

Highly active titania supported ceria catalysts for ammoxidation of picolines

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Abstract

TiO₂ supported ceria catalysts with 20 wt% CeO₂ were prepared by impregnating rutile and anatase polymorphs in aqueous solution of ammonium ceric nitrate [(NH₄)₂Ce(NO₃)₆], characterized by BET surface area measurement and low temperature oxygen chemisorption (LTOC) at –78°C and evaluated for ammoxidation of β- and γ-picolines. Anatase supported catalyst has exhibited higher ammoxidation activities than rutile supported one and pure ceria. Turnover frequencies calculated from ammoxidation rates and irreversible O₂ uptakes in respect to a particular picoline isomer were almost equal for pure supports on one hand and for supported ceria catalysts on the other. The two structural isomers, β- and γ-picolines seem to have exhibited marked steric effect in their reactivity in catalysis on the catalysts. © 1997 Elsevier Science B.V.

Keywords: Titania supported ceria catalyst; Ammoxidation of β- and γ-picolines; Low temperature oxygen chemisorption; Coordinatively unsaturated site

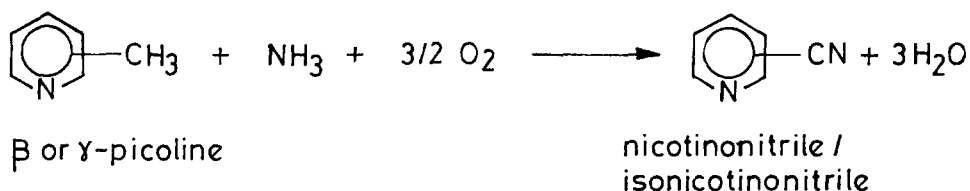
1. Introduction

Research activity is on the increase on the use of ceria in different areas of heterogeneous catalysis [1–6] because of its ability to release and store oxygen, to exist in the redox states of Ce⁴⁺ and Ce³⁺, to form nonstoichiometric oxides under various treatments [7,8] and to be reoxidized to CeO₂ upon exposure to oxidizing environment even at ambient temperature.

However, ceria has not so far been studied as a selective ammoxidation catalyst for picolines.

Vanadia-based catalysts are commonly used for partial oxidation and ammoxidation reactions [9]. In the present preliminary investigation ammoxidation of β- and γ-picolines to nicotinonitrile and isonicotinonitrile, respectively has been studied on CeO₂, the two polymorphs of TiO₂, rutile and anatase, 20% CeO₂/anatase and 20% CeO₂/rutile catalysts. The supported catalysts have exhibited high ammoxidation activities. Low temperature oxygen chemisorption (LTOC) technique developed by Parekh and Weller [10] has been extended for the characterization of the supported ceria catalysts. The ammoxidation products of β- and γ-picolines are industrially important intermediates for the preparation of drugs and pesticides. Equation of the reaction is shown below:

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2. Experimental

Pure CeO_2 was obtained by decomposing ammonium ceric nitrate $[(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6]$ at 500°C in a furnace for 6 h. Two 20% $\text{CeO}_2/\text{TiO}_2$ catalysts with anatase and rutile (Tioxide, UK) as supports were prepared by impregnation method. First the supports were calcined at 500°C in a furnace for 4 h. Exactly 10 g of each dry support was impregnated in 20 ml of ammonium ceric nitrate solution in 9N HNO_3 containing 7.96 g of the salt, for 1 h. The excess water was evaporated on a water bath and the catalyst precursors were dried at 110°C in an oven and finally calcined at 500°C for 4 h.

Activities of these catalysts for ammoxidation of β - and γ -picolines were determined in a vertical borosilicate glass reactor (20 mm i.d. and 350 mm length) enclosed in an electrically heated metal block furnace maintained at 410°C . About 2 g of the catalyst (-18 to $+25$ BSS mesh) was packed in the middle of the reactor in between two beds of glass beads. The temperature of the catalyst bed was measured by a thermocouple inserted into thermowell in the catalyst bed and connected to a temperature controller-indicator.

