

Silica as an Oxidation Catalyst

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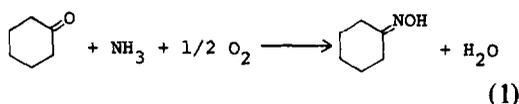
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Whereas silica is not a typical oxidation catalyst, it has been found to be an effective catalyst for the ammoximation of ketones to oximes (e.g., cyclohexanone, ammonia, and oxygen to form cyclohexanone oxime). Attempts to promote the silica catalyst by pretreatment with any combination of the reactants did not result in a higher selectivity to the oxime. In the past, it has been shown that carbon or metal sites are not the centers of the catalysis. All of the active catalysts for the ammoximation reaction are acidic with the best silica catalyst being more acidic than the less active (with respect to oxime production) silica catalysts. It is likely that the acidity of the catalysts results in the generation of >Si-NH_2 species which facilitate the oxidation of the mixture of ammonia and the ketone at 200°C.

INTRODUCTION

During the course of our studies on the novel ammoximation (1, 2) of ketones to oximes, we observed that the best catalysts for reaction (1) were materials which were not the traditional oxidation catalysts.



Recently we have reported a selectivity of 68% for reaction (1) with a silica-alumina catalyst (3), a selectivity of 55% using a silica catalyst (Porasil A) (3), and a selectivity of 23% with γ -alumina (4). Attempts to impregnate oxidizing metals on the silica did not result in improved catalysts.

Besides an induction period (3) for the production of the oxime, reaction (1) is complicated by the formation of an intractable organonitrogen by-product which deposits on the catalyst. Eventually, both the selectivity and the conversion are decreased. All attempts to deposit a similar carbonaceous by-product on inactive catalysts did not improve the activity (to oxime). Other catalysts which show substantial conversions of the ketone in the presence of NH_3 and oxygen (with the formation of a residue on the catalyst) yield

very little oxime. In addition, high-surface-area carbon catalysts tend to be inactive (with respect to oxime production) for reaction (1) (4). By using a wide variety of ketones in place of cyclohexanone, it does not appear that the ammoximation reaction requires the generation of a coproduct (5). Rather, the residue that accumulates on the catalyst must be derived from a competitive aldolization of the ketone over these same silica surfaces.

While no sustained oxidation reactions catalyzed by silica have been reported in the past, there are reports on the oxidative properties of silica-alumina and alumina. By monitoring the ir spectra of the adsorbed species during the reaction, Chapman and Hair (6) demonstrated the oxidation of benzaldehyde to the corresponding benzoate on a silica-alumina surface at 125°C. Earlier, Greenler (7) showed that the alumina surface had considerable oxidative character (with respect to the oxidation of alcohols) at elevated temperatures (400°C). Recently, the ammoxidation of toluene was reported (8) over $\text{SiO}_2\text{-Al}_2\text{O}_3$, $\text{ZrO}_2\text{-Al}_2\text{O}_3$, and $\text{TiO}_2\text{-SiO}_2$ catalysts (>400°C) with the implication that the toluene oxidation proceeds on carbon surface oxides.

A significant part of our work has fo-

cused on why silica should be such an effective oxidation catalyst at such a moderate temperature. In this report, several studies aimed at identifying the origin of this unique oxidation of a mixture of ammonia and a ketone by oxygen over silica, silica-alumina, or alumina catalysts are described. By focusing on the surface acidity of these catalysts, one unique factor for these novel oxidations of mixtures of ketones and ammonia has been determined.

EXPERIMENTAL

The reaction among cyclohexanone, ammonia, and oxygen to yield the oxime was monitored using the automated sampling system described previously (3, 9).

The yield, Y , is the [(moles of oxime produced)/(moles of ketone fed in)] \times 100. The selectivity, S , is the [(moles of oxime produced)/(total moles of ketone reacted)] \times 100. The conversion, C , is the ratio of (Y/S) \times 100.

Acid strength of catalysts. Using the procedures of Walling (10) and Benesi (11), the acid strength of a variety of active and inactive catalysts was determined. The accuracy of the indicators was limited below pH = 0 due to the poor color changes (colorless to pink) (12) associated with the strong acid indicators. However, some qualitative statements could be made with regard to the degree of acidity of various catalysts. Several controls were run with catalysts such as MgO, SiO₂/MgO, or SiO₂/Al₂O₃, and the results were consistent with the values in the literature (11).

