Kinetics of Dehydrogenation of 2-Propanol on $La_{2-x}Sr_xCuO_{4-y}$

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The catalytic properties of mixed oxides $La_{2-x}Sr_xCuO_{4-y}$ ($0.0 \leqslant x \leqslant 1.0$ and y=non-stoichiometry) having K_2NiF_4 structure were investigated with regard to the effect of changes in the lattice parameters, the oxidation state of copper and oxygen nonstoichiometry in order to correlate the catalytic activity with physicochemical properties. The decomposition of 2-propanol was studied by pulse and flow reactor techniques. The flow reactor data was analyzed by statistical methods to deduce the mechanism on the basis of Langmuir-Hinshelwood and Hougen-Watson models. The reaction followed the first order kinetics with dual site surface reaction as the rate controlling step. The kinetic and thermodynamic parameters obtained from flow reactor data are comparable to those obtained from pulse reactor studies. The higher catalytic activity as indicated by low activation energy and higher conductivity value of $La_{1.8}Sr_{0.2}CuO_{3.96}$ among the series have been attributed to the presence of higher concentration of Cu(III).

Rare earth-transition metal oxides crystallizing in perovskite and perovskite-related structures such as double perovskites and mixed oxides having K_2NiF_4 structure are of interest as catalysts for oxidation reactions and electro-catalysts in general and in the treatment of automotive exhausts in particular. The systems with a variety of A and B site ions, are characterized by a greater stability of the structure, stabilization of unusual oxidation states and oxygen vacancies besides offering the possibility of a systematic variation of oxidation states of metal ions. Thus they are excellent model compounds for the correlation of the structure and solid state characteristics with catalytic properties.

In the present study the catalytic properties of lanthanum-copper mixed oxides having K_2NiF_4 structure have been investigated by both flow and pulse reactor techniques. The K_2NiF_4 structure can be considered as an intergrowth of perovskite and sodium chloride type layers resulting in an octahedral environment around the transition metal ion and a coordination of nine for the rare earth metal ion. The lanthanide-copper oxides of compositions, La_2CuO_4 and Ln_2CuO_4 have been investigated for the oxidation of CO, primary alcohols and decomposition of dinitrogen monoxide.[1-3] Literature reports on the use of the micro catalytic pulse reactor for kinetic studies are rather sparse.[4]

Experimental

Preparation and Characterization: All the catalyst compositions in the series $La_{2-x}Sr_xCuO_{4-y}$ ($0.0 \leqslant x \leqslant 1.0$) were prepared in air by solid state reaction. Stoichiometric mixtures of dry La_2O_3 (Indian rare earth Ltd.), $SrCO_3$ (BDH, AR), and $CuCO_3$ (BDH, AR) were heated to 873 K for 6 h. The temperature was further increased to 1073 K for 15 h followed by pelletisation and heating at 1273 K for further period of 15 h. The compounds were characterized by X-ray diffraction pattern and IR spectra. The ratios of Cu(III)/Cu(II) of different compositions were determined by iodometry method.[5] The electrical resistivity measurements were made on pelletised samples with four probe electrical resistivity measurement apparatus in the temperature range 300 to 750 K. The surface area of the samples were measured by BET method.

Kinetics of Decomposition of 2-Propanol: The kinetics of decomposition of 2-propanol was studied by flow as well as pulse technique.

Flow Reactor Technique: The decomposition of 2-propanol was studied in a fixed bed flow (integral) reactor working at atmospheric condition. The kinetics of the reaction was studied by varying the time factor (W/F) in the range 1 to 10 $\mathrm{g\,h\,mol^{-1}}$ of feed at various temperatures between 490 and 560 K. The products were analyzed chromatographycially using TCD.

Pulse Reactor Technique: Pulse microreactor studies were carried out by loading 0.2 g of catalyst in the front portion of a chromatographic column. Constant pulses of 1 μl. of pure 2-propanol were injected into the stream of nitrogen carrier gas. The gas mixture was analyzed by chromatographic column connected to FID. The kinetics of the reactions was followed at different flow rates, 8 to 30 $\mathrm{ml\,min^{-1}}$ of nitrogen gas and at different temperatures in the range 530 to 620 K.

