titanium nitride nanoparticles are due to the presence of the solid catalyst and not due to dissolved molecular species and homogeneous reaction pathways. Only in some special cases homogeneous mechanisms were not identified as such in filtration tests due to re-precipitation of the molecular species on a support [19]. However, in such cases the solution was separated from the solid after complete conversion and thus the educt, necessary for stabilization of the molecular species, was spent. In contrast, here the reaction was stopped at 90% conversion.

The heterogeneity tests are also in agreement with alanate activation carried out as a solid state reaction for hydrogen storage applications if it is assumed that the activation mechanisms induced by TiN are comparable. In the solid state, the formation of molecular species is improbable but a high dispersion of the catalyst particles is crucial for effective activation [12,13].

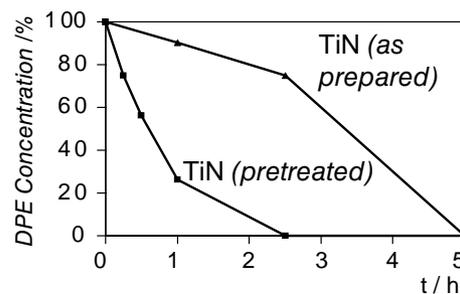


Fig. 3. DPE conversion over the *as prepared* TiN and a pretreated TiN catalyst.

3.2.3. Induction period

Even though dissolution of the particles and formation of homogeneous catalysts can be ruled out, a transformation of the particle surface seems to occur according to our results. We have observed an induction period in the catalytic conversions and obviously 1 or 2 h of catalyst pretreatment are beneficial to obtain the highest activity for the TiN nanoparticles. This induction period is most clearly detected by comparing the reaction rates over *as prepared* titanium nitride nanoparticles and a sample that was stirred for 2 h at 328 K in NaAlH_4 solution (Fig. 3). The activated catalyst shows an exponential decrease of the DPE concentration with time and complete conversion is attained within 3 h. In contrast, the *as prepared* catalyst shows an increasing reaction rate (slope) and conversion is complete after 5 h. Thus, kinetics and total conversion time are completely different for a fresh and a pretreated sample and indicate a formation period for the catalyst. The nature of such an activation could for example be the formation of Ti–H groups on the surface of the particles. The latter would also explain the similarities of the catalytic effects observed with molecular catalysts and the titanium nitride nanoparticles if the formation of blue–violet titanium hydride colloids from molecular species such as TiCl_4 is accepted. Such hydride colloids could have similar catalytic properties, i.e. surface chemistry as compared with surface-modified TiN.

3.2.4. Reuse of the catalyst

The high activity of the solid catalysts also allows to reuse high surface area titanium nitride several times. By centrifugation, the solid can be separated and used in a new reaction. In our case, we have used the catalyst up to four times. Fig. 4 shows the conversion of DPE with time. The catalyst deactivates, but after four runs the conversion is still significantly higher (>99% after 2 h) as compared with the uncatalyzed reaction. Moreover, the Z-selectivity in all four runs is higher than 80% whereas in the uncatalyzed reaction it is typically only 30% (Z). The fact that the solid powder can be used several times furthermore supports that the reaction mechanism is heterogeneous. The reason for the deactivation is unknown. A disadvantage of the nanoparticles is the difficulty of separation. Thus, in some cases the particles form colloidal dispersions that are difficult to filtrate and have

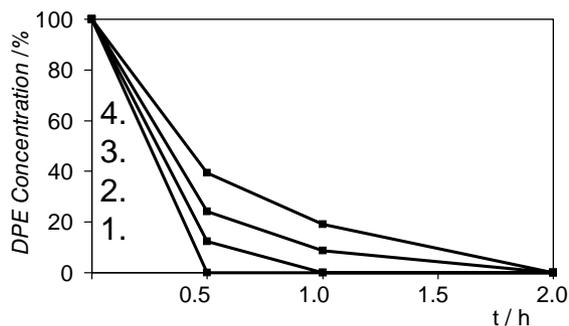


Fig. 4. DPE conversion for a TiN material used in 1–4 cycles.

