CATALYTIC CONVERSION OF ISOPROPYL ALCOHOL ON PURE AND ALKALI DOPED SAMARIUM OXIDE

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The catalytic conversion of isopropyl alcohol (IPA) on pure and alkali doped Sm_2O_3 (10 mole %) was studied in flow system. The reaction is mainly dehydration–dehydrogenation of IPA. The results revealed that, the reaction products are strongly affected by the nature of employed carrier gase. The reaction in oxygen showed the highest activity and selectivity compared to other carriers. The doping process caused a significant decrease in the activity and selectivity of Sm_2O_3 solids. Probable mechanistic routes for the dehydration and dehydrogenation processes are proposed.

The catalytic dehydration and dehydrogenation of alcohols are considered a straightforward means of producing materials of prime industrial importance[1]. Consequently, they have stimulated research interest, and a large number of papers have been published dealing with the subject from a range of important aspects. Part of the catalysts has been based on transition metal oxides[2–10]. These solids generally contain exposed cations, oxygen ions and hydroxyl groups in unusual coordination states[11,12]. These coordinatievly unsaturated sites may be considered as active centers in catalysis by oxides[13]. The surfaces of many oxides have been also studied in terms of acidic and basic sites[14] in addition to reducing or oxidizing centers. On the other hand, less attention was drawn towards the catalytic conversion of alcohols on rare earth metal oxide catalysts. Therefore, the aim of this work is to study the catalytic conversion of isopropyl alcohol over pure Sm_2O_3 and that treated with alkali metal oxides.

EXPERIMENTAL

Materials. Samarium oxide (Sm_2O_3) used was a powder (purity > 99·9%) obtained from Asahi Chemical Industry. Doping of Sm_2O_3 with Li_2O, Na_2O and K_2O (10 mole %) were effected by impregnation from dilute aqueous solutions of nitrate salts (BDH chemicals). The impregnated samples were dried at 110°C, then calcinated in air at 700°C for 5 h.

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Apparatus and procedure. The catalytic conversion of isopropyl alcohol (IPA) was carried: out using a conventional gas flow system at atmospheric pressure, which comprised of two reactors; one of them was used without any catalyst (control reactor). It enabled measurement of the blank conversion which was substracted from that obtained in the second reactor with a catalyst. The reaction gas mixture of IPA with N_2, O_2 or air was introduced into the fixed bed flow reactor. The exit feed was analysed chromatographically using a PYE Unicam gas chromatograph with 20% PEG celite column.

Electrical conductivity was measured using a conductivity cell described elsewhere[15]. Voltage was supplied via 240 Kiethley instrument and the current obtained was measured with 410 A picoameter (Kiethley instrument).

IR spectra of pure Sm_2O_3 and doped oxides were recorded using the Perkin–Elmer spectrophotometer model 599 B in the range of 1 800–600 cm^{-1} and KBr disc technique.

RESULTS AND DISCUSSION

The catalytic activity of the samples was determined using 0·5 g of unsupported catalysts and 1·8% of IPA vapour in the gas feed. The flow rate of carrier gas was 300 ml min^{-1} (STP). It was found that propene and acetone are the major products in the product. Diisopropyl ether has been detected in the products when the reaction was carried out on Sm_2O_3 in presence of air as a carrier gas. The amounts of ether produced were found to decrease progressively with increasing reaction time and then to disappeare after 2 h. All the experimental data recorded after 2 h, the time of attainment of the steady state.

Effect of Reaction Temperature

The influence of the reaction temperature on the conversion of IPA has been tested in presence of air as a carrier gas. The experimental results (Fig. 1) show an increase of conversion of IPA as well as propene yield when the reaction temperature in-

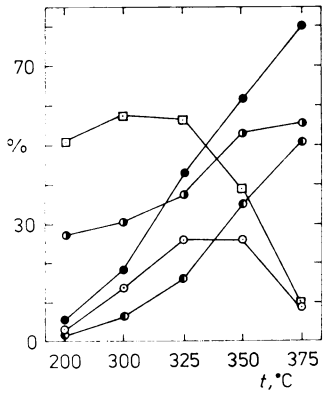

FIG. 1

Activity variation with reaction temperature in presence of air as a carrier gas for pure Sm_2O_3 catalyst calcinated at 700°C for 5 h, ● conversion of IPA, × yield of propene, ◌ selectivity of propene, ⊙ yield of acetone, and ⊡ selectivity of acetone

creases from 200 up to 375°C. On the other hand, the yield of acetone increased with reaction temperature, reaching a maximum value at 350°C, and then decreased suddenly when the temperature rose over this value. These results indicate that under 350°C, the dehydrogenation is faster than the dehydration, whereas a reverse behaviour is observed at the reaction temperature higher than 325°C. The decrease in yield and selectivity for acetone formation may be due to the decomposition of the surface acetate to CO_2, which it detected in the gas mixture at 350°C. The surface acetate is produced via the readsorption of acetone formed during the reaction at higher temperature[6]. It can be concluded that at temperatures higher than 350°C IPA undergoes mainly dehydration reaction on Sm_2O_3 to produce propene.

