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Surface characterization of alumina-supported catalysts prepared by sol–gel method

Part I.—Acid–base properties

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Surface characterization of Al_2O_3, In_2O_3–Al_2O_3 and Ga_2O_3–Al_2O_3 prepared by sol–gel method was made focusing on the acid–base properties. Cyclohexanol conversion as a model reaction revealed that acid sites rather than basic sites are present predominantly on the surface. The presence of Lewis acid sites was confirmed by pyridine adsorption followed by Fourier transform infrared (FT-IR) spectroscopy. In addition, a certain amount of Brønsted acid sites were also revealed by the adsorption of 2,6-dimethylpyridine (DMP). From the adsorption of CO, it was found that the addition of Ga_2O_3 into alumina leads to a decrease of Lewis acid strength but to an increase of the number of sites, while In_2O_3 addition caused a global decrease of Lewis acidic properties of alumina. Using CO_2 as a probe to study the basicity, the number of surface basic sites on alumina was found to be decreased by the In_2O_3 and Ga_2O_3 additives. A good correlation between the catalytic activity for 3,3-dimethylbut-1-ene isomerisation and the surface acidity estimated by CO and DMP adsorption was supposed. The combination of model reactions and adsorption of specific probe molecules gives us detailed information concerning the surface acid–base properties.

1 Introduction

Selective catalytic reduction of nitrogen oxides (NO_x) to N_2 by hydrocarbons (HC-SCR) has recently received extensive attention because of its potential for practical applications in diesel and lean-burn engine exhausts.[1] Most of the reports published so far are related to zeolite catalysts such as Cu-ZSM-5,[2] although metal oxides and noble metals also show activity for this reaction.[3]

It is well known that the catalytic performance of metal oxides is strongly related to their surface properties, for instance, surface composition and surface acidity and basicity. One of the authors first reported the high activity of solid acid catalysts such as H-ZSM-5[4] and Al_2O_3[5] on the reduction of NO with hydrocarbons, and claimed that the number of acid sites is the essential factor for the reaction. Recently, Satsuma *et al.*[6] investigated in detail the relation between the acid properties and the activity of various H-form zeolites, and revealed that the activity is related to the acid amount but not to the acid strength. Acid sites seems to play an important role for NO oxidation[7,8] and hydrocarbon activation.[9]

The present paper is devoted to the study of the surface acid–base properties of various alumina-supported catalysts. Al_2O_3, In_2O_3–Al_2O_3 and Ga_2O_3–Al_2O_3 prepared by sol–gel method were chosen, because these catalysts showed high activity but different catalytic behavior for NO reduction by propene.[10,11] Namely, Ga_2O_3–Al_2O_3 was quite active for the reaction in the wide temperature range between 673 and 823 K, while In_2O_3–Al_2O_3 showed a promotional effect of H_2O on the activity. In the present work, the surface acid–base properties were measured by using two complementary methods: adsorption of specific probe molecules, such as CO, CO_2, pyridine and 2,6-dimethylpyridine (DMP), studied by Fourier transform infrared (FT-IR) spectroscopy and activity for two model reactions (cyclohexanol (CHOL) conversion and 3,3-dimethylbut-1-ene (33DMB1) isomerisation). The former reaction allows us to evaluate the acid–base properties of metal oxides,[12] and the latter reaction is available for characterizing medium strength acid sites.[13]

2 Experimental

2.1 Catalyst preparation

In_2O_3–Al_2O_3 and Ga_2O_3–Al_2O_3 were prepared by sol–gel method. A solution of indium(III) nitrate or gallium(III) nitrate dissolved in ethylene glycol was added to the aluminium boehmite sol solution produced by hydrolysis of aluminum(III) triisopropoxide in hot water (363 K) with a small amount of nitric acid. After the solution was stirred at room temperature for 1 day, the solvents were removed by heating them under reduced pressure. The catalyst precursor thus obtained was

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dried at 383 K in an oven, followed by calcination at 873 K for 5 h in flowing air. The loading of In_2O_3 and Ga_2O_3 was fixed at 5 wt.% and 30 wt.%, respectively. Alumina was synthesized from aluminium boehmite sol as described above. After the sol solution was heated under reduced pressure to remove the solvents, the residue was dried at 383 K and calcined at 873 K for 5 h in flowing air. The BET surface area was found to be as follows: Al_2O_3 207 $m^2\ g^{-1}$, In_2O_3–Al_2O_3 227 $m^2\ g^{-1}$ and Ga_2O_3–Al_2O_3 191 $m^2\ g^{-1}$. Elemental analysis by inductively coupled plasma (ICP) revealed that impurities such as Si and Na in the catalysts prepared were less than 0.01%.

