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Porous Silicon Nitride as a Superbase Catalyst

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The synthesis of a new mesoporous support based on high surface area silicon nitride and its use as a solid superbase is reported. The 2,3-dimethylbut-1-ene isomerization is used as a test reaction to compare the activity of individual catalysts depending on the synthesis conditions of the support. Various impregnation methods and different metal loadings are studied. In particular, potassium catalysts, obtained by impregnation from ammoniacal solution, show high catalytic activity for alkene isomerization. Heat treatments of the support at 1273 K and potassium loadings up to 30% are beneficial for high conversion at low temperature. © 2001 Academic Press

INTRODUCTION

Compared to the vast number of known solid acid catalysts, reports of new solid base materials are still rare, even though base-catalyzed reactions play an important role in the production of fine chemicals (1). It is therefore highly desirable to develop new materials that show a structural chemistry similar to those of known porous framework topologies but with accessible basic sites. Framework topologies, similar to those of zeolites or MCM-41, can be found in nitride-based materials. For example $Si(NH)_2$ is assumed to be isoelectronic and isostructural with SiO_2 (2) and nitrido-sodalites are obtained from the solid state reaction of HPN_2 and divalent metal salts (3), but their pores are very small and inaccessible for organic substrates. We have further explored the synthesis of high surface area nitride-based materials and obtained mesoporous silicon imido nitride with a specific surface area up to 1000 $m^2\ g^{-1}$ and a narrow pore size distribution similar to that of MCM-41 (4). The composition varies between $Si_2N_2(NH)$ and Si_3N_4 depending on the synthesis conditions. The pores are 6 nm in diameter and not ordered. The material is not prone to sintering and can be treated up to 1273 K in vacuum or gaseous ammonia with only little decrease of the specific surface area. Due to the high abundance of $-NH_2$ and $=NH$ functional groups on the inner surface, these compounds are suitable for base-catalyzed reactions such as the Knoevenagel reaction (5).

In contrast to silica-based materials like MCM-41, mesoporous silicon nitride can be used as a support for alkali metals according to our investigations. Thus potassium loaded from ammoniacal solution affords high surface area materials of strong basicity. The impregnated nitrides have superbasic basic sites ($H_- > 26$) and catalyze the isomerization of alkenes. In industry, solid superbases are typically used to convert polycyclic alkenes (6). For example in the Sumitomo process 2000 t of 5-ethylidenebicyclo [2.2.1] hept-2-ene are produced each year (7).

The high activity of solid superbases at low temperature is advantageous to avoid thermal rearrangement and undesirable ring opening reactions that would occur with acidic catalysts. Efficient catalysts for alkene isomerizations are usually stronger than $H_- = 35$ because of the high basicity of the allyl anion formed in the reaction (Fig. 1). In the following, we present the first superbase catalyst based on porous silicon nitride. The isomerization of 2,3-dimethylbut-1-ene (DB-1) to form 2,3-dimethylbut-2-ene (DB-2) is used to evaluate the basic strength of the materials depending on the synthesis conditions (8). The study demonstrates the key role of the support in the synthesis of efficient catalysts for alkene isomerizations.

EXPERIMENTAL

Synthesis of Mesoporous Silicon Nitride

All operations are performed using an argon-filled glove box ($O_2 < 1$ ppm, $H_2O < 1$ ppm) or a vacuum line and dry solvents. Silicon tetrachloride (Arkos 99.8%) is diluted with pentane to a 4% solution and reacted with gaseous ammonia (UHP, Messer) to form a white precipitate. The reaction of 10 ml $SiCl_4$ is complete after 5 h. The precipitate with approximate composition $Si(NH)_2 \cdot 4NH_4Cl$ is filtered out and dried in vacuum. It is then placed in a crucible and heated in a horizontal tube furnace under a flow of gaseous ammonia (UHP, 40 ml min^{-1}, 1 bar) to the desired temperature (873, 1073, or 1273 K) at a rate of 5 K min^{-1} and annealed at that temperature for 2 h. In this way, the NH_4Cl is sublimed and collected at the cold end of the tube.

