Effect of Micropore Filling on Chemisorption by Large Surface Area Materials. Adsorption of O_2 and N_2O by CuZnO Catalysts

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ABSTRACT: In irreversible chemisorption by large surface area catalysts, the partially covered surface takes up additional amounts of adsorbate only if a given threshold pressure is attained. A model is suggested in which micropore filling acts as a precursor state for other gas-solid interactions. The model is applied to the adsorption of oxygen by CuZnO catalysts with various copper contents, and containing particles and interparticle voids of various sizes.

The process of chemisorption often includes slow steps such as surface diffusion, penetration into the bulk, slow chemical reaction, etc. The probability that a slow step takes place considerably increases if the sorbate molecules that reach the surface are prevented from escaping back to the gas phase. This occurs when the adsorbing surface is adjacent to micropores. Sorbate molecules occluded in micropores reside at the surface over a long period of time and have better chances of reacting further.

Most catalysts of practical importance are large surface area materials and generally contain an active component in a finely divided form, with particles in contact with each other or with an inert support. This structure inevitably contains voids of various sizes and chemisorption can take place by the mechanism suggested above. This mechanism can be recognised and distinguished from other possible ones by using an adsorption procedure in which the pressure is increased by small increments during adsorption. Procedures of this type are widely used in measurements of 'differential heats of adsorption' and examination of data concerning amounts and rates of adsorption obtained in these studies gives information concerning the occurrence of the postulated mechanism.

Adsorption at increasing pressures

In a typical experiment, a sample of adsorbent is placed in contact with an amount of gas enclosed in a vessel at a constant volume. Adsorption takes place at a decreasing rate and the pressure drops accordingly. When adsorption has ceased to be measurable, the pressure is increased by a small increment, adsorption resumes, again at a

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decreasing rate. A new increment is added each time the adsorption at the preceding stage has ceased, and the whole process is terminated when an additional increment does not induce further adsorption.

The results often have the following characteristics (see Figures 1 and 2):

(a) At any given stage i, the rate of uptake dn/dt is large at the beginning, and decreases continuously during the stage. The pressure also drops at a decreasing rate from p_{oi} to p_{fi}. However, the rate of adsorption tends to zero while the pressure tends to the non-zero value p_{fi}.

(b) A moderate increase in pressure at the beginning of a new stage, e.g. by a factor of less than two, causes a disproportionately large increase in the rate of adsorption, e.g. by orders of magnitude. A plot of n against t which is almost horizontal often turns into a plot which is almost vertical.

(c) The pressures at the end of the stages p_{fi}, the corresponding uptakes at the end of the stages n_{fi}, and the duration of the stages t_i, increase with the number of stages i. However, the plot of n_{fi} against p_{fi} is convex towards the n_{fi} axis.

(d) The adsorption is largely irreversible, i.e. a decrease in the pressure does not cause significant desorption. Nevertheless, some reversibility is generally observed at the last stages towards the end of the overall process.
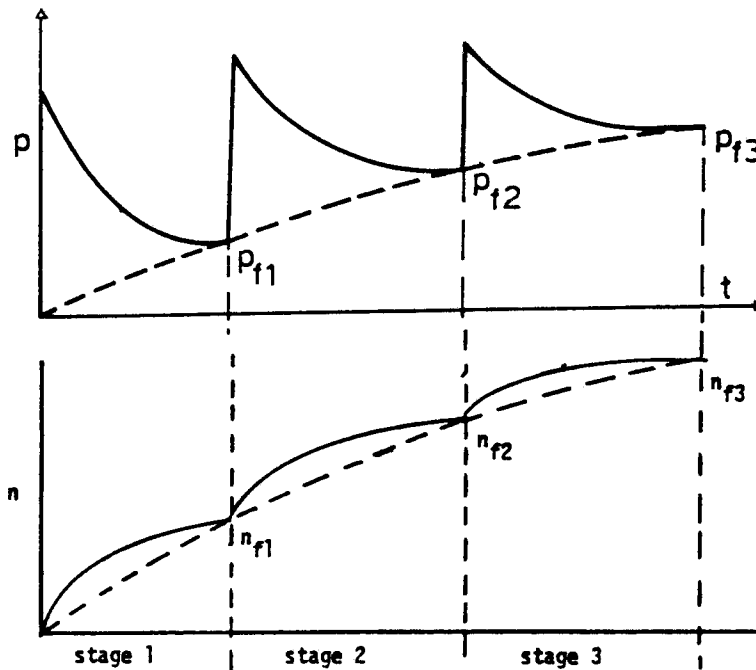

