

Studies on NO_x conversion over transition metal ion (TMI) doped alumina-boria system

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Catalytic decomposition of NO_x has been studied using a fixed bed tubular flow reactor in the temperature range 573-773K, over six aluminium-borate catalysts (containing $2\text{Al}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$ as the major phase and $9\text{Al}_2\text{O}_3 \cdot 2\text{B}_2\text{O}_3$ as the minor phase) doped with different transition metals. The catalyst phases have been characterised by XRD, IR, ESR and ESCA studies on fresh and used catalyst samples. The results indicate structural stability of the catalyst phase over the experimental temperature range and oxidation of Co^{2+} to Co^{3+} accompanied by surface migration of Co^{3+} species. No valence change in the other transition metal ions and surface oxygen enrichment in the used catalyst is observed. Kinetic studies show a first order dependence on NO_x partial pressure in the lower temperature region, except in the case of the mixed doped catalyst. Breaks in the Arrhenius plots at about 673K are noted for all the catalysts.

NO_x constitutes a serious health hazard¹ and stringent permissible limits for NO_x concentration in ambient and industrial atmosphere have been laid down^{2,3}. A need, therefore, exists to develop viable means to convert NO_x to acceptable products; the catalytic decomposition of NO_x becomes attractive from this point of view⁴.

Alumina-boria systems, with or without incorporated transition metal ions (TMI), have been widely used in catalytic reactions. The solid state reaction between alumina and boric oxide has been investigated by many workers⁵⁻⁸. Literature reports indicate that calcination of alumina-boria mixtures in the temperature range 1523-2873K produces definite crystalline phases of the compositions $9\text{Al}_2\text{O}_3 \cdot 2\text{B}_2\text{O}_3$ and $2\text{Al}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$. However, a lower calcination temperature favours an optimum combination of crystallinity, porosity, surface area, and other desirable properties, so that the maximum activity is achieved from active metals dispersed on such supports⁴; such catalysts have also been reported to exhibit a very good thermal and mechanical stability at temperatures of about 2773 to 3273K depending upon the type of active metals present.

In view of the desirable catalytic properties of alumina-boria systems, with or without incorporation of TMI, coupled with the added advantage of structural stability and good mechanical strength⁴ and in

view of insufficient information available regarding the basic performance of the above catalyst, it was considered worthwhile to make a thorough investigation on the alumina-boria system, using NO_x conversion as a model reaction.

Materials and Methods

(A) *Catalyst preparation*: The catalysts were prepared by dry mixing of equimolar proportions of γ -alumina and orthoboric acid (BDH), with required quantity of cobaltous chloride, cupric sulphate or nickel nitrate (BDH). Different samples were prepared by mixing 1 mol% Co(II), Cu(II) or Ni(II); 3 mol% of Cu(II) and a combination of 1 mol% Co(II), Cu(II) and Ni(II) in an agate mortar, with the addition of benzene⁹ to facilitate grinding. A portion of each of these mixtures was oven dried and then DTA studies were conducted to ascertain the calcination temperature. The mixtures were then pelleted under a pressure of $4.9 \times 10^4 \text{ N m}^{-2}$, calcined at 773K for 5h, crushed again, ground in an agate mortar with benzene, oven dried and pelletised as before. Calcination was carried out again at 1023K for 5h to get the final catalysts. Chemical analysis of the final catalysts confirmed that no loss of TMI occurred during the preparative stage.

(B) *NO_x concentration determination*: NO_x was prepared by the action of conc. HNO_3 on copper turnings and its concentration was determined by using a photo-electric colorimeter (Carl Zeiss, Model-ELKO-111), as per the standard method¹⁰.

(C) *Conversion studies*: The conversion studies

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were conducted in a static bed tubular flow reactor placed in a tube furnace whose temperature could be controlled with an accuracy of $\pm 2^\circ\text{C}$. A chromel alumel thermojunction was placed near the centre of the catalyst bed through a thermocouple well, for measurement of catalyst temperature. The feed gas ($\text{NO}_x + \text{air}$) was passed through a preheater tube at flow rates of $3.3 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$, $6.0 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$, $7 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$, $9 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$ and $11.6 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$ by suction at the outlet over the broken pellets (about 10^{-3} m dia) through the sample ($\sim 2\text{g}$) packed between glasswool plugs. For analysis, the inlet and outlet gases were withdrawn in 10 ml portions using a glass syringe.