The catalyst was prereduced in H_2 at 450°C for 2 h and then the temperature of the catalyst bed was lowered to 410°C . A mixture of NH_3 and air (mole ratio 11 : 44) was metered from cylinders and passed through the catalyst bed. Picoline solution in water (mole ratio 1 : 13) was then fed to the reactor at a rate of 2 ml/h with the help of a syringe pump. The products collected in a cold trap at the bottom of the reactor were analysed at intervals of 30 min by gas chromatography using OV-17 column (3 mm \times 3 m). The deviation in estimating the products by GC analysis is $<\pm 2\%$.

The BET surface areas and low temperature oxygen chemisorption (LTOC at 195 K) [10] were measured in a conventional glass adsorption apparatus after

reducing the catalysts in hydrogen (50 ml min^{-1}) at 450°C for 2 h. Oxygen uptakes of $\text{CeO}_2/\text{anatase}$ catalysts with different CeO_2 loadings were determined to see the applicability of LTOC to characterize the catalysts.

3. Results and discussion

The BET surface areas, irreversible O_2 uptakes and O_2 adsorption site densities, and the picoline conversion turnover frequencies (TOFs) of the catalysts are presented in Table 1. Oxygen uptakes are plotted as a function of CeO_2 loading on TiO_2 (anatase) in Fig. 1. Steady state conversions of picolines and selectivities of their respective nitriles obtained on these catalysts are depicted in Fig. 2. Major byproduct in both the reactions is pyridine obtained through dealkylation. It

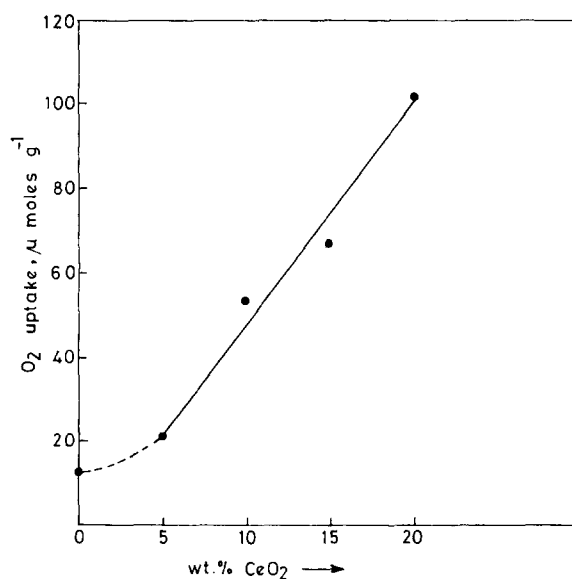


Fig. 1. Oxygen uptake as a function of CeO_2 loading on TiO_2 (anatase).

Table 1

BET surface areas, irreversible O₂ uptakes, O₂ adsorption site densities and conversion TOFs of picolines on CeO₂, TiO₂ supported catalysts and the supports, rutile and anatase

Catalyst	BET surface area ^a (m ² g ⁻¹)	O ₂ uptake ^b (μmol g ⁻¹)	Active site density ^c (cm ⁻² × 10 ⁻¹³)	TOF of picoline ^d conversion (molecules × 10 ³)	
				β-picoline	γ-picoline
CeO ₂	22.5	100	53.54	0.46	1.51
20% CeO ₂ /rutile	43.4	69	19.15	1.48	3.42
20% CeO ₂ /anatase	73.4	102	16.72	1.48	3.54
Rutile	47.5	9	2.28	2.28	9.78
Anatase	83.4	13	1.88	2.67	8.63

^aDetermined by N₂ adsorption at 77 K.

^bDetermined by oxygen chemisorption at solid CO₂+acetone bath temperature (195 K) after reduction at 450 °C in H₂ for 2 h.

^cTaken as equal to number of O-atoms irreversibly chemisorbed on oxygen vacancies created by reduction per cm² of the catalyst surface.

^dTOF calculated from picoline conversions and active site densities.

