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Acid–base properties of supported gallium oxide catalysts

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Abstract

The acid–base properties of supported gallium oxide catalysts have been investigated by microcalorimetry and FTIR spectroscopy of pyridine (acidity) and CO_2 (basicity) adsorption. Pyridine adsorption microcalorimetry has shown that loading supports such as γ-Al_2O_3, TiO_2, and ZrO_2 with gallium oxide in a surface concentration close to the theoretical monolayer, resulted in a decrease of the surface acidity of the catalysts compared to that of the supports, while, in the case of SiO_2, new Lewis acid sites were created. The number of acid sites for the supported and bulk gallium oxide catalysts was in the following order: $Ga_2O_3/SiO_2 < Ga_2O_3/ZrO_2 < Ga_2O_3/TiO_2 \approx Ga_2O_3 < Ga_2O_3/Al_2O_3$. This order is related to the degree of dispersion of gallium oxide on the surface of each support and to the interaction between guest and host oxides. Two types of Lewis acid sites were identified by pyridine adsorption, corresponding to the support and the supported gallium oxide, respectively. The catalysts displayed very weak basicity, except for the samples supported on zirconia and alumina.

Keywords: Adsorption microcalorimetry; FTIR spectroscopy; Acid–base properties; Supported gallium oxide catalysts

1. Introduction

Supported gallium oxide catalysts exhibit interesting catalytic properties for selective catalytic reduction of NO_x by hydrocarbons in the presence of excess oxygen [1] and for the dehydrogenation or aromatization of light alkanes [2].

Previous studies, aimed at developing non-zeolitic de-NO_x catalysts of practical interest, have shown that catalysts containing the non-reducible metallic ion Ga^{3+} supported on metallic oxides [1,3,4], and more specifically on alumina [5], exhibit good catalytic performance [6]. Attempts at explaining the high catalytic activity and selectivity of supported gallium oxide catalysts and identifying the active species have mostly been focused on structural analysis. Thus, the selective catalytic reduction of NO with CH_4 has been shown to be a structure-sensitive reaction depending on the local structure of the Ga^{3+} cation [3,7,8].

Few studies have been reported concerning the correlation between the acidic or basic properties of supported gallium oxide catalysts and their catalytic activity, even though these surface properties are of crucial importance for the choice of a catalyst.

On one hand, supported gallium oxides are preferred to zeolites in the de-NO_x reaction due to their weaker acidity [1,6] and consequently their lower deactivation by formation of carbonaceous deposits when the reductant is a reactive olefin. On the other hand, the Lewis acid sites (as detected by FTIR monitoring of pyridine adsorption) of supported gallium oxides are suspected to be the active sites for the dehydrogenation of ethane [2].

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Connell and Dumesic [9], and Cardona-Martinez and Dumesic [10] have used pyridine adsorption microcalorimetry at 473 K to probe the distribution of acid strength on a series of silica catalysts doped with various oxides, among which Ga_2O_3. The samples showed both Brønsted and Lewis acidity, and the Brønsted acidity was generated by incorporation of Ga^{3+} into the tetrahedral structure of silica.

Gergely and Auroux [11], and Gergely et al. [12] have studied the adsorption of various air pollutants (NO_2, NO, SO_2, NH_3) on Ga_2O_3-supported catalysts and the influence of Ga_2O_3-loading on the surface properties of the alumina and titania used as supports. The titania support and the gallium oxide loadings were different from those used in the present study. Gergely et al. [12] have shown that NO_2, SO_2 and NH_3 are strongly adsorbed, while NO is only physisorbed. The deposition of Ga_2O_3 caused a slight decrease in the acidity as determined by NH_3 adsorption, while the basicity as determined by SO_2 adsorption increased slightly in comparison with the supports.

Parenago et al. [13] have shown that the formation of Lewis acid sites on the dehydroxylated surface of four crystalline modified Ga_2O_3 surfaces is governed by peculiarities of their crystalline structure and is determined by the presence of Ga^{3+} in tetrahedral positions.

The present study aims at gaining a deeper understanding of the catalytic behavior of supported gallium oxides by identifying the active species and the specific contribution of the support. For this purpose, the surface properties of these materials were studied by adsorption calorimetry and infrared spectroscopy.