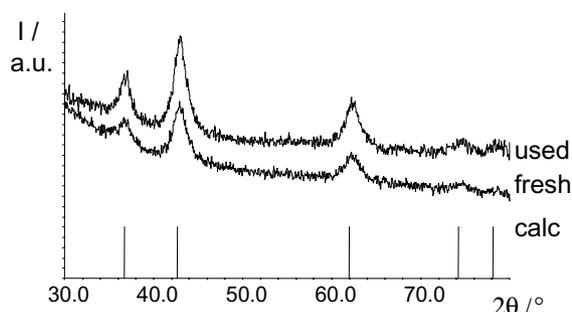


Fig. 5. Powder X-ray diffraction pattern of the *as prepared* TiN (bottom) and the used catalyst (top).

to be centrifuged. One reason for deactivation could thus simply be the fact that some of the smaller particles are not completely separated and are not available for the following cycle. Another reason is a decrease in the specific surface area. For example, a fresh prepared catalyst with a surface area of $160 \text{ m}^2 \text{ g}^{-1}$ had a reduced surface area ($65 \text{ m}^2 \text{ g}^{-1}$) after stirring in a NaAlH_4 solution (THF) for 2 h. However, the reason for such a reduced surface area can also be agglomeration of the particles during isolation and activation for the BET measurement or incomplete removal of adsorbed NaAlH_4 . On the other hand, catalysts isolated after repeated use can still be identified as nanocrystalline TiN in powder X-ray diffraction patterns. A rearrangement in the bulk structure is not observed (Fig. 5). The peaks of the fresh and the re-used material appear at the same positions.

In the case of TiH_2 formation, the increased lattice constant would result in a peak shift and for titanium metal with the bcc structure a pattern different from that of TiN would be expected. Wet chemical analyses show only a slight decrease in the N:Ti ratio (2%) which also confirms the intact bulk structure of TiN after repeated use in the reduction reaction. However, elemental analyses also indicate an increasing amount of aluminum (7.2%) adsorbed on the outer surface of the re-used catalyst after washing and drying. NaAlH_4 decomposition products could be the reason for the deactivation.

3.2.5. Catalyst to alanate ratio

For a high reaction rate and selectivity, high catalyst:alanate ratios are beneficial. With almost stoichiometric amounts of TiN, Z-selectivities up to 90% are observed. Lower TiN:alanate ratios give lower reaction rates but still a high Z-selectivity (Fig. 6). For example, a molar NaAlH_4 :DPE:TiN ratio of 1.8:1:0.1 still gives over 90% conversion after 5 h and a Z-selectivity over 70%.

3.2.6. TiN source

The effect of the TiN precursor on the catalytic properties was also studied using the hydrogen transfer reaction. Titanium nitride nanoparticles prepared from (a) $\text{TiCl}_4(\text{THF})_2$, (b) $\text{TiCl}_4(4,4'\text{-BPY})$, and (c) $\text{TiCl}_4(\text{NH}_3)_2$ were compared. The nanoparticles were all prepared at the same temperature (973 K) by pyrolysis in a NH_3 atmosphere. The reaction rates over the different catalysts are comparable (Fig. 7). Only TiN from $\text{TiCl}_4(\text{THF})_2$ (a) shows a somewhat lower reaction rate. The selectivity is also similar for all samples and close to 90% (Z) after 2 h. Obviously, the catalytic properties do not critically depend on the precursor for the nitride synthesis even though the powders differ significantly in the specific surface area. In fact, (a) has the highest surface area ($200 \text{ m}^2 \text{ g}^{-1}$) whereas for (b) and (c) S_g is lower (b: $140 \text{ m}^2 \text{ g}^{-1}$; c: $90 \text{ m}^2 \text{ g}^{-1}$) and thus (a) should give a higher reaction rate. Therefore, the powders must also vary slightly in the surface chemistry or composition. Organic ligands may hinder sintering and produce higher surface areas in the synthesis of TiN nanoparticles due to the formation of a protective coke coating, but the latter can also lead

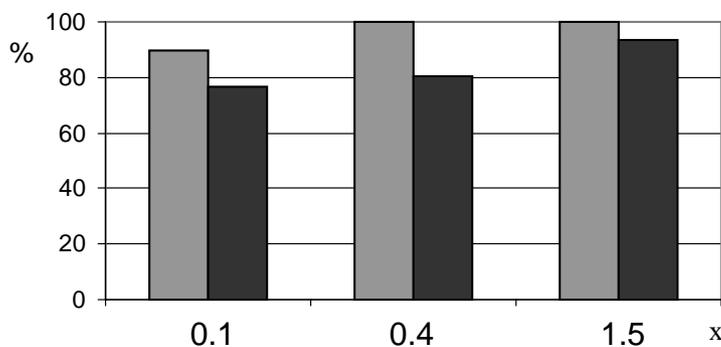


Fig. 6. Variation of the molar catalyst:alanate ratio (NaAlH_4 :DPE:TiN = 1.8:1.0:x; gray: conversion after 5 h, dark: Z-selectivity).

