

Titanium oxide loaded zeolites as photocatalysts for the cyclization of ethylenediamine with propylene glycol

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Received 30 April 2003; accepted 17 July 2003

The photocatalytic activity of titanium dioxide supported on zeolites HZSM-5, HY and H β was evaluated for a novel intermolecular cyclization of ethylenediamine with propylene glycol leading to dihydropyrazine. Titanium dioxide supported on zeolites has been prepared with 2 and 5 wt% of TiO₂ by solid-state reaction, impregnation and sol impregnation methods. From the characterization by XRD, BET, EDAX and TPD of NH₃, it is deduced that in all cases titanium dioxide is in small particles of anatase on zeolites. The highest photocatalytic activity was obtained with 2 wt% TiO₂/H β prepared by solid-state reaction. The acidity determined by TPD of NH₃ was found to be lower for TiO₂/H β than for TiO₂/HZSM-5 and TiO₂/HY. From the above observations, it can be concluded that adsorption, acidity and structure of zeolites have an influence on the activity of supported TiO₂.

KEY WORDS: photocatalysis; titanium dioxide; zeolites; cyclization; dihydropyrazine.

1. Introduction

Photocatalysis over supported TiO₂ was more developed in the recent years for depollution of wastewaters [1–5] than for organic synthesis because most often reactions are not specific. However, the interest in synthetic photocatalysis was experimentally proved [6]. The efficiency of photocatalysts is usually higher when it is used as a powder, but the dispersion on some supports may have an enhancing effect [7–8]. In this context, efforts are increasingly directed toward the development of an integrated photocatalyst—adsorbent matrix suitable for practical application [9–10]. The integrated matrix approach combines adsorption with advanced oxidation by photocatalysis. One of the key properties sought from a support is to provide a hydrophobic surface that adsorbs organic compounds. When the photocatalyst is attached to the adsorbent, there is some chance to improve the photocatalytic efficiency since the problem of encounter between the substrate and the photoactive site is reduced from a three-dimensional to a two-dimensional diffusion problem. This has led to a large number of attempts to anchor TiO₂ on supports on silica, clay and zeolites [4–5, 11–13]. The choice of suitable support for TiO₂ has to take into account several factors. First, TiO₂ has a polar surface and, therefore, it is not a good adsorbent for nonpolar

organic molecules. Second, the support has to be able to enhance catalytic activity through properties ranging from surface acidity to reactive intermediate stabilization. In spite of several titanium dioxide-mediated reactions, examples of intermolecular cyclization are rather limited in literature [14–18]. The intermolecular cyclization over TiO₂/zeolite catalysts was not the theme of many publications except very recently [19–21]. The aim of the present work is to elucidate the effect of method of preparation of TiO₂/zeolites on the intermolecular cyclization reaction of ethylenediamine and propylene glycol using 2–5 wt% titanium dioxide supported on zeolite. The catalysts have been characterized by the more conventional methods such as X-ray diffraction (XRD), BET surface area, energy dispersed X-ray analysis (EDAX) and temperature programmed desorption of ammonia (TPD).

2. Experimental

Titanium dioxide (P25, 80% anatase and 20% rutile, specific surface area 50 m²/g) was from Degussa Corporation. Titanium (IV) isopropoxide (99%) was purchased from Aldrich and used as received. Zeolites HZSM-5 (SiO₂/Al₂O₃ = 30), HY (SiO₂/Al₂O₃ = 4.4) and H β (SiO₂/Al₂O₃ = 20) were from PQ Corporation, USA, Conteka, Sweden and from NCL, India respectively. The chemicals ethylenediamine, propylene glycol, nitric acid, acetonitrile and ethanol were from Ranbaxy, India, of analytical grade of 99% purity. Distilled water was used throughout the study.

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2.1. Preparation of supported TiO₂/zeolite photocatalysts

2.1.1. Solid-state reaction

The catalysts were prepared by thorough mixing of zeolites and ca. 2 and 5 wt% titanium dioxide in an agate mortar with dry ethanol. The catalysts were dried by evaporation to remove ethanol, dried overnight in an air oven at 393 K and finally calcined at 673 K for 6 h.