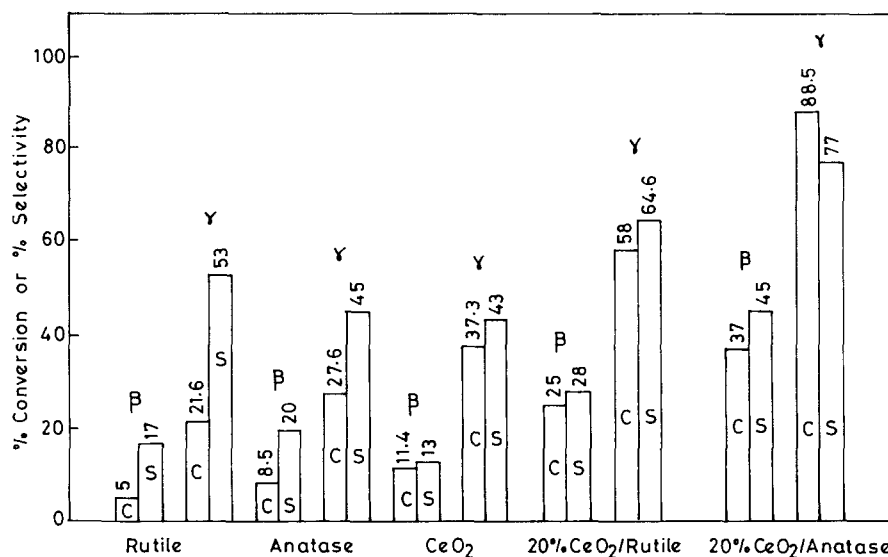


Fig. 2. Conversions (C) of β- and γ-picolines and selectivities (S) of their respective nitriles at 410 °C on rutile, anatase, CeO₂, 20% CeO₂/rutile and 20% CeO₂/anatase catalysts. Experimental conditions: catalyst wt=2 g; mole ratio=picoline : water : ammonia : air=1 : 13 : 11 : 44; gas hourly space velocity (GHSV)=5587 h⁻¹.

was observed that steady state conversions of picolines were obtained within one hour after starting the reaction on all the catalysts.

It is evident from Table 1 that O₂ uptakes determined by the double isotherm method increase in the order, rutile<anatase<20% CeO₂/rutile<CeO₂<20% CeO₂/anatase and the O₂ adsorption site densities are in the order, anatase<rutile<20% CeO₂/anatase<20% CeO₂/rutile<CeO₂.

Pure supports, anatase and rutile have shown lower conversions and selectivities than ceria in the ammoxidation of the two picolines. Anatase supported catalysts have exhibited the highest activity for ammoxidation of picolines (Fig. 2).

The fact that two parallel isotherms are generated on these catalysts by the LTOC technique [10] suggests that Ce⁴⁺ ions have been reduced to Ce³⁺ ions and oxygen is irreversibly adsorbed on oxygen

vacancies [1,11–13] which are usually referred to as coordinatively unsaturated sites (CUS) on cations created by the reduction process. On pure supports the CUS may be located on Ti^{3+} ions obtained by the reduction of Ti^{4+} ions. It may be assumed that all the CUS are equally active in catalyzing the reaction [14,15]. EPR [12] and FTIR [11,13] studies have shown that adsorbed oxygen exists as O_2^- and as O_2^{2-} species on CeO_2 catalysts partially reduced in H_2 at higher temperatures. Fig. 1 shows that O_2 uptakes correlate with CeO_2 loading on TiO_2 (anatase) in the range 5–20 wt% studied suggesting that there is a possible interaction between CeO_2 and TiO_2 (anatase). The O_2 uptake on the supports is low, but on pure CeO_2 it is quite significant. However, the interacted CeO_2 species have shown higher reducibility as is evident from the LTOC data plotted in Fig. 1 (the O_2 uptake is 4–5 times on $\text{CeO}_2/\text{TiO}_2$ (anatase) catalysts if one calculates the uptake per 1 g of CeO_2 in the catalysts). From quantitative TPR study [3] it was shown that the first (around 450°C) of the two peaks is associated with easily reducible surface Ce^{IV} to Ce^{III} . Thus the number of irreversibly adsorbed oxygen atoms measured after reduction at 450°C may be reasonably assumed to be equal to the number of active sites on the catalysts and the active site densities are calculated from BET surface areas and O_2 uptakes. Pure supports have exhibited the highest TOF and the TOF decreases in the order, pure supports > supported ceria catalysts > pure ceria. However, pure supports show lower activities on weight basis because of their lower active site densities (Table 1). Deo et al. [16] have observed that the higher TOF of V_2O_5 catalysts supported on ZrO_2 , TiO_2 , and Nb_2O_5 for methanol oxidation is not related to the terminal $\text{V}=\text{O}$ bond strength determined by Laser Raman spectroscopy. They concluded that the higher activity of $\text{V}_2\text{O}_5/\text{TiO}_2$ and $\text{V}_2\text{O}_5/\text{Nb}_2\text{O}_5$ catalysts should be related to vanadium–oxygen–support (V–O–S) bond strength. Hence the higher TOF of ammoxidation of picolines over $\text{CeO}_2/\text{TiO}_2$ catalysts when compared to pure ceria may also be attributed to a similar facile type of interaction between CeO_2 and TiO_2 surface as in $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts.