The catalytic activity of solids depends strongly on their acid–base properties. In order to study the total acidity or basicity as well as the nature and strength of the acidic or basic sites, it is necessary to use different probe molecules. In this work, pyridine and carbon dioxide were selected as basic and acidic probe molecule, respectively.

Pyridine is the most frequently used basic probe molecule for surface acidity characterization (Lewis and Brønsted sites). The lone-pair electrons of nitrogen are involved in different types of interactions with the surface sites: H-bonded pyridine, molecularly coordinated pyridine on surface cations, and protonated pyridine (pyridinium ions).

CO_2 can act as a weak electron donor or acceptor, but the acceptor characteristics increases when the normally linear molecule becomes bent. In fact, the most common reactions involve positively- or negatively-charged surface sites, giving rise to surface monodentate and bidentate carbonates, hydrogenocarbonyl ions, and superficial carbonyl groups (monodentate or bidentate) [15–17].

2. Experimental

Supported gallium oxide catalysts were prepared by impregnating various supports (γ-Al_2O_3, reference oxide C; SiO_2, reference Aerosil 200; TiO_2, reference P 25 containing 75% anatase phase; ZrO_2, reference VP, all from Degussa) with aqueous solutions of $Ga(NO_3)_3\cdot 9H_2O$ (Fluka, purity $> 99.99\%$). After drying for 18 h at 393 K, the samples were calcined in air flow at 773 K for 8 h. The gallium oxide loading was equivalent to the theoretical monolayer calculated from the density of Ga_2O_3 [14]. Bulk Ga_2O_3 was prepared by oxidative decomposition of gallium nitrate.

Chemical analysis was performed by AES-ICP. BET surface areas were measured using N_2 at 77 K. All the samples were outgassed at 673 K for 4 h prior to the adsorption measurements. X-ray diffraction spectra of powder samples were recorded on a Bruker D5005 diffractometer (Cu Kα source).

The active surface sites were probed by adsorption of CO_2 and pyridine, covering a large domain of acid–base strength, using FTIR spectroscopy and microcalorimetry. The FTIR spectra were recorded on a Bruker Vector 22 spectrometer with a DTGS detector (200 scans per spectrum at 4 cm^{-1} resolution). A self-supported wafer (diameter 18 mm, 40–50 mg), placed in an in situ IR cell with CaF_2 windows, was activated by heating at 673 K under oxygen flow and then outgassed (ca. 10^{-3} Pa) for 1 h at the same temperature. Dry probe molecule adsorption was carried out at 298 K, and the sample was then evacuated for 30 min at the same temperature. The desorption of the probe molecule was monitored by evacuating the sample for 30 min under a dynamic vacuum (10^{-3} Pa) successively at various temperatures, using 50 K temperature intervals up to 673 K. The microcalorimetric studies were performed at 423 K (pyridine) and 303 K (CO_2) in a heat flow calorimeter of Tian–Calvet type (Setaram HT for pyridine adsorption, Setaram C80 for CO_2 adsorption), linked to a conventional volumetric apparatus. The samples were outgassed overnight at 673 K before each experiment. The differential heats of adsorption were measured as a function of coverage by repeatedly sending small amounts of gas onto the catalyst until an equilibrium pressure of about 66 Pa was reached. Then, the sample was evacuated for 30 min at the adsorption temperature, and a second adsorption was subsequently performed in order to determine the uptakes of chemisorption.

3. Results and discussion

The physicochemical characteristics of the supports and supported gallium oxide catalysts are listed in Table 1, which gives for each sample the Ga_2O_3 content (wt.%), the BET surface area, and the acidity and basicity as determined by adsorption microcalorimetry, expressed in terms of initial heats of adsorption and of amounts of chemisorbed pyridine and CO_2, respectively, calculated from the difference between the adsorption and readsorption isotherms under an equilibrium pressure of 27 Pa.

The amount of deposited gallium oxide is close to the theoretical monolayer value calculated from the density of gallium oxide. The surface area decreases sharply for the sample supported on silica, while the decrease of BET surface area is less significant with the other supports. The XRD patterns are the same for the supported samples as for the supports, showing a good dispersion of the amorphous gallium oxide, except for Ga32-Si which is less dispersed. The presence of aggregates of gallium oxide could explain the strong decrease of BET surface area of the Ga32-Si sample.

