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Surface and Catalytic Properties of Yttrium Oxide: Evidence from Infrared Spectroscopy

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Surface and catalytic properties of Y_2O_3 catalysts generated from different inorganic precursors were investigated by the reactions of pyridine and 2-propanol using IR-spectroscopy. Adsorption and reaction studies of pyridine on Y_2O_3 catalysts at different temperatures indicated that, Y_2O_3 exposes Bronsted acid, Lewis acid, and basic sites. The type and strength of these sites are controlled by the origin of the catalyst and pretreatment temperature. The qualitative and quantitative results of 2-propanol revealed that 2-propanol is irreversible adsorbed at 25°C via different surface species. The type, concentration, and reactivity of these species are affected by the origin of the Y_2O_3 catalyst. © 1998 Academic Press

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INTRODUCTION

The increasing availability of metalorganic precursors has facilitated the preparation of high-surface-area porous oxides of the less common metals, such as yttrium oxide, which has been only seldom investigated as a catalyst and support (1–3). Here we report infrared spectroscopy characterizing the acid–base and catalytic properties of porous Y_2O_3 samples formed from the acetate, nitrate, and oxalate of yttrium. Pyridine was used to probe the surface properties, and the decomposition of 2-propanol was used as a catalytic test reaction because the selectivity for dehydration versus dehydrogenation provides a measure of the surface acid–base properties (4–7). The results show that porous Y_2O_3 is basic, with catalytic properties that are dependent on the precursor; some preparations give selective 2-propanol dehydrogenation and some give selective 2-propanol dehydration.

EXPERIMENTAL METHODS

$Y(CH_3COO)_3 \cdot 4H_2O$, $Y(NO_3)_3 \cdot 5H_2O$, and $Y_2(C_2O_4)_3 \cdot 8H_2O$ (Aldrich, 99.9%) were used as precursors for formation of Y_2O_3 by thermal decomposition reactions, which have been described (8). The Y_2O_3 samples referred to below are symbolized with subscripts indicating the precursors (Ac, acetate; Nit, nitrate; and Ox, oxalate) and the temperature applied in the precursor decomposition, in degrees centigrade. For example, YAc700 refers to Y_2O_3 formed by decomposition of yttrium acetate at 700°C for 1 h in static air.

2-Propanol, acetone, and pyridine were spectroscopic grade, BDH (UK). Prior to use they were degassed by freeze-pump-thaw cycles performed under vacuum.

Infrared spectra of surface or gas-phase pyridine and/or 2-propanol and their decomposition products were recorded with wafer samples of Y_2O_3 in a cell with a furnace section (9), where the sample could be heated to various temperatures. In a typical experiment, self-supporting thin wafers (ca 20 mg/cm^2) of the catalysts were prepared from the powder in a hydraulic press. Satisfactory discs could be obtained from YAc700 and YNit500 at pressure of 3–4.5 ton/cm^2. For YOx700 and YNit700, 7 ton/cm^2 was necessary. After that, the disc was placed in a quartz holder mounted in the heatable (upper) part of the cell. The cold part of the cell was equipped with NaCl windows. Spectra were measured with the sample at room temperature. Each sample was heated in a stream of O_2 to 650°C and held for 1 h to clean the surface of carbonate contamination (3), then it was cooled to room temperature under vacuum (10^{-3} Torr). After recording the background spectrum with the sample evacuated, 3 Torr of pyridine or 10 Torr of 2-propanol vapor was introduced into the cell. The sample was then raised to the furnace section and heated in the evolving gas atmosphere, being held at various intermediate temperatures for 10 min and then lowered into the infrared beam for measurement of the spectrum. When the wafer was raised, the spectrum of the gas phase was measured separately. The spectrum of the adsorbed species was obtained by taking the ratio of the spectrum of the wafer in the gas phase to the gas-phase spectrum, or by pumping out the gas phase at each temperature and then measuring the spectrum of the solid. The background spectrum of the initial solid oxide sample under vacuum was also used to give the ratio of the spectrum of the adsorbed species alone.

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The gas phase was analyzed quantitatively for 2-propanol and its gas-phase decomposition products by use of the standard QUANT software (Perkin-Elmer) and a data acquisition system. Accordingly, the amount of gas-phase components (reactant and product) were determined versus the calibration curves relating the IR absorption intensity at a certain analytical frequency to the calibrate gas phase pressure (Torr). The calibration curves were derived from IR spectra data obtained from authentic samples of each of the gas phase components under identical spectroscopic conditions. The absorption intensity (10) at 3665 ± 5 cm^{-1} for 2-propanol, 1740 ± 5 cm^{-1} for acetone and 913 ± 5 cm^{-1} for propene.

RESULTS

Characterization of the Catalysts

Y_2O_3 samples prepared from the various precursors were characterized by X-ray diffractograms matching the relevant ASTM standards; they confirmed that YAc700, YOx700, YNit500, and YNit700 all had the cubic structure (ASTM No. 25-1200). The X-ray data showed that YOx700 and YNit700 were more highly crystalline than YAc700 and YNit500 (8). With respect to the textural properties, the N_2 adsorption isotherms measured at −196°C. The four samples are generally of type IV isotherms of BET classifications, thus revealing a porous character. The texture data and SEM (11) concluded that both YNit at 500°C ($S_{BET} = 58$ m^2/gm) and YAc at 700°C ($S_{BET} = 55$ m^2/gm) products are very similar; they exhibit a wider spectrum of mesoprosity. In contrast, for the 700°C calcination products of YOx ($S_{BET} = 12$ m^2/gm) and YNit ($S_{BET} = 20$ m^2/gm) the surface area is low and the majority of the BET area is due to the external surface and the internal surface is very small; also the majority of the pores are micropores. Moreover, scanning electron micrographs (SEM) indicated that the materials were aggregated with extensive mesopores for YAc700 and YNit500 and micropores for YOx700 and YNit700. Details of the texture properties are given elsewhere (11).