2.2 Infrared spectroscopy

A self-supporting sample disk of about 10 mg cm^{-2} prepared by pressing the catalyst powder was placed in an IR cell with KBr windows. IR spectra were recorded at room temperature with a Nicolet 710 FT-IR spectrometer at a resolution of 4 cm^{-1} after quenching the samples to room temperature. Prior to each experiment, the sample disk was activated for 1 h with oxygen at 13.3 kPa and then evacuated at the same temperature (773 K for CO, CO_2 and pyridine adsorption, 873 K for DMP). Probe molecules (CO, CO_2, pyridine and DMP) were introduced at room temperature on the activated samples and then evacuated at various temperatures. Gas pressure and additional information are reported in the text for each probe.

2.3 Catalytic test reactions

Two kinds of model reactions, CHOL conversion and 33DMB1 isomerisation, were performed in a fixed-bed flow reactor at atmospheric pressure. The reactants, cyclohexanol (vapor pressure: 0.45 kPa) and 3,3-dimethylbut-1-ene (21.2 kPa), were diluted in nitrogen by bubbling the gas through the liquid reactant in a saturator maintained at 308 and 273 K, respectively. Total gas flow rate was fixed at 30 $cm^3\ min^{-1}$. The mole rate of CHOL and 33DMB1 corresponded to 0.45 and 15.3 mmol h^{-1}, respectively. Prior to the activity measurements, the catalysts were calcined *in situ* at 723 K in flowing air, where the catalyst weight was changed from 10 to 60 mg in order to remain below a 20% conversion. The CHOL conversion was carried out at 423 K, while the 33DMB1 isomerisation was performed at five different temperatures (473, 498, 523, 548 and 573 K) to calculate the activation energy. The products were analyzed by on-line gas chromatography (FID) using a capillary Squalane column (50 m, 0.25 mm id) maintained at 323 K for the former reaction and at 303 K for the latter.

3 Results and discussion

3.1 CHOL conversion

The CHOL conversion allows us to characterize the surface acid–base properties of metal oxides.[12] The dehydration of cyclohexanol leading to cyclohexene (CHENE) is generally considered to be catalyzed by acid sites, whereas its dehydrogenation leading to cyclohexanone (CHONE) is catalyzed by acidic and basic sites through a concerted mechanism.[14] The dehydration activity (A_{CHENE}) can be related to the surface acidity, whereas the ratio between the dehydrogenation activity and the dehydration activity ($A_{\mathrm{CHONE}}/A_{\mathrm{CHENE}}$) represents the surface basicity.

In Table 1 are summarized the activities of Al_2O_3, In_2O_3–Al_2O_3 and Ga_2O_3–Al_2O_3 for CHOL conversion at 423 K. All the catalysts showed an activity, mostly related to the acidic sites (high selectivity to CHENE). Apparently, the yield of CHENE on Al_2O_3 was enhanced by the addition of Ga_2O_3, while the opposite was obtained for In_2O_3 addition, leading to the consideration that the number of acid sites on Al_2O_3 is increased by Ga_2O_3 but decreased by In_2O_3. It appears that the value of $A_{\mathrm{CHONE}}/A_{\mathrm{CHENE}}$ was lowered by addition of In_2O_3 and Ga_2O_3 to Al_2O_3, indicating a decrease of the surface basicity of the alumina. Taking these results into account, acidic rather than basic sites seem to be present predominantly on the surface.

Table 1 Activity of Al_2O_3, In_2O_3–Al_2O_3 and Ga_2O_3–Al_2O_3 for CHOL conversion at 423 K

	Formation rate/mmol $h^{-1}\ g^{-1}$		
Catalyst	CHONE	CHENE	$A_{\mathrm{CHONE}}/A_{\mathrm{CHENE}}$
Al_2O_3	0.22	0.83	0.27
In_2O_3–Al_2O_3	0.11	0.64	0.12
Ga_2O_3–Al_3O_3	0.18	1.43	0.12

3.2 Pyridine adsorption

Pyridine adsorption allows us to distinguish between Lewis and Brønsted acid sites.[15,16] The formation of coordinated species, pyL, on Lewis acid sites leads to the appearance of IR bands near 1620–1600 cm^{-1} (ν_{8a}) and 1450 cm^{-1} (ν_{19b}), while the formation of pyridinium ions, pyH^+, on protonic sites gives rise to characteristic bands at 1640 and 1540 cm^{-1}.