Figure 1. Schematic plots of the pressure, and of the quantity adsorbed, against time during adsorption at increasing pressures.
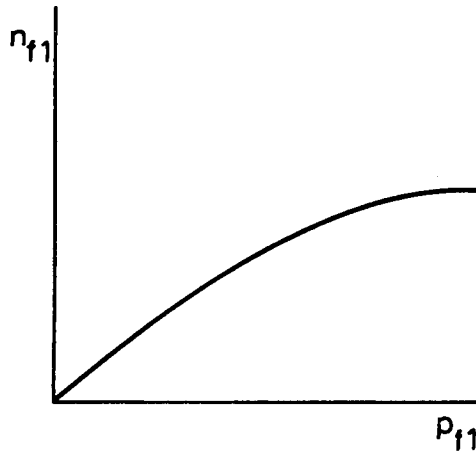
Figure 2. Schematic plot of n_{fi} against p_{fi}.

The significance of these results deserves clarification. For a rapid and reversible adsorption, p_{fi} would represent the equilibrium pressures corresponding to the uptakes n_{fi} and Figure 2 would represent an equilibrium isotherm; however this interpretation does not apply to the cases under consideration, which refer to irreversible adsorption. On the other hand, Figure 1 is not consistent with rapid and irreversible adsorption. For this case, p_{fi} would be zero so long as the surface has not reached saturation (see Figure 3); a finite value of p_{fi} would be obtained only at saturation and further increase of the pressure would not induce further adsorption. Figure 1 does not represent slow and irreversible adsorption either. In slow adsorption, a residual pressure would be observed when the rate has decreased to the extent that adsorption is no longer measurable. However, increase of the pressure would produce a moderate increase in the rate of adsorption, possibly proportional to the increase in pressure. The fact that the rate of adsorption is practically zero at a finite pressure, and rises significantly as a result of a small increase of the pressure, remains unexplained.

One must recognize that the experimental observations schematically represented by Figures 1 and 2 indicate the existence of threshold pressures associated with the states reached by the adsorbent at the end of the stages. Further adsorption takes place if the ambient pressure is greater than the threshold pressure; it does not take place if it is smaller. It can be shown that threshold pressures are associated with pore filling, and the occurrence of a threshold pressure is an indication that a mechanism involving pore filling is valid.

Relationship between threshold pressures and pore filling

In adsorption by non-porous or macroporous solids, the quantity adsorbed at equilibrium is a continuous function of the pressure and has a finite value at any finite pressure. However in capillary condensation in a mesopore or in filling of a micropore,

the quantity adsorbed is a discontinuous function of the pressure. Uptake is zero at any pressure smaller than some threshold pressure, and complete at any pressure higher than this threshold pressure. In capillary condensation, the threshold pressure is the vapour pressure at a gas–liquid interface of a given curvature determined by the radius of the pore. In micropore filling, the threshold pressure is difficult to correlate with the radius of the pore, and is conveniently correlated to an adsorption potential.
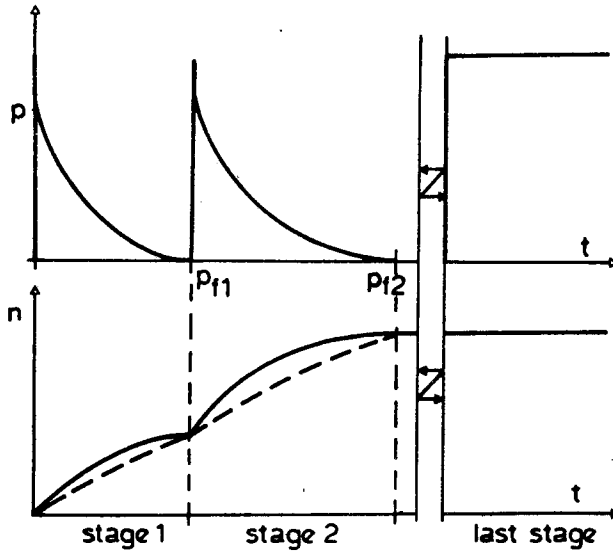

Figure 3. Schematic plots of the pressure, and of the quantity adsorbed, against time during irreversible adsorption at increasing pressures.

