

Temperature-programmed desorption of water and ammonia on sulphated zirconia catalysts for measuring their strong acidity and acidity distribution

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Abstract. Temperature-programmed desorption (TPD) of water and ammonia over ZrO_2 and sulphated ZrO_2 prepared by different methods has been investigated for measuring strong acidity and acidity distribution on sulphated zirconia-type solid super-acid catalysts. The TPD of water provides a simple reliable method for this purpose because of the high stability of water molecules under redox conditions.

Keywords. Temperature-programmed desorption; sulphated zirconia catalysts; acid catalysts; acidity distribution.

1. Introduction

Since the discovery of their strong or super acidity, sulphated zirconia-based catalysts have attracted much attention as process catalysts for a number of reactions.^{1,2} Sulphated zirconia has strong oxidizing abilities at elevated temperatures, and hence commonly used temperature-programmed desorption methods based on the use of ammonia or an organic base as acid probe are not reliable for measuring its strong acidity. This is because of a possible decomposition of the probe molecule by redox or other types of reactions. Okuhara *et al*³ have observed the formation of N_2 via ammonia decomposition above $500^\circ C$ during the TPD of ammonia over sulphated zirconia. In the TPD of pyridine and acetonitrile over sulphated zirconia or other metal oxides, the formation of CO_2 by oxidative decomposition of the probe molecules at above $500^\circ C$ and also the formation of SO_2 and O_2 , originating from SO_4^{2-} decomposition at elevated temperatures, were observed.⁴⁻⁸ Owing to the decomposition of the acid probe, TPD data are too complex to interpret for obtaining information on strong acidity of catalysts. Hence there is a need to find a new acid probe which is stable at elevated temperatures and does not undergo reaction with sulphated zirconia-type catalysts.

Water has both beneficial and adverse effects on the acidity and activity of sulphated zirconia catalysts.⁹⁻¹³ Water is adsorbed on the coordinatively unsaturated Lewis acid sites of the catalyst.^{10,11} It is, therefore, interesting to study TPD of water (which has high stability at elevated temperatures) on sulphated zirconia for measuring its strong acidity. The present work was undertaken for comparing the TPD of water and ammonia over

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ZrO₂ and sulphated ZrO₂ catalysts, prepared by different methods, with the objective of developing a simple but reliable method for measuring the strong acidity and/or acidity distribution of sulphated ZrO₂-based catalysts.

2. Experimental

ZrO₂ and sulphated ZrO₂ (I–III) catalysts were prepared from amorphous Zr(OH)₄ (prepared by its precipitation from an aqueous solution of zirconyl nitrate by ammonium hydroxide solution at a pH of 8.0–8.5, followed by washing with distilled water and drying at 120°C for 20 h). ZrO₂ was obtained by calcining the zirconium hydroxide at 600°C for 4 h. Sulphated ZrO₂ (I) and (II) catalysts (with SO₄²⁻ loading of 6.0 wt.%) were obtained by impregnating zirconium hydroxide with ammonium sulphate and H₂SO₄ respectively, by the incipient wetness technique followed by drying (at 120°C for 20 h) and calcining at 600°C in air for 4 h. Sulphated ZrO₂ (III) was prepared by stirring zirconium hydroxide with 0.5 M H₂SO₄ (15 ml g⁻¹) at room temperature for 1 h, followed by filtering, drying (at 120°C for 20 h) and calcining at 600°C in air for 4 h.

Temperature-programmed desorption of water or ammonia (prechemisorbed at 100°C) over the ZrO₂ and sulphated ZrO₂ (I–III) catalysts was carried out in a quartz reactor (i.d. = 4.5 mm) packed with about 0.1 g catalyst from 50° to 610°C, at a linear heating rate of 20°C min⁻¹ in a flow of moisture-free helium (40 ml min⁻¹). The adsorbate desorbed in the TPD was measured quantitatively by a TCD detector. Before carrying out the TPD, the catalyst was pretreated *in-situ* at 610°C for 1 h in a flow of helium. The ammonia or water was chemisorbed on the catalyst at 100°C by saturating the catalyst with the adsorbate at a lower temperature (50–60°C) and then desorbing the physically adsorbed adsorbate in a flow of pure helium (40 ml min⁻¹) at 100°C for 1 h. The surface area of the catalysts was measured by the single point BET method using a Monosorb Surface Area Analyzer (Quantachrome, USA).

3. Results and discussion

TPD curves for water on ZrO₂ and sulphated ZrO₂ catalysts are presented in figure 1 and that for ammonia on the same catalysts are shown in figure 2. Results for the desorption of water and ammonia on the catalysts at different temperature intervals, obtained from the TPD data, are given in tables 1 and 2 respectively.

NH₃-TPD curves for ZrO₂ and sulphated ZrO₂ catalysts at higher temperatures (above 500°C) are somewhat similar to water-TPD curves for the respective catalysts. However, at lower temperatures, the respective NH₃- and water-TPD curves differ from each other markedly, probably because of the interactions of ammonia with the non-acid sites of the catalysts.