Results

Physicochemical Properties: The phase purity of the composition and tetragonal crystal structure were confirmed by X-ray diffraction patterns. The lattice parameters calculated in the present study are in good agreement with literature reports.[6] The Cu(III)/Cu(II) ratio present in different compositions, crystallographic parameters, room temperature electrical conductivity, and IR absorption bands are given in Table 1.

The variation of Cu(III) content, lattice parameter c, and electrical conductivity ($\sigma_{300\mathrm{K}}$) with strontium concentration (x) are similar in their trend with a maximum at x=0.2. It is shown in Fig. 1. The variation of electrical resistivities of the compositions as a function of temperature showed interesting features. The compositions $0.0 \leqslant x < 0.6$ showed metallic character while compositions with $x > 0.6$ are semiconductors in the temperature range 300—600 K. $LaSrCuO_{3.51}$ showed wide variations in its electrical

Table 1. Catalyst Compositions and Solid State Properties

Composition	Lattice parameters		Cu(III) Content	σ at R.T.	IRγ
	a/Å	c/Å		$\Omega^{-1}cm^{-1}$	cm^{-1}
La_2CuO_4	5.377(2)	13.075(8)	0.0	5.09	690 550 390
$La_{1.8}Sr_{0.2}CuO_{3.96}$	3.739	13.283	0.118	263.5	510 380
$La_{1.6}Sr_{0.4}CuO_{3.80}$	3.742(3)	13.262(4)	0.054	147.7	515 375
$La_{1.4}Sr_{0.6}CuO_{3.72}$	3.749(3)	13.143	0.037	96.7	520 380
$La_{1.2}Sr_{0.8}CuO_{3.62}$	3.793(9)	13.123	0.034	61.3	520 390
$LaSrCuO_{3.51}$	3.805(6)	13.104(4)	0.028	20.0	515 395

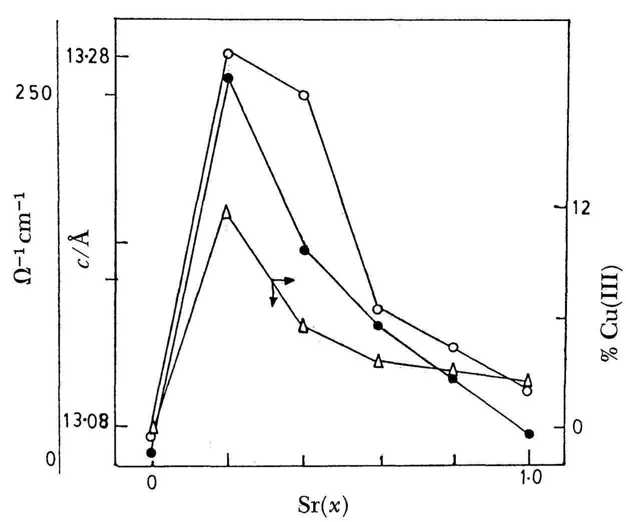

Fig. 1. The effect of strontium concentration (x) in La_{2-x} Sr_xCuO_{4-y} ($0.0 \leqslant x \leqslant 1.0$) on lattice parameter, c (Å): ○, % Cu(III): △, Room temperature electrical conductivity (300 K): ●.

