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# On the interaction between ammonia and SAPO-5

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## Abstract

New data are presented concerning the low-temperature adsorption of ammonia on SAPO-5, the TPD of the low-temperature-adsorbed ammonia, and the high-temperature interaction of ammonia with the SAPO-5 framework.

## INTRODUCTION

SAPO-5 a silicoaluminophosphate crystalline microporous molecular sieve has been intensively investigated in recent years owing to its catalytic properties connected with its acidity [1-7]. It is known, for example, that SAPO-5 acts as a catalyst for the cracking of cumene [1], butane [3-6], and hexane [3], and for the oligomerization of ethylene [1] and propene [1].

Concerning the acidity of SAPO-5, IR spectrometric data have indicated the existence of the following kinds of hydroxyl groups: SiOH, POH and SiOHAl, corresponding to three kinds of Brønsted acidic sites. They are generated by the formal substitution of phosphorus by silicon in the ALPO-5 lattice [2]. The Brønsted acidic centres in SAPO-5 are mainly responsible for interaction with bases [5]. The interaction of ammonia with SAPO-5 has been investigated. According to Hedge et al. [1], the TPD (temperature-programmed desorption) spectra of ammonia adsorbed on SAPO-5 exhibit four maxima in the range 20-500°C. Three TPD peaks above 187°C have been evidenced by Halic et al. [2]. According to Chao and Leu [4], for ammonia initially sorbed at 100°C on SAPO-5, the TPD curve also shows three peaks in the range 200-600°C. A broad TPD peak of ammonia from SAPO-5 located at 170°C was reported by Biaglow et al. [7].

Analysis of the above-mentioned literature data shows differences in the number of ammonia TPD peaks and their corresponding temperatures, as

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well as a lack of quantitative information concerning the adsorption of ammonia on SAPO-5.

This paper reports some results concerning the kinetics of adsorption of ammonia on SAPO-5 at low temperatures, the kinetics of TPD of the adsorbed ammonia and the interaction of ammonia with SAPO-5 at high temperatures.

## EXPERIMENTAL

SAPO-5 was synthesized according to a procedure described elsewhere [8]. The mean size of the crystallites, as determined using a Philips XL 20 SEM, was 26 $\mu$m.

In order to record the isothermal ammonia uptake–time curves, as well as the ammonia TPD curves, a Setaram TG–DSC 111 apparatus was used.

For low-temperature adsorption of ammonia (20–100°C), the standard operating procedure was as follows. The sample of SAPO-5 was heated in the temperature range 20–550°C at 4 K $\text{min}^{-1}$ in flowing nitrogen (20 ml $\text{min}^{-1}$) in order to remove water and the adsorbed template. The sample was held in flowing nitrogen (20 ml $\text{min}^{-1}$) at 550°C for 2 h and in flowing oxygen (17 ml $\text{min}^{-1}$) for 12 h, in order to remove the carbonaceous residue. The sample was then cooled rapidly in flowing nitrogen (20 ml $\text{min}^{-1}$) to the working temperature, at which ammonia was adsorbed isothermally using helium as a gas carrier (14 ml $\text{min}^{-1}$). The non-isothermal desorption of ammonia (TPD) was recorded at a heating rate of 5 K $\text{min}^{-1}$ in flowing nitrogen (20 ml $\text{min}^{-1}$).

For the high-temperature isothermal interaction of ammonia with SAPO-5, the standard treatment was to heat the sample in the temperature range 20–550°C at a rate of 4 K $\text{min}^{-1}$ in flowing nitrogen (20 ml $\text{min}^{-1}$), and then to hold at 550°C in flowing nitrogen (20 ml $\text{min}^{-1}$) for 30 min and at the same temperature in flowing oxygen (17 ml $\text{min}^{-1}$) for 30 min. The sample was then heated in flowing nitrogen (20 ml $\text{min}^{-1}$) at a rate of 10 K $\text{min}^{-1}$ up to the working temperature, when ammonia was interacted with the sample using helium as a gas carrier (14 ml $\text{min}^{-1}$).

If the working temperature was lower than 550°C after changing the oxygen to nitrogen (20 ml $\text{min}^{-1}$), the sample was submitted to rapid cooling until reaching the actual working temperature.