Fig. 1 shows the IR spectra of pyridine species adsorbed on Al_2O_3, In_2O_3–Al_2O_3 and Ga_2O_3–Al_2O_3 formed by introducing 133.3 Pa in equilibrium with the gas phase at room temperature, followed by evacuation at 423 K for 15 min. Only bands characteristic of pyridine adsorbed on Lewis acid sites were observed for all the catalysts, leading to the conclusion that the catalysts tested here possess predominantly Lewis acid sites. In_2O_3 and Ga_2O_3 do not modify the type of acid sites present on alumina.

The intensity of the ν_{19b} band of adsorbed pyridine characterizes the number of Lewis acid sites.[17] The intensity of the IR bands in the region of the ν_{19b} pyridine mode (around 1452 cm^{-1}) is nearly constant for each sample, indicating that there is no great difference in the number of Lewis acid sites.

On the other hand, the position and multiplicity of the ν_{8a} band of adsorbed pyridine is related to the strength and number of the different types of Lewis acid sites. As can be seen in Fig. 1, no great difference in the position of the ν_{8a} bands was observed among the catalysts, meaning that the strength of the Lewis acid sites is almost the same. Obviously, two IR bands were observed at 1622 and 1616 cm^{-1} with all the catalysts. This indicates the presence of the two different Lewis acid sites. Morterra *et al.*[18,19] reported that three types of pyridine species characterized by the ν_{8a} band at 1600–1590 cm^{-1} (site III), 1618–1612 cm^{-1} (site II) and 1626–1620 cm^{-1}

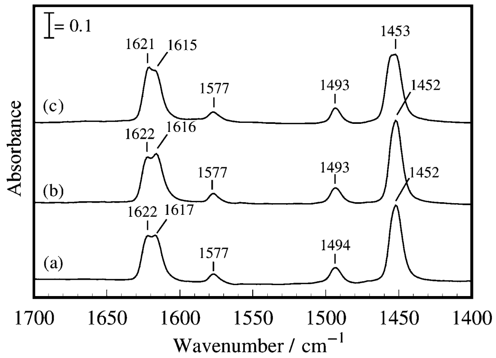

Fig. 1 FT-IR difference spectra of adsorbed pyridine species formed at room temperature, followed by evacuation at 423 K for 15 min. (a) Al_2O_3, (b) In_2O_3–Al_2O_3 and (c) Ga_2O_3–Al_2O_3.

(site I) are present on α- and η-Al_2O_3 surface. They assigned sites I, II and III to coordinatively unsaturated (cus) tetrahedral Al^{3+} cations, to a pair of cus Al^{3+} ions in octahedral and tetrahedral coordination, and to cus octahedral Al^{3+} cations, respectively. Abbattista *et al.*[20] and Nortier *et al.*[21] also observed similar IR bands in the region of the ν_{8a} pyridine mode on several transition aluminas (*e.g.*, γ-Al_2O_3). Referring to their reports, the IR bands at 1622 and 1616 cm^{-1} observed here would be ascribed to pyridine species interacting with sites I and II, respectively. The relative intensity of the bands identifying sites I and II presents slight differences: for Ga_2O_3–Al_2O_3 high wavenumber features are more intense than type II species, whereas for In_2O_3–Al_2O_3 the contrary is true.

3.3 CO adsorption

No great difference in the IR spectra of pyridine species adsorbed on Al_2O_3, In_2O_3–Al_2O_3 and Ga_2O_3–Al_2O_3 was observed (Fig. 1). This is probably due to the fact that pyridine vibrations are much less sensitive to perturbations involving adsorption on Lewis acid sites.[22] On the other hand, CO can largely be used for the surface characterization of cationic centers, which behave as Lewis acid sites, on metal oxide surface,[15,16] because it is a very weak base.