Infrared spectra of catalysts. Preliminary attempts to observe the ir spectrum of the adsorbed reactants and products were made using Porasil A obtained fresh from the container or removed from the reactor after treatment with NH₃ or ketone. Samples of the catalyst (3 mg) were mixed with 100 mg KBr using a mortar and pestle and examined by ir. Also, a special ir cell was built to accommodate compressed catalyst samples under vacuum. With this cell, one could also heat the catalyst wafer under

vacuum or in the presence of a conditioning gas (13).

Ammonia adsorption by catalysts. Using a procedure outlined by Benesi or Hinden (14), a rough estimate of the chemisorption of NH₃ by these catalysts could be obtained rather easily. The technique employed a gas chromatograph (GC) to measure the point at which saturation of the catalyst with NH₃ (by small, sequential injections of ammonia over the catalyst) was achieved. While this technique was used to determine surface acidity, it was of added value in this work because it provided an actual value for the amount of ammonia adsorbed by the catalyst under reaction conditions (200 or 225°C, with 25 cm³/min gas flow over the catalyst). Between 0.1 and 0.4 g of catalyst (60–100 mesh) was weighed into a length [\sim 254 mm (10 in.)] of 3.2-mm ($\frac{1}{8}$ -in.)-o.d. stainless-steel tubing mounted into the GC oven (as if it were a GC column). A sample valve (with a 0.1- or 0.45-cm³ sample loop) was actuated to inject aliquots of ammonia over the catalyst. The catalyst was maintained at an elevated temperature for at least 1 h under a flow of helium. The number of injections (before breakthrough of the ammonia) was used to give an approximate value for the volume of ammonia chemisorbed per gram of catalyst. Unfortunately, the breakthrough of ammonia resulted in a broad peak, the breadth of which made an accurate integration quite difficult; therefore, only a lower estimate for ammonia uptake could be obtained.

RESULTS

Variations in Feed Composition

The effects of pretreating the catalyst with various combinations of NH₃, O₂, or cyclohexanone with respect to the production of the oxime are summarized in Table 1. It is important to note that oxygen must be present to generate the active form of the catalyst. Pretreating Porasil A with 50% NH₃ (balance as helium) did not reduce the conversion or the selectivity of the

TABLE 1
Variations in Feed Composition over the Catalyst^a

Experiment (with standard feeds for 8 h)	Result
A. Turn off all flows after 8 h and flush the catalyst with He for 13 h at 200°C	—Within 5 min after restoring the flows, $S = 38\%$; after 30 min, $S = 50\%$
B. Discontinue cyclohexanone feed after 8 h Restore ketone feed	—Oxime production ceases —Oxime returns to original selectivity
C. Raise temperature of catalyst from 200 to 225°C after 8 h	—No improvement in selectivity —No substantial amounts of oxime liberated from catalyst
Pretreatment	Result
1. With O ₂ (10%) and cyclohexanone (2% as vapor)	—No conversion of the ketone, when NH ₃ was added to the feed, the normal lag ^b in the production of oxime was repeated with the S eventually reaching 50%
2. With NH ₃ (50%)	—No conversion of the NH ₃ ; no N ₂ , N ₂ O, NO or NO ₂ produced. When O ₂ and cyclohexanone were added to the feed, the normal lag ^b in the production of oxime was repeated with the S eventually reaching 50%
3. With NH ₃ (50%) and 10% O ₂	—With conversion of 85% within the first hour which eventually drops to 28% in 8 h; when O ₂ was added to the feed, the normal lag ^b in the production of oxime was repeated with the S eventually reaching 50%
4. With NH ₃ (50%) and cyclohexanone (2%)	—If O ₂ is added in place of the ketone and NH ₃ feed, no oxime was detected after 20 min

^a Balance with He gas; total flow, 21 cm³/min [at 50% NH₃, 2% cyclohexanone (as vapor) and 10% O₂]; temperature, 200°C; catalyst, 1 cm³ of Porasil A.

^b During this induction period (or lag) in the production of oxime, the yield of oxime slowly rises over 2–4 h as the conversion of the cyclohexanone falls.

catalyst. However, treatment of Porasil A at 215°C with hexamethyldisilazane (HMDS) (15, 16) initially prevented the formation of any oxime ($C \sim 30\%$ with some water being formed). Eventually, the selectivity of the catalyst reached 52% at 52% C .

