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Related surface and heat of immersion characterization of some alumina samples

Part IV *$MnCl_2$ and $CuCl_2$-loaded aluminas*

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$MnCl_2$- and $CuCl_2$-loaded aluminas were thermally treated *in vacuo* in the temperature range 20–500 °C. The water loss, specific surface area from nitrogen adsorption measurements and the integral heat of immersion in water were determined for all the samples. The high-pressure hysteresis loop displayed in the adsorption isotherms, together with the limited increase in adsorption values near saturation indicate the dominance of mesopores in the tested samples, as also detected by the V_a–t method of isotherm analysis. Changes in the slope of V_a–t plots suggests that the mesopores rather belong to narrow-ranged mesopore sizes, which are thus considered responsible for adsorption in the t-ranges of 0.5–0.7 and above 0.7 nm. The constancy of V_a (ml g^{-1}) values above $t = 1.2$ nm points out the absence of effective capillary condensation in the high relative pressure region. Variations of BET-surface area and the reciprocal of average pore radius, $\bar{r}^{-1}$ (nm^{-1}), as functions of the heat-treatment temperature indicate that $MnCl_2$-loaded samples display a higher thermal stability than $CuCl_2$-loaded samples; the latter exhibit some aggregation cementation behaviour. At temperatures below 300 °C, the heat of immersion data are not as predicted from changes in water loss and surface-area parameters. Thus, $MnCl_2$-loaded samples display lower heat of immersion values than the respective $CuCl_2$-loaded samples, despite the higher BET areas of the former samples; an effect which may be tentatively interpreted in terms of the capability of the smaller sized Mn^{2+} ions to preserve more water molecules via such processes as complex formation, ion hydration and crystallization, which contribute to lowering the integral heat measured. This apparent discrepancy in the behaviour of integral heat of immersion (J g^{-1}) data with water loss (g g^{-1}) at temperatures below 300 °C is clarified by considering the change in the heat of immersion per unit area, h_i (J m^{-2}) with the temperature of treatment.

1. Introduction

By virtue of the polarity character of an alumina surface, aluminas can be used as drying agents and for selective adsorption and purification processes which involve the removal of some harmful substances from oils during storage.

As an extended interest to these applications, the present investigation is concerned with the study of surface characteristics of manganese chloride- ($MnCl_2$) and cupric chloride- ($CuCl_2$)loaded aluminas based on measurements of nitrogen gas adsorption at − 195 °C and heats of immersion in water at 35 °C. The latter measurements are a continuation of previous investigations [1–3]. In view of the difference in hydration capacities between Mn^{2+} and Cu^{2+} ions, based on the smaller size of Mn^{2+} ions [4], the extent of water loss by dehydration and/or dehydroxylation [5–7] with heat treatment during sample preparation and heats of immersion in water were investigated in terms of the occurrence of crystallization, ion hydration [8] and complex formation processes. Thus, Mn^{2+} ions having the electronic configuration d^5 are capable of undergoing complex formation via Sp^3d^2 hybridization involving six molecules of water per cation. On the other hand, the Cu^{2+} ion of the electronic configuration d^9, coordinates with only four molecules of water per cation via Sp^3 hybridization. Therefore, $MnCl_2$-loaded alumina is predicted to display relatively higher contributions to complex formation and heat of ion hydration [8], in comparison with $CuCl_2$-loaded alumina. These predicted differences in behaviour are considered to influence respective changes in the surface and energetic characteristics of the loaded samples.

2. Experimental procedure

5 g Rhone Poulenc active alumina were soaked in 50 ml 0.2 M solution of either $MnCl_2$ or $CuCl_2$ for 24 h. The loaded aluminas were filtered and the filtrate chloride solutions were removed. The samples obtained were air dried for a prolonged period before use. Both the loading and the drying processes were carried out at room temperature, 20 °C.

Chemical analysis [9] of the original chloride solutions (before loading), as well as of the filtrate chloride

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solutions (after loading) indicated that the uptakes (g %) of anhydrous manganese and cupric chlorides were 7.53 and 12.05, respectively.

Samples of manganese-loaded alumina (MnSA) and copper-loaded alumina (CuSA) were thermally dehydrated *in vacuo* at temperatures of 20, 100, 200, 300, 400 and 500 °C. The manganese-loaded samples were designated MnSA(20), MnSA(100), MnSA(200), MnSA(300), MnSA(400) and MnSA(500), whereas the copper-loaded samples were similarly designated CuSA(20), CuSA(100), CuSA(200), CuSA(300), CuSA(400) and CuSA(500), respectively.