(D) *Characterisation*: The XRD studies were conducted using a Philip's PM 9920/05 X-ray diffractometer with Cu/Fe target at a chart speed of 2 cm min^{-1} . The IR studies were conducted using a Perkin-Elmer IR spectrophotometer, in KBr in the range $200\text{--}4000 \text{ cm}^{-1}$. The ESR experiments for Co(II) were carried out on an X-band (Super heterodyne) spectrometer with scan range 4000G and field set at 2000G . The spectra were recorded at liquid nitrogen temperature. The ESR spectra were recorded for Cu(II) and Ni(II) on a Varian E₁₀₉ X-band spectrometer with scan range 4000G and field set at 3000G . The spectra were recorded at room temperature. The ESCA studies were conducted using an ESCA spectrometer supplied by M/s V.G. Scientific Instruments Ltd., with the powdered catalyst spread over a silver paste under a vacuum of 10^{-9} torr, using carbon standard. No noble gas ions sputtering or gold decoration was used. The source used was AlK_α . The specific surface values of the powdered samples were measured by the BET technique by nitrogen adsorption at liquid nitrogen temperature.

Results

The DTA diagram (Fig. 1) shows two endothermic peaks at 423K and 823K , and an exothermic peak at 1023K . The endothermic peaks may be assigned to moisture loss and evolution of gases, respectively, and the exothermic peak probably indicates a solid state reaction between the components leading to the formation of aluminium borate.

From Table 1 it can be seen that the maximum single pass conversion efficiency is that of the sample doped with 3 mol% Cu. The slope at origin of a typical conversion isotherm gives the initial conversion, plots of logarithms of the slope against the reciprocal of the corresponding temperature (K) give the Arrhenius plots. From the extrapolation of these plots to any desired temperature, the conversion at that temperature can be calculated. This method

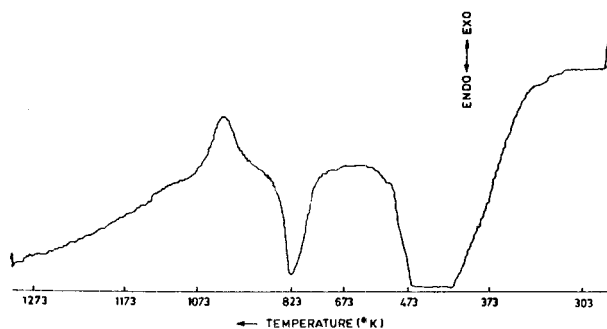


Fig. 1—DTA diagram of the catalyst taken at the preparative stage

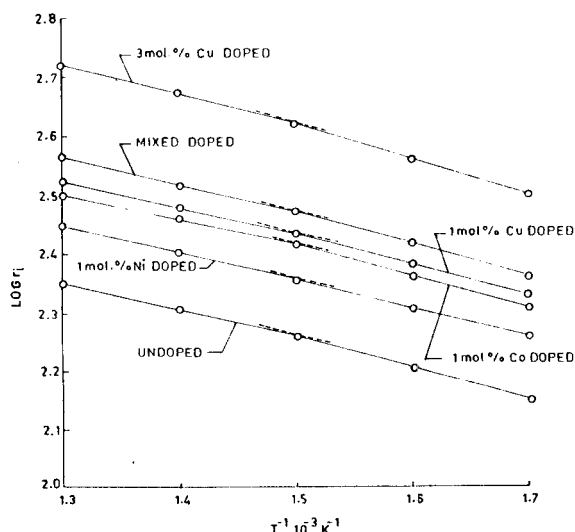


Fig. 2—Arrhenius plots for (a) 3 mol% Cu-doped, (b) mixed doped, (c) 1 mol% Cu-doped, (d) 1 mol% Co-doped, (e) 1 mol% Ni-doped and (f) undoped catalysts

was used to obtain comparative figures for conversion by the different catalysts.

The Arrhenius plots (Fig. 2) indicate a common break temperature of 673K for all the catalyst samples, the slopes in the lower temperature regions being slightly greater than those in the higher temperature region.