The studied supports cover a wide range of acidity as measured by pyridine adsorption, from the weakly acidic silica to the strongly acidic titania and γ-alumina, and sites of different strengths are involved. The order of the number of acid sites, as determined from the chemisorption uptakes, is the following: $SiO_2 \leqslant ZrO_2 < Al_2O_3 < TiO_2$ (see Table 1).

Fig. 1 shows the differential heats of pyridine adsorption versus coverage for the bare supports. All of them display a strong heterogeneity of the sites. While the pyridine uptakes of γ-alumina and titania are nearly equal and the values of initial heats of adsorption very close (see Table 1), we can observe some variation in the strength distribution of the sites, titania presenting relatively higher amounts of weak and strong sites than γ-alumina. The zirconia support, less acidic in terms of pyridine uptake, presents a high value of initial heat of adsorption and a more important contribution of strong acid sites than medium or weak sites.

Fig. 2 shows the IR spectra of the species arising from pyridine adsorption on supports after outgassing at 423 K to remove physisorbed species.

The adsorption bands at 1616 cm^{-1} (shoulder at 1623 cm^{-1}) and 1451 cm^{-1} for γ-alumina, 1608 and 1445 cm^{-1} for zirconia, 1609 and 1447 cm^{-1} for titania, are specific of the 8a and 19b vibration modes, both mainly involving in-plane vibrations of the C_6 ring, and are due to the coordinatively adsorbed

Table 1
Physicochemical characteristics of the supports, bulk and supported gallium oxide catalysts

Samples	Ga_2O_3 content (wt.%)	BET surface area ($m^2\ g^{-1}$)	Acidity		Basicity	
			Q_{init} (kJ mol^{-1})	Chemisorption uptake (μmol pyridine g^{-1})	Q_{init} (kJ mol^{-1})	Chemisorption uptake (μmol CO_2 g^{-1})
Al_2O_3	–	108	152	137	150	22.1
TiO_2	–	55.2	165	141	85	4.8
ZrO_2	–	59.0	230	116	155	59.8
SiO_2	–	208	48	0	0	0
Ga22-Al	22.3	99	250	119	150	17.6
Ga12-Ti	12.1	49.7	245	86	35	1.1
Ga12-Zr	12.7	48.4	230	75	110	16.3
Ga32-Si	32.4	134	250	38	30	0
Ga_2O_3	99.9	77.0	200	86	115	4.7

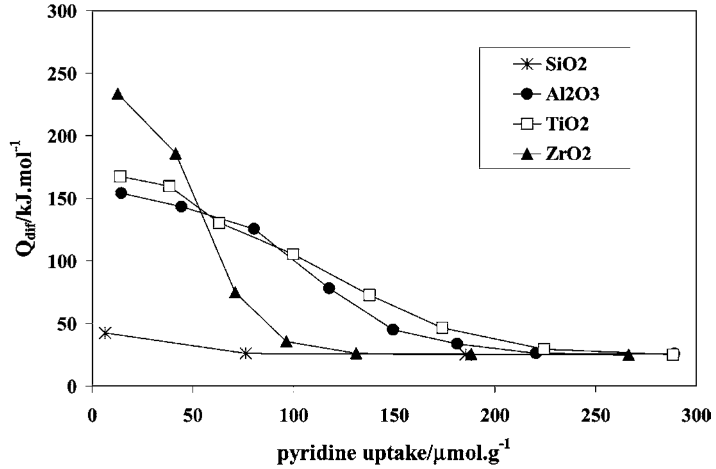

Fig. 1. Differential heats of pyridine adsorption vs. coverage for supports.

pyridine at Lewis acid sites. For amorphous silica, we could not observe any specific band of adsorbed pyridine species, confirming the absence of chemisorbed pyridine as already evidenced by adsorption microcalorimetry (see Table 1).