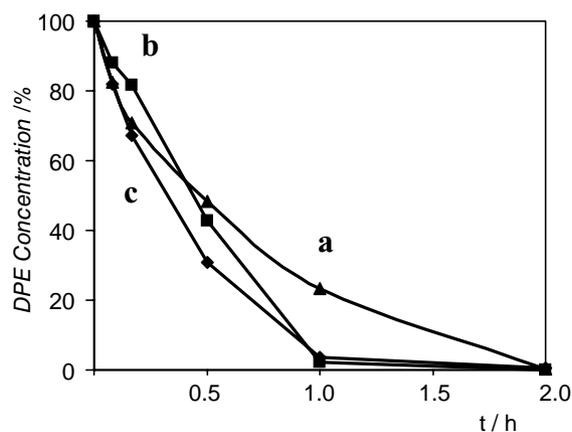


Fig. 7. Conversion over TiN catalysts prepared using different precursors.

to reduced activities due to passivation and shielding of the outer TiN particle surface.

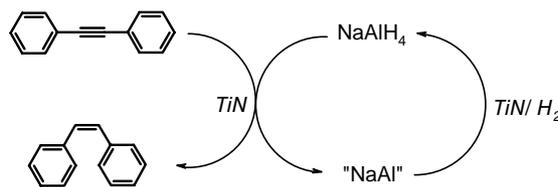
3.2.7. TiN synthesis temperature

Since molecular TiCl_4 is also known to catalyze hydroaluminations, residual Ti–Cl groups could in principle be responsible for the catalytic activity. The presence of molecular TiCl_4 can be ruled out due to the high synthesis temperature for the nitride materials. Within the course of the ammonolysis, chlorine is subsequently replaced by nitrogen, and thus with higher heat treatments, the chlorine content decreases. However, we could not observe a correlation of annealing temperature and activity. Titanium nitride prepared at lower temperatures (773 K) did not give higher reaction rates or better selectivity.

Higher syntheses temperatures result in reduced surface areas and chlorine impurities are not detected in the material. For a $\text{TiCl}_4(4,4'\text{-BPY})$ -derived TiN, a synthesis temperature of 1273 K significantly reduces the activity even though the surface area is still high ($100 \text{ m}^2 \text{ g}^{-1}$). On the other hand, for $\text{TiCl}_4(\text{THF})_2$ -derived titanium nitride nanoparticles synthesized at 973 and 1273 K, the reaction rates in the DPE reduction are almost identical even though the surface area is reduced from 193 to $96 \text{ m}^2 \text{ g}^{-1}$. The results illustrate that reaction rates and selectivity do not scale with the specific surface area of the powders, a fact that is probably due to small variations in compositions and surface chemistry that also depend on the synthesis conditions and affect the catalytic properties.

3.2.8. DPE reduction with molecular hydrogen

A particular interesting approach is to use dihydrogen (H_2) instead of alanates for the hydrogenation since hydrogen is cheaper and easy to handle. According to our experiments, TiN is not an active catalyst in the hydrogenation of DPE. However, in combination with catalytic amounts of NaAlH_4 (10%), the complex hydride and TiN can be used as a co-catalytic system in the reduction with H_2 . In the first reaction step, NaAlH_4 is activated by TiN



Scheme 2. Combination of the catalytic DPE reduction and the catalytic regeneration of NaAlH_4 , both catalyzed by TiN in a cocatalytic system.

to reduce DPE (Scheme 2) and thereby is transformed into an unknown intermediate with reduced hydrogen content, here designated as “NaAl”. The reversible re-hydrogenation of this intermediate is also catalyzed by TiN and restores the complex hydride again. This re-hydrogenation could be mechanistically related to the hydrogenation of NaH:Al in the solid state used in hydrogen storage [12,13].

DPE loaded as a solid together with TiN and NaAlH_4 (molar ratio: 1:0.1:0.1) in an autoclave is reduced with hydrogen (40 bar) with 88.3% conversion after 24 h at 393 K. The main product is *Z*-stilbene (91.7%). In comparison, for DPE, reduced under the same conditions only with NaAlH_4 ($\text{DPE}:\text{NaAlH}_4 = 1:0.1$) but without TiN, the conversion is much lower (56.1%) and the *Z:E* ratio is reversed (60.7% *E*-stilbene and 39.3% *Z*-stilbene).

Thus, the addition of TiN in the hydrogenation reaction significantly enhances the reaction rate and directs the reaction to give a high *Z*-selectivity. The melting point of DPE is 331 K and this hydrogenation is a typical three-phase hydrogenation comparable to other hydrogenation reactions. The reaction scheme is an alternative route to Lindlar-type catalysts. We have not tried to optimize this reaction and the applicability for other substrates still has to be explored.

