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CATALYTIC ACTIVITY OF $\text{Ln}_2\text{MnNiO}_6$ PEROVSKITES FOR ISO-PROPONOL DECOMPOSITION

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MULTIPLE ion-substituted perovskites of the type $\text{A}_2\text{BB}'\text{O}_6$ with transition metal ions at the B site show interesting solid state and catalytic properties. The preparation and characterization of perovskites of the type La_2TiMO_6 ($\text{M} = \text{Cu}, \text{Ni}$ and Zn) have been reported earlier and tested for isopropanol and nitrous oxide decomposition^{1,2}. The present communication deals with the catalytic activity of rare earth-substituted perovskites of the general formula $\text{Ln}_2\text{MnNiO}_6$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Sm}$ and Gd) for isopropanol decomposition.

The oxides $\text{Ln}_2\text{MnNiO}_6$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Sm}$ and Gd) were prepared by firing stoichiometric amounts of the corresponding oxalates at 950°C for 36 hr. A similar procedure had been employed by Blasse³ to prepare a series of compounds La_2MnMO_6 ($\text{M} = \text{Cu}, \text{Co}, \text{Ni}$ and Mg) and by Ganguly¹ to prepare $\text{La}_2\text{MM}'\text{O}_6$ ($\text{M}, \text{M}' = \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{M} \neq \text{M}'$). The formation of single phase was checked by x-ray diffraction using CuK_α radiation. All the compounds crystallised in a cubic lattice and the lattice parameters were found to be approximately twice that of the ABO_3 perovskites ($\sim 3.9\text{\AA}$). The lattice parameters are as follows:

$$\begin{aligned} \text{La}_2\text{MnNiO}_6 &= 7.76 \text{ \AA}; \text{Nd}_2\text{MnNiO}_6 = 7.74 \text{ \AA} \\ \text{Sm}_2\text{MnNiO}_6 &= 7.71 \text{ \AA}; \text{Gd}_2\text{MnNiO}_6 = 7.68 \text{ \AA} \end{aligned}$$

Isopropyl alcohol (BDH spec pure) was distilled before use. The decomposition reactions were followed in a fixed bed-flow type integral reactor⁵. The reactant was fed into the reactor using a motor driven syringe pump. The liquid and gaseous products were analysed using gas chromatograph (Varian 1800) and

Orsat gas analyser. It was found that heating in air (free of CO_2 and moisture) for 4 hr at 400°C restored the activity completely. The reactor was flushed with nitrogen for 10 min before each run to get an inert atmosphere.

The decomposition of isopropyl alcohol was studied in the temperature range $260\text{--}320^\circ\text{C}$ and at contact times 0.2 to 4 sec. All the four catalysts promoted only dehydrogenation to the complete exclusion of dehydration. From the plots of contact time versus mole per cent conversion the initial rates were computed and these were used for making the Arrhenius plots (figure 1).

In order to understand the effect of products on the course of the decomposition, reactions were carried