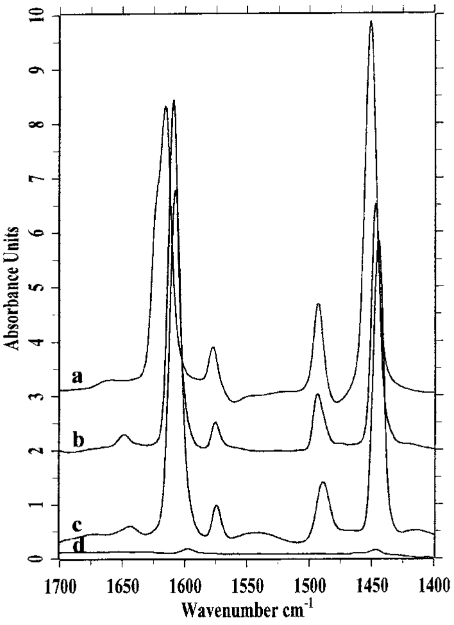

Fig. 2. FTIR spectra (normalized by weight unit) of the surface species after pyridine adsorption at 298 K and outgassing at 423 K on supports: (a) Al_2O_3; (b) TiO_2; (c) ZrO_2; (d) SiO_2.

The absence of bands attributed to pyridinium ions does not indicate the absence of Brønsted sites on the supports. These sites are revealed by ammonia adsorption (formation of ammonium ions). These results confirm that ammonia is more easily protonated than pyridine on oxide surfaces [16], even though the gas phase basicity scale given by proton affinities makes pyridine appear as a stronger base than NH_3 ($PA_{NH_3} = 3540\ kJ\ mol^{-1}$, $PA_{C_5H_5N} = 3816\ kJ\ mol^{-1}$). This is one more instance of the well-known difficulty of defining a single scale for gas phase basicity, proton affinity and pK_a both being natural candidates.

The total acidity (Lewis and/or Brønsted) as determined by the chemisorption uptake of pyridine at 423 K decreased when supporting gallium oxide on alumina, titania or zirconia. For example, Fig. 3 shows the differential heats of adsorption versus coverage for zirconia and supported gallium oxide on zirconia. Although strong sites remain present on the supported sample, the curve shows a sharp decrease of the total number of acid sites. On the contrary, in the case of silica on which adsorption is reversible, new strong acidic centers were created when depositing Ga_2O_3, as shown in Fig. 4. The same behavior can be observed for gallium oxide supported on alumina or titania (see Table 1), presenting an increase in terms of initial heats of adsorption. A few acid sites stronger than those of the corresponding support are created by depositing gallium oxide, though the total acidity is decreased.

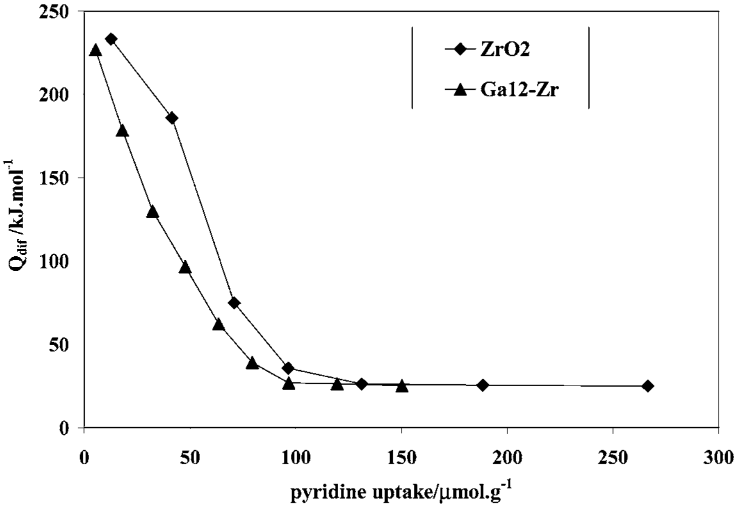

Fig. 3. Differential heats of pyridine adsorption vs. coverage for bare zirconia and zirconia-supported gallium oxide.

Fig. 5 presents the differential heats of pyridine adsorption versus coverage for the various supported catalysts and bulk Ga_2O_3. The strong heterogeneity of the surface acidic sites is evidenced by the absence of a plateau of differential heats in any of the curves.

As can be seen in Table 1 and Fig. 5, the number of acid sites measured by pyridine adsorption on the samples containing gallium oxide varies in the order: Ga32-Si < Ga12-Zr < Ga12-Ti $= Ga_2O_3 <$ Ga22-Al. This order is not directly correlated to the amount of gallium oxide deposited on the surface. It is rather related to the quality of dispersion of Ga_2O_3 on the support and to the specific contribution of each support to the resulting catalyst acidity.

Fig. 6 presents the acid site strength distributions of the supported gallium oxide catalysts and bulk Ga_2O_3, calculated from the differential heats of pyridine adsorption plotted in Fig. 5. This figure gives the number of sites on which the evolved heat belongs to a given interval.