2.1.2. Titanium (IV) isopropoxide impregnation

Titanium (IV) isopropoxide (corresponding to 2 and 5 wt% of TiO₂) was taken in a glass syringe and introduced in a 100-mL round-bottomed flask containing 25 mL of dry ethanol vigorously stirred. The oven-dried zeolite powders (HZSM-5, HY and H β) were immediately added and stirred for 1 h. Warming in a hot water bath during 2–3 h eliminated the solvent. The catalysts were then dried in an air oven at 393 K overnight and finally calcined at 673 K for 6 h.

2.1.3. Titania sol impregnation

The catalysts were prepared by mixing TiO₂ sol with supports in powder (HZSM-5, HY and H β); subsequently the dried solids were calcined at 673 K for 6 h. The TiO₂ sol was synthesized by the method called acid-catalyzed sol–gel formation [9]. The reactant composition was 200 mL of water, 1 mL of 1 M nitric acid and 29.4 mL of titanium (IV) isopropoxide dissolved in 30 mL of ethanol. The resulting slurry was peptized for 7 h. In a typical preparation of supported photocatalyst, 4.9 g of support saturated with 10 mL of water for half an hour was thoroughly mixed under stirring to 3.5 mL of a TiO₂ sol for 1 h. Then, this mixture was dried by evaporation at 323 K for 2–3 h and heated overnight at 393 K. Finally, the solid was calcined at 673 K for 6 h.

A series of samples were prepared with different percentages of titanium dioxide on each zeolite using the above three procedures and are used for the inter-molecular cyclization reaction.

2.1.4. Characterization of photocatalysts

X-ray diffraction patterns of powders were recorded on a Siemens D-5000 diffractometer using Ni-filtered Cu K α radiation. Diffraction patterns were taken over the 2θ range 0–60°. BET surface areas of the catalysts were determined by nitrogen adsorption at liquid nitrogen temperature (77 K), in a pyrex glass high-vacuum adsorption device reaching a 10^{−6} torr vacuum. Energy dispersed X-ray analysis was performed using Oxford Link ISIS-300 with an accelerated voltage of 20 kV.

Temperature-programmed desorption (TPD) of ammonia experiments were carried out on an Auto-Chem 2910 (Micromeritics, USA) instrument. This unit has a programmed furnace with a 1373 K maximum operating temperature. The instrument was connected to a computer that performs tasks such as programmed

heating and cooling cycles, continuous data recording, gas valves switching, data storage and analysis.

In a typical TPD experiment about 200 mg of TiO₂/zeolite sample (dried at 383 K for 16 h) was taken in a U-shaped quartz cell. The catalyst sample was packed in one arm of the sampling tube on a quartz wool bed. The temperature was monitored using thermocouples located near the sample from outside and one on the top of the sample. The gas flows were monitored by highly sensitive mass-flow controllers. Prior to TPD studies, the catalyst sample was pretreated by flowing high-purity helium (50 mL/min) at 473 K for 2 h. After pretreatment the sample was saturated by flowing (75 mL/min) high-purity anhydrous ammonia at 353 K and subsequently flushed with N₂ at 373 K for 2 h to remove the physisorbed ammonia. TPD analysis was carried out from room temperature up to 1073 K (heating rate, 10 K/min). The ammonia concentration in the effluent stream was monitored with the thermal conductivity detector (TCD), and the areas under the peaks were integrated using the software GRAMS/32 to determine the amount of desorbed ammonia during TPD. Thermal conductivity detector calibration was performed by an automated experiment by flowing known volumes of ammonia.

2.1.5. Procedure and analyses

The photocatalytic reaction was carried out in a batch-type cylindrical round-bottomed flask ($\varnothing = 2$ cm, $L = 20$ cm) of 200 mL capacity with a refluxing condenser at the top. About 130 mg of the preactivated (at 473 K for 2 h) TiO₂/Zeolite catalyst was mixed with equimolar ratio (1 : 1) of ethylenediamine (6.7 mL) and propylene glycol (7.4 mL) along with 20 mL of acetonitrile. A constant and continuous stream of molecular oxygen at a rate of 20 mL/h was also provided to the reactor. The reactants were stirred magnetically and simultaneously irradiated with a 250 W HP mercury lamp (Philips, India) for 15 h at room temperature. Irradiation was carried out under oxygen bubbling. After the reaction the mixture was centrifuged along with 20 mL of distilled water to separate the catalyst, in order to recover the adsorbed substrate and products. The supernatant liquid was analyzed with a Chemito 3865 Gas Chromatography unit using a 6 ft, 10% SE-30 packed column with a flame ionization detector (FID). The products were further confirmed by ¹H-NMR, EI-MS and GC-mass spectrometry.