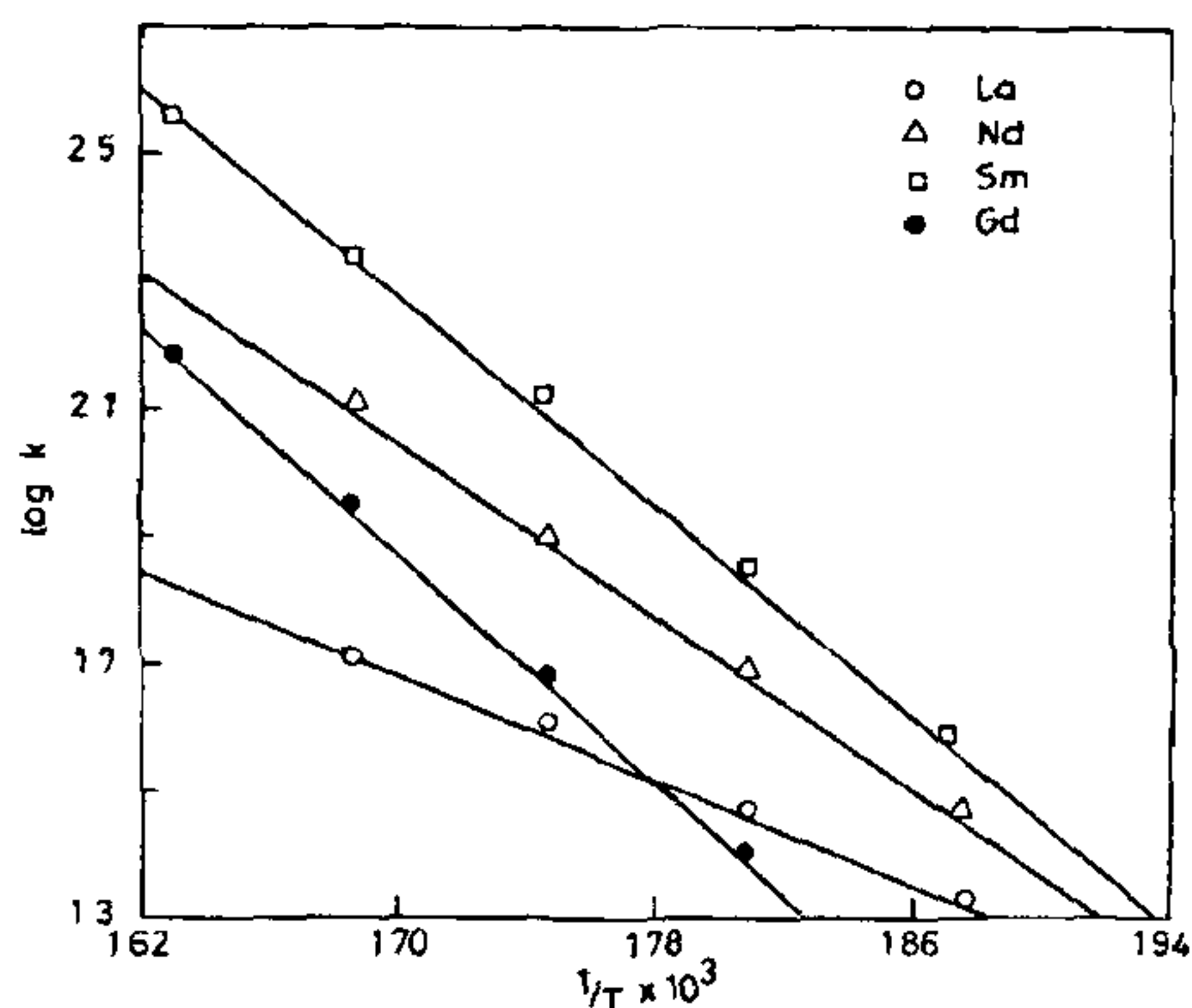


Figure 1. Arrhenius plots for the decomposition of isopropyl alcohol on $\text{Ln}_2\text{MnNiO}_6$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, \text{Gd}$).