A continuous n(p) relationship means that the adsorbent–adsorbate system behaves as a two-component, two-phase system. Surface coverage behaves as a concentration; it adds a degree of freedom to the system and gives the possibility of phase equilibrium at all ranges of pressure. A discontinuous n(p) relationship means that the system behaves as a single-component, two-phase system; adsorbate in the gas phase in equilibrium with occluded adsorbate. The phases are in equilibrium at a single pressure only.

In adsorption by heterogeneous solids containing pores of various diameters, the adsorption is determined by a family of threshold pressures, and the plot of the quantity adsorbed against the pressure for the overall solid may appear to be continuous. Distinction between an n(p) relationship determined by such a heterogeneous porous system and a truly continuous n(p) relationship is difficult when adsorption is reversible, but it is easy for irreversible adsorption. In irreversible adsorption on a nonporous surface, adsorption proceeds so long as adsorbable gas is available at a finite pressure, whereas in an irreversible microporous solid there are pores that are not filled if the pressure is insufficient.

Occlusion in micropores as a precursor state

Micropore filling in chemisorption by large surface area catalysts differs from micropore filling in physisorption by active carbons and other microporous materials. In physisorption, micropore filling is the final state of the adsorption process, and the process can be reversed if the pressure is decreased. In chemisorption by large surface area materials, micropore filling is a precursor state; it gives the sorbate the possibility of reacting further with the solid, and it is followed by slow and irreversible processes responsible for most of the uptake. If the pressure is subsequently reduced, the remaining occluded adsorbate which has not reacted further can be desorbed, but it may be a small fraction of the total quantity sorbed except at the last stages. If, in contrast, pressure is increased further, wider pores are filled and new foci for irreversible sorption are created. The uptake n_i at the end of a stage includes the sorbate occluded in the pores capable of being filled at pressures between 0 and p_{fi}, and the sorbate capable of diffusing from these pores at a measurable rate; it also includes the sorbate capable of diffusing rapidly from the pores filled at pressures between p_{fi} and p_{oi}, as these pores are filled and emptied during the stage.

This model supports and complements a previously developed kinetic model based on measurements at constant pressure and temperature (Aharoni 1984). In that case it was found that the commonly used empirical kinetic equations (Elovich, power, etc.) are in fact approximations to which diffusion equations reduce under certain conditions. The overall kinetics were explained by assuming an ensemble of activated diffusion processes taking place simultaneously with various diffusion coefficients along paths of various lengths. However, the model did not include precise assumptions concerning the nature of these diffusion processes. The observations discussed in the present paper provide the possibility of formulating more specific assumptions. In adsorption at any given constant pressure, micro voids with a range of sizes are filled; they act as foci from which occluded sorbate diffuses. Depending on the nature of sorbent and sorbate, diffusion may be surface diffusion at solid microparticle surfaces or penetration into the bulk of the particles. In both cases, the diffusion process includes formation and breakage of gas–solid chemical bonds, and is activated.

It is remarkable that the kinetics of adsorption on clean and smooth surfaces generally obey kinetic laws totally different from those characteristic of large surface area materials. This is consistent with the assumption that the kinetics in large surface area materials are determined by factors which are absent in smooth surfaces, such as activated diffusion induced by occluded adsorbate. The non-activated chemisorption characteristic of clean and smooth surfaces plays a minor role in uptake by large surface area materials.

Adsorption of O_2 and N_2O by CuZnO catalysts

Measurements of the adsorption of oxygen by reduced CuZnO catalysts (Fubini and Giamello 1984) show that the process has the characteristics discussed above, and gives plots of p against t, n against t, and n_f against p_f consistent with those depicted in

Figures 1 and 2. The adsorption of N_2O on the same adsorbents is consistent with the plots depicted in Figure 3; when a small amount of gas is placed in contact with the solid it is totally adsorbed and no residual pressure remains.

