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CALORIMETRIC CHARACTERIZATION OF SURFACE REACTIVITY OF SUPPORTED Ga_2O_3 CATALYSTS

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Abstract

The surface properties of supported gallium oxide catalysts prepared by impregnation of various supports (γ-Al_2O_3, SiO_2, TiO_2, ZrO_2) were investigated by adsorption microcalorimetry, using ammonia and water as probe molecules. In the case of acidic supports (γ-Al_2O_3, ZrO_2, TiO_2), the acidic character of supported gallium catalysts always decreased in comparison with gallium-free supports; on very weakly acidic SiO_2, new acidic centers were created when depositing Ga_2O_3. The addition of gallium oxide decreased the hydrophilic properties of alumina, titania and zirconia, but increased the amount of water adsorbed on silica. The catalytic performances in the selective catalytic reduction of NO by C_2H_4 in excess oxygen were in the order $Ga/Al_2O_3 > Ga/TiO_2 > Ga/ZrO_2 >> Ga/SiO_2$. This order is more related to the quality of the dispersion of Ga_2O_3 on the support than to the global acidity of the solids.

Keywords: adsorption microcalorimetry, H_2O, NH_3, NO reduction, supported gallium oxide

Introduction

Gallium-containing catalysts exhibit very interesting catalytic properties in the selective catalytic reduction (SCR) of NO_x with hydrocarbons in presence of oxygen and in the dehydrogenation and/or aromatization of alkanes.

In spite of various problems such as hydrothermal instability, fast deactivation, diffusion limitations, progressive degalliation, and modification of the acidity and crystallinity during catalyst regeneration, gallium-promoted zeolites (Ga-ZSM-5, Ga-HMFI, Ga-H-MOR, Ga-H-Y) remain highly effective catalysts [1, 2].

Supported gallium oxide catalysts have been suggested as alternative materials in the selective catalytic reduction (SCR) of NO_x by hydrocarbons [3–11] in order to overcome the atmospheric pollution problems caused by NO_x. Different oxide matrices have been tested as supports for gallium oxide; among them, alumina-supported

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gallium oxide is the most promising candidate for practical applications due to its high activity, selectivity and hydrothermal stability. Attempts to explain the high catalytic activity and selectivity of alumina-supported gallium oxide catalysts and to identify the active species have been mostly focused on structural analysis. Thus, the selective catalytic reduction of NO with CH_4 was proved to be a structure-sensitive reaction depending on the local coordination of the Ga^{3+} cation [5–7].

However the effect of the matrix support on the catalytic performances of supported Ga_2O_3 catalysts has not been investigated in detail, except for samples containing small amounts of gallium oxide and showing low catalytic activity [3].

Moreover, few studies have been reported about the correlation between the adsorption properties of supported gallium oxide catalysts and their catalytic activity. At the same time, the influence of water on the activity of gallium oxide supported on alumina is not clear. It is usually reported that the presence of water either inhibits the de-NO_x reaction (in the case of Ga_2O_3/Al_2O_3) or promotes irreversible deactivation of the catalysts (in the case of gallium-promoted zeolites); however, Hamada *et al.* [8–10] reported an enhancement of the activity for SnO_2- and In_2O_3-doped Ga_2O_3–Al_2O_3.

In this study we investigated the surface properties (acidity, hydrophilicity, adsorption properties) of various supported gallium oxides, tentatively relating them to catalytic performance in the selective catalytic reduction of NO with ethylene in presence of oxygen excess.

Experimental

Supported gallium oxide catalysts were prepared by wet impregnation of various supports (γ-Al_2O_3 (Oxid C, Degussa), SiO_2 (Aerosil 200, Degussa), TiO_2 containing 75% anatase phase (P 25, Degussa), ZrO_2 (VP, Degussa)) with aqueous solutions of $Ga(NO_3)_3\cdot 9H_2O$. After drying 18 h at 393 K, the samples were calcined in air flow at 773 K for 8 h. Gallium oxide loading was equivalent to the theoretical monolayer calculated from the density of Ga_2O_3. This represents about 20.2, 32.8, 11.4 and 12.2 mass% of Ga_2O_3 on Al_2O_3, SiO_2, TiO_2 and ZrO_2 respectively. The samples are named Ga22–Al, Ga32–Si, Ga12–Ti and Ga12–Zr as in Table 1.

Chemical analysis was performed by AES-ICP. The BET surface areas were measured using N_2 at 77 K. X-ray diffraction spectra of powder samples were recorded on a Bruker D5005 diffractometer (CuK_α source).

The microcalorimetric studies were performed in a heat flow calorimeter (C80 from Setaram) linked to a conventional volumetric apparatus, at 423 K for ammonia adsorption and at 353 K for water adsorption [12]. Before each experiment the samples were outgassed overnight at 673 K. 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.