GC/MS were carried out on a HP 5973 Quadrupole GC-MSD using HP-1 MS (cross-linked methyl siloxane) capillary column (15 m $\times$ 0.25 mm $\times$ 0.25 μ m film thickness). ¹H-NMR spectra in D₂O were recorded on a Varian Gemini 200 MHz spectrometer and chemical shifts δ were reported in ppm. Low-resolution EI mass spectra were recorded on a VG 7070H Micromass mass spectrometer at 473 K, 70 eV, with a trap current of 200 μ A and 7 kV acceleration voltage.

3. Results and discussion

It can be seen from the XRD patterns of the TiO_2 -supported zeolites that there is no damage to the parent zeolite structures of HZSM-5 (30), HY (4.4) and $\text{H}\beta$ (20). Examination of supported oxides is complicated by the X-ray of the support as it appears on figure 1. At high coverage of titanium, the anatase peaks approach the line narrowness characteristic of crystalline titanium dioxide. At low coverage the peak of TiO_2 is a little broader, but sufficient to control that the structure of anatase is not modified after the reaction. The XRD patterns of the untreated zeolites are shown in figure 2. A more quantitative and reproducible description of the titania content was obtained by elemental analysis with atomic absorption spectrometry (AAS) and EDAX.

Table 1 summarizes the BET surface area measurements for the bare zeolites and zeolites supporting

titanium dioxide catalysts prepared according to different procedures described above. The results show that there are significant differences between the photocatalysts according to the different procedures used in this work. The catalysts prepared by solid-state reaction method, i.e. P 25 TiO_2 on zeolites show reduced surface areas compared to parent zeolites, indicating the presence of titania on the surface. Further, the catalysts prepared by titanium isopropoxide impregnation and titanium sol impregnation did not show a marked decrease in the surface area, but the presence of titania was evident from elemental analysis. In the case of titanium sol impregnation, an increase of surface area was observed with $\text{H}\beta$ zeolite, but not explained at the present time. The same phenomenon was observed by Reddy *et al.* [22]. In TiO_2 -zeolite composites, changes in microporosity of composites take place, which may affect the catalytic aspects. Therefore, the control of both the dispersed state of TiO_2 and the porosity of the