Heating was carried out using a small electrical tubular furnace (200 W) coupled with a "Shinko thermocontroller" (model DIC-P) of 600 °C range. This thermocontroller was originally calibrated with chromel–alumel thermocouple.

Adsorption of nitrogen at liquid nitrogen temperature was carried out by means of a conventional volumetric apparatus [10]. Highly purified nitrogen was used as adsorbate without further purification. Water losses, $W_0(10^2\,gH_2Og^{-1})$, were estimated using a silica spring balance with a sensitivity of 0.35 mg^{-1}.

Integral heats of immersion in doubly distilled water, H_i ($J\,g^{-1}$) at 35 ± 0.05 °C were determined using a calorimeter as described elsewhere [1, 11].

3. Results and discussion

3.1. Characteristic surface parameters from nitrogen adsorption

Fig. 1a illustrates the adsorption isotherm of sample CuSA(400); all the other isotherms are of similar shape. The adsorption isotherms are invariably of Type IV in the BET classification [12], in view of the presence of high-pressure hysteresis loops and the limited uptakes as the saturation pressure is approached. This may be taken to indicate the absence of effective capillary condensation. The surface areas, $S^{N_2}_{BET}$ ($m^2\,g^{-1}$), were calculated by applying the BET equation [13] to nitrogen-adsorption isotherms in the range of 0.05–0.35 P/P_o, and adopting 0.162 nm^2 for the cross-sectional area of the nitrogen molecule [14]. Computed characteristic surface parameters, together with water losses for MnSA (a) and CuSA (b) samples are given in Table I.

For the nitrogen adsorption isotherms on tested samples thermally heated at temperatures $\leqslant 200$ °C, the internal surfaces in pores vacated from molecular water are considered to contribute to the adsorption of nitrogen molecules. Thermal treatment at temperatures above 200 °C might be considered responsible for dehydroxylation of some structural hydroxyls from the alumina surface [5–7], as well as the loss of water of crystallization, ion hydration [8] and coordinate water of the transition metal complexes.

As indicated from Table I, Column 1, MnSA samples display greater water-loss values than the respective CuSA samples, over the entire range of treatment temperature 20–500 °C. This entails corresponding changes in the $S^{N_2}_{BET}$ areas of the two series of loaded samples (cf. Column 3 of the same table). Such behaviour agrees with the relative capabilities of complex formation of the free/or isolated Mn^{2+} and Cu^{2+} cations and their respective order of ion hydration [8] as well.

The average pore radius, $\bar{r}$ (nm), was calculated using the relation $\bar{r} = 10^3\ (2\,V_p/S^{N_2}_{BET})$, where V_p