Fig. 2 shows the IR spectra of CO adsorbed on Al_2O_3, In_2O_3–Al_2O_3 and Ga_2O_3–Al_2O_3 at room temperature under 1.33 kPa in equilibrium with the gas phase. Two IR bands, which can be assigned to CO species interacting with Lewis acid sites,[22] at around 2230 and 2210 cm^{-1} were observed on all the IR spectra. Apparently, the shape of the IR spectrum is different between In_2O_3–Al_2O_3 and Ga_2O_3–Al_2O_3, whereas the IR spectrum for In_2O_3–Al_2O_3 is very similar to that of Al_2O_3. Recently, two of the authors reported that Ga_2O_3–Al_2O_3 consists of a composite oxide represented by $[Ga_xAl_{(1-x)}]_2O_3$ (where $x < 1$).[23] In the case of In_2O_3–Al_2O_3, the presence of In_2O_3 particles highly dispersed on Al_2O_3 was confirmed by XRD measurement.[24] Therefore, the difference in the features of the IR spectra observed here could be due to the difference in the surface composition of the two doped oxides.

Della Gatta *et al.*[25] reported that CO adsorption on several transition aluminas led to the appearance of two IR bands at 2190 and above 2200 cm^{-1} assigned to CO molecules coordinated to Al^{3+} in octahedral and tetrahedral positions, respectively. As can be seen in Fig. 2, CO adsorption on Al_2O_3 gave rise to bands at 2234 and 2213 cm^{-1}, which can be ascribed to CO molecules coordinated to Al^{3+} in tetrahedral positions (4-coordinate Al^{3+}). In particular, the IR band at higher wavenumber would be due to CO adsorbed on 4-coordinate Al^{3+} ion with unshared coordinative vacancies,[26] because more highly dehydroxylated Al_2O_3, which possesses a lot of defect sites, gave rise to a carbonyl band at higher wavenumber, *ca.* 2240 cm^{-1}.[25] In the case of In_2O_3–Al_2O_3, the same assignment could be applied to the IR bands at 2232 and 2214 cm^{-1}, although a shoulder peak was detected at 2207 cm^{-1}, which might be assigned to CO species adsorbed on In_2O_3. It should be noted that the intensity of the IR band at 2213 cm^{-1} became stronger than that at 2234 cm^{-1} by a factor of *ca.* 1.6 for both Al_2O_3 and In_2O_3–Al_2O_3, suggesting mainly the presence of 4-coordinate Al^{3+} ion without unshared coordinative vacancies.

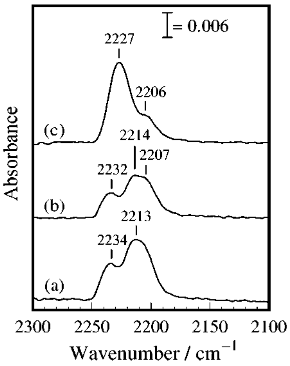

Fig. 2 FT-IR difference spectra of adsorbed CO species after introduction of 1.33 kPa of CO at room temperature. (a) Al_2O_3, (b) In_2O_3–Al_2O_3 and (c) Ga_2O_3–Al_2O_3.

The IR spectrum for Ga_2O_3–Al_2O_3 is quite different. The assignment of the bands at 2227 and 2206 cm^{-1} must be the same as in the case of Al_2O_3. It should be emphasized, however, that it is impossible by CO adsorption to distinguish Al^{3+} and Ga^{3+} in tetrahedral positions acting as Lewis acid sites because of the formation of a solid solution. It was also found that the intensity of the IR band at 2227 cm^{-1} is 3-fold stronger than that at 2206 cm^{-1}. This means that tetrahedrally coordinated surface cations (Al^{3+} and/or Ga^{3+}) with unshared vacancies, which are believed to act as active sites for NO reduction,[27,28] are present predominantly on the surface.

We can hypothesize that the surface density of the Lewis acid sites should be proportional to the intensity of the IR bands because the sample weights and specific surface areas are similar for all the catalysts and the CO pressure in the gas phase is constant. As can be seen in Fig. 2, the maximum intensity of the ν(CO) band was attained for Ga_2O_3–Al_2O_3. It was also found that the peak intensity of IR bands for In_2O_3–Al_2O_3 is weaker than that for Al_2O_3. This is probably due to a decrease in the number of Lewis acid sites for CO adsorption on Al_2O_3 by In_2O_3 particles. It can be concluded that the surface site density decreases in the following order: Ga_2O_3–$Al_2O_3 > Al_2O_3 \geqslant In_2O_3$–$Al_2O_3$.

