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INFLUENCE OF COMPOSITION AND OF ACTIVATION TEMPERATURE UPON THE ADSORPTION AND THERMODESORPTION OF AMMONIA ON ALUMINIUM OXIDE–SILICA GELS

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Aluminium oxide gel and aluminium oxide–silica gels of different compositions were prepared and activated at different temperatures. The adsorption of NH_3 was studied in a McBain type balance at 20 torr and 5×10^{-3} torr at 25°. The thermodesorption of NH_3 was studied at 5×10^{-3} torr between 25 and 550° at a constant heating rate of 4°/min. The desorption was followed by recording the thermogravimetric curve and the pressure oscillations in the system ($p - T$ curve). The influence of composition and activation temperature is discussed. Chemisorption of a monomolecular layer is assumed in three main types of pores, together with the formation of a second monomolecular layer held by hydrogen bonds.

Basic vapours (quinoline) were first used for the determination of the acidity of solid catalysts, by Mills and coworkers [1]. Trimethylamine and pyridine were later applied by Richardson and Benson [2]. Ammonia is also frequently used for the quantitative and qualitative characterization of the catalyst acidity and a considerable number of papers have recently dealt with the interaction of NH_3 and acid catalysts.

This interaction has been studied by means of IR spectroscopy [3–17], gravimetry [5, 16, 18–24], calorimetry [25–35] and gas chromatography [36].

In the present paper an attempt has been made to elucidate the influence of the composition and of activation temperature ($T_{act.}$) on the adsorption and thermodesorption of NH_3 on aluminium oxide–silica gel systems (AlSiG) by using a thermogravimetric method combined with pressure oscillation measurements.

Experimental

Preparation of the systems studied. AlSiG systems were obtained by co-precipitation. Solutions containing silicic acid (4 wt % SiO_2) and aluminium nitrate were treated with ammonium carbonate solution at pH = 5.0–5.5. The precipitate was filtered, washed with water and dried at 105°. The dried precipitate was subjected to a preliminary heat treatment at 400 for 30 min in order to remove any ammonium carbonate and nitrate.

Chemical analyses were carried out after calcination of the samples at 1100° for 3 hrs. The results obtained are presented in Table 1.

Table 1

Compositions of the systems studied

System	Al_2O_3	SiO_2	Molar ratio $Al_2O_3 : SiO_2$
	wt. %		
AlSiG-I	87.9	12.1	1 : 0.25
AlSiG-II	74.2	25.8	1 : 0.60
AlSiG-III	50.0	50.0	1 : 1.70
AlSiG-IV	37.5	62.5	1 : 2.80
AlSiG-V	10.2	89.8	1 : 15.00

The aluminium oxide gel (AlG) was obtained and submitted to thermal treatment exactly as the AlSiG systems.

Apparatus. Measurements were carried out in a McBain type balance connected to a vacuum pump able to attain $5 \cdot 10^{-3}$ torr, and to a Jenaglas reservoir of NH_3. The ammonia was prepared in this reservoir by means of the thermal decomposition of carefully dried diammonium hydrogen phosphate (Merck, p.a.). Drying of the salt was performed in vacuo and by heating up to 70°.

Procedure. 200–500 mg samples of the unactivated material were introduced into the apparatus at atmospheric pressure and 25°. At this temperature the pressure was reduced to $5 \cdot 10^{-3}$ torr, and meanwhile physically adsorbed water was removed. By ensuring a heating rate of 4°/min, the temperature was raised up to the first $T_{act.}$, still under vacuum. Owing to the thermodesorption of water an increase of the pressure occurs. In order to activate the sample, it was kept at $T_{act.}$ for 2 hrs and the pressure again reduced to $5 \cdot 10^{-3}$ torr. After the activation the sample was cooled in vacuo and weighed at 25°. Dry NH_3 was introduced till the pressure reached 20 torr, and the total NH_3 adsorbed was determined. At the same temperature the pressure was reduced to $5 \cdot 10^{-3}$ torr and the observed weight loss corresponded to the first physically sorbed NH_3. By ensuring a constant heating rate of 4°/min the thermodesorption of NH_3 proceeded in two independent ways. The sample weight was recorded as a function of temperature (TG curve), and in addition the pressure was recorded by using a VIT apparatus (made in USSR) with a lamp with thermo cross. Since the vacuum pump worked continuously, the pressure changed only between $5 \cdot 10^{-3}$ and $1 \cdot 10^{-2}$ torr. The magnitude of these changes was proportional to the thermal decomposition rate. Thus, the $p - T$ curve was something like the first derivative of the TG curve, and it was observed to give useful information. Heating of the sample was performed up to the second $T_{act.}$, and the second activation was then carried out by maintaining a constant temperature for 2 hrs. After cooling a new adsorption–thermodesorption run could be carried out.