The sites with strong or medium acid strength are more affected by the deposition of gallium oxide than

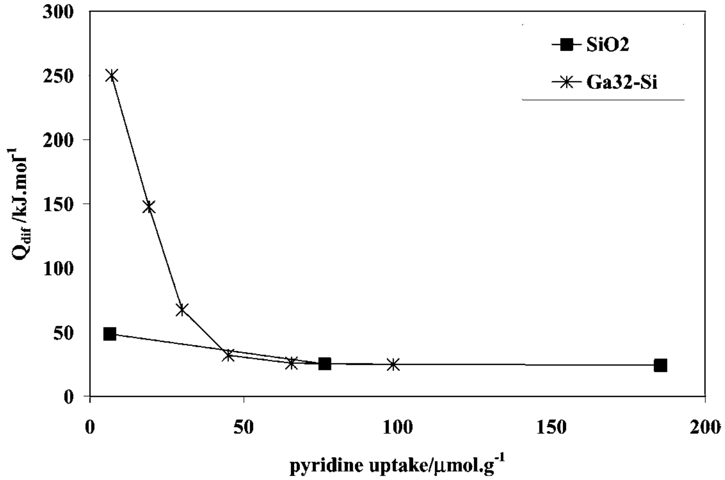

Fig. 4. Differential heats of pyridine adsorption vs. coverage for bare silica and silica-supported gallium oxide.

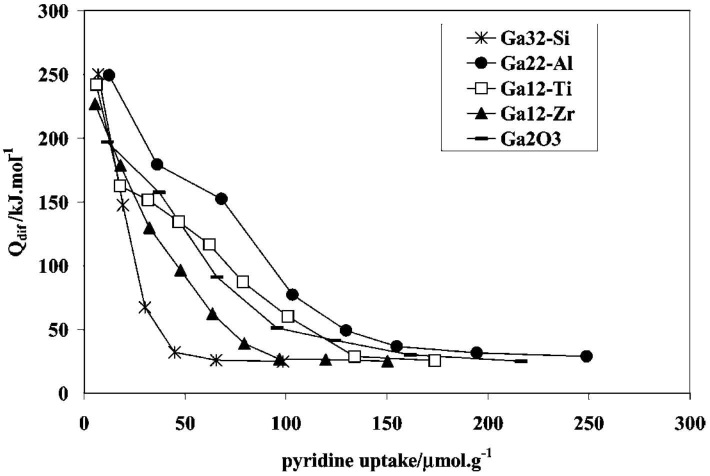

Fig. 5. Differential heats of pyridine adsorption vs. coverage for supported and bulk gallium oxides.

the weak ones. It can be noticed that the Ga22-Al sample, similar to materials already reported to be very interesting de-NO$_x$ catalysts [1,3,4,7,8,18], presents the highest acidity, both in terms of number and strength of acid sites.

The nature, the surface reactivity and the thermal stability of the adsorbed surface species after pyridine adsorption at RT and outgassing at 423 K on the supported gallium oxide samples were determined by FTIR spectroscopy, and the difference spectra are shown in Fig. 7.

Intense bands were observed at 1620 and 1610 cm^{-1} and 1455 and 1448 cm^{-1} (two split broad bands) for Ga12-Ti, 1619 cm^{-1} (shoulder at 1610 cm^{-1}) and 1454 cm^{-1} (shoulder at 1445 cm^{-1}) for Ga12-Zr, 1622 and 1458 cm^{-1} for Ga22-Al, 1621 and 1458 cm^{-1} for Ga32-Si, and 1620 and 1456 cm^{-1} for bulk Ga$_2$O$_3$. These bands are specific of the 8a and 19b vibration modes (in-plane vibrations of the C$_6$ ring), and are due to pyridine coordinatively adsorbed at Lewis acid sites. No bands due to the ring vibrations of the pyridinium ion were detected.