Acid Strength of Catalysts

Table 2 summarizes the acidity of a variety of active ammoximation catalysts using the technique of Walling (10) or Benesi (11). Attempts to use some of the more strongly acidic indicators ($pK < 0$) were complicated by the poor color changes associated with some of these indicators. From this table, it is noteworthy that, compared to the other silica gels, Porasil A is quite acidic.

A silica gel of such high acidity is suspicious. To our knowledge, there is no comparable silica gel available. Since Porasil A is made from H₂SO₄ and sodium silicate, we tested (10) for the presence of free sulfate (in the aqueous phase of a thick slurry of Porasil A in doubly distilled water) by using a saturated BaCl₂ solution. No detectable SO₄²⁻ was observed. Further, no acid was detected in the aqueous phase of a suspension of Porasil A (0.5 g/3 cm³ distilled water) ($pH = 6 \pm 0.5$, overnight). Burwell has shown (17) that silica gels modified with as little as 120 ppm Al³⁺ markedly improved the activity of the silica with respect to olefin isomerization. Traces of alumina (when incorporated into silica) (18) can make very acidic gels, and thus,

TABLE 2
Acid Strength of the Catalysts

Color change ^b (acid/base)	Indicator (p <i>K</i> range)										Apparent p <i>K</i>	S ^a	
	2,4-Dinitroaniline	Methyl violet	4-Nitroaniline	4-Phenylazo-diphenylamine	Methyl yellow	Bromocresol green	4 <i>m</i> -Phenylenediamine	Neutral red	8	8 → 9.8			Phenolphthalein
γ -Al ₂ O ₃ (Girdler T-126)	O/Y	Y/B	O/Y	R/Y	R/Y	Y/B	O/Y	R/A	C/P			4 → 5	Fair
Porasil A ^c	Y	—	—	Y	R	O	Y	C	P			<0	Good
Porasil D	Y	—	—	Y	P	R	Y	P	Y			~2	Poor
CPG-500				Y	R/O	O						2 → 3	Poor
CPG-75		B		Y	O	O						3 → 4	Good
SiO ₂ gel from Alfa (No. 89346) ^d		B		Y	O	O						~3	Good
SiO ₂ gel from Grace (No. 952) ^e		B		Y	O	O						4 → 5	Good
SiO ₂ (No. 3023) from hydrolysis of tetramethylorthosilicate ^f		B		Y	Y	O							
SiO ₂ /Al ₂ O ₃ (No. 3657)	O	Y	Y	Y	Y	Y	C	P	C			5 → 7	Poor
SiO ₂ /Al ₂ O ₃ from Grace (No. 980-25)		Y	O	R	R	O	Y	P	P			<-4	Excellent
(74.5 wt% SiO ₂)	Y		O/Y	R	R	Y	P	P	P			-4 → 0	Fair

^a S = selectivity to oxime; poor, 0-30; fair, 30-40; good, 40-55; excellent, 68%.

^b O = orange; Y = yellow; C = colorless; B = blue; R = red; A = amber; P = pink.

^c S.A. = 450 m²/g; P.V. = 1.0 cm³/g.

^d S.A. = 300 m²/g; P.V. = 1.0 cm³/g.

^e S.A. = 300 m²/g; P.V. = 1.65 cm³/g.

^f Described in Ref. (3).

the trace levels of Al^{3+} found in Porasil A would explain its strong acidity.

Infrared Spectra of Catalysts

Some preliminary attempts to obtain the ir spectrum of the surface species were made using Porasil A fresh from the container or removed from the reactor after treating with ammonia or ketone. Samples of the catalyst dispersed in KBr showed strong, broad diffuse bands centered at 3300 and 1060 cm^{-1} . Weaker bands were detected at 1620, 950, 800, and 470 cm^{-1} . When the catalyst was first swept with 2% cyclohexanone for 1 h, the ir spectrum showed new, weak bands at 2920 and 1440 cm^{-1} . While the broad band at 3400 cm^{-1} might obscure the ν_{OH} vibration, no indication of cyclohexanone H bonded to the silica was apparent.