Infrared Spectra of Y_2O_3 and of Adsorbed Pyridine

The infrared spectra of Fig. 1 represent pyridine adsorbed on YAc700 and YNit700 following evacuation at different temperatures. The spectrum of the higher area YAc700 sample recorded over the frequency range 4000–800 cm^{-1} includes overlapping bands at 3710, 3680, 3640, and 3610 cm^{-1}, and the spectrum of YNit500 includes overlapping bands at 3700, 3650, and 3610 cm^{-1}. The hydroxyl regions characterizing the lower-surface-area samples of YOx700 and YNit700 were not informative because of the low transmission and high scattering. Low-frequency bands (<1560 cm^{-1}), indicative of surface carbonate contaminants (3), were observed for all the samples (as is typical of basic metal oxides), and they disappeared when the samples were treated in O_2 for 1 h at 650°C.

The spectrum of pyridine on YAc700, measured at room temperature (Fig. 1A), includes bands at 1620, 1600, 1540, 1480, and 1440 cm^{-1}, indicating the presence of Lewis acid sites (12–14). The occurrence of the 8_a mode at two different frequencies (1620 and 1600 cm^{-1}) suggests Lewis acid sites of two different strengths (12–15). The band at 1540 cm^{-1} of the 19_b ring vibration mode, accompanied by the 8_a mode at 1620 cm^{-1}, is considered evidence of pyridine bonded to Bronsted acid sites (13).

Pyridine on YNit700 (Fig. 1B) is also represented by a spectrum showing bands (at 1600, 1480, and 1440 cm^{-1}) characteristic of Lewis acid sites. The weakness of the bands and the occurrence of the 8_a mode at one frequency (1600 cm^{-1}) suggest that YNit700 has Lewis acid sites that are weaker than some of those of YAc700.

Figure 1 shows the decreasing intensities of the pyridine bands as the samples were heated and the concomitant growth of new bands at 1560 and 1460 cm^{-1}, which are characteristic of carboxylate surface species (12, 13). The occurrence of the 1560 cm^{-1} band characterizing carboxylate surface species (16) suggests that pyridine reacted with strongly basic sites of YNit700 (12, 13). The bands at 1290, 1180, and 1070 cm^{-1} are assigned to N−O surface species (13), and those at 1460, 1380, 1330, 1040, and 850 cm^{-1} are assigned to carbonate surface species (10, 12, 13). These results suggest (12, 13, 17) highly reactive basic sites associated with hydroxyl groups and/or oxygen ions on the surface.

In summary, these infrared results suggest the following ranking of the basicity of Y_2O_3: YAc700 < YNit500 < YOx700 < YNit700.

Infrared Spectra of Gas-Phase Products Formed from 2-Propanol

Figure 3A shows quantitative analyses of the gas phase resulting from an initial dose of 10 Torr of 2-propanol in the presence of YAc700 and of YOx700, giving rise to acetone and propylene products after consecutive intervals at the temperatures indicated. The corresponding data for YNit500 and YNit700 are also given in Fig. 3B. Infrared spectra of surface species resulting from adsorption of 2-propanol on YAc700 and YNit700 at the temperatures indicated, followed by cooling to room temperature under vacuum, are given in Fig. 4.

Infrared spectra of the gas phase in contact with 2-propanol adsorbed on YAc700 at various temperatures (Fig. 2) include the characteristic bands of 2-propanol (10, 12, 17). At 200°C a small band emerged at 1740 cm^{-1}, which developed in the 250°C spectrum, together with a band at 1250 cm^{-1}, marking the formation of acetone (10, 12); thus,