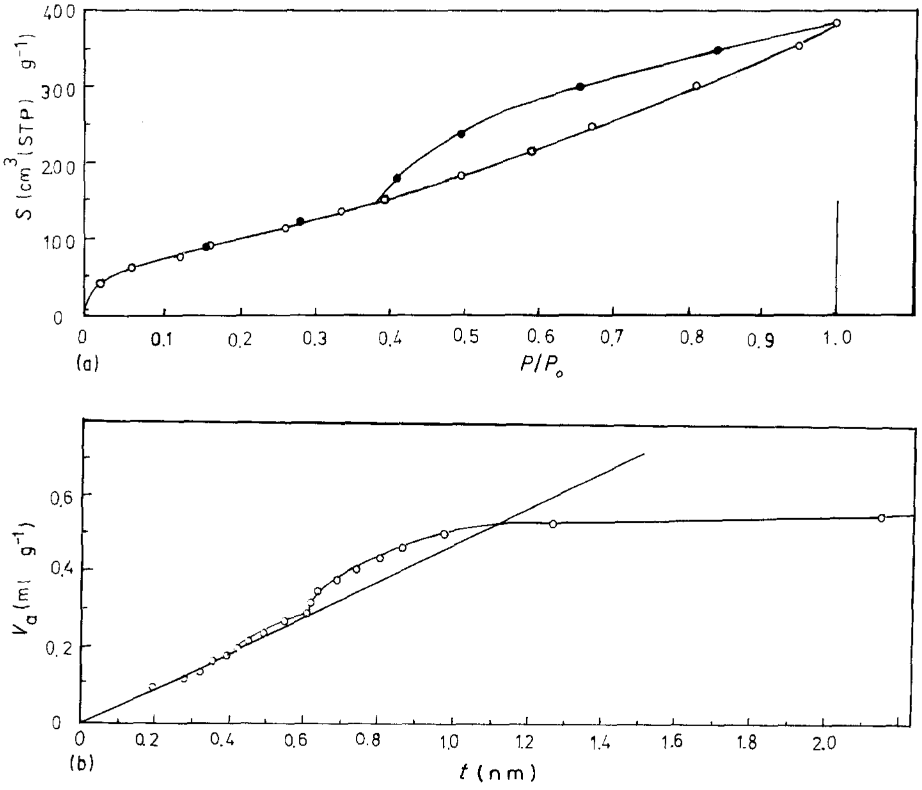

Figure 1 (a) Adsorption–desorption isotherms of nitrogen on sample CuSA(400). (○) adsorption, (●) desorption. (b) V_a–t plot for CuSA (400).

TABLE I Some surface characteristics of nitrogen adsorption on manganese chloride - and copper chloride-loaded aluminas

	Sample MnSA						Sample CuSA					
	1	2	3	4	5	6	1	2	3	4	5	6
Temp. (°C)	W_o (10^2g H_2O g^{-1})	BET-C constant	$S_{BET}^{N_2}$ (m^2 g^{-1})	V_p (ml g^{-1})	S_t^a (m^2 g^{-1})	$\bar{r}$ (nm)	W_o (10^2g H_2O g^{-1})	BET-C constant	$S_{BET}^{N_2}$ (m^2 g^{-1})	V_p (ml g^{-1})	S_t^a (m^2 g^{-1})	$\bar{r}$ (nm)
20	13.07	23–24	417	0.563	420	2.70	3.80	15–16	355	0.543	345	3.06
100	17.17	19–20	498	0.637	500	2.56	6.17	17–18	401	0.575	380	2.87
200	19.61	23	499	0.653	500	2.62	8.80	17–18	447	0.622	440	2.78
300	20.85	21	519	0.661	530	2.55	9.79	17–18	446	0.591	445	2.65
400	21.68	14–15	542	0.669	530	2.60	10.54	17–18	445	0.619	460	2.79
500	21.94	17–18	514	0.676	525	2.63	11.61	13	474	0.637	445	2.69

[a] Reference standard [16]: BET-C $\simeq$ 20–30 was used in V_a–t analysis.

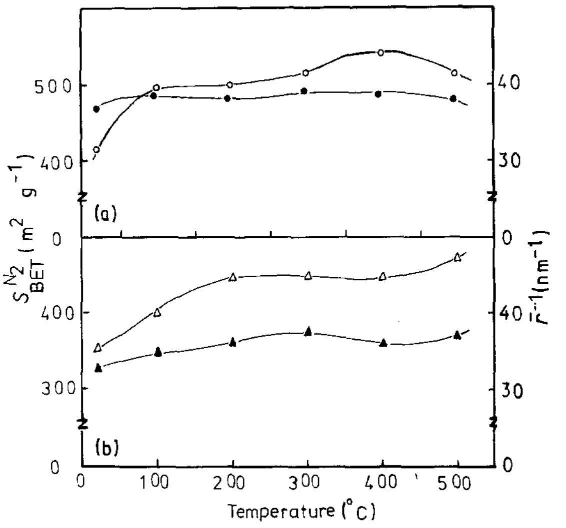

Figure 2 Variation of (○, △) nitrogen surface area and (●, ▲) reciprocal of average pore radius, as a function of heat-treatment temperature: (a) MnSA and (b) CuSA.

(ml g^{-1}) is the total pore volume estimate at $P/P_0 \simeq 1.0$ and $S_{BET}^{N_2}$ is the nitrogen BET-surface area. Computed values of $\bar{r}$ are given in Table I, Column 6.

Fig. 2 shows the variation of nitrogen BET-surface area and reciprocal of the average pore radius, $\bar{r}^{-1}$, both as a function of the treatment temperature. Fig. 2a represents the behaviour of MnSA samples, whereby the coincidence in the changes of the two parameters $S_{BET}^{N_2}$ and $\bar{r}^{-1}$ is less marked, an effect which might refer to the occurrence of some thermal stability of these samples. On the other hand, Fig. 2b representing the behaviour of CuSA samples, shows a relevant coincident change in the two parameters. Thus, the surface area increases with decreasing $\bar{r}$ and vice versa. This indicates that CuSA samples possibly undergo some aggregation cementation changes upon thermal treatment and consequently their BET-surface areas become relatively smaller (cf. Table I, Column 3). These effects appear to be enhanced by the extent of dispersion of $MnCl_2$ on the alumina surface, being higher than in case of $CuCl_2$ upon thermal treatment. Evidently, the lower degree of $MnCl_2$ loading over alumina ($\simeq$ 7.53%) allows for a higher extent of dispersion than in the case of CuSA samples with a higher degree of loading ($\simeq$ 12.05%).