Effect of Reactant Partial Pressure

The content of IPA in the reaction mixture varied between 1·3 and 3·3 mole % when the reaction temperature was fixed at 350°C in presence of air as a carrier gas. The results are given in Table I.

It appears that yield and selectivity for the dehydration and dehydrogenation processes decreased with increase of the partial pressure of IPA. It seems that the catalyst surface becomes saturated with chemisorbed alcohol molecules at relatively small partial pressure.

Effect of Nature of the Carrier Gas

The effect of the nature of carrier gas on the conversion of IPA over Sm_2O_3 calcined at 700°C have been carried out at 350°C in the presence of N_2, O_2 and air. The variation of conversion, yield and selectivity with time-on-stream is presented in Figs 2–4. The results show that the surface sites are influenced by the presence of these gases. The published work on the oxides of 3*d*-transition metals indicated:

TABLE I

Variation of conversion, yield and selectivity with IPA content in the reaction mixture over pure Sm_2O_3 at the reaction temperature of 350°C

Reactant content mole %	Conversion %	Yield, %		Selectivity, %	
		propene	acetone	to propene	to acetone
1·3	85·5	50·0	33·3	58·5	38·9
1·8	75·3	42·0	27·5	56·1	36·6
2·4	67·2	31·5	15·7	46·1	23·0
3·3	60·5	27·5	12·5	45·5	20·7

(i) oxygen content of the oxide surfaces can vary in a complex manner with temperature and oxygen pressure[16-18] and (ii) the activity and/or selectivity of some pure unsupported oxides for dehydration and/or dehydrogenation of secondary alcohols could be strongly altered by prior reduction or oxidation of the oxide surface[19].

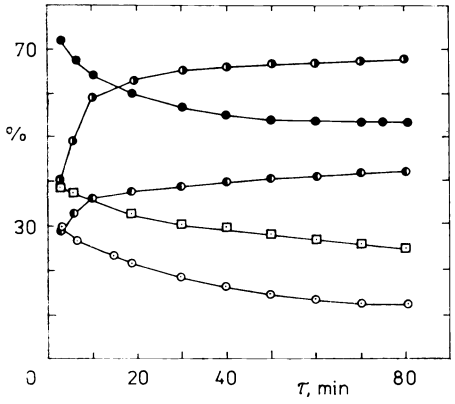

FIG. 2

Activity variation with time-on-stream in presence of N_2 as a carrier gas for pure Sm_2O_3 catalyst calcinated at 700°C for 5 h, ● conversion of IPA, × yield of propene, ⊗ selectivity of propene, ⊙ yield of acetone, and □ selectivity of acetone

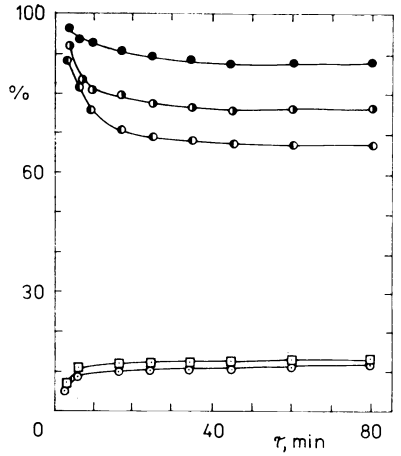

FIG. 3

Activity variation with time-on-stream in presence of Sm_2O_2 as a carrier gas for pure Sm_2O_3 catalyst calcinated at 700°C for 3 h, ● conversion of IPA, × yield of propene, ⊗ selectivity of propene, ⊙ yield of acetone and □ selectivity of acetone

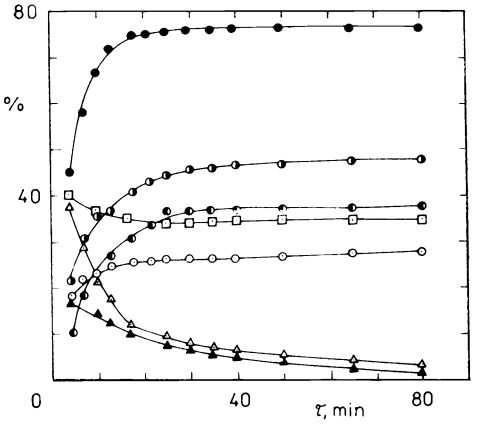

FIG. 4

Activity variation with time-on-stream in presence of air as a carrier gas for pure Sm_2O_3 catalyst calcinated at 700°C for 5 h, ● conversion of IPA, × yield of propene, ⊗ selectivity of propene, ⊙ yield of acetone, □ selectivity of acetone, ▲ yield of ether and △ selectivity of ether