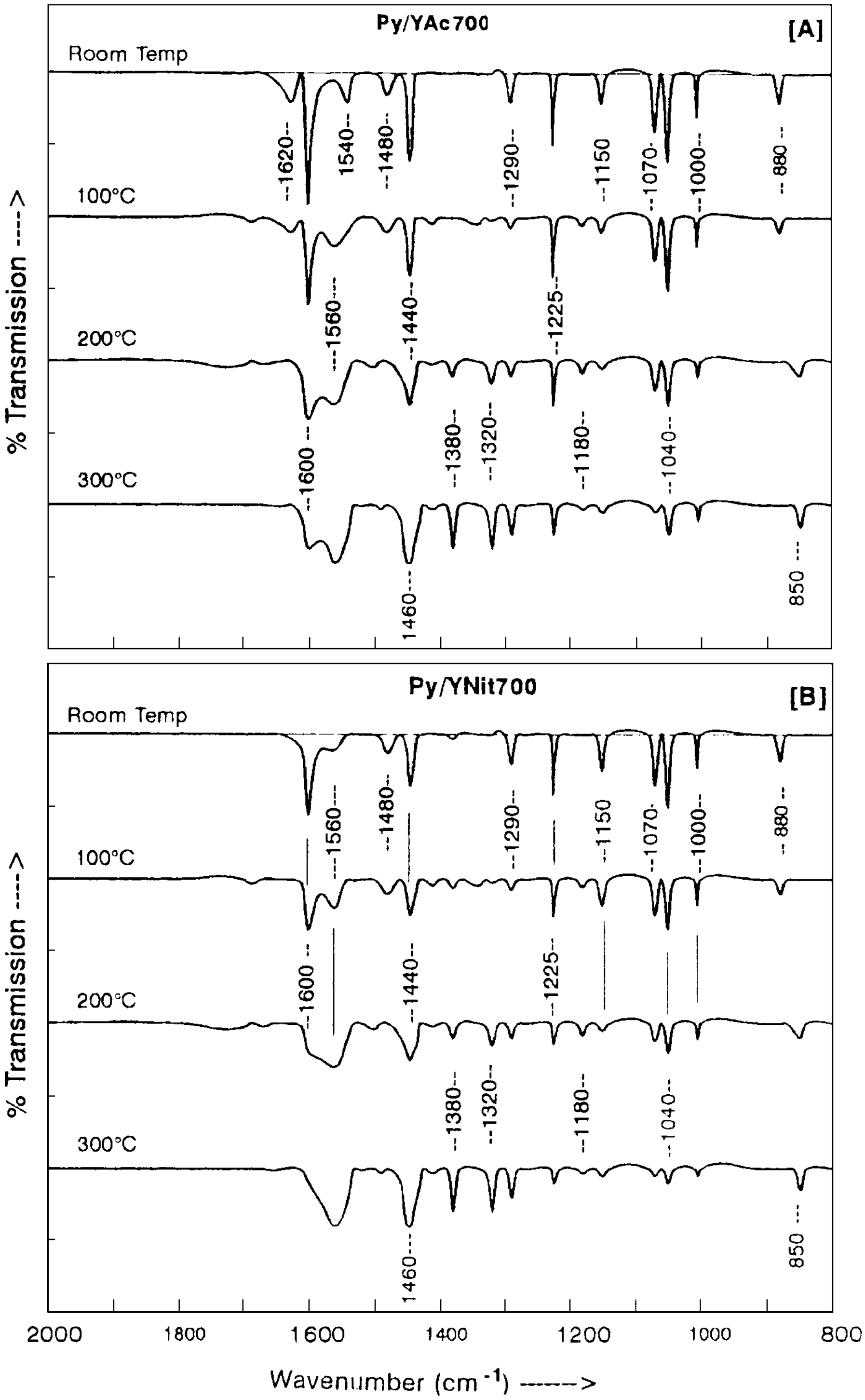


FIG. 1. IR spectra of the surface species from the adsorption and surface reactions of 3 Torr of pyridine at the temperature indicated on [A] Yac700 and [B] YNit700.

we infer that 2-propanol dehydrogenation started at about 200°C. At 250°C, additional bands appeared at 1650 cm^{-1} (doublet) and 915 cm^{-1}, indicating propene; evidently, the dehydration of 2-propanol set in at about 