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A REDOX COMBINED PHOTOCATALYSIS: NEW METHOD OF N-ALKYLATION OF AMMONIA BY TiO_2/Pt SUSPENDED IN ALCOHOLS

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Abstract: Ammonia was efficiently N-alkylated into tertiary amines by room-temperature photoirradiation at > 300 nm in the presence of platinized titanium dioxide suspended in alcohols, such as methanol, ethanol, and ethylene glycol. A couple of processes, photocatalytic dehydrogenation of alcohols and thermal hydrogenation of an imine intermediate, account for the ammonia N-alkylation.

Our recent reports have shown that platinized TiO_2 (TiO_2/Pt) particle suspended in non-aqueous solvents such as acetonitrile[1] and alcohols[2] is capable of promoting a photocatalytic preparation of N-alkyl and N-alkylidene derivatives of alkylamines at room temperature, as well as in aqueous solutions.[3] The present paper describes the further application of the photocatalytic N-alkylation to the novel process for selective preparation of tertiary alkylamines from ammonia (NH_3) dissolved in alcohols.

The TiO_2/Pt catalyst was prepared by mixing anatase TiO_2 powder (Merck) with Pt black (Nakarai Chemicals, 5 wt%).[1-3] The suspension of TiO_2/Pt (52.5 mg) in alcohol (5.0 cm^3) was purged by Ar, and purified NH_3 gas (0.1 mmol) was injected through a rubber septum fitted to the reaction vessel. Photoirradiation was achieved by a 400-W high-pressure mercury arc at room temperature under magnetic stirring.

The results are shown in Table 1. N-Alkylation of NH_3 proceeded efficiently in aliphatic mono- and diols to produce tertiary amines as well as H_2. Although exact measurement of primary and secondary amines was unsuccessful,[4] it is obvious that tertiary amine was a main photocatalytic product. Quantum yield of the tributylamine formation was roughly estimated as 0.4 %.

The fact that photoirradiation in the absence of NH_3 led to almost equimolar formation of H_2 and aldehydes suggests the primary step of the N-alkylation to be a well-documented photocatalytic dehydrogention of the alcohols[5-10] followed by the condensation of aldehydes with NH_3.[11]

$$RCH_2OH \longrightarrow RCHO + H_2 \qquad (1)$$

$$RCHO + NH_3 \longrightarrow [\ RCH(OH)NH_2\ ] \longrightarrow RCH{=}NH + H_2O \qquad (2)$$

Table 1 Photocatalytic N-alkylation of ammonia by platinized TiO_2 suspended in alcohols.[a]

Alcohol (RCH_2OH, R =)	Product/μmol				Efficiency[b] /%
	Primary amine	Secondary amine	Tertiary amine	H_2	
H	≃ 0	≃ 0	9.2	121.7	18.5
CH_3	≃ 0	≃ 0	25.3	65.5	58.7
$CH_3CH_2CH_2$	≃ 0	7.1	60.1	105.3	64.9
$HOCH_2$	——[c]	——[c]	41.2	51.4	70.6

[a] Ammonia (0.1 mmol), alcohol (5.0 cm^3), and platinized TiO_2 catalyst (52.5 mg) were placed in an test tube (180 mm × 18 mmφ, transparent for the light of wavelength > 300 nm) and irradiated by a 400-W high-pressure mercury arc for 20 h under Ar at room temperature.
[b] Efficiency of tertiary amine formation, see text. [c] Not determined.