3.2. Pore structure analysis

The porosity character of thermally treated samples was qualitatively detected by the V_a–t method [15]. A representative graphical illustration for V_a–t plot analysis is given in Fig. 1b for sample CuSA(400) which has a straight-line portion passing through the origin, and thus the S_t area (m^2 g^{-1}) can be readily estimated from its slope. At $t \sim 0.5$ nm the plot displays some upward deviation from linearity which appears to increase in slope over $t \sim 0.7$–0.9 nm and thereafter decreases markedly until $t \sim 1.2$ nm. These V_a–t plot features are almost invariably displayed by the various tested samples and are considered to indicate the dominance of mesoporosity character in the samples. The noted decrease in slope of the V_a–t plot at

$t \geqslant 0.9$ nm indicates the prevalence of rather narrow-ranged mesopore sizes which thus contribute to limited multimolecular adsorption. The mesopore sizes appear to be distributed in two ranges which are responsible for the adsorption over the t-ranges 0.5–0.7 and 0.7–0.9 nm. Moreover, the insignificant changes noted in V_a above $t \simeq 1.2$ nm are considered to indicate the absence of effective capillary condensation in the nitrogen adsorption on the tested samples.

The correct choice of the reference data [16] in the V_a–t method [15] is inferred from the fair agreement between the computed S_t areas and the corresponding $S_{BET}^{N_2}$ areas, cf. Table I.

Conclusions on the mesoporosity characters of the tested samples revealed from the t-method of isotherm analysis [15], are also emphasized by the invariable existence of the high-pressure hysteresis loop in the nitrogen isotherms.

3.3. Heats of immersion in water

Fig. 3a shows the variation of the integral heat of immersion, H_i (J g^{-1}), as a function of heat-treatment temperature. For both MnSA and CuSA, H_i increases with treatment temperature, the increase being more gradual above 300 °C. The marked increase in H_i up to 300 °C may be correlated with the water loss produced which comprises varying contributions from molecular bound water, water of crystallization, ion hydration [8] and coordinated water, depending upon the extent of thermal treatment. It can be seen that, in each series of loaded samples, the H_i values for 400 and 500 °C samples are close together. At this stage of high thermal treatment temperatures, the internal and external surfaces of the samples become largely depleted from the water molecules in its differently bound forms.

Fig. 3b and c illustrate the variation with temperature of treatment of surface area and water-loss parameters, respectively. It can be seen that despite the higher water loss associated with the development of higher BET-area values (cf. Fig. 3b and c) displayed by MnSA samples compared to the respective CuSA samples, the H_i values of MnSA, heated at temperatures $\leqslant 300$ °C, are evidently lower than those of the respective CuSA samples (cf. Fig. 3a). This noted discrepancy can be tentatively interpreted in terms of the capability of Mn^{2+} ions to preserve more water molecules via complex formation, ion hydration [8] and crystallization processes which can effectively contribute to lowering of the measured H_i values. The energetics of immersion behaviour of the tested samples can be better considered in terms of the heat of immersion per unit area parameter, h_i (J m^{-2}), as a measure of the interactions between the adsorbent-loaded surface and the immersion liquid (water). Accordingly, its value is determined by the extent of surface depletion by water loss and the magnitude of water uptake on the depleted surface via immersion. Tentatively, it is considered that water uptake via the immersion route does not necessarily involve effects which reflect the exact reverse behaviour that takes place in the water-loss process. Differences in h_i values for corresponding MnSA and CuSA samples were found to decrease progressively as the dehydration temperature increased (cf. Table II). At 500 °C, when dehydration is considered complete, the noted difference in h_i values is markedly reduced in view of the reduction in shielding effects by water molecules for the metal ions, becoming thus more available to contribute to the magnitude of heat of immersion measured.