For all the catalysts, the γ -picoline TOFs are more than twice the β -picoline TOFs (Table 1). It is interesting to note that the intrinsic activities in respect of a particular isomer are almost equal for pure supports on one hand and for the supported ceria catalysts on the

other. From these results it should be inferred that the two structural isomers with methyl group at different positions from nitrogen atom show marked steric effect in catalysis on these materials. γ -picoline with methyl group farther away from nitrogen is perhaps more favorably activated than β -picoline on the catalyst surface for participation in the reaction. Interacted CeO_2 species of supported catalysts have shown increased O_2 uptakes as well as increased conversions and selectivities in the ammoxidation of β - and γ -picolines to their corresponding nitriles.

Hitherto, it is suggested that irreversible oxygen chemisorption obtained by applying LTOC technique to hydrotreating catalysts [17] and supported V_2O_5 catalysts [18] can be related to the general state of dispersion of active phase on the support. The present study (Fig. 1) has shown that LTOC technique can be applied for measuring the CUS on supported ceria which catalyzes ammoxidation reaction. The present investigation has revealed that highly active ammoxidation catalysts can be synthesized by dispersing ceria on suitable supports.

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References

- [1] T.X.T. Sayle, S.C. Parker, C.R.A. Catlow, J. Chem. Soc. Chem. Commun. (1992) 977.
- [2] A. Naydenov, R. Stoyanova, D. Mehandjiev, J. Mol. Catal. 98 (1995) 9.
- [3] F. Zamar, A. Trovarelli, C. de Leitenburg, G. Dolcetti, J. Chem. Soc. Chem. Commun. (1995) 965.
- [4] S. Murata, K. Aika, T. Onishi, Chem. Lett. (1990) 1067.
- [5] G. Wrobel, M.P. Sohier, A.D. Huysser, J.P. Bonnelle, J.P. Marq, Appl. Catal. A. 101 (1993) 73.
- [6] S. Bernal, F.J. Botana, J.J. Calvino, G.A. Cifredo, J.A. Pereg-Omil, J.M. Pintado, Catal. Today 23 (1995) 23.
- [7] M.P. Rosynek, Catal. Rev. Sci. Eng. 16 (1977) 111.
- [8] J.H. Shyu, W.H. Weber, H.S. Gandhi, J. Phys. Chem. 92 (1988) 4964.
- [9] A. Anderson, J.O. Bovin, Naturwissenschaften 72 (1985) 209.
- [10] B.S. Parekh, S.W. Weller, J. Catal. 47 (1977) 100.

- [11] J. Soria, A.M. Arias, J.C. Conesa, *J. Chem. Soc. Faraday Trans. 91* (1995) 1669.
- [12] A.M. Arias, J. Soria, J.C. Conesa, X.L. Seoane, A. Arcoya, R. Cataluna, *J. Chem. Soc. Faraday Trans. 91* (1995) 1679.
- [13] C. Li, K. Domen, K. Maruya, T. Onishi, *J. Am. Chem. Soc.* 111 (1989) 7683.
- [14] K.V.R. Chary, K. Narsimha, K.S. Rama Rao, B. Rama Rao, P. Kanta Rao, *J. Mol. Catal.* 58 (1990) L13.
- [15] P. Kanta Rao, V.V.D.N. Prasad, K. Somasekhara Rao, K.V.R. Chary, *J. Catal.* 142 (1993) 121.
- [16] G. Deo, I.E. Wachs, *J. Haber, Crit. Rev. Surf. Chem.* 4 (1994) 141.
- [17] W. Zmierczak, G. Murali Dhar, F.E. Massoth, *J. Catal.* 77 (1982) 432.
- [18] N.K. Nag, K.V.R. Chary, B.M. Reddy, B.R. Rao, V.S. Subrahmanyam, *Appl. Catal.* 9 (1984) 225.