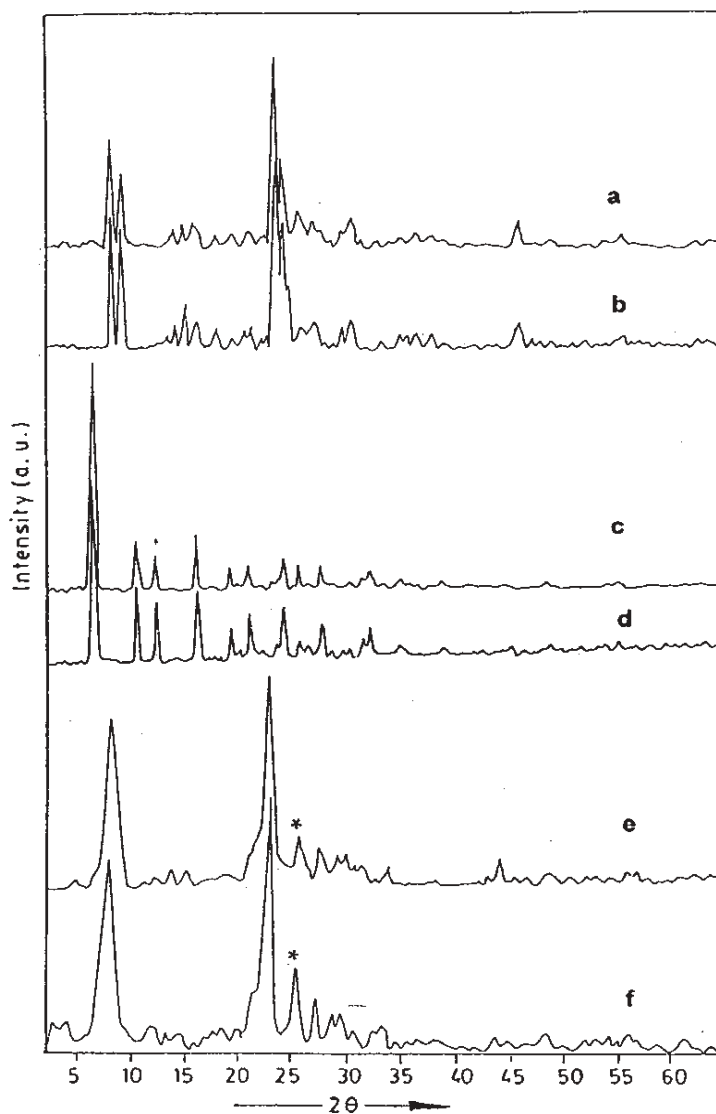


Figure 1. XRD patterns of TiO_2 /zeolites prepared by solid-state reaction (a) 2 wt% TiO_2 /HZSM-5 (30) (b) 5 wt% TiO_2 /HZSM-5 (30) (c) 2 wt% TiO_2 /HY (4.4) (d) 5 wt% TiO_2 /HY (4.4) (e) 2 wt% TiO_2 /H β (20) and (f) 5 wt% TiO_2 /H β (20). * indicates the anatase phase of TiO_2 .

