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Thermochimica Acta 379 (2001) 95–99

thermochimica acta

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Site energy distribution of copper catalytic surfaces from volumetric data collected at various temperatures

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Abstract

Two catalysts prepared on a titanium silicate (ETS-10) matrix by loading 6 and 11 wt.% of copper were studied by employing nitrogen monoxide as adsorbate to probe the surface properties of copper centres. Volumetric isotherms of NO adsorption were collected at different temperatures (19–70°C). A thermodynamic model was applied to the isotherms in order to describe the behaviour of the NO–Cu system in terms of surface energy distribution of Cu sites. The higher loading copper sample had more energetic interaction with NO ($-171 < \Delta_a H\,(\mathrm{kJ/mol}) < -44$), with higher heterogeneity, than the less loaded one ($-111 < \Delta_a H\,(\mathrm{kJ/mol}) < -41$). The properties of the Cu sites were related with the activity measured in the SCR of NO with ethylene.

Keywords: Copper catalysts; NO adsorption; Volumetry; Site energy distribution

1. Introduction

The catalytic properties of heterogeneous solid catalysts are governed by their surface characteristics. Gas-phase adsorption methods using suitable probes, chosen on the basis of their chemical and electronic characteristics, appear to be the most promising in order to study the thermodynamic properties of the surface sites.

The collection of experimental adsorption isotherms and/or curves of differential heats of adsorption can reveal the more or less marked degree of heterogeneity of the surface sites. However, the temperature at which the adsorption is performed can deeply influence the results obtained. Higher temperatures depress the adsorption on the more energetic sites, so that definite types of surface sites can only be observed in a certain temperature interval. In order to overcome this problem, the authors recently have proposed a model [1–3] based on a fitting procedure applied to the volumetric and/or calorimetric adsorption data collected at different temperatures. The model allows the determination of the thermodynamic parameters of adsorption (temperature of half-coverage at unit pressure, $T^0_{1/2}$, equilibrium constant of adsorption, and entropy of adsorption) for each type of site. The model interprets the adsorption on the heterogeneous surface as a summation of single isotherms, each one relevant to a definite type of site. The dependence of the adsorption constant for each type of site is obtained on the basis of the van't Hoff equation. The determination of the pre-exponential factor in the van't Hoff equation was obtained through the new parameter $T^0_{1/2,i}$ which represents the temperature of half-coverage at unit pressure for a given type of site. The model allows the site distribution to be obtained in terms of number of sites

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0040-6031/01/$ – see front matter
PII: S0040-6031(01)00607-4

versus enthalpy of adsorption, which reflects the heterogeneous character of the surface of the solid with respect to the adsorption of a chosen adsorbate.

In this study, the adsorption of NO on copper catalysts was taken into account. NO has already been used by the authors as probe molecule to study the surface copper centres of zeolitic (Cu/ZSM-5) and oxidic (Cu/SiO_2–Al_2O_3) catalysts [4]. NO is a strong Lewis base, able to stabilise the formation of both mono- and dinitrosyls of Cu^+ and Cu^{2+} cations [5]. In recent years, large and medium pore zeolite structures and other molecular sieves exchanged with Cu and various cations have been studied for reducing NO with hydrocarbons (SCR process) [6]. The synthesised microcrystalline ETS-10 material (titanium silicate) [7] was used as support matrix for the preparation of copper based catalysts, in comparison with the Cu–ZSM-5 system [4]. A very large number of papers on the characterisation of the species formed by interaction of reactant molecules (i.e. NO, O_2, CO) with the surface centres appeared in the literature [8–14], most of them employing infrared spectroscopy. However, only few papers are devoted to the study of the energy of surface centres and their distribution on the surface [4,15].

The adsorption of NO on two copper titanium–silicate catalysts was studied with the aim of determining the energy distribution of Cu surface centres. Correlations between both the nature and the energy of the Cu surface species and the catalyst activity in NO reduction with C_2H_4 in excess oxygen are proposed.

2. Experimental

The samples have been prepared by loading 6 and 11 wt.% of copper on a microcrystalline titanium silicate (ETS-10, from Engelhard) matrix [4]. The starting material was the Na^+/K^+ form of ETS-10, containing about 8 wt.% of TiO_2. A conventional base-exchange procedure using copper acetate was carried out to prepare samples at low and high Cu loading (6 and 11 wt.% Cu, Cu/ETS-6 and Cu/ETS-11, respectively). The amount of Cu introduced was less than the total exchange capacity of ETS-10. The powders were dried at 120°C, calcined at 550°C for 5 h, then crushed and sieved as particles of 0.25–0.35 mm size.