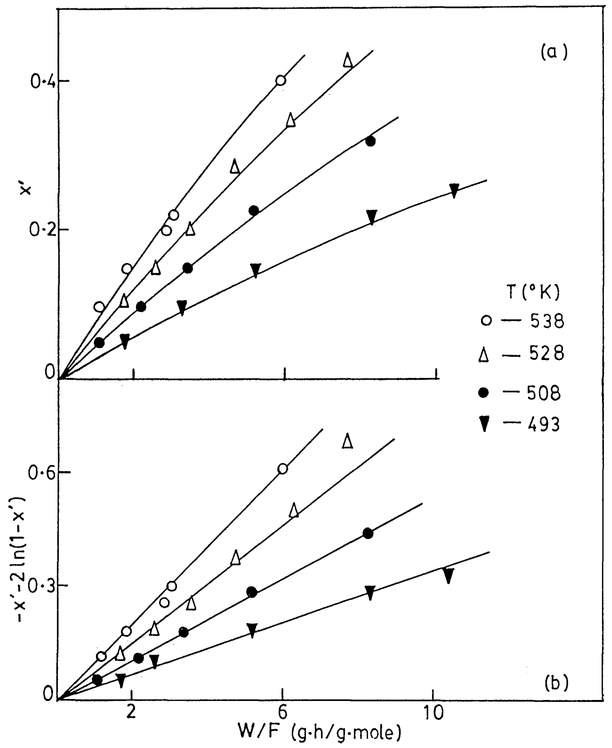

Fig. 2. Effect of time factor on dehydrogenation of 2-propanol on $La_{1.8}Sr_{0.2}CuO_{3.96}$. (a) Plot of W/F vs. x': (b) Plot of W/F vs. $-x'-2\ln(1-x')$.

behavior in that, the resistivity remains constant in the temperature range 300 to 500 K indicating semimetallic nature and undergoes a transition to metallic in the temperature range 550 to 623 K.

Catalytic Properties: Flow Reactor Studies: All the catalyst compositions in the series $La_{2-x}Sr_xCuO_{4-y}$ ($0.0 \leqslant x \leqslant 1.0$) exhibits selectivity towards dehydrogenation of 2-propanol. The fractional conversion vs. W/F plot is shown in Fig. 2(a) for a representative sample of $La_{1.8}Sr_{0.2}CuO_{3.96}$. The experimental data were analyzed on the basis of integral method by using the Eq. $-x'-2\ln(1-x')=kP/RT\ (W/F)$ where x' is the fractional conversation, k is rate constant, P is total pressure, R is gas constant, and T is temperature of the catalyst bed. The plot of $-x'-2\ln(1-x')$ vs. W/F gave straight lines passing through the origin at all temperatures for all the catalyst compositions confirming the order of the reaction to be one (Fig. 2(b)). The rate constants were calculated from the slopes of the straight lines. The energy of the activaion for the catalyzed reaction was obtained from Arrhenius plot. The kinetic parameters are listed in Table 2.

The kinetic parameters have also been determined based on reaction mechanism approach using Hougen-Watson models.[7] The experimental conditions such as flow rate and particle size were so chosen as to eliminate the physical steps that occur during catalytic reactions. The chemical steps involved are considered to be three consecutive steps based on Langmuir-Hinshelwood mechanism, namely adsorption, surface reaction, and desorption as rate control-

Table 2. Kinetic and Thermodynamic Parameters for the Isopropanol Dehydrogenation on the $La_{2-x}Sr_xCuO_{4-y}$ Series

Composition	T	k	k	K_A
	K	lr atm g^{-1} h^{-1} (Integral method)	lr atm g^{-1} h^{-1} (Method based on mechanism)	mol^{-1} (Method based on mechanism)
La_2CuO_4	558	4.81	6.70	0.78
	538	3.19	3.21	0.90
	528	1.94	2.10	1.01
	508	0.83	0.91	1.10
		E_a=93±0.5 kJ mol^{-1}	E_a=92±0.5 kJ mol^{-1}	
		ln A=21.93 h^{-1}.	ΔH=4±0.1 kJ mol^{-1}	
$La_{1.8}Sr_{0.2}CuO_{3.96}$	538	4.70	5.19	0.68
	528	3.39	4.41	0.69
	508	3.19	3.32	0.70
	493	1.42	1.89	0.71
		E_a=54±0.6 kJ mol^{-1}	E_a=54±0.5 kJ mol^{-1}	
		ln A=13.91 h^{-1}.	ΔH=2±0.5 kJ mol^{-1}	
$La_{1.6}Sr_{0.4}CuO_{3.80}$	538	7.43	7.86	0.88
	520	4.26	4.08	1.00
	493	1.94	1.74	1.41
		E_a=64±0.5 kJ mol^{-1}	E_a=65±0.4 kJ mol^{-1}	
		ln A=16.37 h^{-1}.	ΔH=22±0.5 kJ mol^{-1}	
$La_{1.4}Sr_{0.6}CuO_{3.72}$	538	5.70	6.10	0.80
	518	3.15	3.37	1.09
	498	1.93	1.97	1.14
		E_a=66±0.5 kJ mol^{-1}	E_a=66±0.5 kJ mol^{-1}	
		ln A=16.65 h^{-1}.	ΔH=20±0.4 kJ mol^{-1}	
$La_{1.2}Sr_{0.8}CuO_{3.62}$	538	4.20	4.72	0.80
	518	3.21	3.01	0.90
	508	2.55	1.81	1.01
	498	1.18	1.11	1.11
		E_a=71±0.4 kJ mol^{-1}	E_a=71±0.4 kJ mol^{-1}	
		ln A=17.4 h^{-1}.	ΔH=12±0.5 kJ mol^{-1}	
$LaSrCuO_{3.51}$	538	2.99	2.20	1.62
	528	2.04	1.27	1.72
	518	1.53	0.99	1.78
	498	0.87	0.50	1.87
		E_a=74±0.5 kJ mol^{-1}	E_a=74±0.5 kJ mol^{-1}	
		ln A=17.23 h^{-1}.	ΔH=6±0.4 kJ mol^{-1}	