This procedure enabled us to perform 4–5 activations of a single sample at different temperatures, and to carry out the corresponding adsorption–thermodesorption experiments without removing the sample from the apparatus, thus completely avoiding the contact of the AlSiG systems with the atmosphere.

Results and discussion

The total amount of NH_3 adsorbed at 25° and $p = 20$ torr is given in Table 2. The decrease of the amount of NH_3 adsorbed with increasing $T_{act.}$ is obvious from the this Table. It means the diminishing of the specific surface area with increasing $T_{act.}$ The influence of the SiO_2 content is interesting. Small amounts of SiO_2 diminish the number of active sites. This number has a clear maximum at AlSiG-II, containing 25.8% SiO_2.

At 25° and $5 \cdot 10^{-3}$ torr more than half of the adsorbed NH_3 is desorbed. This NH_3 is weakly bound by physical sorption. Its amount is given in Table 3.

Table 2

Total NH_3 adsorbed, m.e./g

$T_{act.}$	AlG	System				
		I	II	III	IV	V
465	2.22	1.72	3.02	2.45	2.53	2.66
550	—	1.46	2.47	2.25	1.94	2.11
620	2.01	1.36	2.26	2.05	1.84	1.86
720	1.69	1.21	1.99	1.75	1.64	1.65
820	1.36	0.95	1.59	1.59	—	1.12

Table 3

NH_3 desorbed in vacuo at 25°C, m.e./g

$T_{act.}$	AlG	System				
		I	II	III	IV	V
465	1.26	0.99	1.49	1.45	1.32	1.51
550	—	0.79	1.37	1.32	1.12	1.16
620	1.18	0.75	1.26	1.21	1.10	1.11
720	0.95	0.68	1.16	1.01	1.00	1.03
820	0.72	0.49	0.74	0.96	—	0.65

The difference between the amounts given in Tables 2 and 3 represents the more strongly adsorbed NH_3. Its quantity is given in Fig. 1. As seen, the higher $T_{act.}$, the less NH_3 is adsorbed, while the composition of the sample has a considerable influence on the adsorption capacity. The highest values were obtained with AlSiG-II.

TG and $p - T$ curves were obtained for the thermal desorption of NH_3 in vacuo. One of these curve pairs, for the AlSiG-IV system activated at 550°, is given in Fig. 2. The shape of the $p - T$ curves suggests that the thermal desorption occurs in four stages corresponding to the temperature intervals 25–155,

Table 4

Amounts of NH_3 desorbed (in m.e./g) between 25 – 155° [*a*] and 155 – 550° [*b*], and their ratio [*R*]

$T_{act.}$	System																	
	AlG			I			II			III			IV			V		
	a	*b*	*R*	*a*	*b*	*R*	*a*	*b*	*R*	*a*	*b*	*R*	*a*	*b*	*R*	*a*	*b*	*R*
465	0.47	0.49	0.96	0.35	0.38	0.92	0.61	0.92	0.66	0.48	0.53	0.90	0.40	0.52	0.77	0.61	0.54	1.12
550	—	—	—	0.31	0.36	0.86	0.47	0.63	0.75	0.41	0.51	0.80	0.39	0.43	0.91	0.45	0.50	0.90
620	0.41	0.42	0.98	0.29	0.32	0.91	0.46	0.51	0.90	0.40	0.44	0.91	0.37	0.38	0.97	0.33	0.43	0.76
720	0.35	0.39	0.90	0.26	0.28	0.93	0.40	0.43	0.93	0.34	0.41	0.83	0.31	0.33	0.94	0.28	0.34	0.82
820	0.31	0.33	0.94	0.22	0.24	0.92	0.38	0.28	1.35	0.31	0.31	1.00	—	—	—	0.21	0.26	0.81