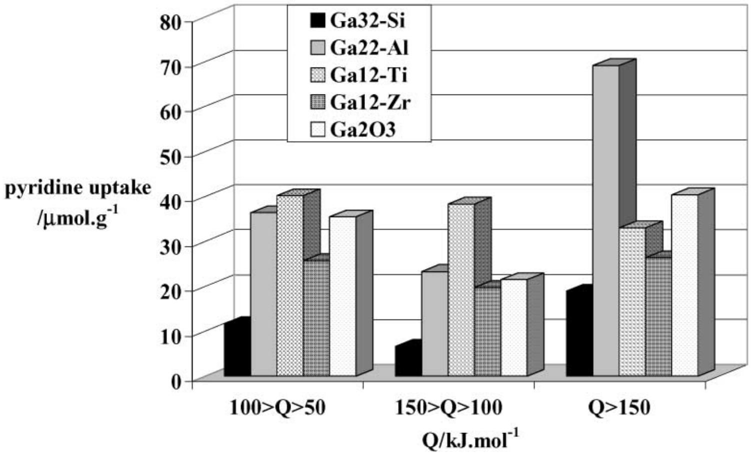

Fig. 6. Strength distribution of acid sites (determined by pyridine adsorption) of the supported catalysts and bulk gallium oxide.

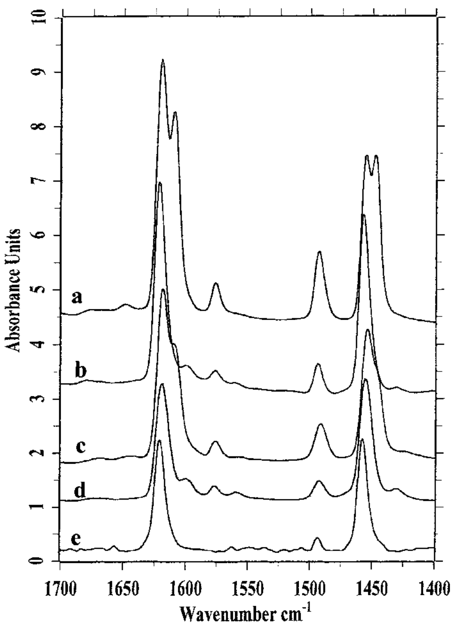

Fig. 7. FTIR spectra (normalized by weight unit) of the surface species after pyridine adsorption at 298 K and outgassing at 423 K on supported gallium oxide catalysts: (a) Ga12-Ti; (b) Ga22-Al; (c) Ga12-Zr; (d) Ga_2O_3; (e) Ga32-Si.

The observation of the 8a vibration mode band, considered as the most sensitive one for coordinatively adsorbed pyridine, reveals the presence in Fig. 7 of specific bands characteristic of pyridine adsorbed on Lewis sites [9,19]. No such bands was observed for silica. This indicates that depositing gallium oxide on SiO_2 creates Lewis sites which can be tentatively attributed to gallium sites. This is in full agreement with calorimetric results. In the case of Ga12-Ti sample, two distinct bands at 1620 and 1610 cm^{-1} were observed, which can be attributed to two different types of Lewis sites. The band at 1610 cm^{-1}, already observed when adsorbing pyridine on the bare TiO_2 support, is related to pyridine coordinated to Ti^{4+} sites of TiO_2. The band at 1620 cm^{-1} (similar to Ga32-Si and Ga_2O_3) could be related to gallium sites present on the surface. The relative intensities of these two bands could be indicative of the dispersion of Ga_2O_3 on the support surface. In the case of Ga12-Ti, a significant fraction of the titania surface could be not covered by gallium oxide. The same trend is observed for the Ga12-Zr catalyst, but in this case the band which can be attributed to the adsorbed pyridine on the non-covered support is much less intense, showing a higher degree of dispersion of gallium oxide on zirconia. In the case of Ga22-Al only one single band at 1622 cm^{-1} is observed. This band might overlap the 1616 cm^{-1} band observed for gallium-free alumina. This result demonstrates that pyridine adsorption probing by FTIR spectroscopy cannot distinguish between Ga^{3+} and Al^{3+} surface sites. For all supported gallium oxide samples, the band around 1620 cm^{-1} is thought to be related to the presence of the Ga^{3+} cations of the surface, since the same band is observed when adsorbing pyridine on bulk gallium oxide. Based on this interpretation it can be suggested that, for all gallium oxide-supported catalysts, gallium oxide has been more or less dispersed on the bare support. This is in agreement with the microcalorimetric measurements. For acidic supports, the total acidity of the gallium-based samples is decreased compared to that of the supports. In the case of silica (non-acidic support), some acidic sites were created.