Table 1 Physicochemical characteristics of supports and supported gallium oxide catalysts

Sample	Ga_2O_3 content/ mass%	BET surface area/m^2 g^{-1}	Acidity		Water adsorption	
			Q_{init}/ kJ mol^{-1}	NH_3 uptake[a]/ µmol NH_3 g^{-1}	Q_{init}/ kJ mol^{-1}	H_2O uptake[a]/ µmol H_2O g^{-1}
Al_2O_3	–	108	215	206	265	468
TiO_2	–	55.2	200	217	200	274
ZrO_2	–	59.0	210	156	325	255
SiO_2	–	208	20	58	50	50
Ga22–Al	22.3	99	195	195	335	309
Ga12–Ti	12.1	49.7	140	140	225	156
Ga12–Zr	12.7	48.4	190	124	215	187
Ga32–Si	32.4	134	160	175	290	212

[a]Total amount adsorbed under an equilibrium pressure of 27 Pa, calculated from the primary isotherm

Ga_2O_3-supported catalysts were tested in NO reduction by ethylene in a high oxidizing atmosphere ($NO–C_2H_4–O_2$). The catalytic runs were performed in a fixed-bed quartz tubular reactor introducing about 0.1 g of catalyst in powder form. The gases, 2% NO/He, 2% C_2H_4/He, and pure O_2, were fed from independent mass flow controllers (Bronkhorst, Hi-Tec.). For all runs the final feed mixture was composed of 0.5% NO, 0.5% C_2H_4, and 9% O_2, with He as balance, at a total flow-rate of 5.5 L h^{-1}. Space velocity corresponded to 50 000 h^{-1} (GHSV). The reaction was studied at ten different temperatures between 523 and 773 K, maintaining each temperature for 3 h. The outflow gas was analyzed by using a gas chromatograph equipped with a TCD detector (Chrompack) mounting a 60/80 Carboxen-1000 column (Supelchem) for the separation of O_2, N_2, N_2O, NO, C_2H_4, CO and CO_2.

Results and discussion

The physicochemical characteristics of supports and supported gallium oxide catalysts are listed in Table 1, which gives for each sample the Ga_2O_3 content (mass%), the BET surface area, the acidity and the water adsorption properties as determined by adsorption calorimetry, expressed in terms of initial heats of adsorption (noted Q_{init}) and amounts of adsorbed probe molecule 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 BET surface area decreases sharply for the sample supported on silica, while the decrease is less important 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 (indicated by XRD measurements) could explain the strong decrease of BET surface area of the Ga32–Si sample.

The differential heats of ammonia adsorption *vs.* coverage are represented in Fig. 1 for the supports and in Fig. 2 for the supported Ga_2O_3 catalysts. The acidity of supports expressed in terms of NH_3 sorption uptakes varies over a wide range, from very weakly acidic silica to acidic titania and γ-alumina, as shown in Table 1. The total acidity of the supports, expressed in terms of number of acid sites, varies in the order: $SiO_2 \ll ZrO_2 < Al_2O_3 \approx TiO_2$. All supports except for silica present small populations of strong acid sites, with comparable strengths, as indicated by the very similar values of initial heats of adsorption. The absence of a plateau in the shape of the differential heat curves shows the heterogeneity of the adsorption sites of the supports.

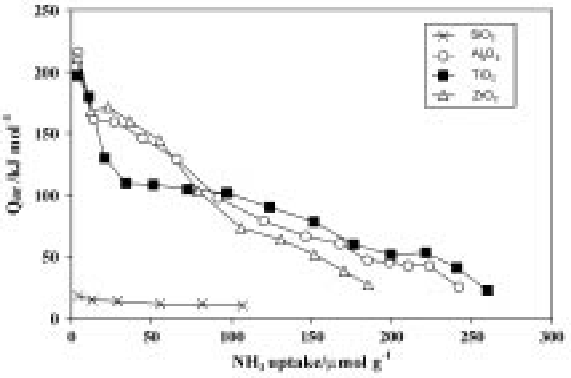

Fig. 1 Differential heats of ammonia adsorption at 423 K *vs.* coverage for supports

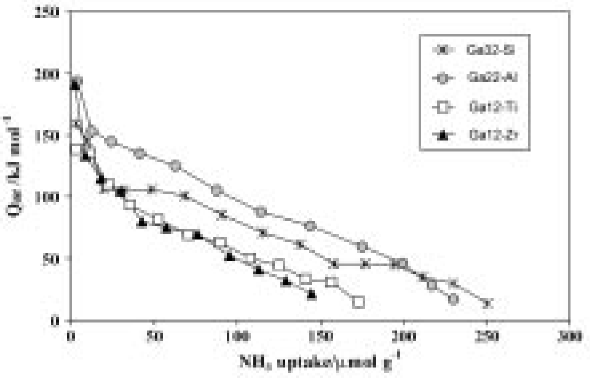

Fig. 2 Differential heats of ammonia adsorption at 423 K *vs.* coverage for supported gallium oxide catalysts