Table 1 lists the apparent Arrhenius parameters for the six catalysts and it also includes the relative activities at two selected temperatures below and above the point of break, namely 623K and 723K respectively, calculated from the Arrhenius plots. While not much difference in the high temperature activation energies is noted for the different catalysts, the low temperature activation energy value shows a more pronounced variation from catalyst to catalyst. The lowest activation energies at the higher temperature are shown by 1 mol% Cu-doped and

Table 1—Apparent Arrhenius parameters, activity at selected temperatures and maximum per cent conversion per g catalyst for NO_x conversion over the catalysts studied

Catalyst	Mol% doped	Dopant metal	Apparent activation energy (kJ/mol)		Activity		Apparent pre-exp. factor $\times 10^3$		Maximum % conversion/g catalyst
			723K	623K	723K	623K	723K	623K	
	0	—	8.97	9.59	20	16	0.91	1.02	22
	1	Ni	8.50	9.59	25	20	1.05	1.29	28
	1	Cu	8.50	9.59	30	24	1.20	1.51	34
	1	Co	9.59	9.97	29	23	1.45	1.59	32
	3	Ni,Cu,Co (in equimolar proportions)	9.59	10.9	33	26	1.66	2.13	36
	3	Cu	9.59	11.5	47	36	2.35	3.31	52

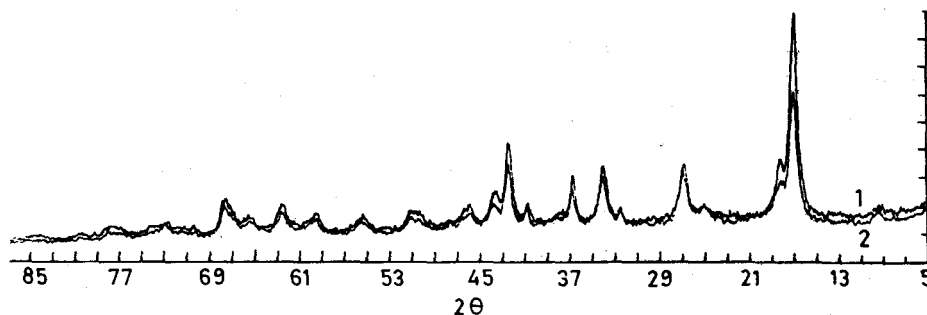


Fig.3—XRD of the catalyst (Co-doped) (1) before and (2) after use in the reaction

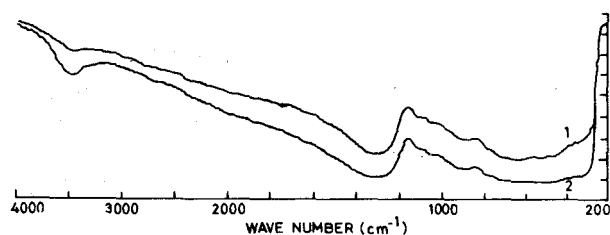


Fig. 4—IR spectra of the catalyst (Co-doped) (1) before and (2) after use in the reaction

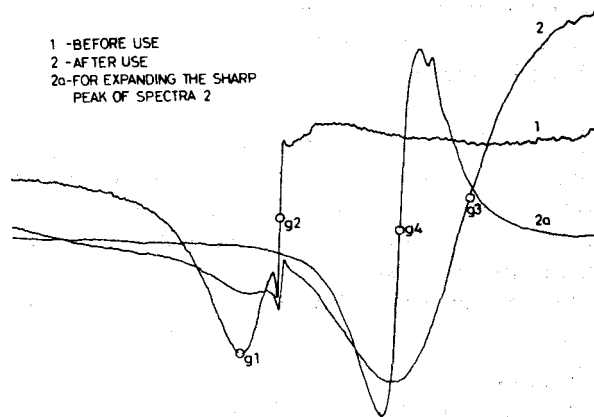


Fig.5—ESR patterns of the fresh and used catalysts (Co-doped)

1 mol% Ni doped samples, which, however, are not very active in view of their relatively lower pre-exponential factors. The undoped catalyst has somewhat higher activation energy and the lowest activity in the series. The most active catalyst among the present catalysts, namely 3 mol% Cu-doped sample, has a relatively higher activation energy which is offset by its highest pre-exponential factor. Similar considerations also apply to the low temperature region.

From Fig. 3, we note that the major phase formed by the solid state reaction between γ -alumina and

orthoboric acid is $2\text{Al}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$. The minor phase is $9\text{Al}_2\text{O}_3 \cdot 2\text{B}_2\text{O}_3$. Traces of unreacted γ -alumina are indicated but no free boria. The doped TMI is in a too finely dispersed state to be detected by XRD. There appears to be no detectable structural change in the course of the catalytic reaction.