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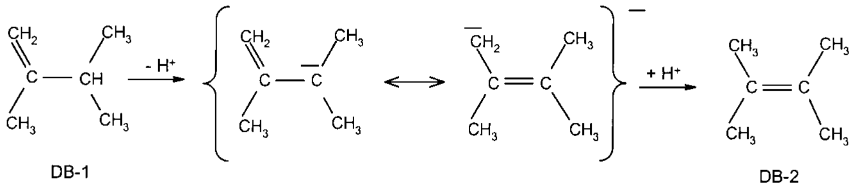

FIG. 1. Mechanism of the base-catalyzed 2,3-dimethylbut-1-ene isomerization.

The resulting powder in the crucible has a high surface area between 700 and 1000 $m^2\ g^{-1}$ depending on the annealing temperature.

Impregnation of Silicon Nitride

One hundred milligrams of the support together with the desired amount of potassium (sodium, lithium) and a trace of Fe_2O_3 (<1 mg) are loaded in the reactor. At 210–230 K, 2 ml ammonia (UHP, Messer) are condensed in the reactor. The blue solution turns gray after a few minutes. After 1 h the reactor is warmed up to room temperature and the ammonia is sublimed off. The reactor is placed in a tube furnace and heated to 573–673 K in vacuum (10^{-4} mbar). The highest conversion is obtained with a catalyst synthesized by loading 30 mg potassium on 100 mg of the support, the latter being synthesized at 1273 K (Table 2).

Characterization of the Catalyst

Nitrogen physisorption experiments were performed on a Micromeritics 2000 instrument. The average mesopore diameter was obtained from the desorption branch of the isotherm using the BJH method (9). For IR measurements the air sensitive powder was mixed under argon with KBr and pressed into a pellet. ^{29}Si MAS NMR experiments were carried out on a Bruker Avance 500WB instrumet using a single pulse excitation.

Evaluation of the Catalytic Activities

2,3-Dimethylbut-1-ene (DB-1, Fluka, 98%) was distilled prior to use and stored under argon (98.6% by GC). For the test reaction, 2 ml DB-1 were added to the catalyst and stirred. After 10 min, the catalyst was filtered out and the product mixture was analyzed with a Carlo Erba gas chromatograph using a DB-1 glass column. For the test reactions conducted below room temperature, all operations were performed at the designated temperature (Table 2).

RESULTS AND DISCUSSION

Synthesis of Mesoporous Silicon Nitride

In the course of silicon nitride synthesis, first the precursor silicon diimide ($Si(NH)_2$) is precipitated at 295 K in an organic solvent together with NH_4Cl,

$$SiCl_4 + 6\,NH_3 \xrightarrow{solvent} [Si(NH)_2\downarrow\ +\ 4\,NH_4Cl\downarrow].$$

Organic solvents like pentane afford mesoporous materials with a high specific surface area up to 1000 m^2g^{-1}, whereas the use of polar solvents results in a significant reduction of the inner surface area (4). The NH_4Cl is removed by sublimation at elevated temperatures in an ammonia flow reactor.

$$[Si(NH)_2\downarrow + 4\,NH_4Cl\downarrow] \xrightarrow{NH_3,\ heat} Si(NH)_2 + 4\,NH_4Cl\uparrow\ .$$

Sublimation is the key step to obtain high surface area materials, whereas in the manufacture of dense silicon nitride from $Si(NH)_2$ washing with liquid ammonia is used to remove excess NH_4Cl. This reduces the surface area further and destroys the narrow pore size distribution. A high concentration of ammonia in the sublimation is necessary to avoid rehalogenation of the diimide. At 723 K, most of the NH_4Cl can be sublimed (Cl content < 2%).