The CuZnO catalysts were prepared by precipitation of the metals as carbonates, decomposition to the oxides at 583K and reduction of CuO to Cu by hydrogen at 483K (Fubini and Giamello 1984, Giamello *et al*. 1984). Samples containing 3, 15 and 30 mol% Cu were used. The following experimental observations provide further information on the nature and mechanism of adsorption of oxygen: (1) Adsorption by ZnO
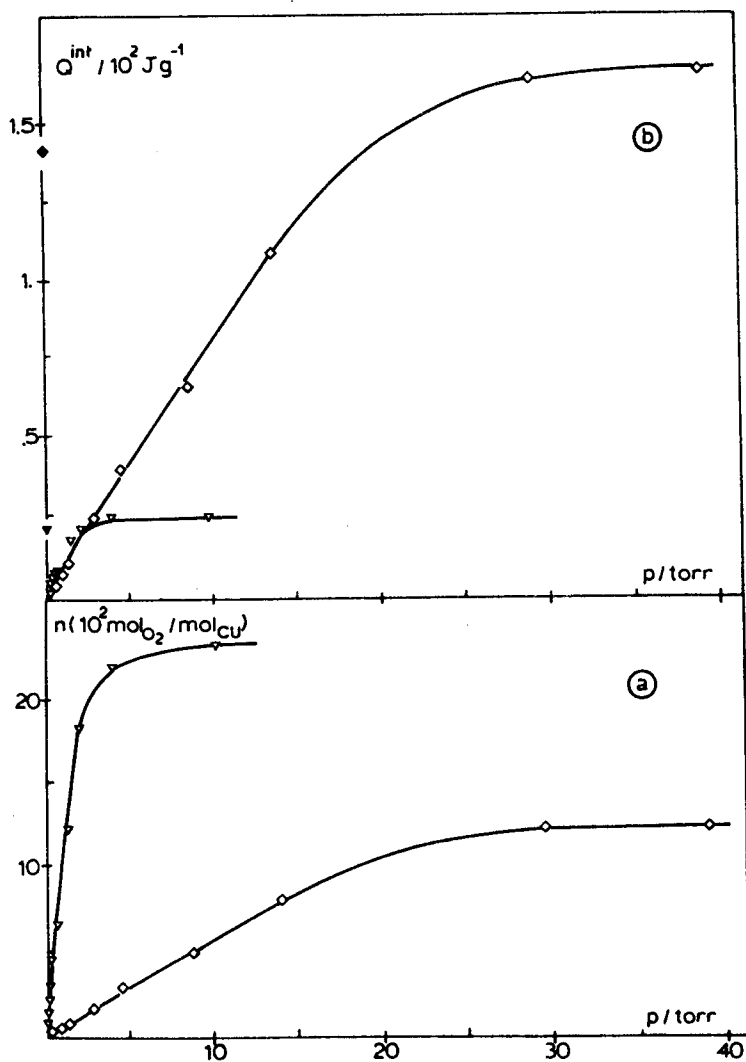

Figure 4. The adsorption of oxygen by catalysts with various CuZnO ratios. Plots against p_{fi}. (a) Adsorption at the end of the various stages expressed per mol copper in the catalyst. (b) Integral heat of adsorption at the end of the various stages per g catalyst (the integral heat is proportional to the number of moles adsorbed except in the latter stages). Catalyst content: ◇ 30% Cu; ∇ 3% Cu.

containing no copper was negligible. (2) The heat of adsorption was constant and corresponded to the heat of formation of Cu_2O (181 kJ/0.5 mol O_2) during most of the process. It was slightly higher at the very beginning of the process and dropped to low values towards the end. (3) If the quantity of oxygen adsorbed was related to the surface area of the copper, it appeared that the uptake was many times greater than that corresponding to a monolayer.

These observations indicate that sorption of oxygen takes place at the copper component of the catalyst and that it is associated with bulk oxidation of this metal. Bulk oxidation involves slow diffusional processes, and it is reasonable to assume that it is promoted if the sorbate is previously occluded in micropores. The quantity n_{fi} thus represents the quantity of sorbate occluded in the pores filled at stage i plus the quantity that diffuses at a measurable rate into the bulk of the copper starting from these pores. During most stages of the process, the quantity of sorbate taken up by the copper is significantly larger than that remaining in the pores. In the final stages, the sorbate occluded in the pores becomes relatively important, the process becomes reversible and the value of the differential heat diminishes.

The adsorption of N_2O can also be attributed to uptake by the copper component of the catalyst, as no significant adsorption is observed with pure ZnO. The mechanism of uptake seems to involve decomposition of N_2O and oxidation of Cu to Cu_2O, although the observed evolution of heat is greater than expected for this reaction. When the quantity of adsorbate taken up is related to the surface area of the copper, it appears that coverage is less than a monolayer. As the process does not include slow penetration into the bulk of the copper as for oxygen uptake, it can occur at a significant rate when molecules from the gas phase strike the surface. Promotion by micropore filling is negligible, and the kinetics represented by Figure 3 are applicable.