250°C. After the temperature had been raised to 300°C, the spectrum showed that bands characteristic of alcohol and acetone had become almost undetectable; propene bands grow stronger, and bands in the νCH region (3100–2800 cm^{-1}) were restructured. Furthermore, new bands emerged at 3010 and 1310 cm^{-1}, indicating CH_4. At 350°C, the alcohol and

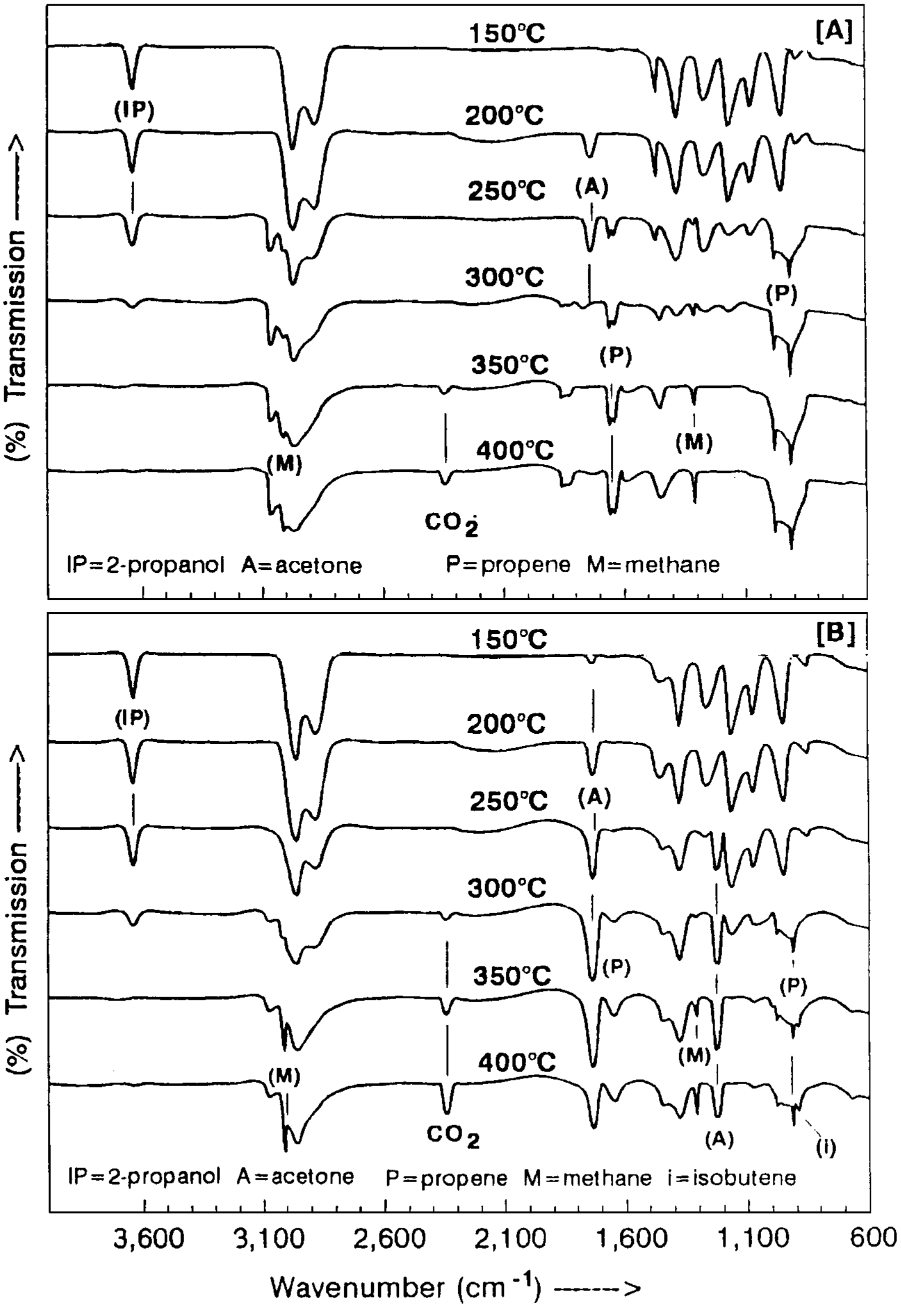
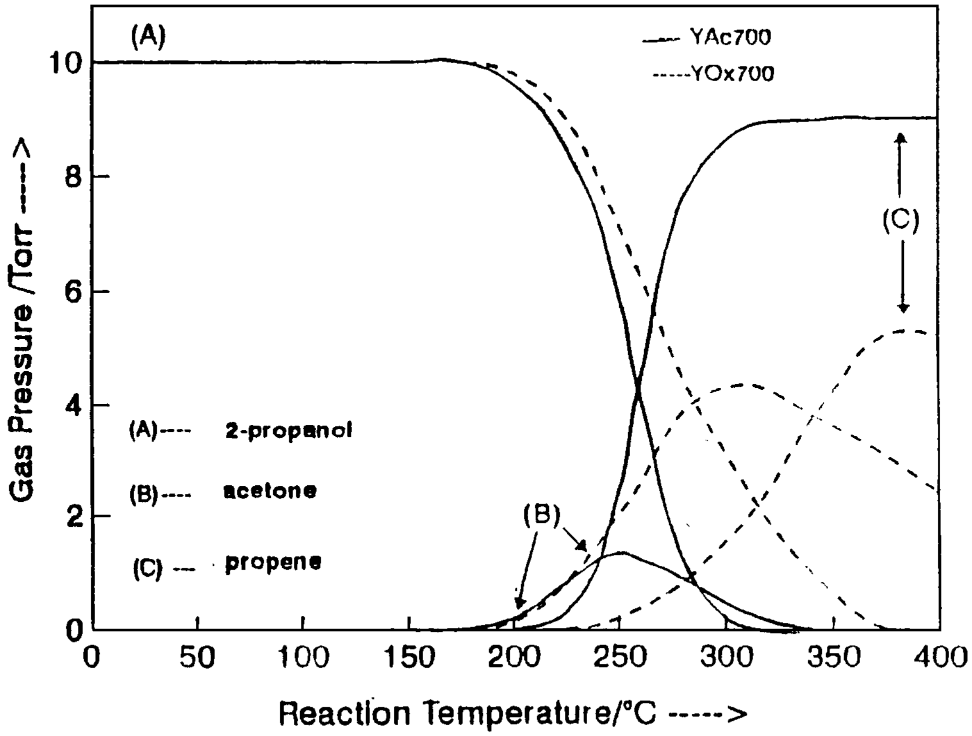