Using the special ir cell built to accommodate a solid catalyst sample under vacuum, the spectrum of a pure sample of Porasil A (25 mg pressed to 6 tons) gave a very broad band from 3800 to 3200 cm^{-1} even at 200°C under vacuum. Heating the pellet for 5 h at 400°C narrowed the absorption to between 3750 and 3400 cm^{-1} . However, it was not until the pellet was treated at 585°C for 2 h (under vacuum) that a distinct band at 3750 cm^{-1} could be observed. (There was still a slight shoulder on this band.) This sample was treated in the sample cell with ammonia (at 720 Torr) [dried over Na/K alloy (19)] at 25 or 200°C for 2 h, and then evacuated while heating to 200°C for 1 h. This treatment with ammonia (under conditions comparable to reaction conditions) did not produce any distinctive peaks which could be assigned to $\nu_{\text{N-H}}$. However, the spectrum of the pellet exposed to ammonia did show a shoulder on the low-energy side of the band at 3750 cm^{-1} (down to 3300 cm^{-1}).

Using the same ir cell described in the preceding paragraph, a 24-mg pellet of Porasil A was dried at 220 or 400°C under vacuum and then exposed to ~10 Torr of pyridine (dried over BaO) for 1 h (at room

temperature) following the procedure of Parry (20). Evacuation of the pyridine at room temperature produced strong bands at 1592 and 1442 cm^{-1} as observed by Parry (20) which he attributed to Lewis acid sites. On heating to 150°C for 3 h, these bands are considerably reduced in their intensity and a weak, but distinct, band appears at ~1546 cm^{-1} (which was previously buried under the 1592- cm^{-1} band), indicative of some very limited Brønsted acidity. As a control, the poorer silica gel catalyst (No. 3023, Table 2) displayed similar responses (via ir) except no band was detected in the 1540- cm^{-1} region. As expected, the silica-alumina catalyst (No. 3657, Table 2) displayed a much stronger band at 1548 cm^{-1} as well as stronger bands at 1593, 1490, and 1440 cm^{-1} . On heating at 150°C under vacuum for 3 h, the band at 1593 cm^{-1} disappeared, leaving bands at 1545, 1490, and 1453 cm^{-1} .

Ammonia Adsorption by Catalysts

Using a thermal conductivity detector to measure the saturation of a catalyst by ammonia at reaction temperatures (14), a rough estimate of the adsorption capacities of the catalyst for ammonia can be obtained. The results of the relative amounts of ammonia adsorbed by several ammoxidation catalysts are summarized in Table 3. Once again, Porasil A is observed to adsorb much more ammonia than other silica gels. As expected, the silica-aluminas adsorb large quantities of ammonia. Further, pretreating the Porasil at 400°C for 2 h increases its capacity to adsorb ammonia; however, this pretreatment does not improve the selectivity for the ammoxidation of cyclohexanone.

DISCUSSION

While silica is not a traditional oxidation catalyst, it apparently behaves as an oxidation catalyst for the ammoxidation of ketones (1-3). It is impossible to absolutely rule out carbon or metal centers as the site of oxidation, although previous studies

TABLE 3
Adsorption of NH_3 by Catalysts

Catalyst	Catalyst temp. (°C)	Pretreatment ^a conditions	NH_3 adsorbed (cm ³ /g)	Comments ^b
Porasil A	200	200°C, 75 min;	0.5	Virgin catalyst
		400°C, 2 hr;	1.6	
Blackened Porasil A	200	200°C, 30 min	0	Catalyst at peak activity
		200°C, 2 hr		
Si-gel (No. 3023) ^c	200	200°C, 2 hr	0	Poor catalyst
CPG-500 (No. 4045) ^d	200	200°C, 2 hr	0.1	Fair catalyst
CPG-75 (No. 4280) ^d	200	200°C, 2 hr	0.2	Good catalyst
Porasil D (No. 4290)	200	200°C, 2 hr	0	Poor catalyst
$\gamma\text{-Al}_2\text{O}_3$ (Girdler T-126)	200	250°C, overnight	9.	Fair catalyst
$\text{SiO}_2/\text{Al}_2\text{O}_3$ (No. 3657)	200	200°C, 45 min;	9.	Best catalyst to date (described in Ref. (3))
		400°C, 2 hr;	19.	
$\text{SiO}_2/\text{Al}_2\text{O}_3$ (No. 3657)	225	200°C, 30 min	13.	Best catalyst to date (described in Ref. (3))
		225°C, 2 hr		
Blackened $\text{SiO}_2/\text{Al}_2\text{O}_3$ (No. 3657)	225	225°C, 1.5 hr	1.	Catalyst at peak activity

^a With helium at 20 cm³/min.