Table 5

Amounts of NH_3 desorbed in the intervals 155 – 265° [*a*], 265 – 385° [*b*] and 385 – 550° [*c*] in m.e./g

$T_{act.}$	System																	
	AlG			I			II			III			IV			V		
	a	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*
465	0.29	0.16	0.04	0.19	0.13	0.06	0.46	0.32	0.14	0.31	0.16	0.06	0.28	0.18	0.06	0.31	0.19	0.04
550	—	—	—	0.16	0.12	0.08	0.35	0.21	0.07	0.29	0.15	0.07	0.24	0.12	0.07	0.26	0.17	0.07
620	0.25	0.13	0.04	0.16	0.10	0.06	0.28	0.17	0.06	0.25	0.13	0.06	0.22	0.11	0.05	0.24	0.13	0.06
720	0.23	0.11	0.05	0.15	0.09	0.04	0.25	0.13	0.05	0.22	0.13	0.06	0.16	0.09	0.08	0.18	0.10	0.06
820	0.21	0.09	0.03	0.13	0.07	0.04	0.18	0.08	0.02	0.19	0.09	0.03	—	—	—	0.14	0.08	0.04

155 – 165, 265 – 385 and 385 – 550°. All the $p - T$ curves have a similar shape and they are not significantly influenced by the temperature of activation or the composition of the system. This is obvious from Figs 3 and 4.

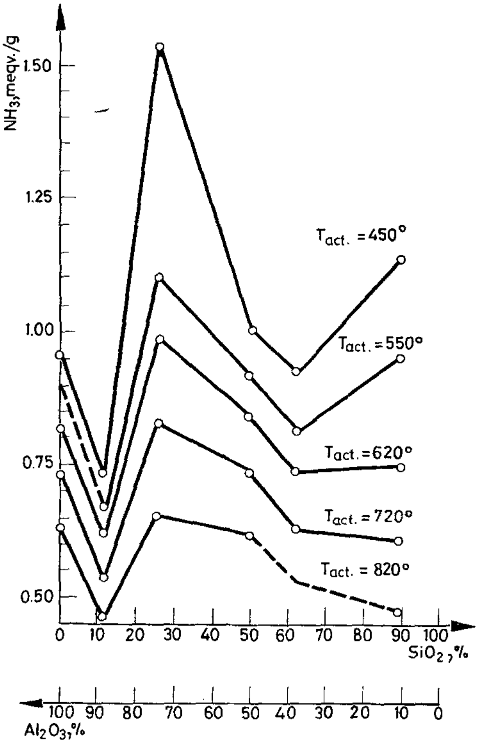

Fig. 1. NH_3 thermodesorbed between 25 and 550° as a function of the composition and activation temperature

The peaks on these $p - T$ curves might be evidence for the existence of acid centres of differing strengths. A quantitative picture of these centres can be obtained on the basis of the NH_3 thermally desorbed in the corresponding temperature ranges. In Table 4 are presented the amounts of NH_3 desorbed between 25 – 155 and 155 – 550°, respectively, and the ratio

$$R = \frac{NH_3 \text{ desorbed between } 25-155^\circ}{NH_3 \text{ desorbed between } 155-550^\circ}$$

Since R is near 1, it can be assumed that on the surface of the solid there is a chemisorbed monomolecular layer and on this a second one, perhaps hydrogen-bonded and it is this second monomolecular hydrogen-bonded layer which is desorbed up to about 155°. In this temperature range, in the main a single peak appears on the $p - T$ curves, but there are sometimes two, close to one another. In the other three temperature ranges, there are several peaks corresponding to the chemisorbed NH_3 in each range. This general picture is consistent with the above assumption.