The ν(CO) frequency increases with the strength of interaction between CO and the Lewis acid sites.[29] It is clear that the ν(CO) band for Al_2O_3 is located at a position *ca.* 2 and 7 cm^{-1} higher than that for In_2O_3–Al_2O_3 and Ga_2O_3–Al_2O_3, respectively. Taking the Δν shifts of the ν(CO) band from the gas phase value as a scale for the Lewis acidity of the centers,[29] it can be concluded that the Lewis acidity of Al^{3+} ions in pure alumina is decreased by the addition of In_2O_3 and Ga_2O_3.

3.4 2,6-Dimethylpyridine adsorption

As described above, the presence of Brønsted acid sites was not evidenced by pyridine adsorption on Al_2O_3, In_2O_3–Al_2O_3 and Ga_2O_3–Al_2O_3 (Fig. 1). However, according to the hypothesis of Tanabe *et al.*,[30] generation of new acid sites (Brønsted acid sites) by chemically mixing two metal oxides is expected. DMP is often used to probe surface Brønsted acid sites.[17,31–34] The ability of DMP to detect Brønsted acid sites can be related to the steric hindrance of the nitrogen atom, which tends to prevent its coordination but not its protonation[31] and to its higher basicity (pK_a is 6.7 for DMP and 5.2 for pyridine).[32]

As shown in Fig. 3(A), DMP adsorption under 133.3 Pa in equilibrium with the gas phase on Al_2O_3, In_2O_3–Al_2O_3 and Ga_2O_3–Al_2O_3 followed by evacuation at room temperature leads to the appearance of four distinct IR bands at 1653, 1615, 1605 and 1582 cm^{-1} and a shoulder band at 1628 cm^{-1}. The band at 1605 cm^{-1} could be due to hydrogen bonded and/or physisorbed species,[33] because it completely disappeared by evacuation at 423 K (Fig. 3(B)). The IR band at 1615 cm^{-1} can be ascribed to DMP species interacting with Lewis acid sites.[32] In accordance with the results of CO adsorption, it appears that the number of Lewis acid sites on the Al_2O_3 surface increases with addition of Ga_2O_3 and decreases with addition of In_2O_3. In particular,

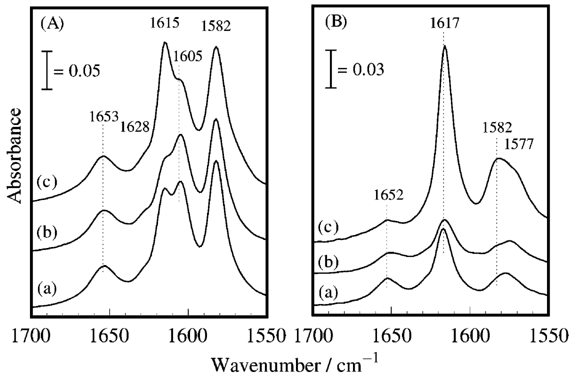

Fig. 3 FT-IR difference spectra of adsorbed 2,6-dimethylpyridine species remaining after evacuation at (A) room temperature and (B) 423 K for 15 min. (a) Al_2O_3, (b) In_2O_3–Al_2O_3 and (c) Ga_2O_3-Al_2O_3.

Ga_2O_3–Al_2O_3 seems to possess a higher amount of strong Lewis acid sites, which can not be desorbed even at 423 K (Fig. 3(B)).

It should be noted that two bands at 1653 and 1628 cm^{-1} were detected in the IR spectra for all the catalysts. These bands are in agreement with those reported in the literature for protonated DMP species on pure or fluorinated alumina.[32] Therefore, we can consider that the catalysts tested here possess a certain amount of Brønsted acid sites. Moreover, as can be seen in Fig. 3(A), addition of Ga_2O_3 to alumina seems to promote the number of Brønsted acid sites on the mixed compound. Alumina, however, possesses a lot of strong Brønsted acid sites compared with In_2O_3–Al_2O_3 and Ga_2O_3–Al_2O_3, as a distinct band at 1652 cm^{-1} was still observed even after evacuation at 423 K.