ling steps.

The rate controlling steps involved in the dehydrogenation of 2-propanol and the corresponding equations are given below:

$$\underset{(A)}{C_3H_7OH} \rightarrow \underset{(B)}{CH_3COCH_3} + \underset{(C)}{H_2} \qquad (1)$$

Adsorption rate controlling

$$r=k(C_A-C_BC_C/K_{eq})/(1+K_AC_BC_C/K_{eq}+K_BC_B+K_CC_C) \qquad (2)$$

Surface reaction rate controlling

$$r=kK_A(C_A-C_BC_C/K_{eq})/(1+K_AC_A+K_BC_B+K_CC_C)^n$$

n = number of surface active sites. (3)

Desorption rate controlling

$$r=kK_{eq}(C_A/C_B-C_C/K_{eq})/(1+K_AC_A+K_BC_B+K_{eq}K_C(C_A/C_B)) \qquad (4)$$

The true rate expression and therefore the reaction mechanism that governs the heterogeneously catalyzed reaction was determined by statistical method of parameter estimation and model discrimination. The kinetic data have been analyzed by nonlinear estimation method with the help of a computer program. The initial rates (r_{obs}) derived from W/F vs. x' plot and gas phase concentration from conversion data were used for computing the values of rate constants and adsorption equilibrium constants for all the possible mechanisms.

Models were discriminated against, if the estimated rate constants and/or adsorption equilibrium constants were negative or if the temperature coefficients of those estimated parameter values were of the wrong sign. For all the compounds the best fit model was found to be the mechanism involving dual site surface reaction with negligible adsorption of products as the rate controlling step. A dual site surface reaction mechanism based on Hougen-Watson approach envisages the interaction of surface adsorbed species with an adjacent active center forming a complex which then decomposes to the product. This model gave positive values for all the coefficients over the entire temperature range and fits well with the Arrhenius equation.

Table 3. Kinetic and Thermodynamic Parameters on $La_{2-x}Sr_xCuO_{4-y}$ from Pulse Reactor Studies

Composition	E_a	ΔH	kK_A at 573K
	kJ mol^{-1}	kJ mol^{-1}	mol atm^{-1} g^{-1} s^{-1}$\times10^{-6}$
La_2CuO_4	92±0.5	8±0.5	2.90
$La_{1.8}Sr_{0.2}CuO_{3.96}$	50±0.6	7±0.5	9.36
$La_{1.6}Sr_{0.4}CuO_{3.80}$	60±0.6	9±0.5	4.61
$La_{1.4}Sr_{0.6}CuO_{3.72}$	62±0.4	11±1.0	4.55
$La_{1.2}Sr_{0.8}CuO_{3.62}$	66±1.0	12±0.5	4.25
$LaSrCuO_{3.51}$	89±1.0	10±0.5	5.59

Further, the validity of the rate expression was checked by calculating the rates for all the temperatures using the equation.

$$r_{\text{cal}}=\frac{A_1\,e^{-(E_a/RT)}A_2\,e^{-(\Delta H/RT)}[C_A-C_BC_C/K_{\text{eq}}]}{(1+A\,e^{-(\Delta H/RT)}C_A)^2} \tag{5}$$

The calculated reaction rate values (r_{cal}) and the experimental values (r_{obs}), obtained graphically from x' vs. W/F curves fall on the same line for entire temperature range for each of the compositions confirming the validity of the selected mechanism.