During the heat treatment silicon diimide decomposes via the following idealized pathway:

$$Si(NH)_2 \xrightarrow{1073\ K} Si_2N_2(NH) \xrightarrow{1273\ K} Si_3N_4.$$

However, the intermediates are not stochiometric compounds and the composition of the powder depends on the dehalogenation temperature and the ammonia concentration. After annealing at 1073 K, the composition is close to $Si_2N_2(NH)$. At 1273 K the material is amorphous Si_3N_4. The abundance of amide, imide, and nitride ions varies with different heat treatments of the support. IR measurements indicate a high abundance of proton containing functional groups (Fig. 2) if the dehalogenation is carried out at moderate temperatures (700–800 K). In our study, we have used mesoporous silicon nitride synthesized at 873 K (SIN873), 1073 K (SIN1073), and 1273 K (SIN1273) with specific surface areas of 990, 865, and 700 $m^2\ g^{-1}$, respectively.

Impregnation of Mesoporous Silicon Nitride

The basicity of the catalyst obtained by impregnation of high surface area silicon nitride depends on the alkali metal and the impregnation method used. Lithiation of silicon diimide is achieved using n-butyllithium in an inert solvent

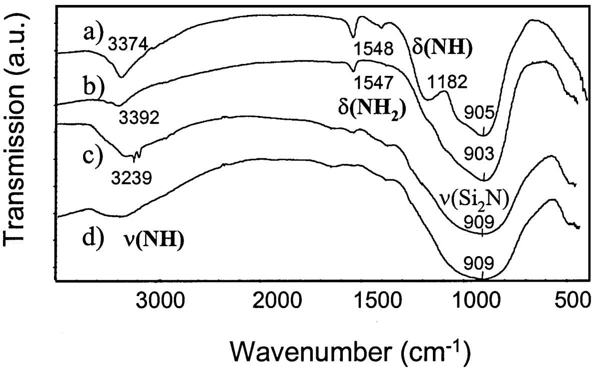

FIG. 2. IR spectra of silicon imido nitrides before and after impregnation; (a) SIN723, (b) SIN1273, (c) KNH_2 loaded on SIN1273, and (d) activated catalyst.

like hexane. This method produces pyrophoric samples, but the catalyst shows no significant activity for DB-1 isomerization (Table 1). Sodium is loaded from ammoniacal solution. The metal is dissolved in liquid ammonia to give a blue solution. Catalysts obtained by this procedure show only minor activity.

Efficient catalysts are obtained by deposition of alkali metal amides (Table 1). The principle method of impregnation is the same as for sodium from ammoniacal solution but a trace amount of Fe_2O_3 is added before ammonia is condensed to the mixture of potassium and the nitride support. The blue solution turns gray after 10 min due to the formation of alkali metal amide. Potassium amide shows the highest conversion (Table 1) and is more efficient than lithium and sodium catalysts. Some earlier studies on potassium-supported alumina (10) suggest that the amide formation is a necessary step to obtain suberbasic catalysts of high efficiency.

TABLE 1

DB-1 Isomerization Results for Alkali Metal Loaded High Surface Area Silicon Nitride Using Various Impregnation Methods

Active metal	Activation (K)	DB-1 isomerization conditions[a]	Conversion (%)
Li (from n-BuLi)	None	295 K, 1 h	<0.1
Li (from n-BuLi)	573	295 K, 12 h	<0.1
Na(NH_3), 30%	None	295 K, 24 h	0.2
Na(NH_3), 20%	413	313 K, 15 h	0.8
Na(NH_3), 20%	573	313 K, 17 h	4.1
$LiNH_2$, 8%	673	295 K, 15 h	<0.1
$LiNH_2$, 8%	973	295 K, 90 min	21.3
$NaNH_2$, 18%	673	295 K, 10 min	43.0
KNH_2, 30%	None	295 K, 10 min	20.2
KNH_2, 30%	673	295 K, 10 min	92.8

[a] 100 mg support, 2 ml DB-1.