3.5 CO_2 adsorption

Generally, CO_2 has been used as a probe to study the basicity of metal oxides.[35] CO_2 is also known to act as a base, leading to the appearance of IR bands in the 2420–2350 cm^{-1} range by adsorption on acid sites.[36] As can be seen in Fig. 4, exposure of Al_2O_3, In_2O_3–Al_2O_3 and Ga_2O_3–Al_2O_3 to 1.33 kPa of CO_2 caused the appearance of an intense band around 2350 cm^{-1}, which is due to the asymmetric $\nu_{as}(CO_2)$ stretching mode of linear CO_2 species coordinated with cus cations. A well-defined band at 2350 cm^{-1} is present in the spectrum for Ga_2O_3–Al_2O_3, while a band at 2346 cm^{-1} with a shoulder at 2360 cm^{-1} was observed in the IR spectra for Al_2O_3 and In_2O_3–Al_2O_3. Since the upward shift of the vibrational modes with respect to gaseous CO_2 (2349 cm^{-1}) is known to depend upon the strength of the Lewis acid sites,[37] Al_2O_3 and In_2O_3–Al_2O_3 seem to possess Lewis acid sites of greater strength than those of Ga_2O_3–Al_2O_3. This is in agreement (even if at a lower spectroscopic resolution) with the results reported above due to CO adsorption.

When CO_2 is adsorbed on basic sites, it gives rise to hydrogencarbonates (characterized on γ-Al_2O_3 by bands at 1645, 1480 and 1235 cm^{-1}) and/or to carbonate species (1450 cm^{-1} band) depending upon the adsorption sites, OH^- or cus O^{2-}.[35] Normally on alumina, only surface basic hydroxy groups are found. As can be seen in Fig. 4, intense IR bands at *ca.* 1645, 1485 and 1237 cm^{-1} were observed for all the catalysts. They are assigned to hydrogencarbonates, as confirmed by the sharp δ(OH) mode at 1237 cm^{-1}. This assignment would also be supported by the fact that a well-resolved band at *ca.* 3608 cm^{-1} was detected. This band is due to the ν(OH) stretching mode of hydrogencarbonates formed from the interaction of surface basic hydroxy groups (at around 3750 cm^{-1}) with CO_2.[35] For all the catalysts, particularly Al_2O_3 and In_2O_3–Al_2O_3, broad IR bands at 1800–1860 cm^{-1} and a weak band at *ca.* 1200 cm^{-1} were also detected. According to Parkyns,[38] these bands could be ascribed to "organic-type" carbonate species. In this case a larger amount of basic sites should be ascribed to those catalysts. Alternatively, we could assign the above-mentioned bands to a perturbed adsorption state of CO_2 on Lewis acid sites.[37] In the latter case, the driving phenomenon for carbonate species formation on these materials will be surface acidity.

Concerning the overall intensities in the spectral range below 2000 cm^{-1}, it appears that there are slight differences between the catalysts. The most intense IR bands were obtained for Al_2O_3, and the amount of surface basic sites seems to decrease in the sequence $Al_2O_3 \geqslant In_2O_3$–$Al_2O_3 >$ Ga_2O_3–Al_2O_3. It is also clear that the bands due to hydrogencarbonates for Al_2O_3 are hardly affected by the presence of In_2O_3, while some of those for Ga_2O_3–Al_2O_3 are shifted of *ca.* 7 cm^{-1} to lower wavenumbers.

3.6 33DMB1 isomerisation

33DMB1 isomerisation is a relatively simple reaction with only two main products: 2,3-dimethylbut-1-ene (23DMB1) and 2,3-dimethylbut-2-ene (23DMB2). Interestingly, the two isomers were formed in almost equal amounts on all the catalysts irrespective of reaction temperature. In the present work, the catalytic activity was evaluated from the sum of the reaction rates for the formation of 23DMB1 and 23DMB2.

Table 2 gives the activities of Al_2O_3, In_2O_3–Al_2O_3 and Ga_2O_3–Al_2O_3 for the 33DMB1 isomerisation performed at five different temperatures. We could obtain good reproducibility with an experimental error of less than 5% for each experiment. Obviously, the highest activity was attained on Ga_2O_3–Al_2O_3, and it decreased in the order

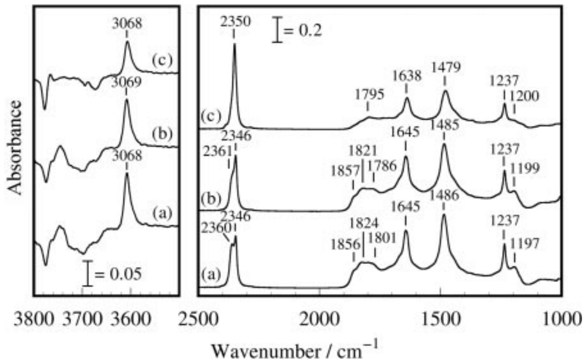

Fig. 4 FT-IR difference spectra of adsorbed CO_2 species after introduction of 1.33 kPa of CO_2 at room temperature. (a) Al_2O_3, (b) In_2O_3–Al_2O_3 and (c) Ga_2O_3–Al_2O_3.