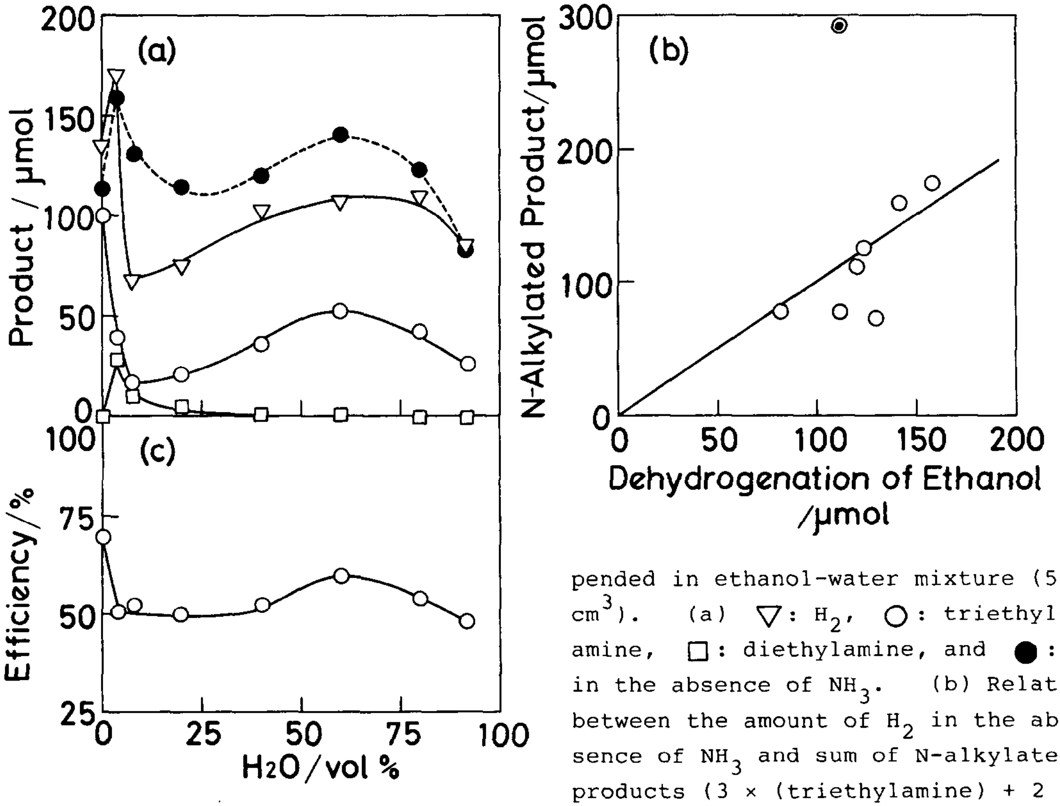

Fig. 1 Effect of H_2O on the photocatalytic N-ethylation of ammonia (0.1 mmol) by TiO_2/Pt (52.5 mg) suspended in ethanol-water mixture (5.0 cm^3). (a) ▽: H_2, ○: triethylamine, □: diethylamine, and ●: H_2 in the absence of NH_3. (b) Relation between the amount of H_2 in the absence of NH_3 and sum of N-alkylated products (3 × (triethylamine) + 2 × (diethylamine)); ◉: in neat ethanol and ○: in ethanol-H_2O mixture. (c) Efficiency of N-alkylation.

The resulting imine intermediate would undergo thermal hydrogenation catalyzed by Pt to yield primary amine.

$$RCH{=}NH + H_2 \xrightarrow{Pt} RCH_2NH_2 \qquad (3)$$

Further N-alkylation would lead to secondary and tertiary amines. The hydrogenation (reactions 3, 4, and 5) proceeds in the dark[12] as confirmed by the fact that dark treatment of NH_3 (0.1 mmol) and acetaldehyde (0.3 mmol) dissolved in ethanol (5.0 cm^3) with Pt black (2.5 mg) in the presence of H_2 (ca. 1 mmol) led to the mixture of secondary and tertiary amines.

$$\begin{array}{lr} RCH_2NH_2 + RCHO \xrightarrow[-H_2O]{} [\ RCH_2N{=}CHR\ ] \xrightarrow[H_2/Pt]{} (RCH_2)_2NH & (4) \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad + & \\ (RCH_2)_2NH + RCHO \xrightarrow[-OH]{} [\ (RCH_2)_2N{=}CHR\ ] \xrightarrow[H_2/Pt]{} (RCH_2)_3N & (5) \end{array}$$

Figure 1(a) shows the effect of H_2O added to the ethanol system. A small amount (4-8 vol%) of H_2O reduced the tertiary amine yield, while increased the yields of H_2 and secondary amine. Maximum yields of these products were commonly observed with H_2O around 60 vol%. Similar dependence of the photocatalytic ethanol dehydrogenation, as measured by the H_2 yield (see, reaction 1), was obtained by the photoirradiation in the absence of NH_3 as also shown in Figure 1(a). The remarkable enhancement of this H_2 yield by the addition of small amount of H_2O is attributable to facilitated formation of hydroxyl radical to abstract hydrogen from alcohol.[10,13] Figure 1(b) is the replots of the H_2 yield against the sum of N-alkylated products. Almost equimolar relation except for the case of neat ethanol shows that the hydrogenation step leading to N-alkylation in the dark strongly depends on the amount of N-alkylation agents, H_2 and acetaldehyde, produced by reaction 1. It follows that the dependence shown in Figure 1(a) is accounted for by the primary photocatalytic process, but not by the hydrogenation in the dark. Deviation of the datum in the absence of H_2O from the linear relation shows the increase of concentration of the imine intermediates in reactions 2, 4, and 5, due to the discounted reverse reaction in neat ethanol.

On the basis of the reaction scheme described above, efficiency of the tertiary amine formation is defined as

$$\text{Efficiency/\%} = 100 \times 3Y_{tert} / (Y_H + Y_{prim} + 2 \times Y_{sec} + 3 \times Y_{tert}) \qquad (6)$$

where Y_H, Y_{prim}, Y_{sec}, and Y_{tert} are yields of H_2, primary, secondary, and tertiary amines, respectively (see also Table 1). The efficiency in the neat ethanol system (69 %) was higher than those in the ethanol-H_2O mixtures (50-60 %).

In this reported non-aqueous photocatalytic system, a couple of aldehyde and H_2 as the N-alkylation agents are produced *in situ* from the stable material, alcohol, at room temperature and at ambient pressure. This is advantageous for preparing amines from alcohols compared with the conventional catalytic process operated under severe conditions.[14,15]

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