The computed values of rate constants and adsorption equilibrium constants for all the catalyst compositions are given in Table 2. From the Arrhenius plots of $\ln k$ vs. $1/T$ and $\ln K_A$ vs. $1/T$, the values of E_a and ΔH were also calculated and presented in Table 2.

Pulse Reactor Studies: All the catalyst compositions showed selectivity towards the dehydrogenation reaction under pulse reactor conditions also.

The chromatographic elution of unconverted reactant and product were devoid of peak broadening. Apparently the adsorption of 2-propanol was relatively a fast step. The elution of the product acetone preceeds that of the reactant. Further the retention volumes of acetone under identical experimental conditions in the presence and in the absence of catalyst were found to be identical, indicating that desorption of product was not the rate controlling step. Under these conditions, it was fair to assume that surface reaction was the rate controlling step.

The quantitative treatment of pulse micro reactor data for the evaluation of kinetic and thermodynamic parameters has been explained elsewhere.[8] The conversion reaction was found to follow the first order kinetics from the observed straight line plots of $\ln(1/1-x)$ vs. $1/F$ for all the compositions and the products of rate constants and adsorption equilibrium constants were calculated. The energy of activation for the reaction was obtained from the plot of $\ln kK_A$ vs. $1/T$ at constant flow rate which is equivalent to plot of $\ln(\ln(1/1-x))$ vs. $1/T$. The ΔH values were calculated from retention volume data.[4] The observed kK_A, E_a, and ΔH values are presented in Table 3.

Discussion

The Effect of Strontium Content on the Catalytic Activity: The catalytic activity of the series may be compared either on the basis of E_a or rate constant at particular temperature. The values of E_a obtained from both pulse and flow reactor techniques are nearly identical in magnitude and variation of E_a with stronitum content shows in both cases a similar trend as shown in Fig. 3. The energy of activation for dehydrogenation reaction decreases steeply as x increases from 0.0 to 0.2 and shows an increasing trend with further increase in x. Similar trend is observed in the variation of Cu(III)/Cu(II) ratio with strontium content. The higher catalytic activity observed in $La_{1.8}Sr_{0.2}CuO_{3.96}$ may be attributed to the presence of maximum Cu(III) concentration. The higher concentration of Cu(III) apparently facilitate the electron transfer from the adsorbate to the catalyst surface. Similar behavior of p-type semiconductors facilitating the dehydrogenation reaction is well documented in literature.[9,10]

The variation of the product of rate constant and adsorption equilibrium constant attained from pulse reactor technique shows a maximum at x=0.2, and decreases as x increases upto 0.8 as shown in Fig. 3. The trend is similar to the variation of structural characterstics (lattice parameter, c), chemical composition (ratio of Cu(III)/Cu(II)) and room temperature electrical conductivity as shown in Fig. 1. The slight

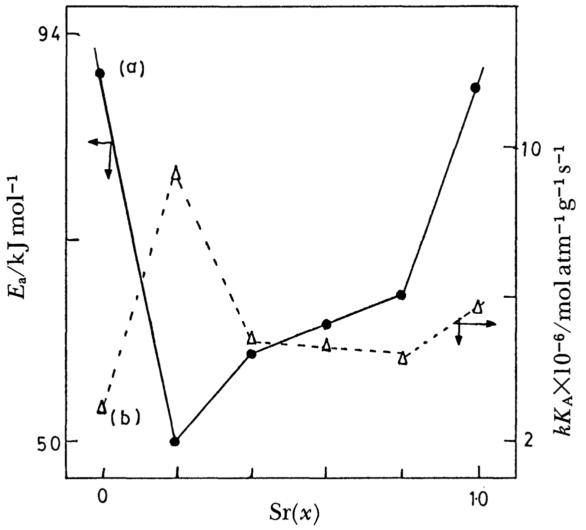

Fig. 3. Variation of E_a (●) and kK_A (△) with strontium concentration (x).