^b With respect to catalysis of reaction (1) (see Ref. (4)); see footnote *a*, Table 1.

^c Prepared from hydrolysis of tetramethylorthosilicate.

^d CPG = controlled pore glass. CPG-500 is a silica with a narrow pore size distribution centered at 500 Å.

aimed at these issues seem to eliminate these possibilities.

All attempts to pretreat the silica gels with any one of the reactants still resulted in an induction period (with respect to oxime formation) once all the reactants were passed over the catalyst. Pretreatment of the Porasil A with NH_3 did not poison the catalyst while hexamethyldisilazane initially prevented the formation of any oxime. Ammonia is much less effective than HMDS (an irreversible specific poison for Brønsted-acidic hydroxyls) (16). The restoration in selectivity of the HMDS-treated catalyst can be explained by the eventual hydrolysis (catalyzed by NH_3) or decomposition of the esterified Porasil A. While the strong acid sites would be tied up with NH_3 and an equilibrium would exist between the weakly acidic sites and NH_3 , one has to

recall that NH_3 is being activated by the catalyst at the same time. The experiments with HMDS did suggest that, when hydroxyl groups are removed, the formation of oxime ceases.

The stability of the blackened catalyst (over 14 h at 200°C under flowing helium) demonstrates that the induction period (which is observed over ~4 h) for achieving a high selectivity to the oxime reflects the time required to activate the catalyst surface. It appears that the apparent high conversions that are initially observed reflect the formation of an overlayer on the catalyst as well as the strong adsorption of the ketone on the catalyst. The generation of this residue either removes sites which lead to decomposition of the cyclohexanone or serves to generate a carbonaceous site which now contains the active site. The

latter is unlikely in view of our earlier attempts to prepare carbon-based catalysts for this reaction (4). Whatever occurs, the activated catalyst is stable to 200°C for at least 13 h since the selectivity rises abruptly to 50% when the original feed mixture is initiated.

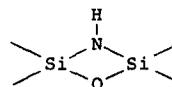
Importance of Surface Acidity of the Virgin Catalyst

There is no easy way to determine the surface acidity of catalysts (21). Two detailed reviews (11, 22) on the methods and results of correlations of surface acidity with catalytic activity offer no satisfactory method. Four techniques which have been employed in the past are: (1) the aqueous method, (2) the nonaqueous method, (3) the monitoring of the adsorption of gaseous bases by GC, calorimetry (23), or gravimetrically, and (4) the infrared spectroscopic method. In the literature, the general approach is to compare results obtained from these techniques and draw conclusions regarding the relevance of surface acidity to catalytic activity. Any results obtained with our catalyst must be taken with the realization that the presence of moisture [from reaction (1)] profoundly (24) affects surface acidity by generating surface hydroxyl groups.

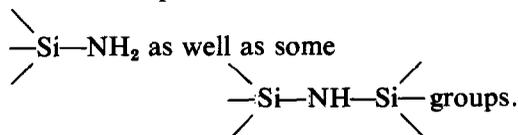
Some observations can be made with regard to the surface acidity of a variety of catalysts using the traditional indicator technique (11, 22, 25). Commercial silica gels, such as Grace No. 952 and Alfa No. 89346, are only weakly acidic and somewhat less effective than Porasil A. γ -Alumina is only weakly acidic, consisting of a large number of Lewis acid sites but few weakly acidic Brønsted sites. The controlled pore glasses (which may contain some boron) and Porasil D are acidic. Porasil A is more strongly acidic and seems way out of line. As expected, the active silica-alumina catalyst is strongly acidic. However, from the poor performance of a commercial silica-alumina catalyst (Grace No. 980-25), high surface acidity does not imply that the catalyst

will be an effective catalyst for the ammoxidation of cyclohexanone.