In the case of the NH₃-TPD on all the sulphated ZrO₂ catalysts, the observed high temperature desorption peak at above 500°C may be at least partly due to the N₂ formed in the decomposition of strongly adsorbed ammonia³. This makes the ammonia-TPD unreliable for measuring the acidity distribution on sulphated ZrO₂. However, in the case of water as an acid probe, there is no possibility of its decomposition at elevated temperatures. Hence, the TPD of water seems to be a much better tool for measuring the acidity distribution (i.e. the number and strength of acid sites) on sulphated zirconia and other solid super-acids with redox sites. Comparison of the results in tables 1 and 2 shows that the acidity distribution on all the sulphated zirconia catalysts from the NH₃-TPD is appreciably different from that obtained from the water-TPD.

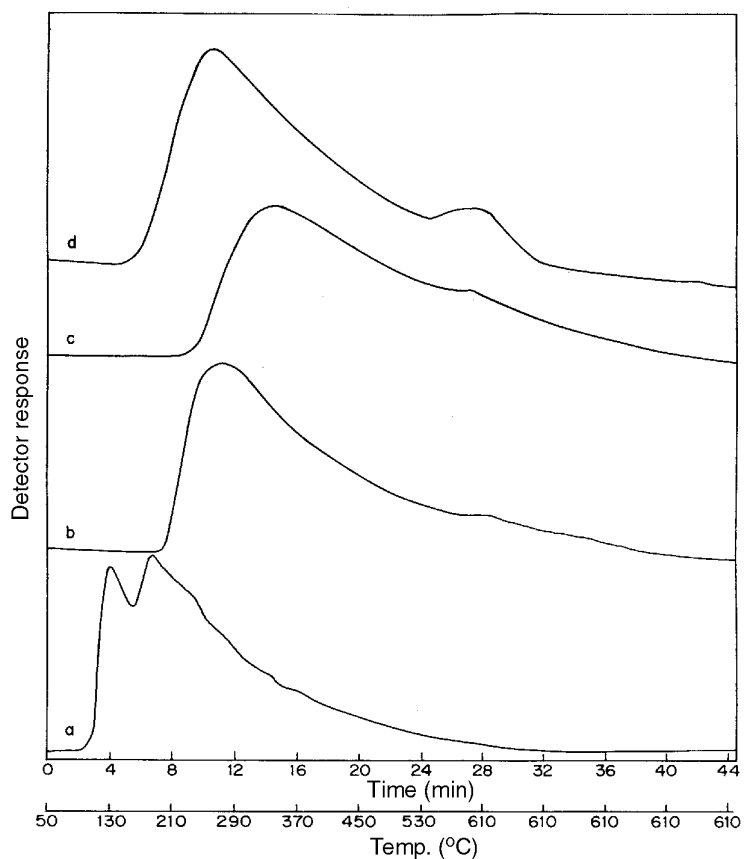


Figure 1. TPD of water over ZrO_2 and sulphated ZrO_2 (I–III) catalysts. (a) ZrO_2 ; (b) sulphated ZrO_2 (I); (c) sulphated ZrO_2 (II); (d) sulphated ZrO_2 (III).

Table 1. Data for the desorption of water (chemisorbed at $100^\circ C$) on ZrO_2 and sulphated ZrO_2 (I–III) catalysts at different temperature intervals.

Catalyst	Surface area ($m^2 g^{-1}$)	Water chemisorbed at $100^\circ C$ ($mmol g^{-1}$)	Water desorbed ($mmol g^{-1}$)		
			50–150°C	150–500°C	>500°C
ZrO_2	45.4	0.103	0.015 (14.6%) ^a	0.084 (81.6%)	0.004 (3.8%)
Sulphated ZrO_2 (I)	94.1	0.160	0.0 (0.0%)	0.095 (59.35%)	0.065 (40.65%)
Sulphated ZrO_2 (II)	78.0	0.262	0.0 (0.0%)	0.112 (42.9%)	0.150 (57.1%)
Sulphated ZrO_2 (III)	66.5	0.368	0.0 (0.0%)	0.255 (69.34%)	0.112 (30.66%)

^aValues in parentheses are the percentage of chemisorbed water desorbed in the corresponding temperature intervals