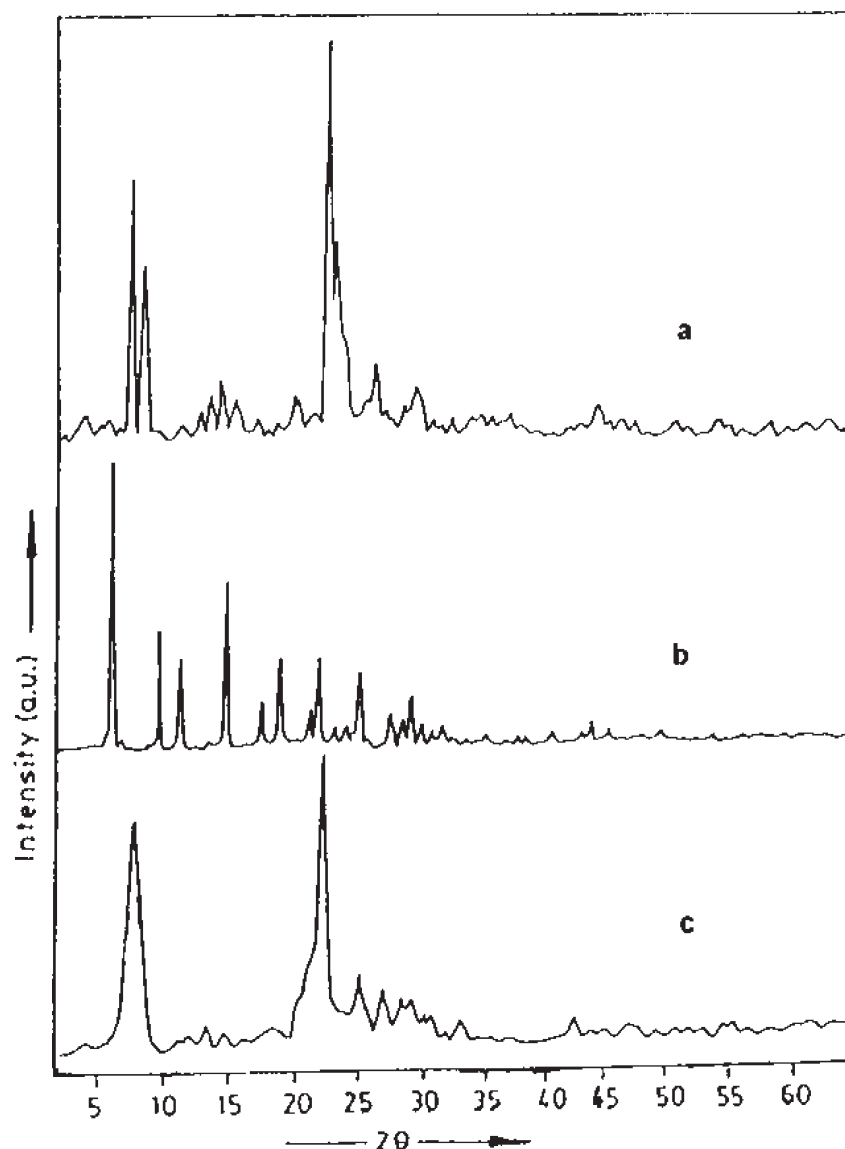


Figure 2. XRD patterns of untreated zeolites (a) HZSM-5 (30), (b) HY (4.4) and (c) H β (20).

zeolite is important to improve the adsorption and catalytic activities. Xu *et al.* [9] and Chen *et al.* [23] also reported the change in microporosity of zeolite by TiO₂ modification. The latter suggests that TiO₂ brings a slight collapse of the regular microstructure of HY during repeated modification process and/or a plausible pore stacking that reduced the surface area. The reduction in the surface areas was also observed by Xu *et al.* for titania-loaded zeolites [9].

EDAX analysis (table 2) showed that Ti is present in the samples and also that it is not uniform as it results from bulk phase analysis. It has been reported [24–25] that the observable crystallites of TiO₂ may appear on the surface of the zeolite when TiO₂ exceed the monolayer capacity (2.8 wt%).

Ammonia TPD results for the catalysts prepared by different procedures show variations with reference to the parent zeolites. The catalysts resulting from solid-

state reaction, i.e. 2 wt% TiO₂/HZSM-5 (30) and 5 wt% TiO₂/HZSM-5 (30), have shown higher acidity compared to HY and H β . The present reaction is favored by a moderate acidity and hydrophobicity and hence H β has shown higher yield. There was not much observable difference in the acidity values for the catalysts prepared by Ti^{IV} isopropoxide impregnation and TiO₂ sol impregnation compared to bare zeolites, but the incorporation of titania is the key factor that is essential for the cyclization reaction.

3.1.1. Photocatalytic activity

The present study has been initiated keeping in view that heterogeneous photocatalysis happens on the surface of titanium dioxide catalyst and adsorption may be modified by the distribution of titania on zeolite and the acidity of the support. We have studied the intermolecular cyclization of ethylenediamine and propylene

Table 1
Results obtained over different TiO₂/zeolite catalysts for the intermolecular cyclization of ethylenediamine with propylene glycol under pure oxygen

Catalyst	Surface area ^d (m ² /g)	Acidity ^e (mmol/g)	Yield ^f of DHP (indoor) (%)	Yield ^g of DHP (solar) (%)
	420	—	—	—
2 wt% TiO ₂ /HZSM-5 (30) ^a	350	0.37	13.0	12.0
5 wt% TiO ₂ /HZSM-5 (30) ^a	320	0.32	11.0	8.90
2 wt% TiO ₂ /HY (4.4) ^a	400	0.25	13.6	11.7
5 wt% TiO ₂ /HY (4.4) ^a	341	0.22	12.0	10.5
2 wt% TiO ₂ /H β (20) ^a	406	0.20	20.4	18.7
5 wt% TiO ₂ /H β (20) ^a	400	0.22	15.5	14.3
HZSM-5 (30)	420	—	—	—
2 wt% Ti/HZSM-5 (30) ^b	401	0.24	12.0	11.5
5 wt% Ti/HZSM-5 (30) ^b	392	0.22	10.7	9.50
2 wt% Ti/HY (4.4) ^b	334	0.25	9.50	8.60
5 wt% Ti/HY (4.4) ^b	392	0.28	8.75	7.71
2 wt% Ti/H β (20) ^b	479	0.42	16.5	15.5
5 wt% Ti/H β (20) ^b	465	0.49	14.0	13.7
HY (4.4)	500	—	—	—
2 wt% Ti/HZSM-5 (30) ^c	378	0.24	8.50	7.50
5 wt% Ti/HZSM-5 (30) ^c	334	0.21	6.45	5.36
2 wt% Ti/HY (4.4) ^c	428	0.56	9.50	5.69
5 wt% Ti/HY (4.4) ^c	400	0.60	6.75	4.69
2 wt% Ti/H β (20) ^c	527	0.52	5.65	4.00
5 wt% Ti/H β (20) ^c	518	0.55	4.35	3.50
H β (20)	425	—	—	—