Some of the characteristics of the pore structure and its effect on the adsorption of oxygen can be deduced by comparing results obtained for catalysts with various copper contents (Figure 4). The data are plotted as the cumulative adsorption at the end of the various stages versus the corresponding pressures. The quantities adsorbed are expressed directly as mol O_2, or indirectly by the integral heat of adsorption which is proportional to the number of moles adsorbed during most of a given run. The pressures used in the plots are those at the end of the stages (p_{fi}), disregarding effects which arise because the stages start at higher pressures p_{oi}. Adsorption per mole of copper [Figure 4(a)] as well as adsorption per gram of catalyst [Figure 4(b)] are considered. Similar results were obtained in experiments where the adsorption of oxygen was preceded by that of N_2O [Figures 5(a) and (b)].

Figures 4(a) and 5(a) show that when adsorption is expressed as mol O_2/mol Cu, it decreases when the ratio Cu/ZnO increases. This relationship is valid for any pressure. On the other hand, Figures 4(b) and 5(b) show that when the adsorption is expressed per g catalyst, the maximum value attained is larger when the copper content is greater. An interesting feature of these results is the fact that the plots for catalysts with various copper contents coincide until the adsorbate quantities approach their specific maxima, i.e. at any value of p_{fi} all the catalysts adsorb the same quantity of oxygen irrespective of the copper content, provided adsorption has not yet
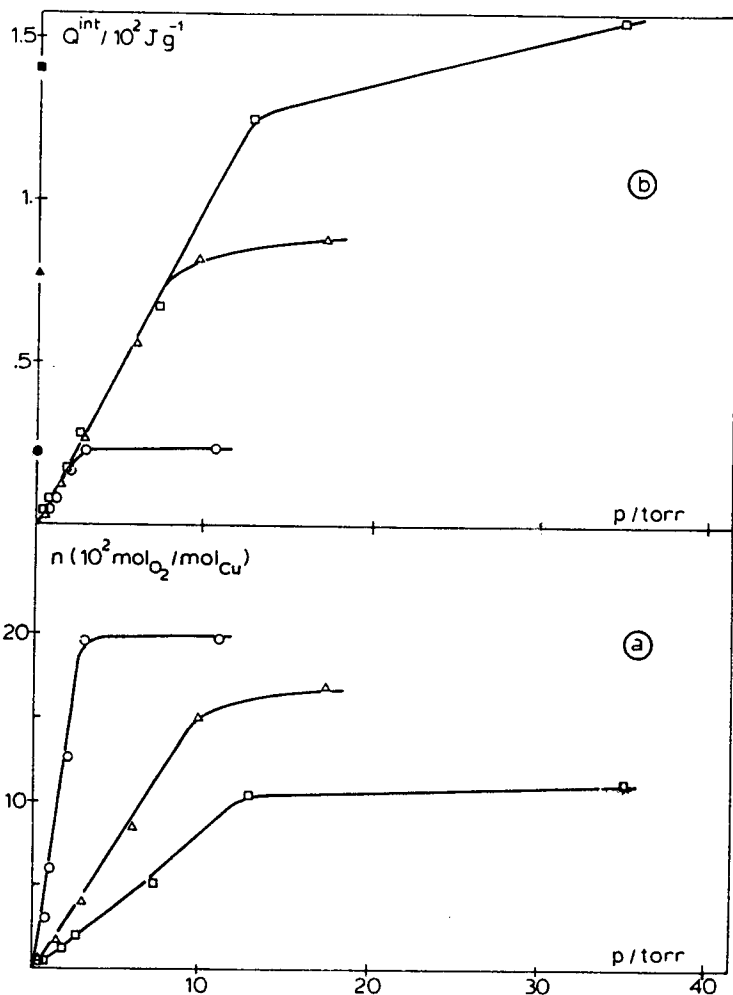
Figure 5. The adsorption of oxygen by catalysts with various CuZnO ratios, after initial exposure to N_2O (see caption for Figure 4). Catalyst content: ⊔ 30% Cu, previous uptake 119 mol N_2O/g Cu; Δ 15% Cu, previous uptake 45 mol N_2O/g Cu; o 3% Cu, previous uptake 19 mol N_2O/g Cu.

attained its maximum value. When the adsorption for a given copper content approaches its maximum value, the plot deviates and becomes less steep.