The samples were characterised by various analyses: inductive coupled plasma (ICP) for the determination of copper content, powder X-ray diffraction (XRD) (Philips PW1877 diffractometer), N_2 adsorption isotherms at 77 K (Sorptomatic 1900 apparatus, Fisons Instruments). Microcalorimetry determinations of the heats of NO adsorption were performed using a differential heat flow calorimeter (C80, Setaram) equipped with a standard volumetric adsorption device and a capacitance manometer (Datametrics) for pressure measurements. The adsorption was performed at 30°C up to ca. 1 mbar.

Complete NO adsorption isotherms (up to ca. 30 mbar) were collected by an automatic static apparatus (Sorptomatic 1900, chemisorption version, Fisons Instruments) at different temperatures (40–70°C). The equilibrium pressure was determined at the point at which the pressure was stable within 0.02 mbar for 7 min.

The samples were pretreated at 400°C under vacuum (ca. 16 h) prior to the microcalorimetric and volumetric analyses.

The computation method used to determine the energy distribution of Cu sites in terms of NO adsorption enthalpy is reported in [3]. The stoichiometry of adsorption was assumed to be NO/Cu = 1. Because NO can be adsorbed as mononitrosyl (NO/Cu = 1) and dinitrosyl (NO/Cu = 2) species, the assumption of NO/Cu = 1 could lead to an overestimation of the number of the Cu-adsorption sites. However, mononitrosyl species are predominant at low NO pressure ($P_{NO} < 20$ mbar) [14]. Only data with $P_{NO} \leq 10$ mbar were taken into account in the computations.

Activity tests for catalytic reduction of NO by C_2H_4 in excess oxygen (NO–C_2H_4–O_2) were carried out in a fixed bed reactor in the temperature range 150–500°C at GHSV of 7500 h^{-1} with 0.4% of both NO and C_2H_4 and 4% of O_2 in the feed. The reactor outflow was analysed by a GC equipped with a TCD detector.

3. Results and discussion

3.1. Catalyst properties and activity

The ETS-10 molecular sieve consists of a combination of tetrahedral silica and octahedral titanium units [7,16]. XRD patterns of the two catalysts were indistinguishable from that of the parent matrix, indicating that the crystal structure remained unperturbed by the copper exchange procedure. In the case of

Cu/ETS-11, a slight decrease in crystallinity could be observed and low intensity peaks characteristic of CuO appeared in the 2θ region of 36–39°. The texture of the samples was studied in terms of total, external and internal surface area by constructing *V–t* curves (*t*-plot method) from the nitrogen adsorption isotherms. Both the matrix and the samples possessed microporosity (mean pore radius 10 Å) and high surface area (480, 396, and 307 m^2/g for ETS-10, Cu/ETS-6, and Cu/ETS-11, respectively). The contribution of the internal surface to the total surface area of ETS-10 was very important (about 90%). For Cu/ETS-6 a slight decrease (about 20%) of internal surface area compared with the parent matrix was observed. A more important decrease was found for Cu/ETS-11 (about 40%).

Concerning the oxidation state of the copper species, previous studies by X-ray photoelectron spectroscopy (XPS) on Cu/ETS series samples [4] have confirmed that pretreatment at 400°C under vacuum creates a larger proportion of Cu^+ for the high loading copper samples than for those at low loading. Nearly 100% Cu^+ was found on the pretreated Cu/ETS-11, while on both the fresh samples only Cu^{2+} species were detected.

Both Cu/ETS-6 and Cu/ETS-11 were active and selective towards N_2 production in the NO–C_2H_4–O_2 reaction [4]. As expected, the N_2 yield followed a volcano-shaped curve with a maximum temperature around 300°C. The differences that emerged between the two catalysts in terms of maximum N_2 yield were not very important (about 23%). However, the oxidation of C_2H_4 to CO_2 attained its maximum value (at 325°C) only on Cu/ETS-11, whilst CO_2 yield was 60% at 300°C and 97% at 500°C on Cu/ETS-6. Therefore, Cu/ETS-6 was more selective than Cu/ETS-11 as indicated by the competitiveness factors (CF) of 10 and 4% at 300°C for Cu/ETS-6 and Cu/ETS-11, respectively. This behaviour seems to confirm that small CuO-like aggregates, such as those present on Cu/ETS-6, are more active towards NO reduction and do not possess enhanced oxidation properties.