After depositing gallium oxide on the surface of supports, the total acidity (in terms of number of sites) is in the order: Ga12–Zr≈Ga12–Ti<Ga32–Si<Ga22–Al. In comparison with the bare support, the Ga12–Zr and Ga22–Al samples were slightly less acidic, while a large decrease in the number of acid sites was observed for Ga12–Ti, as determined by NH_3 adsorption. The acid sites present on the surface of these catalysts are weaker than those existing on the supports, as shown by the initial

heats of adsorption in Table 1. The new strong acid sites titrated on Ga32–Si sample can be attributed to Ga^{3+} cations present on the surface.

NH_3 and H_2O, both donors with lone-pair electrons able to interact with cation surface sites, are frequently used as probe molecules to characterize the surface properties of catalysts. These two molecules differ by their proton affinity (PA_{NH_3}= 3573 kJ mol^{-1}, PA_{H_2O}=2891 kJ mol^{-1}). With this assumption water adsorption should define the same scale of acidity as ammonia, but smaller values in terms of number of sites are to be expected due to the lower *PA* in comparison with ammonia. However, since in our case the adsorption temperature was lower for water than for ammonia, it is more meaningful to compare the ordering of the catalysts according to their adsorbed amounts rather than the amounts themselves.

The ordering of the samples according to their hydrophilic character was close to that for acidity, both in the case of supports: SiO_2<<ZrO_2≈TiO_2<<Al_2O_3 and supported gallium oxide catalysts: Ga12–Ti<Ga12–Zr<Ga32–Si<Ga22–Al. As shown in Fig. 3, the hydrophilic behavior of supports varies between mere water physisorption (in the case of SiO_2) and chemisorption of a large amount of water (for γ-alumina). After gallium oxide deposition (more or less dispersed as a monolayer on the surface

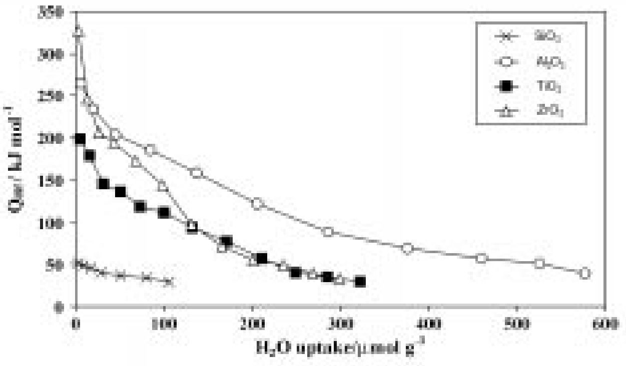

Fig. 3 Differential heats of water adsorption at 353 K *vs*. coverage for supports

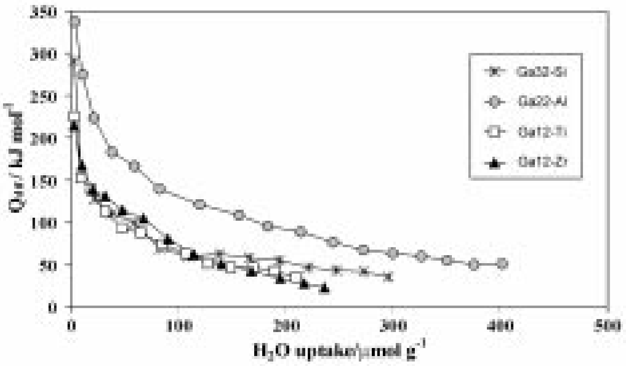

Fig. 4 Differential heats of water adsorption at 353 K *vs*. coverage for supported gallium oxide catalysts

of support), the surface properties tested by water adsorption indicate a similar hydrophilic behavior of all catalysts (as can be seen in Fig. 4) irrespective of the initial behavior of the support, with the notable exception of γ-alumina. This demonstrates that on the other supports the hydrophilic properties are mainly dictated by the gallium oxide (isomorphous with Al_2O_3).

Figures 5 and 6 present the distribution of strength of water adsorption sites on the supports and supported gallium oxide samples respectively, as determined from the variations with coverage of the differential heats of water adsorption by counting the number of sites over which the heat evolved during adsorption is in a given interval. It is worth noting that the strong and weak acid sites were more affected by gallium oxide deposition than those of intermediate strength. At the same time, a bigger contribution of the weak water adsorption sites in comparison to the strong and medium ones was evidenced for supported gallium oxides. The population of strong water adsorption sites (Q>150 kJ mol^{-1}) was hugely decreased in the case of catalysts supported on alumina, zirconia and titania.