^aCatalysts prepared by solid-state reaction.

^bCatalysts prepared by Ti(IV)isopropoxide impregnation.

^cCatalysts prepared by TiO₂ sol impregnation.

^dMeasured by BET method with liquid N₂ at 77 K.

^eMeasured by TPD of NH₃ with AutoChem 2910 (Micromeritics, USA).

^fYields obtained after 15 h irradiation.

^gYields obtained after 48 h irradiation.

Table 2
Results of elemental analysis for Ti content by AAS and EDAX

Catalyst	AAS (%)	EDAX (%)
2 wt% TiO ₂ /HZSM-5 (30)	1.38	1.27
5 wt% TiO ₂ /HZSM-5 (30)	4.36	4.30
2 wt% TiO ₂ /HY (4.4)	1.29	1.26
5 wt% TiO ₂ /HY (4.4)	4.16	4.12
2 wt% TiO ₂ /H β (20)	1.19	1.20
5 wt% TiO ₂ /H β (20)	4.09	4.12
2 wt% Ti/HZSM-5 (30)	1.20	1.19
5 wt% Ti/HZSM-5 (30)	4.28	4.21
2 wt% Ti/HY (4.4)	1.26	1.15
5 wt% Ti/HY (4.4)	4.05	4.02
2 wt% Ti/H β (20)	1.10	1.20
5 wt% Ti/H β (20)	4.01	4.00
2 wt% Ti/HZSM-5 (30)	1.30	1.21
5 wt% Ti/HZSM-5 (30)	4.26	4.20
2 wt% Ti/HY (4.4)	1.25	1.22
5 wt% Ti/HY (4.4)	4.12	4.11
2 wt% Ti/H β (20)	1.16	1.12
5 wt% Ti/H β (20)	4.03	4.10

glycol. It was observed that 2 wt% P 25 titania-modified zeolites by solid-state reaction are more active than the other two methods of preparation (table 1). It can be deduced that P 25 is more active than TiO₂ prepared from Ti^{IV} isopropoxide and that 2 wt% TiO₂ leads to the most efficient coverage of zeolite. It has been reported by Xu *et al.* [9] that 2.8 wt% titania corresponds to full coverage of surface of zeolite. The reactions have been carried out with a catalyst amount of 130 mg, and it was observed that further increase did not show better reaction yields. Reactions in dark after larger time period than the reaction time did not show any cyclized product. Solar irradiations were also carried out in comparison with indoor irradiations. The values are reported in table 1. They confirm that 2 wt% TiO₂/H β is most efficient with respect to other percentage of titania. However, it can be noted that yields are a little lower than in artificial light. It may be attributed to a significantly lower reaction rate because of the lower percentage of UV light and the involvement of other reactions that may compete with photocyclization. To

Table 3
Control experiments for the photocatalytic synthesis of dihydropyrazine (DHP)

Conditions	Irradiation period (h)	Yield (%)
Light, O ₂	15	0
Zeolite, light, O ₂	15	0
TiO ₂ /zeolite, dark, O ₂	15	0
TiO ₂ , dark or light, O ₂	15	0
TiO ₂ /zeolite, light, N ₂	15	0
TiO ₂ /zeolite, light, O ₂	15	20.4