The IR patterns shown in Fig. 4 also corroborate that free boria is not present since its characteristic

Table 2—The calculated g -values obtained from ESR spectra

Description of the spectra	g -values
1. Spectra No. 1 taken before use as a catalyst in NO_x conversion.	g_1 -4.91589 g_2 -4.24116
2. Spectra No. 2 taken after use as a catalyst in NO_x conversion.	g_3 -2.57499
3*. Spectra No. 2a taken after use as a catalyst in NO_x conversion.	g_4 -2.00277

*Spectra 2a taken for expanding the sharp peak of spectra 2.

IR absorption at 530 cm^{-1} (medium strength) was not obtained. The structure of the catalyst is such that B—O bond is weakened due to the neighbouring Al atoms. Weak but multiple bands in the range $1150\text{--}850\text{ cm}^{-1}$ suggest that traces of a tetraborate type of species also exist. However, this could not be confirmed by XRD.

From the ESR patterns, it is seen that while no change in the oxidation state of Cu and Ni occurs as a result of the catalytic reaction, Co^{2+} changes to Co^{3+} after participating in NO_x conversion (Fig. 5, Table 2).

From Table 3, it is seen that oxygen dispersion increases in the used catalyst; also, Co appears as a surface dispersed species in the used catalyst. The binding energies of $\text{B}_{1s_{3/2}}$ and of $\text{Al}_{2p_{3/2}}$ and $\text{Al}_{2p_{1/2}}$, as well as their surface dispersion, are seen to decrease in the sample used in the catalytic conversion. This could be due to a surface restructuring for accommodating increased oxygen dispersion in the used catalyst. The dispersion trends were calculated from FWHM values²².

A first order dependence on NO_x partial pressure was noted in the lower temperature region, except in the case of the mixed doped catalyst. This observation suggests that the available adsorption sites are far too numerous to affect the reaction order, leading to a pseudo-first order dependence.

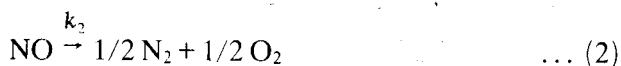
The average value of BET surface area measured for all the catalysts was found to be $13.5\text{ m}^2\text{ g}^{-1}$.

Discussion

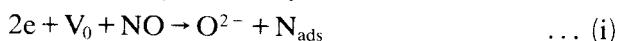
The unusually low activation energies obtained in these studies could be an indication of external diffusion limitations. The catalysts were found to have low specific surface and consequently low porosity. Normally, it should not be associated with diffusion control processes; still, we took the added precautions of using different quantities of the catalysts in the tubular flow reactor and obtained the conversion per unit mass of the catalyst in each case. The values obtained are comparable, suggesting that there is little probability of diffusion control. Because of limitations in the analytical procedure used

by us, we could not determine very low concentrations, to get conversion near the origin in conversion versus time plots, which is the usual practice to check external diffusion limitations. Hence, we employed the usual statistical method. Arrhenius plots were then constructed and the apparent Arrhenius parameters were calculated in the usual manner.

The decomposition of NO_x is assumed to be a two step process (Eqs. 1, 2), as proposed by Wikstrom and Nobe¹¹



The adsorption of NO has been proposed to be unimolecular followed by dissociative chemisorption of NO at oxygen vacancy sites¹² as shown below:



Where V_0 is an oxygen vacancy. If the above mechanism proposed by Voorhoeve is applicable in the present case, there should be two types of oxygen in the used catalyst, one obtained from NO decomposition and the other from adsorbed oxygen.

Louis Raj *et al.*¹³, working on the kinetics of N_2O decomposition on a perovskite surface, also proposed two different oxygen species, one obtained from N_2O decomposition and the other from the adsorbed oxygen.

Ross and Fairbridge¹⁴, working on NO and oxygen reaction with 1-butene over Mn(III) oxide, postulated two O_{1s} binding energy values, 530 eV for chemisorbed oxygen on metal oxides and 533 eV for a molecular oxygen species¹⁵. Thus, oxygen is activated and adsorbed on the catalyst surface as O^- and O_2^- species¹⁶. Both the Louis Raj *et al.*¹³ mechanism and that proposed by Ross and Fairbridge¹⁴, predict two $\text{O}_{1s_{1/2}}$ binding energies. However, our ESCA studies gave only one $\text{O}_{1s_{1/2}}$ binding energy, both for the fresh and for the used catalyst, which corresponded to that of the molecular oxygen species proposed by Ross and Fairbridge¹⁴.

We noted breaks in the Arrhenius plots at 673K for all the catalysts studied. In the case of very low activation energies, small differences are often taken to be due to experimental errors. However, we noted such breaks in a number of cases. Since we got nearly identical readings in repeated runs, we could not assign the breaks to experimental errors. In addition, we employed the usual statistical methods to ascertain that breaks in the Arrhenius plot do exist.