FIG. 2. IR Spectra of (IP) 2-propanol (10 Torr) and its decomposition products [(A) acetone, (P) propene, (M) methane, (I) isobutanol in contact with [A] YAc(700) and [B] YNit 700 for 10 min at the indicated temperature.

acetone bands had disappeared, and new bands appeared at 2340 and 670 cm^{-1}, indicating CO_2 (10). The bands representing CH_4 and CO_2 were intensified at 400°C. Since the disappearance of acetone and the appearance of CH_4 and CO_2 occurred at roughly the same temperature (300–400°C), we suggest that the former was converted into the latter.

Spectra similar to these (Fig. 2B) were recorded for the gas phase formed from 2-propanol in contact with YNit700. The results are different from those obtained for YAc700 (Fig. 2A), as follows: (i) acetone first appeared at 150°C and increased in amount at 300°C; (ii) propene first appeared at 300°C, and acetone remained up to 400°C; (iii) new bands indicative of CO (at 2145 cm^{-1}) and isobutylene (at 890 cm^{-1}) were detected.

The gas-phase spectra of 2-propanol products in the presence of YOx700 and YNit500 are closely similar in many respects, including (i) complete decomposition of the



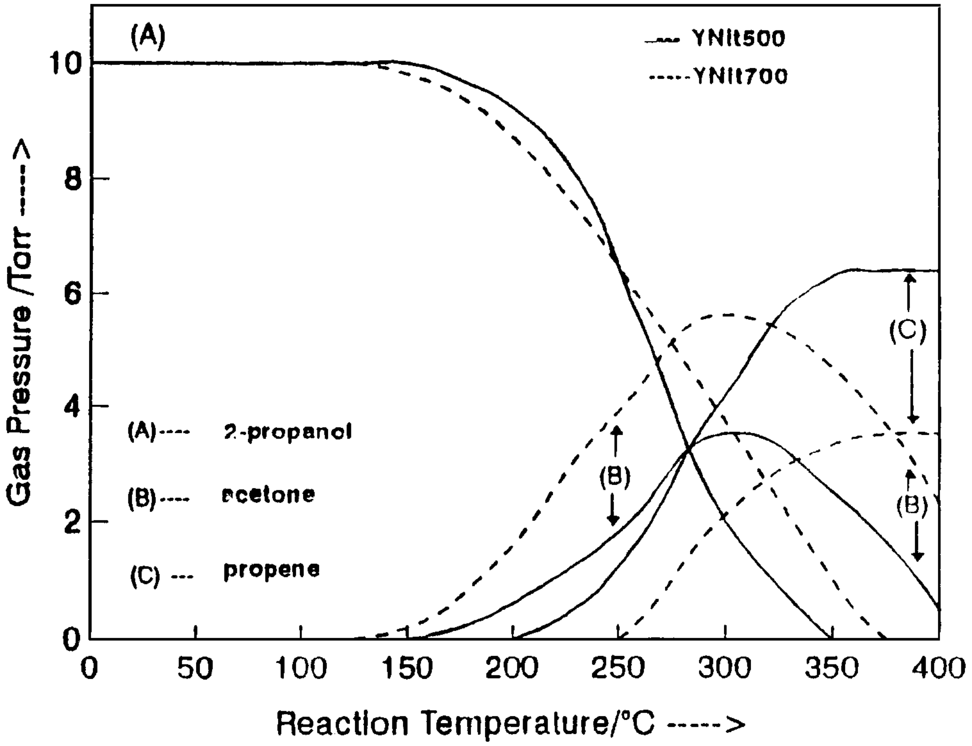


FIG. 3. IR quantitative analysis of the gas-phase composition resulting from 10 Torr 2-propanol (A), decomposing over YAc700, YOx700, YNit500, and YNit 700 to give acetone (B) and propene (C) after consecutive 10-min intervals at the temperatures indicated in Fig. 2.

initial dose of alcohol achieved at 350°C, (ii) formation of CH_4 and isobutylene at 400°C, as for YNit700 (Fig. 2B).

It must be noted that, when a 10 Torr of 2-propanol is admitted to the cell without any catalyst and heated up to 400°C, no decomposition products (dehydration and/or dehydrogenation) were detected.

On the basis of activity and selectivity factors, the above results are represented quantitatively in Fig. 3. It is clear that the initial amount of 2-propanol remains invariant until 150°C and commences to decline detectably on approaching 200°C. Acetone and propene are shown to emerge simultaneously into the gas phase near 200°C. The rate of alcohol decomposition appears to maximize at ca 250°C for YAc700 and YNit500, and at ca 275°C for YOx700 and YNit700. The alcohol completely decomposed at ca 350°C. YAc700 has a higher activity and selectivity (ca 90% at 300°C) for the propene formation in comparison to the other catalysts, most probably due to the higher surface acidity (Bronsted acid sites). In contrast, YNit700 which contains higher surface basicity, appears to have a higher activity and selectivity for the dehydrogenation reaction (65% at ca 300°C) (acetone formation). Both YOx700 and YNit500 are nearly similar in activity and selectivity. Both are working as dual functions for dehydrogenation (≈38% at ca 300°C)/dehydration (≈60% at ca 375°C) reactions, but YNit500 dehydrates more than YOx700.

In summary, YAc700 has a higher activity and selectivity for propene formation than the other Y_2O_3 catalysts, suggesting a stronger Bronsted acidity. YNit700, characterized by a stronger basicity, is more active and selective for dehydrogenation to give acetone.

In comparison with the earlier studies, Y_2O_3, obtained from Y-acetate at 700°C in atmosphere of air, is the more active and selective dehydration catalyst than that of Gd_2O_3 (12), La_2O_3 (17), Sm_2O_3 (12), and Nd_2O_3 (4), obtained from the same precursor (acetate) under the same conditions.

Infrared Spectra of Surface Species Formed from 2-Propanol

Spectra of surface species obtained from adsorption and surface reactions of 2-propanol (10 Torr) for 10 min on YAc700 and YNit700 show that the 25°C spectra have many features in common, even with the 150°C spectra. The hydrogen-bonded νOH bands (at 3500–3000 cm^{-1}) disappeared from the spectra of YNit500, YNit700, and YOx700 after 5 min of evacuation at 25°C, consistent with the suggestion that a small portion of the alcohol molecules were weakly hydrogen bonded to surface OH groups. This result indicates that the surface hydroxyls of YNit500, YNit700, and YOx700 are anionic in nature (8, 12, 18); they are weak hydrogen-bond donors, in comparison with YAc700, which has Bronsted acid sites.

The absorptions in the δCH region and at frequencies <1500 cm^{-1} are listed, assigned, and compared with the corresponding absorptions of $Y(C_3H_7O)_3$ (19) in Table 1. The observations above indicate, as expected, the presence of adsorbed alcohol and corresponding 2-propoxide species (10). Since the spectra in Fig. 4 were obtained after evacuation of the cell at the temperatures indicated, the band at 1280 cm^{-1} of the δOH (in plane) mode must have originated from freely bending hydroxyls of alcohol molecules held on the surface by bonds that are stronger than hydrogen bonds (20). A similar absorption in the δOH region has been assigned (10, 12, 21) to coordinated (undissociated) alcohol molecules. These species were observed at temperatures up to 250°C.

TABLE 1

Frequencies (cm^{-1}) of Absorptions in the νCH Region and Below 1500 cm^{-1} from Surface Species Produced by 2-Propanol Adsorption on Y_2O_3 (as YAc700, YNit500, YNit700), Compared with Those of $Y(OC_3H_7)_3$ (as Reported in Ref. (26))

Assignment	Y_2O_3	$Y(OC_3H_7)$ (26)
νas(CH_3)	2960vs	2955vs
2xνas(CH_3)	2915s	2920vs
ν(CH_3)	2840	2850vs
	2615w	2607w
δas(CH_3)	1440m	1460vs
	1370m	1376s
δs(CH_3)		1363sh
δ(CH_3)		1354m
		1336m
δ(OH)	1280b	
ν(CO)	1165vs	1168vs
ν(CC)	1130s	1123s
	1010	1005vs
CH_3 rock	970s	974s
		950m
		835m
	815	822m

Note. Absorptions at 2955, 2920, 2850, 1460, and 1376 cm^{-1} are overlapped by absorptions from Nujol.