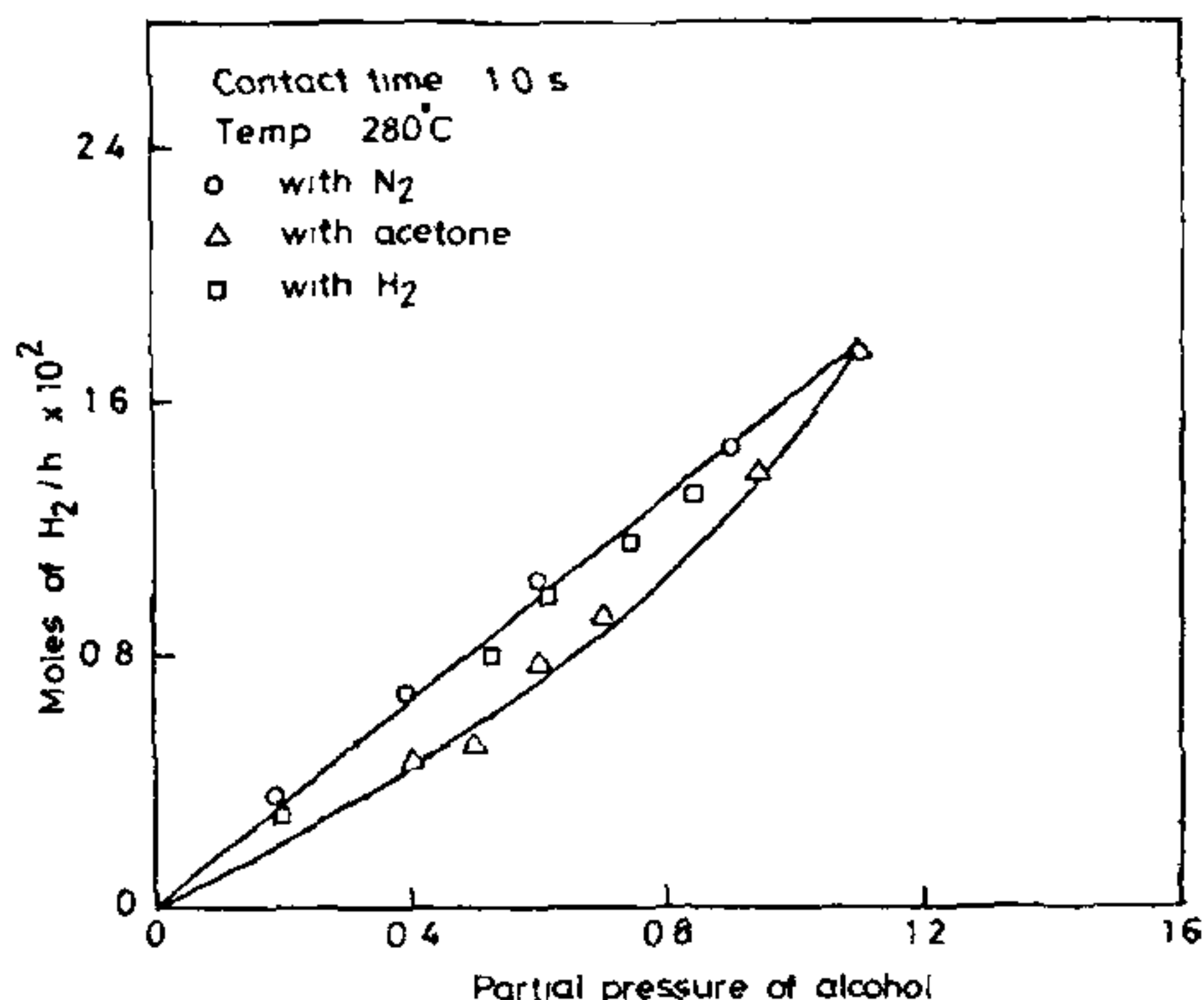


Figure 2. Effect of products on the decomposition of iso-propyl alcohol on $\text{Gd}_2\text{MnNiO}_6$.

out in the presence of the products acetone and hydrogen, with nitrogen as diluent. The results given in figure 2 for Gd_2MnNiO_6 show that (i) acetone suppresses the dehydrogenation reaction rate at all partial pressures. (ii) hydrogen does not affect the dehydrogenation reaction.

The effect of products on the other catalysts is also the same. Hence it is possible that acetone desorption is the rate-determining step of the reaction on these catalysts.

A plot of $\log A$ versus E_a shows a linear relationship (figure 3), which indicates that the active centre is