The source of ammonia used was the coordination compound $[Ni(NH_3)_6]Br_2$, synthesized according to Flóra [9], and kept at 132°C by means of a constant temperature paraffin-oil bath. An amount of 5–6 g of this compound introduced in a vessel was sufficient is generate dry ammonia for 5–6 h in the above-mentioned conditions.

For the TPD experiments, in addition to the samples obtained by isothermal adsorption of ammonia, samples were also obtained by room temperature exchange of SAPO-5 (calcined and oxygen-treated at 550°C) with an ammonia buffer at pH 9.

## TPD DATA HANDLING

In order to obtain the values of the non-isothermal kinetic parameters of ammonia desorption in the framework of the "reaction order" model, three integral methods were applied: the Coats and Redfern [10]; the Flynn and Wall for constant heating rate [11]; and the modified Coats–Redfern [12]. The experimental data were processed using a program written in BASIC [13]. The same program allows the generation of the desorption curve using the determined experimental values of the kinetic parameters in the coordinates ($\alpha$, T°C) and fitting it to the experimental points, where $\alpha$ is the degree of conversion.

## RESULTS AND DISCUSSION

### Low-temperature adsorption of ammonia

Figure 1 shows a typical ammonia uptake–time curve obtained at 19.46°C. The maximum uptake of ammonia amounts 13.5%. The oscillating

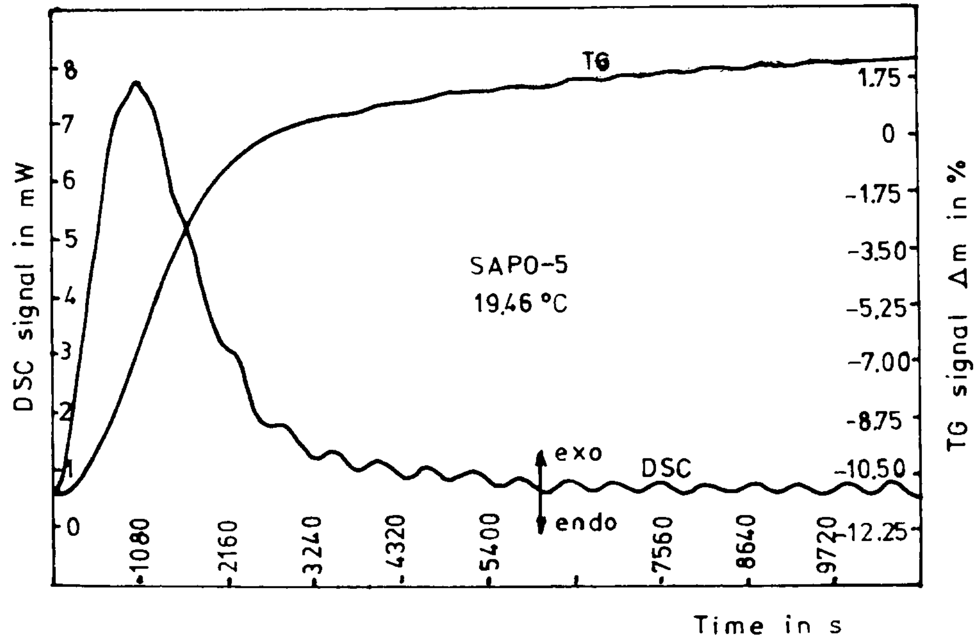

Fig. 1. Isothermal ammonia uptake–time curve ($T = 19.46$°C).

TABLE 1

Maximum ammonia uptake for various temperatures

| Temperature of adsorption/°C | Maximum uptake/wt.% |
|---|---|
| 19.46 | 13.5 |
| 39.37 | 11.2 |
| 59.28 | 4.1 |
| 79.19 | 3.3 |
| 99.45 | 2.4 |

character of the DSC curve, as well as the oscillations which modulate the adsorption of ammonia, are obvious. Similar isotherms were obtained at 39.37, 59.28, 79.19 and 99.45°C. The maximum uptake of ammonia expressed in weight percentages is listed in Table 1.