It appears that the amount adsorbed at a given stage i is not the only quantity which depends on the pressure p_{fi} rather than on the copper content. The rate of adsorption at a given stage i also depends on the pressure rather than the copper content. Figure 6 depicts plots of the thermokinetic parameter $t_{0.5, i}$ (the time at which the thermogram drops to half the maximum value) against p_{fi}. The plots for the various copper contents all coincide.

These results may be explained by assuming that in catalysts with low copper content, the copper particles are small and intimately mixed with the ZnO particles so that

the interparticle voids are narrow in diameter. In catalysts with a higher copper content, larger particles are present in addition to the finer ones, and correspondingly larger pores are present in addition to the narrower ones. The increase in particle size and in pore size is related to the increase in copper content via a definite relationship which is valid for all compositions.
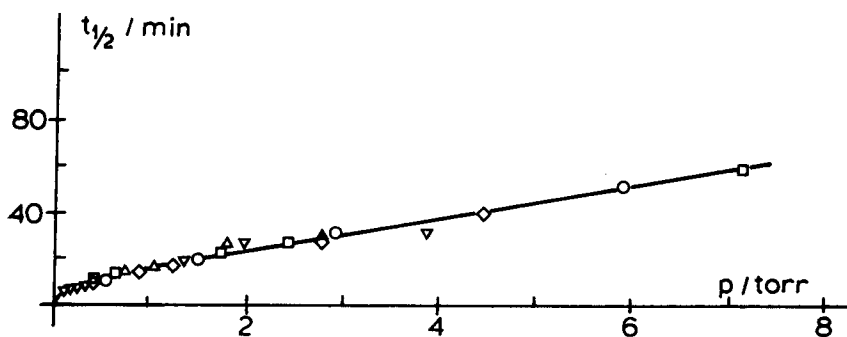

Figure 6. Plots of $t_{0.5, i}$ versus p_{fi}. Catalyst content: □ 30% Cu, △ 15% Cu, o 3% Cu.

The literature on the morphology of CuZnO catalysts mentions observations that provide some support for these assumptions (Metha *et al*. 1979, Dominiquez *et al*. 1983, Ghiotti and Boccuzzi 1987). It has been shown, for instance, that in catalysts containing 300 mg Cu/g catalyst, an amount of copper estimated at ca. 150 mg is in the form of crystalline particles with sizes in the range 3–27 nm and with a definite crystallographic orientation with respect to ZnO particles. The remaining copper does not appear as a copper phase distinct from the ZnO phase; it is either dissolved in the ZnO or is composed of particles smaller than 2 nm intimately mixed with the ZnO. This apparent phase comprises copper included in the ZnO before reduction of the catalyst as well as copper included during the reduction process. In catalysts containing 30 mg Cu/g catalyst, most of the copper appears to be included in the ZnO phase having originated from copper included before reduction. These results are consistent with the above model if we assume that the copper included in the ZnO phase is in the form of finely divided particles, and that the fraction originally included comprises the particles with the smallest sizes. According to these assumptions the catalyst containing 300 mg Cu/g catalyst and the catalyst containing 30 mg Cu/g catalyst should behave in the same way at low pressures, viz. the same quantity at a given p_{fi} and the same rate of adsorption. The catalyst containing 300 mg should be capable of further adsorption when pressure is increased, while the one containing 30 mg attains saturation at a low pressure.

Interesting effects caused by pre-adsorption of N_2O are revealed when the plots of Figure 5(b) (adsorption of O_2 on catalysts previously subjected to the adsorption of N_2O) are compared with the plots in Figure 4(b) (adsorption of O_2 on untreated catalysts). As expected, the quantity of oxygen finally adsorbed by the N_2O-treated

catalysts is smaller than that finally adsorbed by the untreated catalyst. However, the quantity adsorbed by the N_2O-treated catalysts at any given pressure is larger. This suggests that treatment by N_2O causes narrowing of the micropores, and that when adsorption of O_2 is subsequently performed it takes place at lower pressures.

Quantitative correlations between particle size, uptake of sorbate at various pressures and kinetics of adsorption will be discussed in further work.

ACKNOWLEDGEMENT

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