The reduction of NO by C_2H_4 over supported gallium oxide catalysts was investigated in severe lean conditions at very high space velocity (50,000 h^{-1}). Significant differences emerged among the supported Ga_2O_3 catalysts in terms of temperature of onset of reactions (NO conversion to N_2 and C_2H_4 conversion to CO and CO_2), activity, and selectivity.

As shown in Table 2, Ga22–Al is the most active and selective catalyst. The reduction of NO to N_2 by C_2H_4 started at a low temperature, and so did the parallel combustion of C_2H_4 by O_2. The N_2 production always increased with temperature, reaching 82.2% at 773 K. At this temperature, C_2H_4 conversion was not quantitative; therefore, the selectivity of the catalyst could be calculated in terms of competitiveness factor (*c.f.*, defined as the ratio between the amount of C_2H_4 used by NO to form N_2 and that used by O_2). Ga_2O_3-based catalysts supported on TiO_2 and ZrO_2 were active towards N_2 formation, but their activity and selectivity were lower than those of the Al_2O_3 supported catalyst (Table 2). A complete absence of activity towards N_2 formation was observed on Ga32–Si; at high temperatures only a slight combustion of C_2H_4 could be observed.

Table 2 Significant results for the $NO:C_2H_4:O_2$ reaction over the Ga_2O_3 supported catalysts

Sample	NO conversion to N_2		C_2H_4 conversion to CO+CO_2		Selectivity[b,c]
	T_{onset}[a]/K	Conversion[b]/%	T_{onset}[a]/K	Conversion[b]/%	*c.f.*/%
Ga22–Al	533	82.2	583	91.1	15.0
Ga12–Ti	613	33.9	648	53.3	10.6
Ga12–Zr	653	32.8	653	59.2	9.2
Ga32–Si	–	<5	713	25.4	<3

[a] T_{onset} corresponds to 15–20% of conversion to N_2 and to CO+CO_2
[b] data at a reaction temperature of 773 K
[c] selectivity in terms of competitiveness factor (*c.f.*)

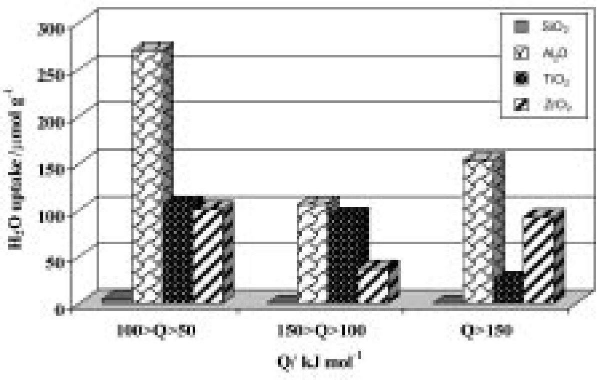

Fig. 5 Strength distribution of water adsorption sites of the supports

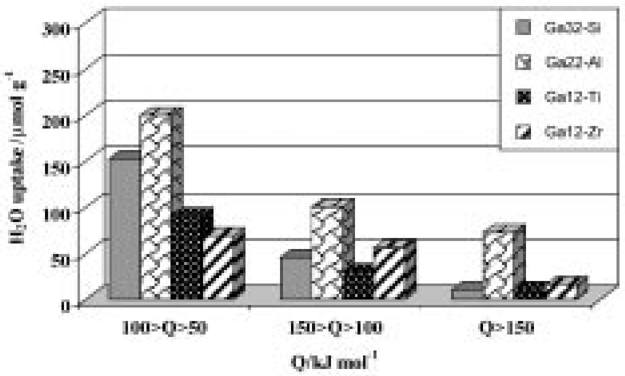

Fig. 6 Strength distribution of water adsorption sites of the supported gallium oxide catalysts

Differences in the degree of dispersion of Ga_2O_3 on the surface of the support and in the Lewis-type acidity (coordinatively unsaturated Ga^{3+} centers on the surface) could be invoked to rationalize the catalytic results.

Conclusions

The importance of the Lewis acidity (unsaturated surface cations) and of the rather hydrophobic character of gallium oxide species strongly bonded to the support for the activity and selectivity in NO_x reduction by C_2H_4 has been demonstrated. Gallium oxides deposited on titania and zirconia were less acidic and less effective in the de-NO_x process than Ga_2O_3 supported on alumina. Ga_2O_3 on silica, which is badly dispersed on the surface and displays a more hydrophilic character than the support, was inactive in the SCR of NO. This behavior underlines the importance of the surface OH groups in the reaction mechanism. However the NO conversion to N_2 is more related to the dispersion of the gallium active centers on the supports than to the global acidity of the catalysts.

The highly stable supported gallium oxide catalysts, tested in the reaction of NO reduction by ethylene in oxygen rich atmosphere, have demonstrated their interest as an alternative to metal exchanged zeolites in the aim of reaching the future emission standards.

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