The absorptions of ν(C−O)/ν(C−C), at 1165 and 1130 cm^{-1} (Fig. 4, Table 1) have been observed (10) on TiO_2, ZrO_2, and HfO_2 and assigned to two different alkoxide species (20–22). The higher frequency band is assigned to an alkoxide coordinated to a single cation and the other, to an alkoxide bridge bonded to two cations. Rossi *et al.* (22) provided experimental evidence of the existence of these two types of 2-propoxide species on TiO_2 by 2-propoxide-d6 adsorption and infrared spectroscopy. The spectra of species adsorbed on YAc700, YOx700, YNit500, and YNit700 are very similar, including a band at 1165 cm^{-1} (indicating a terminally bonded alkoxide) and a band at 1130 cm^{-1} (indicating a bridge-bonded alkoxide). The spectra of YAc700 and YOx700 had the same feature in which the absorption band at 1165 cm^{-1} is stronger than that at 1130 cm^{-1}, in contrast with both YNit500 and YNit700, indicating that

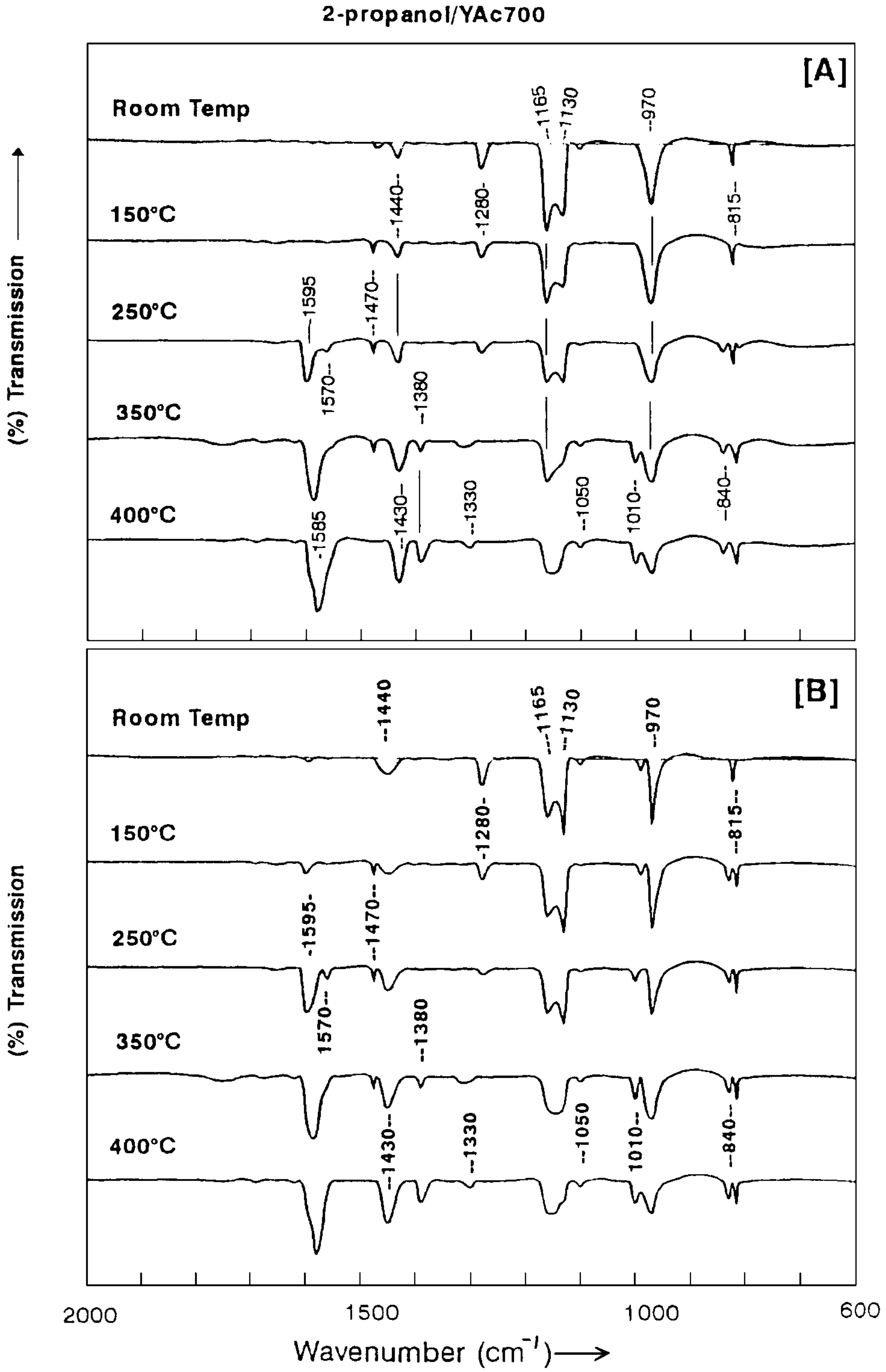


FIG. 4. IR spectra of the surface species from the adsorption and surface reactions of 10 Torr of 2-propanol at the temperature indicated on [A] YAc700 and [B] YNit700.

the nature of Lewis acid sites is affected by the origin of the catalyst.

Spectra recorded after the temperature had been raised to 150°C (Fig. 4) include additional bands at 1595 cm^{-1} (YNit700) and 1470 cm^{-1}. They were enhanced when the temperature increased to 250°C. The bands at 1595 and 1470 cm^{-1} were assigned (16) to the surface acetate. We recall that acetone first appeared in the gas phase at about

150°C. At 250°C, carbonate surface species (bands at 1570, 1430, 1380, 1330, and 1050 cm^{-1}) were also detected. It is known (10, 16) that surface acetate decomposes at high temperatures to give surface carbonates, which decompose at higher temperatures to give CO_2 in the gas phase.