3.2. NO adsorption measurements and interpretation model

The differential heats of NO adsorption measured at 30°C on ETS-10 and on the two Cu catalysts showed a continuous decrease of the heats in a short uptake range, following the order: ETS-10 ≪ Cu/ETS-6 ≪ Cu/ETS-11. Initial heats of NO adsorption were 75 kJ/mol over ETS-10, while over both Cu/ETS catalysts the initial adsorption heats were as high as 110–130 kJ/mol and the average heats in the range 80–90 kJ/mol. A steep decrease of the adsorption heat curve for the catalyst with low copper content and a less marked decreasing trend for the catalyst with high copper content were observed [4]. This behaviour reveals a more or less marked heterogeneous character of the Cu sites towards NO adsorption, with few Cu centres at high enthalpy (>100 kJ/mol) and a large predominance of less enthalpic ones. The total amounts of NO adsorbed at a given pressure (0.15 mbar) were 1.23, 16.97 and 35.64 μmol/g for ETS-10, Cu/ETS-6, and Cu/ETS-11, respectively. After pumping at the adsorption temperature (30°C), the amounts of NO still adsorbed on the samples were 57, 34, and 22% of the total amounts of NO adsorbed for ETS-10, Cu/ETS-6, and Cu/ETS-11, respectively. This evidence confirms the low strength of the bonding between NO and the copper sites over both the catalysts.

To determine the distribution of Cu centres in terms of number of Cu sites versus enthalpy of adsorption, volumetric adsorptions of NO were accomplished at different temperatures (40–70°C). Each point of the low temperature isotherms laid above those corresponding to the same pressure at higher temperatures. This is in agreement with thermodynamics, because NO adsorption, being an exothermic reaction, is less favoured at a higher temperature. The experimental adsorption data were interpreted following a mathematical model described previously [1–3]. The NO adsorption isotherms were considered as summations of single Langmuir isotherms, each of them relevant to sites of a definite type. The dependence of the adsorption constants on temperature was expressed by the van't Hoff equation. The adsorption enthalpy of each *i*th type of site ($\Delta_a H_i$) was considered constant in the temperature range investigated and the pre-exponential factor of the van't Hoff equation was expressed as a function of the "half-coverage temperature at unit pressure", $T^0_{1/2,i}$. The latter parameter, defined in previous papers [1,2], is characteristic of each type of site. For the two catalysts, the $\Delta_a H_i$ and $T^0_{1/2,i}$ values as well as the number of sites of each type (n_i) were determined by an optimisation procedure simultaneously exploiting the data collected at the

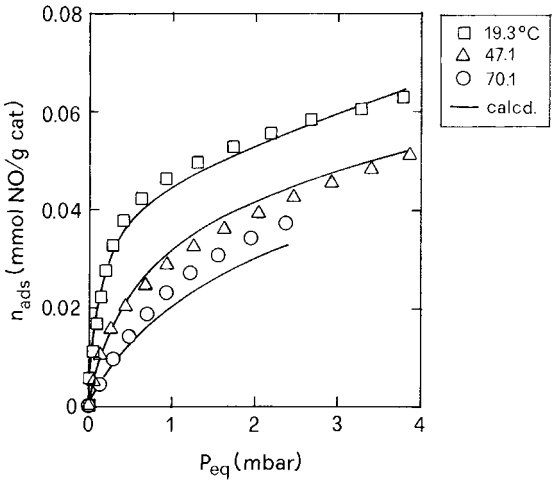

Fig. 1. Experimental and calculated (lines) isotherms of NO adsorption over Cu/ETS-6 collected at four different temperatures.

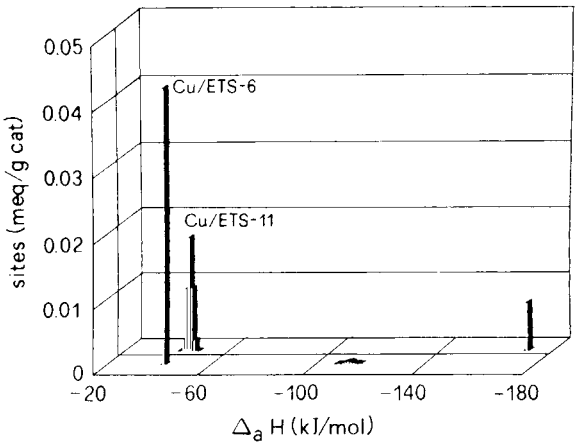

Fig. 3. Copper site energy distributions in terms of enthalpy of NO adsorption over the two catalysts determined by the optimised thermodynamic parameters with the employed model, starting from the isotherms of NO adsorption measured at different temperatures.

various temperatures. Preliminary computations showed an adsorption-enthalpy distribution with $\Delta_a H_i$ values grouped around a small number of maxima. For the final computations, a Gaussian distribution function of the enthalpies around the maxima was assumed in agreement with other authors [17]. The comparison between experimental and calculated isotherms, shown in Figs. 1 and 2, evidences the quality of the fit.