Activation of the Catalyst

Without activation, potassium amide loaded on silicon nitride shows 20.2% conversion at room temperature (Table 1), whereas after heating in vacuum the equilibrium composition for the DB-1 isomerization (92.8%) is attained within 10 min. The activation of the catalyst by heating in vacuum has two functions. One is to remove solvent molecules from the active surface and to empty the pores of the catalyst so that the substrate can access active sites. The second is the formation of superbasic sites during the heat treatment. In the case of potassium amide loaded from ammoniacal solution the amide decomposes at elevated temperatures. Table 1 indicates that for sodium and potassium, an activation at 673 K improves the catalyst to a significant level, whereas for lithium amide much higher temperatures are needed. It has been argued that potassium nitride is formed during the activation (10),

$$3KNH_2 \xrightarrow{heat} K_3N + 2NH_3\uparrow.$$

The loss of NH vibrational modes of the KNH_2 in the IR spectrum of the activated catalyst (Figs. 2c and 2d) confirms this view, but K_3N has never been synthesized as a neat solid. Usually, potassium metal forms during the decomposition.

Optimization of the Catalytic Activity

We have studied the activity for the DB-1 isomerization at 253 K (Table 2) to show the influence of the support and its composition, the amount of potassium loaded, and the activation temperature after impregnation.

TABLE 2

DB-1 Isomerization Results at 253 K for Potassium Amide Loaded on High Surface Area Silicon Nitride

Support[a]	Potassium loading (mg/100 mg support)	Activation (K)	Conversion[b]
SBA-15	30	573	0
SIN873	30	673	7.4
SIN1073	30	673	24.0
SIN1273	30	673	39.1
Al_2O_3	8	573	85.7
SIN1273	20	673	9.0
SIN1273	25	673	19.8
SIN1273	30	673	39.1
SIN1273	35	673	17.7
SIN1273	40	673	15.2
SIN1273	30	573	13.1
SIN1273	30	623	14.2
SIN1273	30	673	39.1
SIN1273	30	723	28.3
SIN1273	30	773	25.2

[a] SIN873, SIN1073, SIN1273 synthesized at 873, 1073, and 1273 K, respectively; SBA-15 (13) was dried in vacuum at 770 K, $S_g = 480\ m^2\ g^{-1}$; Al_2O_3: Degussa C, $S_g = 100\ m^2\ g^{-1}$;

[b] 100 mg support, 2 ml DB-1, 10 min.

The conversion of DB-1 heavily depends on the basicity of the support (Table 2). Potassium promoted SBA-15, an ordered mesoporous silica, shows no activity for alkene isomerization. However, superbase catalysts are obtained using alumina (86% DB-1 conversion at 253 K). The silicon nitride materials are also active at 253 K (up to 39% conversion). The conversion depends on the heat treatment of the support. It is higher for nitrides with a composition close to Si_3N_4 that were obtained using a dehalogenation temperature of 1273 K (SIN1273) as compared to materials obtained at 873 K (SIN873), although the specific surface area is lower for the former. This can be attributed to two different factors. The first is incomplete dehalogenation (up to 2%Cl) in samples heated not higher than 873 K. The nature of the chlorine species is still unknown. It could be NH_4Cl or Si–Cl in long chain chlorosilazanes formed during the precursor precipitation. Both react with potassium amide to form inactive KCl. The second significant difference between nitride supports synthesized at different temperatures is the amount of amide and imide groups on the inner surface. They are present in samples annealed at 723 K (Fig. 2a: δ(NH): 1182 cm^{-1}, δ(NH_2): 1548 cm^{-1}) but less abundant at 1273 K (Fig. 2b). The conversion results suggest that the proton-containing groups of the support deactivate superbasic sites. The $-NH_2$ groups are sufficiently acidic in character to give protolysis reactions. The resulting Si–NHK groups are not basic enough to contribute to the DB-1 conversion.

The metal loading was optimized for SIN1273 supported potassium. A maximum conversion was observed with 30 mg potassium per 100 mg support (Fig. 3). This is about three times higher compared to alumina-supported samples and corresponds to the higher surface area of the nitrides (700 m^2 g^{-1} for materials synthesized at 1273 K compared to 243 m^2 g^{-1} for the alumina used in (10)). Since silicon nitride based materials are known to react with alkali metals to form ternary nitrido silicates at higher temperatures (11), the high thermal and chemical stability of our supports was quite surprising. Figure 4 shows the nitrogen physisorption measurement of a nitride synthesized at 1273 K before potassium impregnation and after (30% loading, activated in vacuum). The BET surface area is reduced by 30% due to the higher density of the material, but the pore morphology is retained with only a little decrease in the average pore diameter from 5.8 to 5.4 nm, indicating a smooth coverage of the Si_3N_4 surface. The corresponding ^{29}Si MAS NMR spectra before and after impregnation are almost identical and show a broad line centered at 47.2 ppm, which is characteristic of amorphous silicon nitride and the less well defined local structure herein (12).