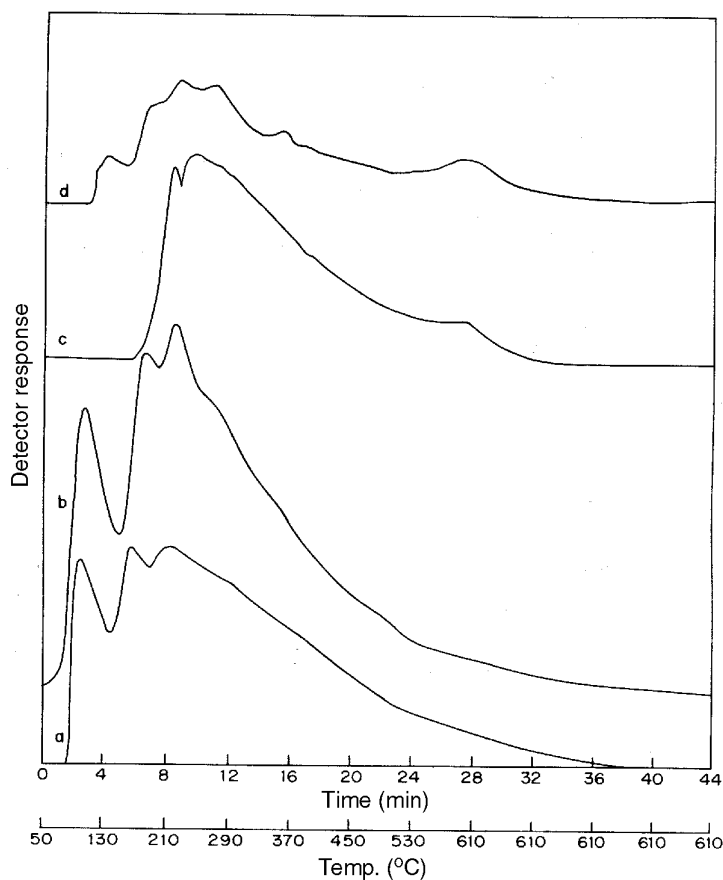


Figure 2. TPD ammonia over ZrO_2 and sulphated ZrO_2 (I-III) catalysts. (a) ZrO_2 ; (b) sulphated ZrO_2 (I); (c) sulphated ZrO_2 (II); (d) sulphated ZrO_2 (III).

Table 2. Data for the desorption of NH_3 (chemisorbed at $100^\circ C$) on ZrO_2 and sulphated ZrO_2 (I-III) catalysts at different temperature intervals.

Catalyst	NH_3 chemisorbed at $100^\circ C$ ($mmol\ g^{-1}$)	NH_3 desorbed ($mmol\ g^{-1}$)		
		50-150°C	150-500°C	>500°C
ZrO_2	0.388	0.058 (14.9%) ^a	0.313 (80.7%)	0.017 (4.4%)
Sulphated ZrO_2 (I)	0.497	0.079 (15.9%)	0.382 (76.9%)	0.036 (7.2%)
Sulphated ZrO_2 (II)	0.427	0.0 (0.0%)	0.365 (85.5%)	0.062 (14.5%)
Sulphated ZrO_2 (III)	0.422	0.02 (4.7%)	0.312 (74.0%)	0.090 (21.3%)

^aValues in parentheses are the percentage of chemisorbed ammonia desorbed in the corresponding temperature intervals

From comparison of the water TPD curves (figure 1) and water desorption data (table 1) for ZrO_2 with that for sulphated ZrO_2 (I–III) catalysts, the following important observations can be made.

- Because of sulphatation, the TPD curve is shifted towards higher temperatures, indicating an increase in the strength of Lewis acid sites present in the catalyst.
- The high temperature TPD peak (at about 600°C) is observed only for the sulphated zirconia catalysts, indicating the presence of strong Lewis acid sites on them but little or no strong acid sites on the ZrO_2 (i.e. without sulphatation).
- The water (chemisorbed at 100°C) desorbed from all the zirconia catalysts at the temperature below 150°C is 0.0%, but that between 150° and 500°C and above 500°C is much higher than that desorbed from the ZrO_2 without sulphatation.

This indicates the absence of weak acid sites (measured in terms of the water desorbed from 50° and 150°C) and the presence of a larger number of both intermediate and strong acid sites (measured in terms of the water desorbed from 150° to 500°C and above 500°C respectively) on the sulphated ZrO_2 catalysts. The catalysts can be arranged for their total acidity (measured in terms of the water chemisorbed at 100°C) and strong acidity, in the following order.

For total acidity: Sulphated ZrO_2 (III) > sulphated ZrO_2 (II) > sulphated ZrO_2 (I) > ZrO_2 .

For strong acidity: Sulphated ZrO_2 (II) > sulphated ZrO_2 (III) > sulphated ZrO_2 (I) \gg ZrO_2 .

The catalyst order for both the total and strong acidity is, however, different, when it is obtained from NH_3 -TPD data (table 2).

The surface areas of the catalysts (table 1) are in the order [$(NH_4)_2SO_4/ZrO_2 > H_2SO_4/ZrO_2 > ZrO_2$], which is consistent with that observed earlier.^{1,14} The observed lower strong acidity of sulphated- ZrO_2 (I) (table 1) is also consistent with the fact that the sulphatation by ammonium sulphate (as compared to that by sulphuric acid) provides sulphated zirconia having lower catalytic activity.²

4. Conclusions

The present study leads to the following important conclusions.

- (1) The acidity distribution obtained from the TPD of water is quite different from that obtained from the TPD of ammonia.
- (2) The TPD of water provides a more reliable method for measuring strong (or super) acidity and acidity distribution on the sulphated zirconia-based catalysts. It may also be used for measuring acidity of other solid super-acids having the redox function.
- (3) The number of intermediate and strong acid sites on sulphated zirconia is strongly influenced by the sulphatation agent (e.g. ammonium sulphate or sulphuric acid) used and also by the method of sulphation (e.g. incipient impregnation or stirring with impregnating solution) used.

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