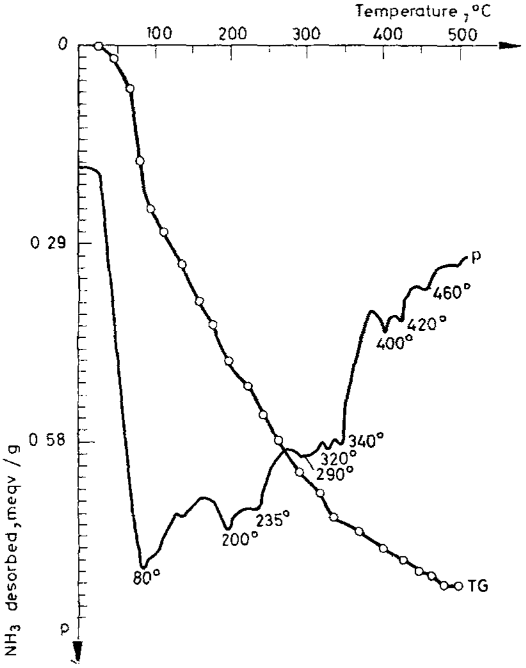

Fig. 2. The TG plot (NH_3 thermodesorption) and $p - T$ curves of the AlSiG-IV system for $T_{act.} = 550°$

In Table 5 the desorption of the chemisorbed NH_3 is presented for the three main temperature ranges.

The amount desorbed can be seen to decrease systematically in the order $a > b > c$. On the other hand, with increasing $T_{act.}$ a shows a tendency towards increasing relative weight, and b a decreasing one. The decrease of the relative contribution of c to the overall chemisorbed NH_3 is very obvious in the case of AlSiG-II. These facts suggest that the acid centres responsible for the chemisorption are of the same strength, but they are disposed in pores of different sizes. There are presumably three main types of pores, corresponding to the three temperature ranges. The bulk of NH_3 chemisorbed is in the large pores (desorption between 155 and 265°). With increasing $T_{act.}$ the number of pores is reduced and especially the number of the narrow ones. This is why the relative weights of b and c decrease with increasing T_{act}.

It is very important that all data presented in Tables 2–5 and Fig. 3 have a maximum value for AlSiG-II. The only exceptions are the *c* values in Table 5, but this is not important, since it can be explained by the effects of experimental errors on their very small values. All these data suggest that the adsorption capacity has a well-defined maximum near the molar ratio $Al_2O_3 : SiO_2 = 1 : 1$.

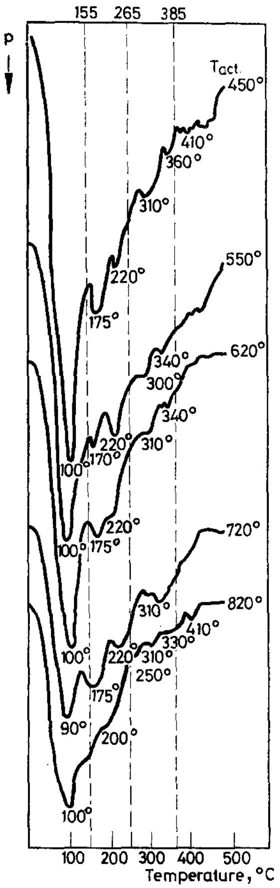

Fig. 3. $p - T$ curves of AlSiG-II for different activation temperatures

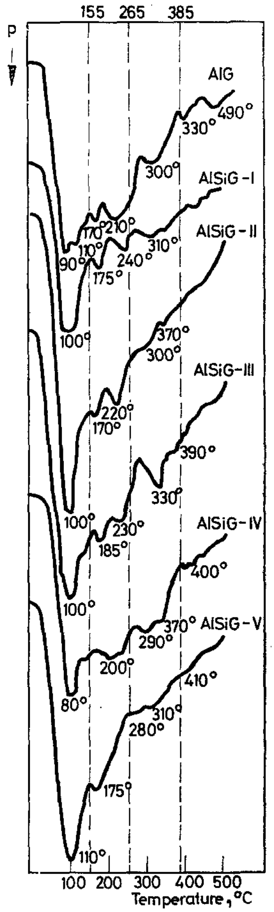

Fig. 4. $p - T$ curves of different systems. $T_{act.} = 550°$ (for AlG $T_{act.} = 620°$)

Conclusions

1. Increase of $T_{act.}$ leads to the decrease of the adsorbed NH_3.
2. The composition of the solid system has a considerable influence on the adsorptive capacity, and irrespective of $T_{act.}$ a well-defined maximum is observed near the molar ratio $Al_2O_3 : SiO_2 = 1 : 1$.