Owing to the presence of the acidic surface centres in SAPO-5, it is unclear in the investigated temperature range whether ammonia is physisorbed, or merely held on the surface by weak bonds.

Even though there were oscillations modulating the isothermal ammonia uptake–time curves, an attempt was made to obtain kinetic information. In order to fit a specific kinetic equation, the isothermal curves for 19.46, 39.37 and 59.28°C, which permit a more reliable treatment of the data, were used. Considering the maximum ammonia uptake for each isothermal curve as corresponding to the total conversion of ammonia in the adsorbed state, the following equation was found to fit the experimental data

$$\alpha = kt^p \tag{1}$$

where $t$ is the time, and the rate constant $k$ and the exponent $p$ are specific for a given adsorbate–adsorbent system. Working our data in the coordinates ($\ln \alpha$, $\ln T$) yielded the results listed in Table 2.

Inspection of Table 2 shows that the integral kinetic eqn. (1), which is a variant of the Bangham and Burt equation [14], is satisfactorily fulfilled. Because of the decrease in $p$ with temperature, we appreciate that it is not

TABLE 2

Values of $k$ and $p$ for the isothermal adsorption of ammonia on SAPO-5

| Temperature/°C | $k/\mathrm{s}^{-p}$ | $p$ | $\lvert r\rvert$[a] |
|---|---|---|---|
| 19.46 | $1.70 \times 10^{-3}$ | 1.74 | 0.9773 |
| 39.37 | $4.16 \times 10^{-3}$ | 1.62 | 0.9805 |
| 59.28 | $1.10 \times 10^{-2}$ | 1.58 | 0.9806 |

[a] $r$ is the correlation coefficient of the linear regression.

possible to estimate the activation energy. Nevertheless, the increase in the rate constant *k* with temperature, even expressed in different units, indicates that ammonia is somehow involved in a chemical interaction with SAPO-5, despite the decrease in the maximum uptake of ammonia with temperature.

### *TPD of the low-temperature adsorbed ammonia*

Figure 2 shows the TG curve as well as the DSC curve (the latter can be considered as a TPD curve) for ammonia adsorbed on SAPO-5 at 19.46°C. There a single peak at 130°C and all the adsorbed ammonia was desorbed during the TPD experiment. For higher temperatures of adsorption, the peak is shifted towards lower temperature (for $T_{ads} = 39.37$°C, $T_{peak} = 111$°C and for $T_{ads} = 59.28$°C, $T_{peak} = 97$°C). These results indicate that the strength of the ammonia adsorption bond on SAPO-5 decreases with an increase in the temperature of adsorption.

The sample obtained by exchange yielded similar TPD curves. At a heating rate of 10 K $min^{-1}$, the peak temperature was 136°C. A weak peak assigned to the desorption of water was also observed at 54°C.