increase in kK_A value for the composition x=1.0 may be attributed to the decrease in variation in electrical resistivity in the temperature range 560 to 623 K, wherein it shows a transition from metallic to semiconductor. The K_A and ΔH values also depend on the strontium concentration and their variations with x are shown in Fig. 4. The K_A values for compositions x=0.0, 0.4, 0.6, and 0.8 are almost identical. However, for x=0.2 there is a distinct lowering of K_A value indicating the surface concentration of adsorbed species to be low. The variation of ΔH vs. x also shows a minimum value at x=0.2 and a maximum at x=0.4.

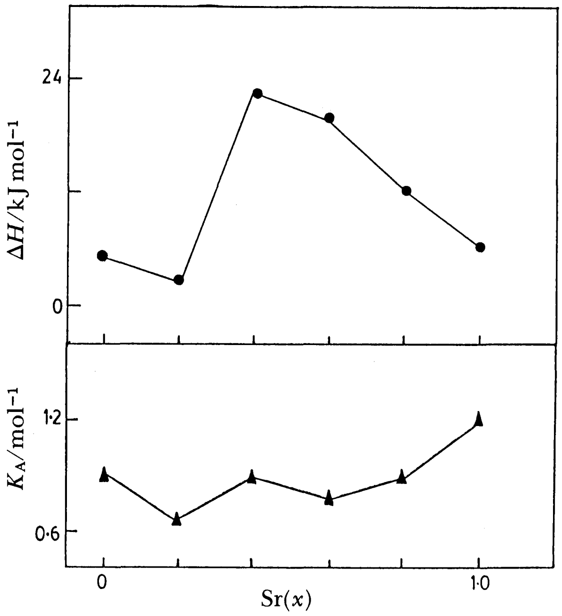

Fig. 4. The effect of strontium concentration (x) on thermodynamic parameters. (a) Plot of heat of adsorption ΔH vs. x: (b) Plot of adsorption equilibrium constant K_A vs. x.

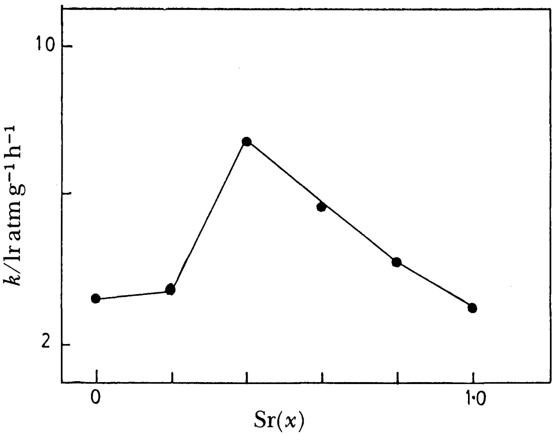

Fig. 5. Variation of rate constant at 538 K with x in $La_{2-x}Sr_xCuO_{4-y}$.

The rate constant for the composition x=0.2 is slightly lower than those of x=0.6 and 0.8 while the E_a value for x=0.2 is lowest when compared to the values for all other compositions. For the composition having x=0.4 the rate constant shows a maximum but with higher E_a value (Fig. 5).

Conclusion

The dehydrogenation of 2-propanol on $La_{2-x}Sr_xCuO_{4-y}$ ($0.0 \leqslant x \leqslant 1.0$) follows first order kinetics with surface reaction as rate limiting step. The kinetic parameters obtained from both flow and pulse reactor techniques are comparable. Among the series the compound $La_{1.8}Sr_{0.2}CuO_{3.96}$ in which the Cu(III) concentration is high, performs high catalytic activity.

Since the steady state and unsteady state yield comparable results, it is inferred that the kinetic data derived from the pulse reactor technique can be used for scaling up of the reaction parameters. Hence this technique is advantageous in that, it requires extremely small quantities of catalysts and reactant and less time consuming compared to conventional fixed bed flow reactor.

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