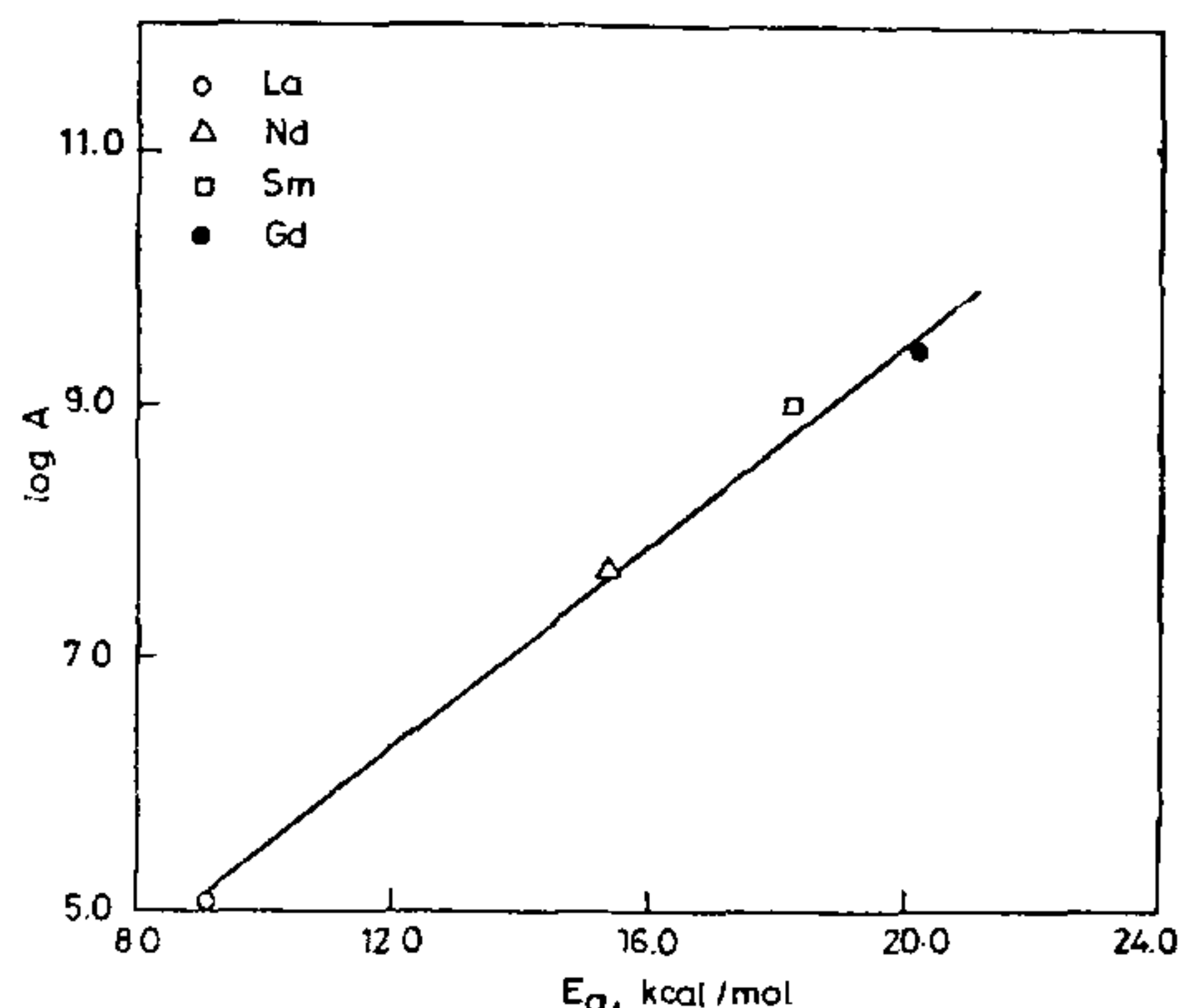


Figure 3. Compensation effect for the decomposition of iso-propyl alcohol in the system Ln_2MnNiO_6 ($Ln = La, Nd, Sm, Gd$).

primarily the divalent transition metal ion, *i.e.*, Ni^{2+} . It has been reported earlier² on a similar series of catalysts *viz* La_2TiMO_6 ($M = Cu, Ni$ and Zn) that the acetone desorption is the rate-determining step for isopropanol decomposition and that the transition metal ions are the active centres. The present investigation suggests that the alcohol decomposition involves a similar type of mechanism in the case of Ln_2MnNiO_6 catalyst and the rare earth ions seem to modify the activity of the transition metal ions in the reaction.

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STUDIES ON TELLURIUM (IV) CHLORIDE COMPLEXES WITH N, N' - SUBSTITUTED THIOUREAS.

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ALTHOUGH thiourea and its derivatives generally reduce $Te(IV)$ in acid solution to form divalent tellurium complexes, stable complexes of tetravalent tellurium have also been isolated in the case of tetramethyl thiourea¹⁻³. No reports are available on the complexes of $Te(IV)$ with N,N'-disubstituted thioureas. The present paper deals with the synthesis of $TeCl_4$ complexes with benzoyl thiourea (bztu), N-benzoyl N'-methyl thiourea (bzmetu), N-benzoyl N'-ethyl thiourea (bzetu), N-benzoyl N'-phenyl thiourea (bzPtu), N-benzoyl N'-o-chlorophenyl thiourea (bz-o-ClPtu), N-benzoyl N'-m-tolyl thiourea (bz-m-totu), N-benzoyl N'-o-tolyl thiourea (bz-o-totu), N-benzoyl N'-o-nitrophenyl thiourea (bz-o- NO_2 Ptu), N-benzoyl N'-o-methoxyphenyl thiourea (bz-o-MeOptu), N'-benzoyl N'-2,5 diethoxyphenyl thiourea (bz-2,5 diEtoPtu), N-benzoyl N'- β -hydroxyethyl thiourea (bz- β -OHetu), N-benzoyl N'-furfuryl thiourea (bz-fur. tu) and morpholine 4-thiocarbonic acid benzamide (MTBzA). These adducts have been analyzed and further characterized with the aid of conductance, spectral and thermoanalytical data.

The ligands were synthesised in accordance with published methods⁴.

The complexes were prepared by stirring a solution of ligand and $TeCl_4$ in 1:2 mole ratio in dry benzene for 2-3 hr (26-27°C) at room temperature when they precipitated completely. The products were quickly filtered under vacuum, washed with the solvent and dried in vacuo over P_2O_5 . Care was taken to exclude moisture throughout the synthesis. The complexes were analyzed for tellurium, nitrogen, sulphur and chlorine by standard procedures⁵. The analytical data are presented in table I.

The molar conductivity was measured in DMSO ($1 \times 10^{-3} M$) using HICO conductivity bridge. The infrared spectra were recorded on PF-597 spectrometer; The NMR spectra in $CDCl_3$ and d_6 DMSO were recorded on Varian I-60 instrument and the thermograms (0-500°C) were recorded on a Stanton balance at a heating rate of 6°C/min.