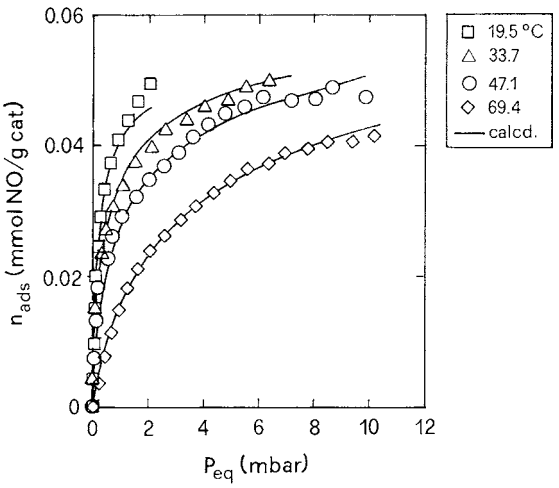

Fig. 2. Experimental and calculated (lines) isotherms of NO adsorption over Cu/ETS-11 collected at three different temperatures.

Both catalysts showed a significant quantity of sites associated with $\Delta_a H_i$ values close to −14 kJ/mol (nearly the heat of vaporisation of NO). The energy distributions of the sites with higher $\Delta_a H_i$ values, corresponding to more energetic interaction of NO with copper sites, are shown in Fig. 3. Sites of a same type, close to −41 kJ/mol, were found (0.0422 meq/g_{cat}) for Cu/ETS-6, which showed only a few more energetic sites (0.001 meq/g_{cat}) broadened around −111 kJ/mol. For Cu/ETS-11, most of the sites (0.040 meq/g_{cat}) were distributed between −47 and −41 kJ/mol, with a maximum at −44 kJ/mol, and a small but not negligible amount of sites (0.007 meq/g_{cat}) was found close to −171 kJ/mol. Taking into account the most representative populations of Cu sites (around 40–50 kJ/mol) and the different Cu loadings of the two samples, the numbers of sites were as high as 0.703 meq/g_{Cu} for Cu/ETS-6 and 0.364 meq/g_{Cu} for Cu/ETS-11. This indicates better copper dispersion for the low loading copper sample than for that at higher loading, which presents copper aggregates in small particles as revealed by XRD results.

The computations allowed us to decompose the global isotherms into isotherms relevant to each type of site as shown, as an example, in Fig. 4.

The copper site energy distribution obtained for the two catalysts is in agreement with the direct calorimetric data, from which a heterogeneity of Cu sites,

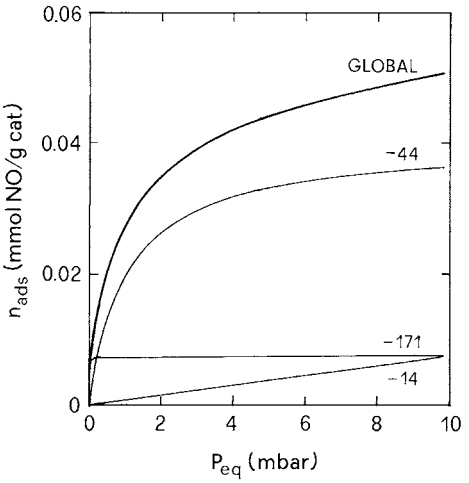

Fig. 4. Calculated isotherms of NO adsorption at 47.1°C for each type of site of different $\Delta_a H_i$ for Cu/ETS-11, obtained by the decomposition of the experimental isotherm through the optimised thermodynamic parameters.

with a large predominance of low enthalpy NO–Cu interaction, could be observed. Only quite small CuO-like aggregates are present on Cu/ETS-6, while larger aggregates are also present on Cu/ETS-11, as reported above. The former ones are those stabilising low energy interaction with NO and are more involved in the NO reduction than the latter ones. In fact, the differences evidenced between Cu/ETS-6 and Cu/ETS-11 in terms of activity and selectivity in the reduction of NO by C_2H_4 in excess oxygen were not very important. This behaviour suggests that isolated copper sites can be viewed as active sites while larger copper aggregates do not possess activity towards NO reduction [18].

The model employed here for the description of the energy distribution of copper sites (in terms of enthalpy of adsorption) introduced in a host structure of catalytic importance, can also provide other useful physico-chemical parameters. In particular, the molar entropy of adsorption of the adsorbate species can be determined [19,20]. This parameter is diagnostic of the mobility of adsorbate layers. A mobile adsorbate can play an active role in catalysis, as it is more involved in transformations along the surface than an immobilised adsorbate. Insight into this aspect is still in progress and will be discussed in a future paper.

4. Summary

Experimental data of NO adsorption on two copper containing catalysts were collected at different temperatures. The data were interpreted using a previously presented mathematical model which permitted the study of the heterogeneity of the two catalysts by determining the energy distribution of the different types of copper sites on the surface. The quality of the results confirms the validity of the model in the study of heterogeneous surfaces once a suitable probe has been individuated.

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