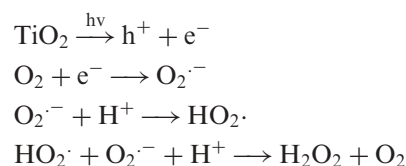
prove that intermolecular photocyclization is a photocatalytic reaction, experiments were carried out in different conditions: presence or absence of light, of oxygen and of catalyst. The results are gathered in table 3. No reaction was observed in the absence of light, with bare zeolite, and in the absence of oxygen. It is much more efficient under pure oxygen than in air-saturated solution. It is the reason why typical experiments were carried out under oxygen bubbling. The kind of zeolite used also has an influence on the efficiency of the reaction. It may be due to several parameters: size of pores, acidity and hydrophobicity. The best conditions are found with H β . The cyclization of ethylenediamine and propylene glycol over TiO₂/Zeolite catalysts show remarkable alterations in product yields over the three zeolites used. The internal structure of the three types of zeolites that have been used to support TiO₂ vary in size and shape, i.e. faujasite Y, 7.4 Å, three-dimensional channels with a cage, pentasil ZSM-5, 5.3 × 5.6 and 5.1 × 5.5 Å, two interconnected channels and H β , 7.5 × 5.7 and 6.5 × 5.6 Å, three-dimensional channels. Differences observed in product yields obtained in this study between the faujasite, pentasil and H β as the support reveal that to obtain good product selectivity an appropriate size of cavity has to be used. The channels in zeolites have to be sufficiently large to permit the shape changes occurring during the reaction but also small enough to eliminate the formation of some by-products. As can be seen in table 1, cyclization is favored by moderate acidity, the highest acidities being associated to the lowest yields. The best conditions in our investigation was found with 2 wt% TiO₂/H β that is in good agreement with results of Xu *et al.* for the photooxidation of 4-chlorophenol and acetophenone.

As seen from the results given in table 1, 2 wt% TiO₂/HZSM-5 and 2 wt% TiO₂/HY show more or less the same activity and yield of dihydropyrazine, but the yield is significantly lower than with H β . The hydrophobicity and acid site strength of zeolites influence the activity of these zeolite systems in the order H β > HZSM-5 $\cong$ HY. This order illustrates that the cyclization is favored by a combination of moderate hydrophobicity and acidity (H β). The highest activity of 2 wt% TiO₂/H β may possibly be explained by the structure of H β , which

is a combination of both HZSM-5 (channel pore system, high Si/Al ratio) and Y (12-ring pore system) zeolites [26].

3.1.2. Plausible reaction mechanism

A mechanism involving the intermediate formation of methyl dihydropyrazine is proposed since the formation of this product was previously reported, and it was experimentally proved that methyl dihydropyrazine is photo-demethylated in our present experimental conditions. The observed reaction involves an oxidation since it does not occur in the absence of oxygen. When titanium dioxide is exposed to UV light ($\lambda < 308$ nm), electrons are promoted in the conduction band and positive holes are formed in the valence band. In the presence of oxygen, the recombination is limited by trapping the electrons, which leads to the formation of hydrogen peroxide.