3. At p = 20 torr more than half of the NH_3 adsorbed is weakly, physically sorbed and this is desorbed in vacuo at 25°.

4. In vacuo the NH_3 adsorbed presumably forms two monomolecular layers. The first one is chemisorbed on the acid centres, the second layer is strongly physically sorbed on the first one, perhaps through hydrogen bonds. This second layer is desorbed thermally up to about 155°.

5. The chemisorbed part is adsorbed presumably on acid centres of the same strength, disposed in three main types of pores of different sizes.

6. Increase of $T_{act.}$ diminishes the number of all pores, but the number of narrow pores decreases more rapidly than the number of larger ones.

7. Measurement of the pressure oscillation under dynamic temperature conditions and continuous functioning of the vacuum pump allows the recording of a derivative type $p - T$ curve very sensitive to small changes in the thermal desorption rate.

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Résumé — On a préparé des gels d'oxyde d'aluminium et des gels de silice et d'oxyde d'aluminium de diverses compositions; les préparations ont ensuite été activées à différentes températures. On a étudié l'adsorption de NH_3 à l'aide d'une balance de type McBain à 25° sous des pressions de 20 et de 5.10^{-3} torr ainsi que la désorption thermique sous 5.10^{-3} torr entre 25 et 550° avec une vitesse de chauffage de 4°/mn. On a suivi la désorption en enregistrant les courbes thermogravimétriques et les oscillations de pression dans le système (courbes $p - T$). On a discuté l'influence de la composition et de la température d'activation. On suppose une chemisorption d'une couche monomoléculaire dans trois types principaux de pores ainsi que d'une seconde couche monomoléculaire maintenue par ponts d'hydrogène.

Zusammenfassung — Aluminiumoxyd und Aluminiumoxyd-Kieselsäure Gele von verschiedener Zusammensetzung wurden erzeugt und bei unterschiedlichen Temperaturen aktiviert. Die Adsorption von NH_3 wurde mit Hilfe einer McBain Waage unter 20 und $5 \cdot 10^{-3}$ Torr Druck bei 25°, weiterhin die Thermodesorption von NH_3 unter $5 \cdot 10^{-3}$ Torr Druck zwischen 25 und 550° mit 4°/Min. Aufheizungsgeschwindigkeit untersucht. Die Desorption wurde durch die thermogravimetrische Kurve und durch Registrieren der Druckschwankungen in dem System ($p - T$ Kurve) verfolgt. Man diskutiert den Einfluß von Zusammensetzung und Aktivierungstemperatur. Man nimmt eine Chemisorption einer monomolekularen Schicht in drei Porenhaupttypen gemeinsam mit der Ausbildung einer zweiten durch Wasserstoffbindungen gebundenen monomolekularen Schicht an.

Резюме — Приготовлен гелькокиси алюминия и окись алюминия-силикагелы различного состава и активированы при различных температурах. Изучена адсорбция аммиака (NH_3) на весах типа Мак Бен при 20 мм рт. ст. и $5 \cdot 10^{-3}$ мм рт. ст. и температура 25°. Изучена термодесорбция при $5 \cdot 10^{-3}$ мм рт. ст. в пределах температур 25° — 550° при постоянной скорости нагрева 4°/мин. Десорбция сопровождается регистрированием термогравиметрической кривой и осцилляцией давления в системе (p—T кривая). Обсуждено влияние состава и температуры активации. Высказано предположение о наличии мономолекулярного слоя в трех главных типах пор, вместе с образованием второго мономолекулярного слоя, удерживаемого водородными связями.