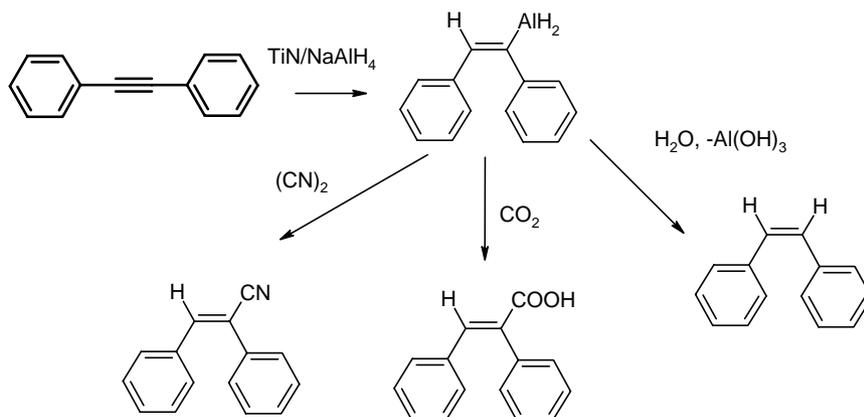
3.2.9. Activation of other complex hydrides

Lithium alanate is not cheaper as compared with NaAlH_4 but more widely in use due to its higher solubility in organic solvents. We have therefore also tested the activation of LiAlH_4 with ultrafine TiN particles. In that case, the catalytic acceleration was not as pronounced as observed for NaAlH_4 . At 328 K, the reaction rate was lower and the *Z:E* ratio was 50:50 after 24 h (conversion >99%). Thus, the selectivity is slightly changed. LiAlH_4 has a higher thermodynamic stability compared with NaAlH_4 and needs probably higher temperatures for activation. The higher stability of LiAlH_4 also precludes applications in hydrogen storage [12].

Reactions with LiBH_4 and NaBH_4 were even less effective and only gave very low conversions (<10%) after 24 h.

3.2.10. Mechanism

The understanding of mechanisms in catalytic reactions is sometimes crucial for the creative development of new applications. In our first approach, the main interest was to develop high surface area titanium nitride as a material for catalytic applications, and therefore evaluation of catalysts varying in the specific surface area was performed.



Scheme 3. Proposed hydroalumination mechanism for the TiN-catalyzed reaction. Besides water quenching, other known quenching reactions are illustrated.

Interestingly, the stereoselective hydrogenation with complex alanates is also feasible using molecular catalysts. This approach has been applied recently for the hydrogenation of alkynols with great success [20]. Initially, such reactions were uncovered by Ashby [14]. Even though the intermediates in these reactions were never characterized by means of X-ray crystallography and specific NMR data allowing identification of the addition products are rare, Al–C bond formation was postulated in most of the cases, for catalyzed reactions, as well as for uncatalyzed addition reactions and thus the reaction was termed hydroalumination (Scheme 3). In that case, prove for intermediates containing Al–C bonds were based on various quenching reactions which can be used to transform the intermediate into a more valuable product. The latter shows also that hydroaluminations are extremely versatile reactions which allow to synthesize a variety of products.

Identification and characterization of the intermediates was only recently realized by Uhl [21] who has reported the structure of several hydroalumination products. In the case of DPE hydroaluminations, structural data or NMR investigations have not been carried out. We have therefore separated the intermediates from the catalyst and measured NMR spectra after various reaction times. Identification of the intermediates and assignment of the lines to particular structural fragments is difficult in that case since the spectra show complicated multiplets which indicate oligomers. However, an important result from NMR data is that neither the lines of DPE nor signals of any of the stilbenes can be recognized in the spectra. From that observation, we conclude that an intermediate is formed in the course of the reaction, probably a hydroalumination product.

Highly dispersed titanium nitride catalyzes the decomposition of NaAlH₄. The nanoparticles facilitate the subsequent decomposition into Na₃AlH₆ and Al [12,13]. On the other hand, pure AlH₃ is known to add stereoselective to DPE to form Z-stilbene. The role of TiN in the hydrogenation of DPE could thus be to facilitate the dissociation of NaAlH₄ into NaH and AlH₃ if a suitable substrate is present. Hereafter, AlH₃, formed on the TiN particle surface, adds to DPE

and forms Z-stilbene after hydrolysis of the hydroalumination intermediate.

4. Conclusion

We have for the first time reported complex hydride activation using high surface area titanium nitride catalysts. Hydrogenations can be carried out with complex hydrides as well as with gaseous molecular hydrogen. The activation by TiN results in a significant acceleration of hydrogen transfer and a very high stereoselectivity with over 90% Z-stilbene, whereas the uncatalyzed reaction produces only 30% Z-stilbene. NMR studies suggest that the mechanism of the reaction proceeds via a hydroalumination intermediate.

Acknowledgements

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