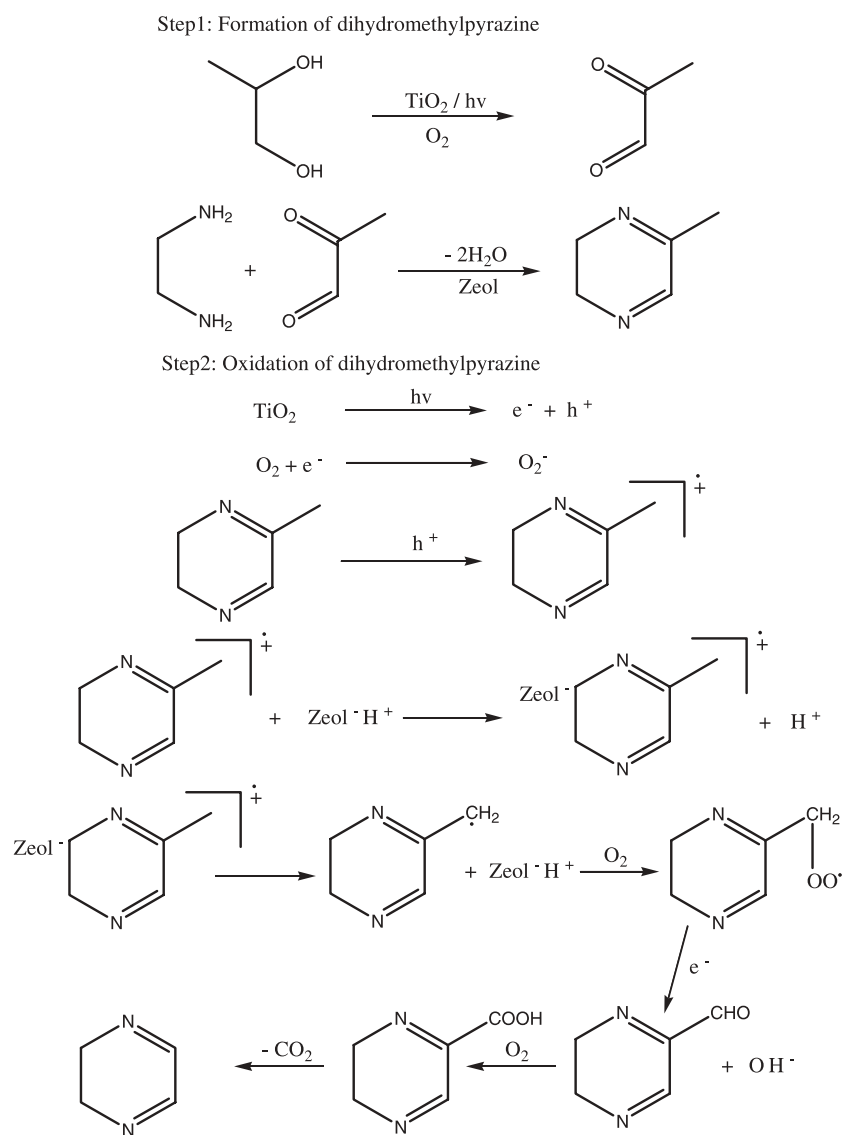


It may be assumed that the preferential adsorption of ethylenediamine leads propylene glycol to undergo oxidation to keto-aldehyde (step 1, scheme 1) at the oxidizing site of TiO₂. The keto-aldehyde formed undergoes cyclization with ethylenediamine to give dihydromethylpyrazine (DHMP) with a loss of 2 moles of water. Zeolite probably favors this reaction by trapping water formed. The second step is the oxidation of methyl group induced by positive holes h^+ produced on the surface of TiO₂. The zeolite is expected to stabilize the radical cation as was proposed by Beaune *et al.* [27] and also reported in our recent papers [19–21]. It is known that zeolite catalysts can stabilize reactive intermediates in several photochemical reactions [28–29]. Thus, the proposed mechanism of step 2 lets us understand that the reaction is pH dependent. Dihydropyrazine carbaldehyde intermediately formed undergoes further oxidation to the corresponding acid, which in turn forms dihydropyrazine by decarboxylation. The acid was actually detected in small amounts in the mixture.

The reaction was attempted with ethylene glycol instead of propylene glycol, but no cyclic product was observed. It may be deduced that the electron-donating substituent, i.e. methyl group of propylene glycol, may favor the oxidation mechanism [30].

4. Conclusion

The formation of DHP through intermolecular photocatalytic cyclization of ethylenediamine and pro-



Scheme 1. A plausible reaction mechanism for the formation of dihydropyrazine (DHP).

pylene glycol at room temperature in the presence of molecular oxygen is reported for the first time. The formation of dihydropyrazine was obtained with a yield of 20.4% over 2 wt% $\text{TiO}_2/\text{H}\beta$ catalysts prepared by solid-state reaction. A reaction scheme is proposed involving the intermediate formation of dihydromethylpyrazine. TiO_2 and zeolite have synergic roles, the former by producing oxidizing species and the latter by adsorbing the substrate and trapping water released in the reaction. The optimum conditions are 2 wt% $\text{TiO}_2/\text{H}\beta$.

The use of TiO_2 supported on zeolite may be a promising method in synthetic photochemistry.

Acknowledgments

One of the authors, Kambala V. Subba Rao, is thankful to CSIR, New Delhi, for Senior Research Fellowship. We thank Dr. Pierre Boule, UBP, France, for his helpful discussions in improving the manuscript.

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