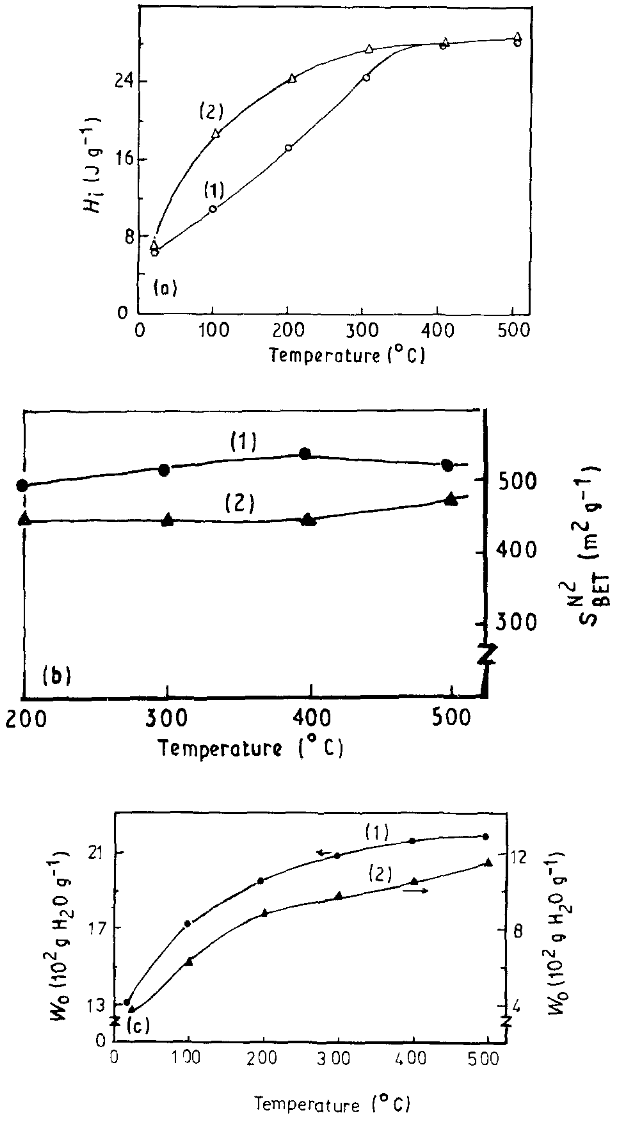

Figure 3 (a) Variation of the integral heat of immersion as a function of heat-treatment temperature: (1) MnSA and (2) CuSA. (b) Surface area–temperature plot: (1) MnSA and (2) CuSA. (c) Variation of water loss as a function of the heat-treatment temperature: (1) MnSA and (2) CuSA.

However, the occurrence of some reversible dehydration hydration aspects can be inferred from the corresponding changes with the treatment temperature of the water loss, W_o (g H_2O g^{-1}) and of the integral heat of immersion, H_i, when both parameters are normalized to unit nitrogen area (m^2). Thus, values of h_i and W_o were computed and given in Table II. The corresponding changes noted in the two parameters h_i and W_o with temperature can be considered indicative of the dependence of heat of immersion on the magnitude or the extent of dehydration of water in its differently bound forms.

TABLE II Heats of immersion in water of various manganese chloride- and copper chloride-loaded aluminas

Temperature (°C)	Sample MnSA			Sample CuSA		
	1	2	3	1	2	3
	H_i ($J g^{-1}$)	h_i^a ($10^3 J m^{-2}$)	W_0^a ($10^4 g H_2O m^{-2}$	H_i ($J g^{-1}$)	h_i^a ($10^3 J m^{-2}$)	W_0^a ($10^4 g H_2O m^{-2}$)
20	6.44	15.44	3.136	7.23	20.37	1.071
100	11.12	22.33	3.445	18.39	45.87	1.540
200	17.14	34.35	3.930	24.16	54.05	1.970
300	25.16	48.49	4.020	27.38	61.39	2.194
400	28.55	52.67	4.000	28.05	63.03	2.371
500	28.84	56.11	4.270	29.39	62.00	2.450

[a] Values of the heat of immersion and water loss calculated based on total BET-surface areas (Table I).

4. Conclusions

Heats of immersion in water can be considered as a measure for the affinity of the investigated samples for interaction with water as the immersion liquid. Therefore, the bearing of water dehydration, as well as its influence on changes of the BET-surface area, influences more the respective change in heat of immersion parameter. Accordingly, the heat of immersion in water, together with the accessibility of the pore space to nitrogen molecules (surface-area measurements by nitrogen gas or by the smaller water molecule as well) can be considered as convenient measures for the proper choice or use of these tested materials as water getters or desiccants.

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