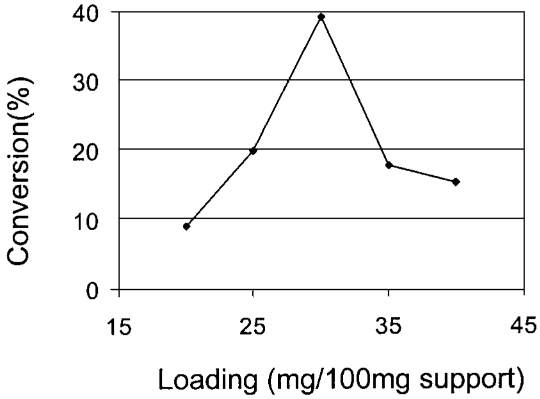

FIG. 3. Optimization of the potassium loading for silicon nitride supported catalysts.

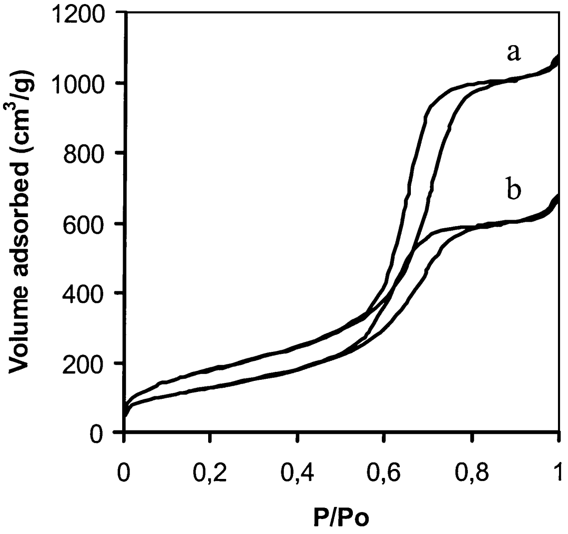

FIG. 4. (a) Nitrogen physisorption isotherms for silicon nitride prepared at 1273 K; (b) the same material after impregnation with 30% potassium and activation.

The highest activity was observed for samples heated to 673 K in vacuum (10^{-4} mbar) after impregnation (Table 2).

All tests showed high selectivity close to 100% to 2,3-dimethylbut-2-ene. Side products were below the level of impurities of the substrate (<0.7%).

CONCLUSION

Potassium loaded high surface area silicon nitride was found to be an efficient superbase catalyst suitable for alkene isomerization reactions. The nitrides exhibit remarkable chemical and thermal stability, which is necessary to avoid significant loss of the specific surface area during the preparation of the catalyst. The activity is comparable to that of alumina-supported potassium. At 295 K, complete conversion of DB-1 is achieved in 10 min. The highest activity at 253 K was observed for supports heat treated in ammonia at 1273 K. With a high amount of potassium (30%) and an activation temperature of 673 K the activity was at an optimum.

The nature of the superbasic site is unknown. The significant impact of the support and the impregnation procedure on the catalyst performance indicates the presence of a distinct phase that is neither pure potassium nor K_3N but an intermediate composition stabilized by functional groups on the supports surface.

Further development of high surface area nitride chemistry seems necessary to enhance the performance of the catalyst using higher annealing temperatures or dopants. However, the results are encouraging to further study the use of high surface area silicon nitride materials in heterogeneous catalysis under nonoxidizing conditions since the low sintering tendency of the material also allows for high temperature applications. According to our recent research results the pore size of silicon nitride can also be tailored in the micropore range. This could allow the preparation of shape selective superbase catalysts and is currently being studied.

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