Table 2 Activity of Al_2O_3, In_2O_3–Al_2O_3 and Ga_2O_3–Al_2O_3 for 33DMB1 isomerisation at different temperatures

Reaction temperature/K	Rate for isomerization of 3,3-dimethylbut-1-ene/mmol h^{-1} g^{-1} Al_2O_3	In_2O_3–Al_2O_3	Ga_2O_3–Al_2O_3
473	2.2	1.6	5.8
498	6.7	2.7	22.7
523	21.9	8.2	78.0
548	62.7	14.0	224.4
573	118.6	18.7	633.1
	Activation energy/kJ mol^{-1}		
	93	59	106

Ga_2O_3–Al_2O_3 > Al_2O_3 > In_2O_3–Al_2O_3. It is reported that the 33DMB1 isomerisation proceeds *via* secondary carbenium ions on Brønsted acid sites.[39] However, Duprez *et al.*[14,40] reported that this reaction proceeds on several aluminas that generally possess no Brønsted acidity. Perot *et al.*,[41,42] from a study of the isomerisation of but-2-ene selectively deuterated in the allylic and vinylic positions, claimed that alumina may have a weak protonic acidity. In the present work, it was revealed by DMP adsorption that there are a number of Brønsted acid sites on the surface of all the catalysts (Fig. 3). DMP adsorption showed that the number of Brønsted acid sites on Al_2O_3 was increased by addition of Ga_2O_3 and decreased by addition of In_2O_3. This tendency is in good agreement with that of the catalytic activity described above, so that the catalytic activity seems to be closely related to the amount of Brønsted acid sites.

The activation energies determined from the Arrhenius plots for 33DMB1 isomerisation are also given in Table 2. Obviously, they are quite similar for Al_2O_3 and Ga_2O_3–Al_2O_3: 100 ± 6 kJ mol^{-1}. This is consistent with the results reported by Martin and Duprez for alumina.[14] On the other hand, the value obtained for In_2O_3–Al_2O_3 is quite low: 59 kJ mol^{-1}. The activity reported in Table 2 was measured after the reaction reached the steady state. The steady state activity was obtained for Al_2O_3 and Ga_2O_3–Al_2O_3 immediately after the beginning of the reaction irrespective of the reaction temperature, while the difference between the initial and the steady state activity of In_2O_3–Al_2O_3 increased with increasing reaction temperature. For instance, the reaction rate at 573 K decreased from 37.5 to 18.7 mmol h^{-1} g^{-1} after about 1 h on stream. This might be due to the appearance of other reactions, for instance, partial oxidation of 33DMB1, at higher temperatures. It can be presumed that the surface properties of In_2O_3–Al_2O_3 are slightly different from those of Al_2O_3 and Ga_2O_3–Al_2O_3.

4 Conclusion

Adsorption of probe molecules on alumina-based catalysts prepared by the sol–gel method revealed differences in their surface acid–base properties. When pyridine was adsorbed on alumina-based catalysts, only bands indicative of pyridine adsorbed on Lewis acid sites were observed in the IR spectra for all the catalysts. However, the adsorption of 2,6-dimethylpyridine confirmed the presence of a number of Brønsted acid sites on the catalyst surface. From adsorption of CO it was found that the surface density of Lewis acid sites was increased on addition of Ga_2O_3 into alumina, while it was decreased on addition of In_2O_3. The presence of basic OH groups on the surface of alumina-supported catalysts was observed from CO_2 adsorption. Although no great difference in their surface basic strength was observed, the presence of In_2O_3 and Ga_2O_3 was found to decrease the amount of basic sites of alumina. A good correlation between the activity for model reactions (CHOL conversion and 33DMB1 isomerisation) and the adsorption of probe molecules was observed. The catalytic activity for both reactions occurring on the acid sites was found to be closely related to the number of acid sites but not to their strength.

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