The intensities of the absorption bands (at 1165 and 1130 cm^{-1}), characteristic of 2-propoxide species were modified as the temperature increased. The band at 1165 cm^{-1} was weakened first in the spectrum of YAc700 (Fig. 4A); i.e., the bridge-bonded 2-propoxide is thermally more stable than the terminally bonded 2-propoxide. This is in agreement with earlier studies for 2-propanol with Gd_2O_3 (12) and La_2O_3 (17) catalysts obtained from GdAc and LaAc at 800°C, but in contrast, with other studies, for 2-propanol over CeO_2 (21) obtained from ammonium ceric nitrate hydrate and TiO_2, ZrO_2, and HfO_2 (10). It was found that, the bridged 2-propoxide species are less stable, in comparison with the terminal one.

The bridge-bonded 2-propoxide on YNit700 (Fig. 4B) remained the more strongly bonded species at temperatures up to 250°C. When the temperature increased to 350°C, the range of dehydration reaction, the bridged 2-propoxide decomposed. These results may indicate that terminal propoxide species are intermediates for acetone formation. Spectra obtained at 400°C (Fig. 4) indicate the disappearance of absorption bands of acetate and a further weakening of the 2-propoxide absorptions. In contrast, there was a gradual increase in the carbonate absorptions.

The above results indicate that the nature of the Lewis acid sites is strongly influenced by the nature of the precursors used; the Y_2O_3 formed from the acetate or oxalate is different from that formed from the nitrate.

DISCUSSION

Mechanistic Pathways of 2-Propanol Adsorption and Surface Reactions

The four Y_2O_3 samples share a common cubic structure of the bulk, but the textures are different, with YAc700 and YNit500 being nearly the same in texture but different from YOx700 and YNit700, which are similar to each other; however, both YAc700 and YOx700 are generated from the same intermediate ($Y_2O_2CO_3$) at the same temperature, 700°C, but the texture is different. The four samples have different Lewis acid sites and they are all strongly basic, as indicated by the pyridine cracking (Fig. 1). YAc700 has absorption from four types of surface OH and shows Bronsted acidity, indicated by the proton transfer to pyridine. In contrast, the other three samples show no Bronsted acidity; one might speculate that surface OH groups were generated during the decomposition of the acetate precursor, but not during the decomposition of the oxalate and nitrate precursors.

Alcohol molecules could be held to the surface of metal oxide surfaces through hydrogen bonding and/or via coordination to Lewis acid sites. The formation of 2-propoxide could occur in two straightforward ways, as in Eqs. [1] and [2]

$$\mathrm{ROH} + \mathrm{Y}^{3+} + \mathrm{OH}^{-}_{(s)} \rightarrow \mathrm{RO}^{-}\cdots\mathrm{Y}^{3+}_{(s)} + \mathrm{H_2O} \qquad [1]$$

$$\mathrm{ROH} + \mathrm{Y}^{3+} + \mathrm{O}^{2-}_{(s)} \rightarrow \mathrm{RO}^{-}\cdots\mathrm{Y}^{3+}_{(s)} + \mathrm{OH}^{-}_{(s)}. \qquad [2]$$

Reaction [1] can only occur on hydroxylated surfaces, e.g., on YAc700, whereas reaction [2] predominates on largely dehydroxylated surfaces such as those of YNit700 and YOx700. The δOH absorption at 1280 cm^{-1} (Fig. 4) indicates the presence of coordinated molecules. The differences in the Lewis acid sites characterized by pyridine adsorption (Fig. 1) are responsible for the formation of the two types of 2-propoxide species (terminal and bridged bonded) with different concentrations (Fig. 4). These species are probably formed by reaction [2].

The Dehydrogenation Reaction

The spectroscopic evidence suggests that the 2-propoxide species are reactive intermediates, because the bands indicating their presence on the surface are weakened as the dehydrogenation reaction commences. Furthermore, there is evidence that acetone formation proceeds via alkoxide surface species (23, 24).

The acetone formation could take place via a first step described in Eq. [2], and the second step might be written as

$$\begin{aligned} &\mathrm{(CH_3)_2CH\bar{O}}\cdots\mathrm{Y}^{3+}_{(s)} + \mathrm{OH}^{-}_{(s)} \\ &\quad\rightarrow \mathrm{(CH_3)_2C{=}O} + \mathrm{H_2} + \mathrm{O}^{2-}_{(s)} + \mathrm{Y}^{3+}_{(s)}. \end{aligned} \qquad [3]$$

The terminal 2-propoxide species (absorption at 1165 cm^{-1}) are important in the dehydrogenation reaction (10, 12).

This mechanism is supported by the simulation methods (1) for the oxidation coupling of methane. Iett and Saiful Islam reported that the O-hole (large polarons) are created from the filling of oxygen vacancies by reactant molecular oxygen ($\mathrm{Vo}^{**} + 1/2\mathrm{O}_{2(g)}$ $(\mathrm{Oox} + 2\mathrm{H}^{*})$. These holes facilitate the hydrogen abstraction from CH_4 and increase the catalytic activity of the rare earth oxide catalyst. The method of preparation and pretreatment and doping critically affect the number of holes.

Secondary Reactions of Acetone

At 350–400°C, the dehydrogenation product (acetone) was largely consumed. It has been established (10, 23, 25) that at these temperatures, adsorbed acetone takes part in a bimolecular reaction (similar to aldol condensation) with a gas-phase acetone molecule to give gas-phase isobutylene and surface acetate species, as follows:

$$(CH_3)_2C{=}O\cdots Y^{3+}_{(s)} + CH_3COCH_{3_{(g)}} + HO\cdots Y^{3+}_{(s)} \rightarrow (CH_3)_2C{=}CH_2 + CH_3CO_2\cdots Y^{3+}_{(s)} + H_2O. \qquad [4]$$

CH_4 and CO_2 are formed in the gas phase by the decomposition of the surface acetate, as in Eq. [5] and/or analogous surface reactions involving acetone and water (the dehydration product) as in Eq. [6].

$$CH_3CO_2\cdots Y^{3+}_{(s)} + OH^-_{(s)} \rightarrow CH_4 + CO_2 + Y^{3+}_{(s)} + O^{2-}_{(s)} \qquad [5]$$

$$CH_3COCH_3 + H_2O \rightarrow 2CH_4 + CO_2. \qquad [6]$$

The fact that water was not observed in the gas phase (Fig. 2) is consistent with the suggestions. Such a reaction necessitates the involvement of surface acid sites or hydrogenolysis by H_2 (arising from the alcohol dehydrogenation), since water is not a reagent by itself to split C–C bonds to form CH_4 and CO_2. The possible role of H_2O as a reactant could be in the water gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$) because CO_2 is an unlikely primary product of acetone decomposition. CH_4 can also give CO_2 by steam reforming (26).