Thus, in case of (IPA + N_2), Fig. 2 shows that at the beginning of the reaction, the yield and selectivity of propene and acetone have equal values while on increasing the reaction time, a progressive decrease in the conversion of IPA as well as the yield and selectivity towards the formation of acetone is observed. On the other hand, the yield and selectivity of propene formation are increased by increasing the reaction time. This behaviour indicates that the active sites responsible for the dehydrogenation reaction are decreased by the consumption of some lattice oxygen during the reaction. The participation of lattice oxygen in the decomposition of CH_4, C_2H_6 and C_2H_4 over Sm_2O_3, in presence or absence of oxygen, has been studied previously[20]. The removal of some lattice oxygen in absence of O_2 was detected by the appearance of carbon oxides in the product. In fact, the loss of some lattice oxygen during the reaction is accompanied by the creation of anionic vacancies according to the following mechanism

$$Sm_2O_3 \rightarrow 2\,Sm|Sm|' + |O|^{\bullet\bullet} + \tfrac{1}{2}\,O_2 + 2\,e\,, \qquad (1)$$

where $Sm\,|Sm|'$ represents Sm^{2+} replacing Sm^{3+} and $|O|^{\bullet\bullet}$ are oxygen vacancies. Accordingly, the creation of anionic vacancies acting as acidic sites (electron acceptors) in the chemisorption, which results in propene formation is responsible for such increase. On the other hand, the loss of basic lattice oxide O^{2-}, which acts as electron donor during the reaction, is responsible for the decrease of acetone formation.

Figure 3 shows the variation of the reaction products of IPA over Sm_2O_3 in presence of O_2 gas. At the start of the reaction, the conversion of IPA reached 96%, was followed by continuous decrease on increasing the time-on-stream and attained 86% after 1 h. Also, a progressive decrease in both yield and selectivity of propene formation was observed. On the other hand, the yield and selectivity of acetone formation showed a little increase at the beginning of the reaction and reached the steady state after 20 min. It is of interest to mention that the high catalytic activity attained for dehydration–dehydrogenation of alcohols over various oxides in the presence of gaseous oxygen in an initial step is followed by fast reoxidation by gaseous oxygen of metal oxide sites reduced in the first step[21,22]. Furthermore, we concluded previously[20] that the reactivity of adsorbed oxygen for converting methane into C_2 hydrocarbons was higher than that of lattice oxygen atoms. However, according to equation (*1*), the released electrons should enhance the adsorption of oxygen on the catalyst surface as follows:

$$O_{2gas} \rightleftarrows O_{2ads} \xrightarrow{+e} O_2^- \xrightarrow{+e} 2\,O^- \xrightarrow{+2e} 2\,O^{2-}\,. \qquad (2)$$

From equation (*2*), the reoxidation by oxygen is assumed to lead to the formation of lattice O^{2-} ions through simultaneous transfer of four electrons from the cation.

However, a stepwise transfer of electrons involving O_2^-, O_2^{2-} and O^- as intermediates might be expected[23,24]. The formation of adsorbed oxygen is accompanied by the formation of acidic sites, i.e. by an increase the oxygen anion vacancies. Therefore, the higher yield of propene, compared to that obtained in absence of O_2, can be understood on the basis of an increase of electron acceptor sites. On the other hand, a small difference between the values of acetone yield in absence and presence of O_2 has been observed. Also, the fast establishment of the steady state may be attributed to the fast reduction and reoxidation of donor sites in presence of O_2 in the gas phase.

Important results have been obtained when the reaction of IPA on Sm_2O_3, in presence of air, at 350°C has been carried out. The results presented in Fig. 4 indicate an increase in the conversion as well as the yield of propene on increasing the time-on-stream. More interesting is the detection of diisopropylether in the reaction products with a 38% selectivity at the initial period. This means that the ratio of oxygen in the gas phase is an important factor for the distribution of the reaction products.

It follows from the above results that the catalytic behaviour is strongly dependent on operating conditions especially on the composition of the gaseous phase above the catalyst surface. However, it was pointed out recently that the removal of two hydrogen atoms from IPA to give H_2 and acetone involves likely at some stage a basic site to accept H^+ from the OH group, and an acidic site to accept H^- from the tertiary carbon atom, the two sites preferably existing close together. On the other hand, the dehydration reaction can proceed on the acid–base pairs of sites[25]. Ultimately, the acidic $Sm^{3+}_{(s)}$ site could accept an OH^-, and the basic $O^{2-}_{(s)}$ site a proton to give another $OH^-_{(s)}$. Product water would then be produced from the two $OH^-_{(s)}$ species. Accordingly, the dehydrogenation can proceed as follows:

$$(CH_3)_2\text{—}CH\text{—}OH + Sm^{3+}_{(s)} + O^{2-}_{(s)} \rightarrow (CH_3)_2\text{—}CHO^- \cdots Sm^{3+}_{(s)} + OH^-_{(s)}\,, \quad (3)$$

where (s) denotes a surface species.