Table 3 lists the values of the non-isothermal kinetic parameters

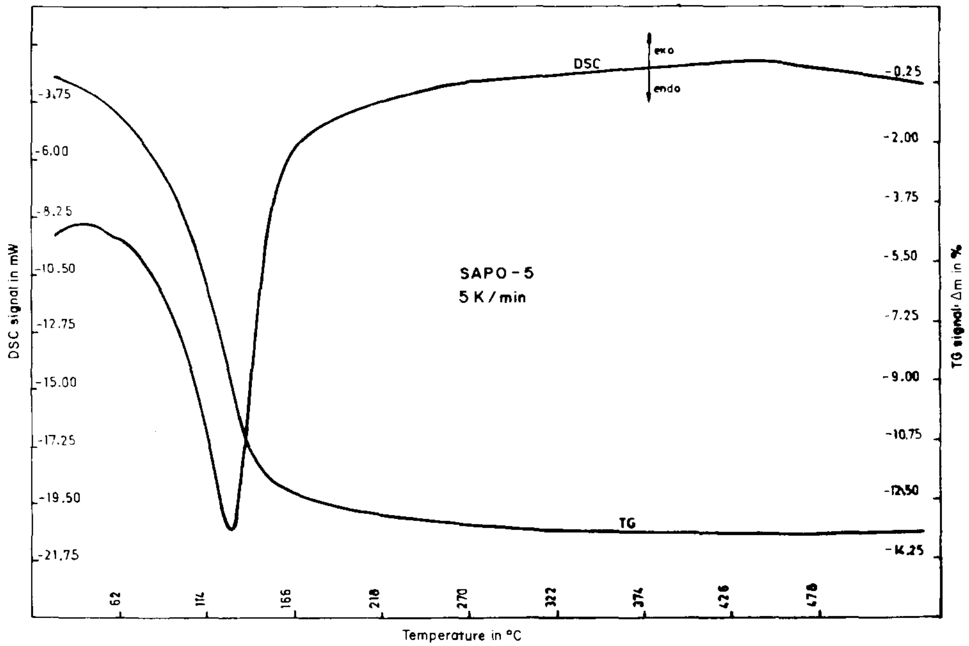

Fig. 2. TPD curves for ammonia adsorbed at $T = 19.46$°C.

TABLE 3

Kinetic parameters of ammonia TPD

| Kinetic parameter | Method | | |
|---|---|---|---|
| | Coats–Redfern | Flynn–Wall | Modified Coats–Redfern |
| $T_{\mathrm{ads}}$ = 19.46°C | | | |
| $E/(\mathrm{J\,mol^{-1}})$ | 40.964 | 45.144 | 41.382 |
| $A/(\mathrm{s^{-1}})$ | $8.57 \times 10^2$ | $7.23 \times 10^3$ | $1.08 \times 10^3$ |
| $n$ | 1.4 | 1.4 | 1.3 |
| $\|r\|$ | 0.9965 | 0.9973 | 0.9958 |
| $T_{\mathrm{ads}}$ = 39.37°C | | | |
| $E/(\mathrm{J\,mol^{-1}})$ | 63.335 | 62.260 | 60.774 |
| $A/(\mathrm{s^{-1}})$ | $3.25 \times 10^6$ | $4.26 \times 10^6$ | $1.40 \times 10^6$ |
| $n$ | 2.1 | 2.0 | 1.9 |
| $\|r\|$ | 0.9987 | 0.9969 | 0.9982 |
| $T_{\mathrm{ads}}$ = 59.28°C | | | |
| $E/(\mathrm{J\,mol^{-1}})$ | 45.562 | 47.652 | 40.546 |
| $A/(\mathrm{s^{-1}})$ | $4.86 \times 10^3$ | $1.88 \times 10^4$ | $9.37 \times 10^3$ |
| $n$ | 2.1 | 2.0 | 1.8 |
| $\|r\|$ | 0.9989 | 0.9991 | 0.9986 |

(activation energy $E$, pre-exponential factor $A$, and reaction order $n$) for the desorption of ammonia from SAPO-5. There is a satisfactory agreement between the values of the TPD kinetic parameters obtained by the three above-mentioned methods. (The modified Coats–Redfern method leads to the lowest value of the reaction order but the difference is not significant.)

Figure 3 shows the regenerated ($\alpha$, $T$) desorption curve obtained using the listed values of the Coats–Redfern kinetic parameters for $T_{\mathrm{ads}}$ = 19.46°C and the corresponding experimental points. As can be seen, the experimental points lie practically on the curve confirming the correctness of the values obtained for the kinetic parameters.

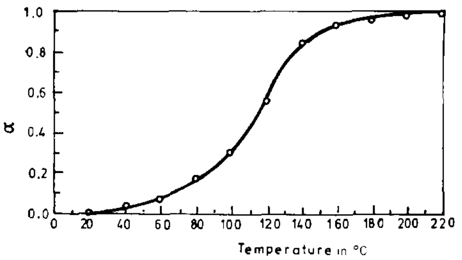

Fig. 3. Regenerated desorption curve in coordinates ($\alpha$, $T$°C): ——, calculated curve; ○, experimental points.