The ir method (26-29) can provide a quantitative picture as to the nature and number of acidic sites. The appearance of a weak band at 1546 cm^{-1} on exposure of a heated sample of Porasil A at 220 or 400°C to pyridine suggests the presence of some Brønsted-acidic sites. However, the number of these sites is certainly much less than those on traditional silica-aluminas. Nonetheless, these experiments support the earlier observations that Porasil A contains a limited number of strong acid sites unlike most traditional, pure silica gels. However, ammonia adsorption on Porasil A is complicated by the generation of NH_4^+ and the presence of broad ν_{OH} vibrations due to water and surface hydroxyl groups (30). Only when the sample is dried at elevated temperatures have distinct ν_{OH} bands been observed (31). Thus, at 200°C, the surface of the silica gel is still hydroxylated. In the presence of ammonia, these Si—OH bonds are expected to be in equilibrium with ammonia to yield Si— NH_2 species. The ir experiments do emphasize that Porasil does interact with water very strongly. Further, while no definite $\nu_{\text{N-H}}$ vibration was observed, ammonia does react with (or is adsorbed by) the partially dehydrated Porasil even at 200°C. According to the literature, ammonia adsorbed on porous glass (29, 32) is reported to generate bands at 3320 and 3400 cm^{-1} in the ir attributable to $\nu_{\text{N-H}}$ vibrations. Evidence (30) has also been presented for



groups on the surface of silica gel. Therefore, under reaction conditions, the silica surface is expected to contain a number of



Further, ketones are known to physisorb

(33, 34) at the silica surface via hydrogen bonding through surface hydroxyl groups. This interaction has been observed by a shift in frequency of ν_{OH} with adsorption of acetone on silica (~ 7 kcal/mole) (34).

For the ammoximation of ketone, the chemisorption of ammonia not only provides some assessment as to the number of Brønsted and Lewis acid sites, but also the technique tells us how much of one of our major reactants is adsorbed on the catalyst.

As expected, the results in Table 2 indicate that the virgin silica-alumina catalyst (No. 3657) takes up large amounts of ammonia; however, even Porasil A can adsorb some ammonia (~ 0.5 cm³/g) at 200°C whereas other fairly inactive silica gels adsorb very little ammonia. These results can be converted into the number of molecules of NH₃ per gram of catalyst at either 200 or 225°C. Then, dividing by the surface area (284 m²/g), this is equivalent to ~ 0.5 molecules of NH₃ per square nanometer of the silica-alumina catalyst (measured at 220°C with 0.4 atm of NH₃). For Porasil A, the same calculation yields ~ 0.02 molecules of NH₃ per square nanometer of Porasil A (measured at 200°C with 0.4 atm of NH₃). From the literature (35), the average OH site density is ~ 4 OH/nm² (at $\sim 150^\circ\text{C}$) for silica gels. The value we obtain for silica-alumina also includes ammonia adsorbed by Lewis acid and Brønsted acid sites. While the value for Porasil A is much lower than that for silica-alumina, Porasil A does adsorb some ammonia under reaction conditions.

Interestingly enough, there does appear to be some correlation between the ability of the catalyst to adsorb ammonia and its selectivity as a catalyst for ammoximation. The increase in selectivity for ammoximation appears to vary dramatically with surface acidity. However, the amount of ammonia adsorbed by the catalyst does not allow one to predict the effectiveness of the catalyst. The large amounts of ammonia adsorbed by γ -alumina suggest that Lewis acid sites are not very effective for the am-

moximation of cyclohexanone. The values for the blackened Porasil A or blackened silica-alumina are not anomalous. In fact, these catalysts already contain large amounts of ammonia (or organonitrogen bases) as evidenced by the evolution of ammonia-like products as the temperature of the catalyst is raised above 200 or 225°C.

Thus, while silica is not a typical oxidation catalyst, it is an effective catalyst for the selective oxidation of mixtures of ammonia and ketones. Surface hydroxyl groups are clearly important for the ammoximation of cyclohexanone. Perhaps, the same surface hydroxyl groups which give silicas their acidity can also be used to activate ammonia via the formation of >Si-NH_2 species. Interaction of these surface amines (or imides) with adsorbed ketone could yield organic imines, and these surface-activated imines could then react with O₂ to yield the oxime. Due to the strength of the Si-O bond, silica can only provide the necessary surface to activate NH₃ and ketone for oxidation by some sort of O₂ activated species.

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