In Table 1, also reported are the initial heats of adsorption and the amounts of carbon dioxide chemisorbed at room temperature under an equilibrium pressure of 27 Pa. The comparison of the CO_2 uptakes on supports and supported gallium oxide catalysts suggests that weakly basic Ga_2O_3 is also covering some of the basic sites of γ-alumina, titania and zirconia. After depositing gallium oxide on zirconia, an amphoteric support which displays the largest and strongest population of basic sites, the CO_2 uptake decreases much more than in the case of the alumina-supported catalyst. On silica, the deposited gallium oxide does not seem to create a specific basicity. This is in agreement with the adsorption of CO_2 measured by FTIR spectroscopy, where no carbonate bands were observed.

Fig. 8 presents the differential heats of CO_2 adsorption versus coverage on the supported gallium oxide catalysts and bulk Ga_2O_3. Ga22-Al is the only sample that displays a relatively strong basicity.

In terms of amounts of formed species after CO_2 adsorption, the general trend is a decrease after Ga_2O_3 deposition (except for silica), but the most dramatic difference between the FTIR spectra of the support and supported sample was observed in the case of zirconia. The infrared bands corresponding to carbonate vibrations are much less intense for Ga12-Zr than for ZrO_2. This behavior is confirmed by the calorimetric

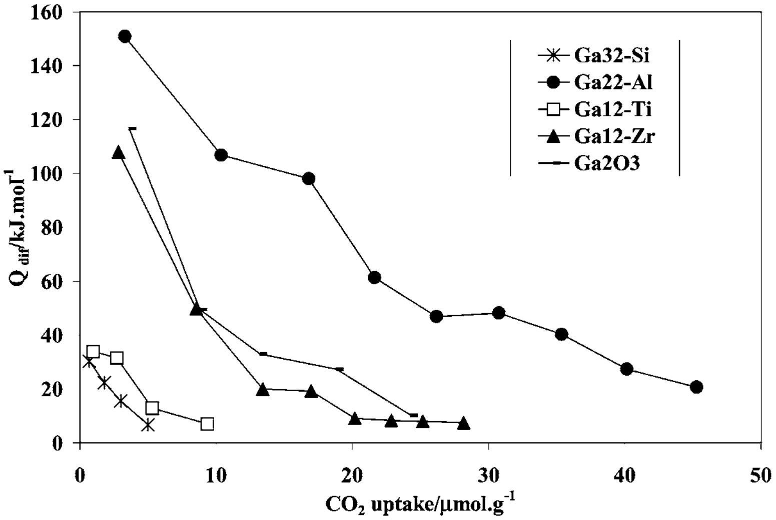

Fig. 8. Differential heats of CO_2 adsorption vs. coverage for supported and bulk gallium oxides.

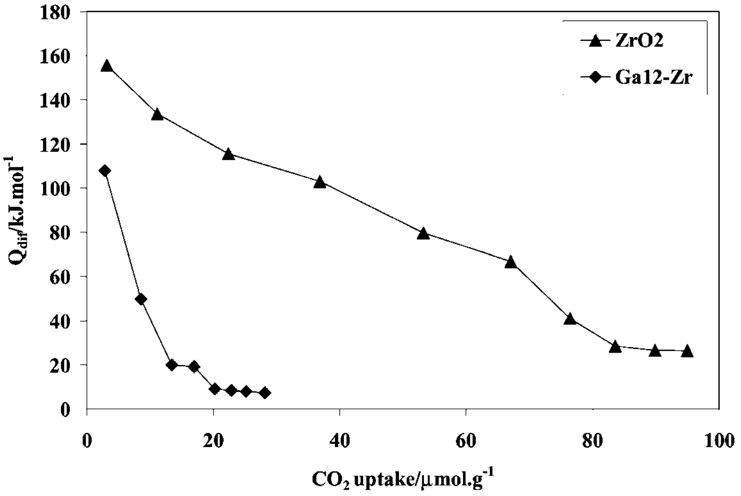

Fig. 9. Differential heats of CO_2 adsorption vs. coverage for zirconia and zirconia-supported gallium oxide.

experiments and can be seen in Fig. 9 where the differential heats of CO_2 adsorption are plotted versus coverage for bare ZrO_2 and zirconia-supported gallium oxide. From Figs. 8 and 9 it can be deduced that a high proportion of the surface basic sites of zirconia are covered by gallium oxide. Considering the previously discussed acidity measurements, it can be concluded that the zirconia surface might be almost completely covered by a layer of Ga_2O_3.