Acetone on YNit500, YNit700, and YOx700 reacts further to give both acetone and isobutylene. These products suggest that the dehydration reaction may create surface hydroxyl groups which are mainly responsible for the surface reaction of acetone to give isobutylene and CH_4 in the gas phase, probably by Eqs. [4] and [5].

The Dehydration Reaction

Dehydration of 2-propanol to give propene is widely used to characterize the acidity of metal oxide catalysts (7). This reaction occurs on both hydroxylated and dehydroxylated surfaces. A number of investigators (10, 25, 27) postulated alkoxide species as the surface intermediate for alcohol dehydration. Other proposed mechanisms for alcohol dehydration (28) do not involve alkoxide ions directly, but rather adsorbed alcohol or oxonium ions.

The results presented here suggest the presence of coordinated alcohol molecules on the surface, indicated by the δOH absorption at 1280 cm^{-1} (Fig. 4), which are still present up to temperatures of 250°C (dehydration started) and are also important with the alkoxide species in the dehydration reaction. Moreover, the results suggest that the Lewis acid sites required for the dehydration are different from those involved in the dehydrogenation and the type of Lewis acid sites required for dehydration activity depend not only on the surface area and nature of surface hydroxyl groups but also on the parent material and pretreatment conditions, as indicated by the higher dehydration activity of YOx700 ($S_{BET} = 12$ m^2/g) than that of YNit700 ($S_{BET} = 20$ m^2/g). Indeed, pyridine adsorption revealed the existence of Bronsted acid sites and two different kinds of Lewis acid sites of distinct acid strengths on YAc700, an active dehydration catalyst. For the lower acidity sample (YNit700), the O^{2-} basicity is most probably important for the dehydration reaction, and accordingly, the proposed (10, 12) reaction described by Eqs. [7] and [8] would be the most suitable dehydration pathway:

$$O^{2-}\cdots HCH_2{-}(CH_3)CH{-}HO\cdots HO \rightarrow CH_3CH{=}CH_2 + H_2O + O^{2-}_{(s)} + HO^-_{(s)}, \qquad [7]$$

$$O^{2-}\cdots HCH_2(CH_3)CH{-}OH\cdots Y^{n+}_{(s)} \rightarrow CH_3CH{=}CH_2 + HO{-}Y^{n+}_{(s)} + HO^-_{(s)}. \qquad [8]$$

Moreover, the H_2O formed during the dehydration of the coordinated alcohol molecules on the other samples, YNit500, YOx700, and YNit700, created surface hydroxyl groups with acidic character (12) which enhances the dehydration activity. This acidity explains the higher dehydration selectivity at temperatures >300°C that was observed for YNit500, YOx700, and YNit700.

CONCLUSIONS

1. Both YAc700 and YOx700 are the final decomposition products of the same stable intermediate, $Y_2O_2CO_3$ (11), but they differ in surface area and texture. YAc700 has a surface area of 55 m^2/g, whereas that of YOx700 is only 12 m^2/g; evidently, the parent material strongly influences the physical properties of the resulting Y_2O_3.
2. YAc700 has surface Bronsted acid sites, as well as Lewis acid sites of at least two different strengths, as well as four surface OH groups, most of which are anionic in nature, as indicated by pyridine cracking.
3. YNit500 has surface Lewis acid sites, strong basic sites, and several kinds of hydroxyl groups with anionic nature. Pyridine on the surface cracked at room temperature, forming surface carboxylates on the dehydroxylated, low-surface-area YNit700, which incorporated strongly basic sites. The order of the acidity strength is YAc700 > YNit500 > YOx700 > YNit700.
4. 2-Propanol adsorbed strongly on Y_2O_3 in the form of coordinated molecules and terminal and bridged-bonded 2-propoxide species. The amount of terminal 2-propoxide species is higher than the bridged one for both YAc700 and YOx700. This may indicate that both samples have the same Lewis acid sites, most probably because both are generated from the same intermediate $Y_2O_2CO_3$. In support of this suggestion, both YNit500 and YNit700 have the same Lewis acid sites but different ones with YAc and YOx700.
5. The terminal 2-propoxide are initial surface species for alcohol dehydrogenation. Coordinated alcohol molecules and terminal 2-propoxide are possible surface intermediate for the dehydration reaction. The bridged

2-propoxide species are the surface intermediate for the dehydration activity above 250°C. The surface texture play no role on the cracking of pyridine and decomposition of alcohol.

6. Acetone molecules, the dehydrogenation product, take part at 350°C in surface bimolecular reaction to give isobutylene, methane, CO_2, and acetate surface species. The reaction is associated with $Y^{3+}{-}OH^-$ pair sites. The O^- holes created from the filling of oxygen vacancies by reactant molecular oxygen ($Vo^{**} + 1/2O_{2(g)}$ ($Oox + 2H^*$) are controlled the catalytic activity of Y_2O_3. The method of preparation, pretreatment, and nature of the gas evolved during the decomposition critically controlled the number of holes.

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