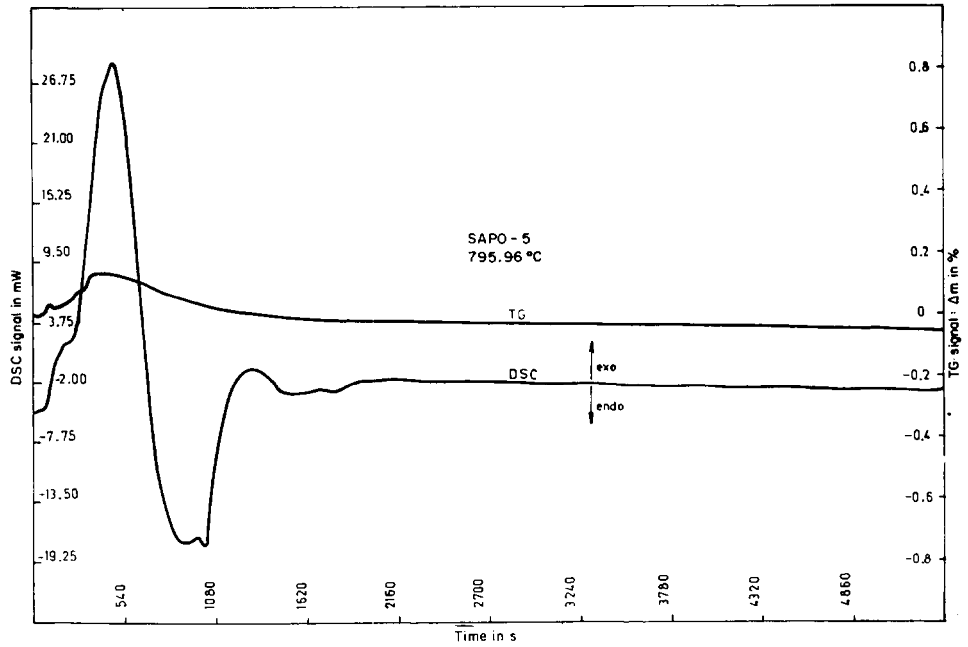

Fig. 4. TG and DSC curves for the time evolution of the system ammonia-SAPO-5 at 795.96°C.

There is a trend to higher values of the order of desorption $n$, from $n = 1.4$ at $T_{ads} = 19.46$°C, to $N = 2$ at $T_{ads} = 39.37$°C and $T_{ads} = 59.28$°C. For the last two temperatures, the Coats–Redfern method gave the same value of the desorption order, $n = 2.1$, but the values of the activation energy and pre-exponential factor were different. Nevertheless, for the rate constant at 100°C, the Arrhenius equation yields the results

for $T_{ads} = 39.37$°C, $k_{100°C} = 4.89 \times 10^{-3}\ s^{-1}$

and

for $T_{ads} = 59.28$°C, $k_{100°C} = 2.28 \times 10^{-3}\ s^{-1}$

i.e. relatively close values. This indicates the existence of a compensation effect, the decrease in the activation energy from $T_{ads} = 39.37$°C to $T_{ads} = 59.28$°C being compensated by a corresponding decrease in the pre-exponential factor.

The increase in the desorption order with the temperature of adsorption implies that structural units consisting of more than one ammonia molecule are desorbed when ammonia is adsorbed at higher temperatures. This is owning to a decrease in the interaction between ammonia and the SAPO-5 surface with an increase in the adsorption temperature. In such conditions, the ammonia molecules adsorbed at higher temperatures also interact with each other and thus form structural units which undergo desorption as one entity.

This result is in agreement with the previously reported shift in the TPD curve peak with the temperature of adsorption.

### *High-temperature interaction of ammonia with SAPO-5*

Figure 4 shows the isothermal TG and DSC curves for the interaction of ammonia with SAPO-5 at 795.96°C. A relatively small weight increase (0.14%) is followed by a small weight decrease which is accompanied by heat release. In ten hours of interaction of ammonia with SAPO-5, the weight decrease amounts to 0.38%. Qualitatively, the same trend in weight increase and decrease was found for 596.86 and 497.31°C. The reported weight changes are probably due to the amonolysis of SAPO-5.

## CONCLUSIONS

The isothermal low-temperature adsorption of ammonia on SAPO-5 is described by a Bangham–Burt-type equation. The order of the ammonia desorption from SAPO-5 increases with the temperature of adsorption. At higher temperatures, the interaction of ammonia with SAPO-5 is accompanied by low successively positive and negative weight changes, probably due to amonolysis.

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