4. Conclusion

Using adsorption microcalorimetry and FTIR spectroscopy as complementary methods, it was shown that the deposition of amphoteric gallium oxide (more acidic than basic) modifies, in variable proportions, the acid–base properties of the supports; this makes it possible to estimate specific contributions of the support and of the guest oxide.

Lewis acidity, the only type of acidity observed by pyridine adsorption, depends on the existence of exposed metal cations at the surface, and factors such as ionic charge, degree of coordinative unsaturation and band gap strongly influence this acidity. In this study, it was shown that the most important Lewis acidity (the highest number of coordinatively unsaturated surface cations) is observed on the alumina-supported gallium oxide catalyst. This catalyst has a specific local structure (superficial spinel) different from bulk gallium oxide and was revealed as highly effective in SCR of NO_x.

It is suggested that the acid–base strength of the supported gallium oxide catalysts is mainly determined by the topological distribution of Ga_2O_3 and by the ability of the support to form tight bonds based upon strong interactions between guest and host oxides. This in turn can be very dependent on the chemical nature and thermal history of the support.

References

[1] K. Shimizu, A. Satsuma, T. Hattori, Appl. Catal. B 16 (1998) 319.

[2] K. Nakagawa, C. Kajita, Y. Ide, M. Okamura, S. Kato, H. Kasuya, N. Ikenaga, T. Kobayashi, T. Suzuki, Catal. Lett. 64 (2000) 215.

[3] K. Shimizu, M. Takamatsu, K. Nishi, H. Yoshida, A. Satsuma, T. Hattori, Chem. Commun. (1996) 1827.

[4] T. Maunula, Y. Kintaichi, M. Inaba, M. Haneda, K. Sato, H. Hamada, Appl. Catal. B 15 (1998) 291.

[5] H. Hamada, Catal. Today 22 (1994) 21.

[6] K.A. Bethke, M.C. Kung, B. Yang, M. Shah, D. Alt, C. Li, H.H. Kung, Catal. Today 26 (1995) 169.

[7] K. Nishi, K. Shimizu, M. Takamatsu, H. Yoshida, A. Satsuma, T. Tanaka, S. Yoshida, T. Hattori, J. Phys. Chem. B 102 (1998) 10190.

[8] K. Shimizu, M. Takamatsu, K. Nishi, H. Yoshida, A. Satsuma, T. Tanaka, S. Yoshida, T. Hattori, J. Phys. Chem. B 103 (1999) 1542.

[9] G. Connell, J.A. Dumesic, J. Catal. 105 (1987) 285.

[10] N. Cardona-Martinez, J.A. Dumesic, J. Catal. 127 (1991) 706.

[11] B. Gergely, A. Auroux, Res. Chem. Intermed. 25 (1999) 13.

[12] B. Gergely, A. Redey, C. Guimon, A. Gervasini, A. Auroux, J. Therm. Anal. 56 (1999) 1233.

[13] O.O. Parenago, Y.N. Pushkar, A.O. Turakulova, G.P. Murav'eva, E.V. Lunina, Kinet. Catal. 39 (1998) 268.

[14] H.E. Ries, K.J. Laidler, W.B. Innes, F.G. Ciapetta, C.J. Plank, P.W. Selwood, in: P.H. Emmett (Ed.), Catalysis. Part I. Fundamental Principles, Vol. I, Book Division Reinhold Publishing Corporation, New York, 1954, p. 258.

[15] V.E. Henrich, P.A. Cox, in: The Surface Science of Metal Oxides, Cambridge University Press, Cambridge, 1994, pp. 247–285.

[16] G. Busca, Catal. Today 41 (1998) 191.

[17] A. Auroux, A. Gervasini, J. Phys. Chem. 94 (1990) 6371.

[18] A.L. Petre, A. Auroux, A. Gervasini, M. Caldararu, N.I. Ionescu, J. Therm. Anal. Calal. 64 (2001) 253.

[19] M. Lenarda, L. Storaro, G. Pellegrini, L. Piovesan, R. Ganzerla, J. Mol. Catal. A: Chem. 145 (1999) 237.