The second step could be

$$(CH_3)_2\text{—}CHO^- \cdots Sm^{3+}_{(s)} \rightarrow (CH_3)_2C{=}O + H \cdots Sm^{3+}_{(s)} \quad (4)$$

followed by

$$OH^-_{(s)} + H \cdots Sm^{3+} \rightarrow Sm^{3+}_{(s)} + H_2 + O^{2-}_{(s)}\,. \quad (5)$$

The dehydration would have reaction (*3*) as the first step, and reaction (*6*) would then be followed by the condensation of the two $OH^-_{(s)}$ to give water

$$(CH_3)_2CHO^- \cdots Sm^{3+}_{(s)} \rightarrow CH_3\text{—}CH{=}CH_2 + OH \cdots Sm^{3+}_{(s)} \quad (6)$$

and

$$OH^-_{(s)} + OH\cdots Sm^{3+}_{(s)} \rightarrow H_2O + Sm^{3+} + O^{2-}_{(s)} \,. \qquad (7)$$

The Catalytic Decomposition of IPA on Doped Sm_2O_3 *Oxides*

The catalytic decomposition of IPA on Sm_2O_3 treated with Li_2O, Na_2O and K_2O (10 mole %) calcined at 700°C has been tested in presence of air as carrier gas using the same conditions as mentioned above. The experimental results, shown in Fig. 5, indicate a noticeable relative in the dehydration-dehydrogenation activities on doping Sm_2O_3 with alkali metal oxides. The electrical conductivity measurements with pure and alkali-treated oxides has been carried out in flow of air. Plots of $\log \sigma$ values versus $1/T$ gave straight lines, the calculated ΔE_a are 0·74, 0·88, 0·98 and 105 eV for pure Sm_2O_3 and those doped with Li_2O, Na_2O and K_2O, respectively. These values indicate that the increase in the Fermi potential should retard the reaction between IPA and the catalyst surface. Morrison et al. reported that, if the Fermi potential increases, the selectivity should decrease. Moreover, the IR absorption spectra of these samples (Fig. 6) show a significant change in the vibration bands characteristic to samarium oxide which means that the foreign ions are

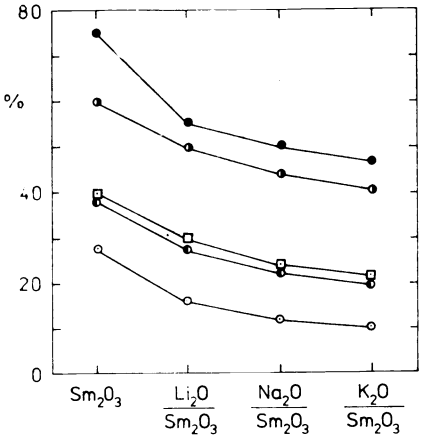

FIG. 5

Activity variation with Li_2O/Sm_2O_3, Na_2O/Sm_2O_3 and K_2O/Sm_2O_3 (10 mole % dopants) calcinated at 700°C for 5 h in presence of air as a carrier gas, ● conversion of IPA, ⊗ yield of propene, ⊘ selectivity of propene, ○ yield of acetone and □ selectivity of acetone

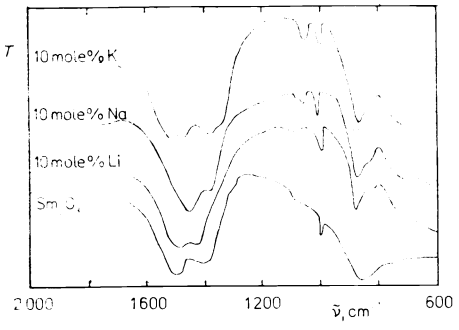

FIG. 6

IR absorption spectra of pure Sm_2O_3 and doped with 10 mole % Li_2O, 10 mole % Na_2O and 10 mole % K_2O (the samples calcinated at 700°C for 5 h)

effectively incorporated into its crystal lattice. Consequently, these results clearly point to an important changes in the surface sites responsible for the dehydration–dehydrogenation reactions. The direction of relative change of activity is

$$Sm_2O_3 > Sm_2O_3\text{–}Li_2O > Sm_2O_3\text{–}Na_2O > Sm_2O_3\text{–}K_2O\ .$$

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