The Voorhoeve's¹² mechanism suggests that the

Table 3—The relative FWHM values alongwith binding energies and peak intensities of Co-doped catalyst for NO_x conversion

Elements with orbitals	B.E. (eV)		FWHM (eV)		Peak intensity (meter $\times 10^{-2}$)	
	Fresh	Used	Fresh	Used	Fresh	Used
Al _{2p_{1/2}} Al _{2p_{3/2}}	74	73	2.55	2.25	4.40	2.90
O _{1s_{1/2}}	532	532	2.80	3.00	9.80	11.00
B _{1s_{1/2}}	194	192	2.80	2.50	2.50	2.00
C _{1s}	286	286	3.20	3.35	1.10	1.90
Co _{2p}	—	793.5	—	—	—	—

initial step is the dissociative chemisorption of NO at the oxygen vacancy sites (step i). The NO may be present as such in NO_x or NO_x may consist entirely of NO₂, in view of the easy oxidation of NO to NO₂ in presence of air. If NO₂ is predominant, it must first dissociate to NO¹¹. The NO thus formed could then undergo dissociative chemisorption. These chemisorption sites could be oxygen vacancies (V₀). The adsorbed nitrogen could then continue to form nitrogen molecules in a surface reaction, which subsequently desorbs. The (step i) above highlights the role of oxygen vacancies in the adsorption of NO. The incorporated TMI probably helps in the creation of oxygen vacancies leading to increased NO adsorption. This contention is corroborated by the fact that higher pre-exponential factors are observed in the TMI doped samples. The difference is more pronounced in the lower temperature regions. The pre-exponential factors are consistently higher in the low temperature zones. The lower value of the pre-exponential factor in the high temperature zones suggests that oxygen vacancy concentration is lowered at higher temperatures, probably because of surface migration of oxide ions. In terms of activation energies in the two temperature zones, the higher temperature activation energies are consistently lower, which also suggests higher mobility of surface oxygen and/or oxygen vacancies. The breaks in the Arrhenius plots noted in our studies probably reflect the mobility differences of these species in the two temperature zones.

The NO₂ molecule can attach to a lewis base site (such as an oxygen vacancy) through the electron deficient nitrogen atom, as nitro species ($-\text{NO}_2$) or through a π -bonded electron deficient oxygen atom, as nitrite species ($-\text{NO}$). The nitro species is more stable compared to the nitrite species¹⁷. NO can adsorb more strongly on reduced transition metal oxides¹⁸, probably acting as a ligand for coordinately unsaturated surface atoms. It can adsorb as a chelate with oxygen end bound to the metal¹⁹, accompanied with oxidation of the catalyst^{18,20}. Our ESR, studies (Fig. 5) show that oxidation does occur in the used cobalt doped catalyst.

An increase in peak intensity of oxygen has been reported for NO conversion over a silica molybdena catalyst by Best *et al.*²¹. Similar increase in peak intensity along with increased value of FWHM of O_{1s_{1/2}} (Table 3), probably indicates an increase in surface dispersion of oxygen in the used catalyst. We can assume (Table 3), a Co_{2p} peak at 793.5 eV (though it is small and difficult to identify due to background noise) in the used catalyst, whereas in the case of the fresh catalyst it could not be identified. This suggests a higher dispersion of Co_{2p} in the former in comparison to the latter. This result, considered along with the ESR result, suggests the oxidation of Co²⁺ to Co³⁺ in the course of the catalytic reaction and probable migration of the Co³⁺ species to the substrate. This should be favoured by the smaller size of Co³⁺ ions. Such an oxidation might appear to be unlikely because of the high stability of CoAl₂O₄, which may be formed during Co doping. However, the very low concentration of cobalt could result in a high dispersion of this spinel with consequent small particle size and high reactivity. Thus, a redox cycle Co²⁺/Co³⁺ could be established, which would necessitate the preconditioning and regeneration step. However, the sustained activity of the catalyst system observed by us suggests that the regeneration is a dynamic process occurring simultaneously with the catalytic reaction.

It is noted that the activity enhancement is due to pre-exponential factor, suggesting the predominant role of oxygen vacancies in the catalytic reaction. Since the catalyst is structurally quite stable, with favourable mechanical properties, it can well be used for the removal of NO_x pollutants in the form of afterburners in automobile exhausts chimney emission etc.

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