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Surface acidity investigation of Al_2O_3 supports and Ni-Mo/Al_2O_3 catalysts using the temperature-programmed desorption of *tert*-butylamine

A.T. Townsend [+], M.J. Ridd * and F.P. Larkins **

Department of Chemistry, University of Tasmania, Hobart, Tasmania, 7001 Australia

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The relative acid site densities of a range of Ni-Mo/Al_2O_3 based catalysts were measured by the temperature-programmed desorption of *tert*-butylamine. The catalysts investigated possessed different surface areas and active species loadings. The effect of active species impregnation on the acidity of blank aluminas was also determined. Similarly the effect of sulphiding on catalyst acidity was also addressed.

Keywords: Surface acidity; *tert*-butylamine; Ni-Mo/Al_2O_3 catalysts

1. Introduction

The temperature-programmed desorption of a nitrogen base is a widely accepted technique for the characterisation of the surface acidity of heterogeneous catalysts. A range of bases have been reported in the literature, including ammonia [1,2], pyridine [1–3], and *tert*-butylamine [4–6].

Catalyst acidity has been found to be an important parameter in the design of catalysts for the hydrotreating of petroleum and heavy liquids, particularly shale and gas oils, as well as coal-derived liquids [7]. It is well known that increased acidity leads to increased coke formation during the upgrading of such liquids, resulting in catalyst deactivation and a shorter catalyst life [8]. Acidic sites are also thought to be responsible for cracking, isomerisation and dealkylation reactions [6].

[+] Author to whom correspondence should be addressed.

* Now at the Legislative Research Service, Parliament House, Canberra, ACT, 2600 Australia.

** Department of Chemistry, University of Melbourne, Parkville, Victoria, 3052 Australia.

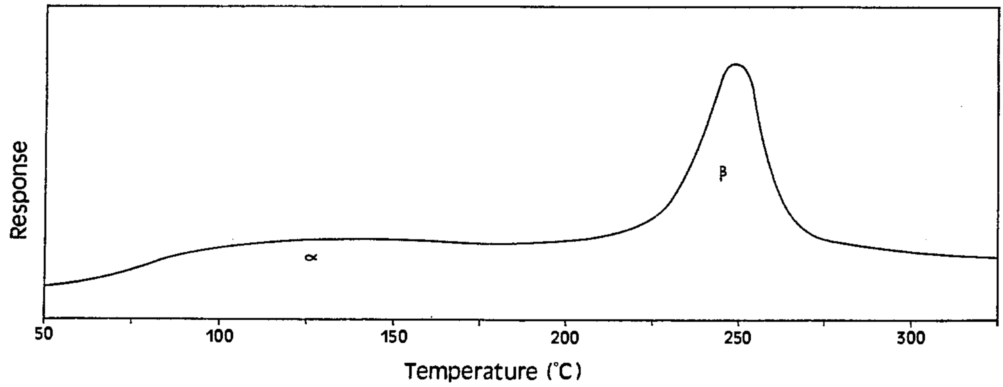

Fig. 1. A typical temperature desorption profile of *tert*-butylamine from the Shell 424 commercial catalyst.

Both Brønsted and Lewis acid sites have been found on the surface of catalysts used in the upgrading of heavy feeds [9]. Similar definitions as applied to acidic solutions may also be applied to solid acids.

A temperature-programmed desorption method using *tert*-butylamine (TBA) has been used extensively recently by McCormick and coworkers [6,7,10–12] in the study of acidic supports as well as metal-doped catalysts for the upgrading of coal-derived liquids. TBA was chosen as a probe molecule as it possessed sufficient volatility for introduction into a carrier gas stream, and the desorption products are normally detected at temperatures below 400°C, allowing for rapid analysis and GC oven compatibility [6]. Catalyst acidities were given as relative acid site density values (RAD's), a dimensionless quantity defined as the desorption peak area divided by the catalyst surface area.

In the typical desorption profile of a nitrogen containing base such as TBA two peaks are normally observed (fig. 1). For consistency the terminology used by McCormick [6] will be used here to distinguish between the two peaks. The first at lower temperatures (α-peak) arises from any weakly bound physisorbed gas, while the peak at higher temperatures is caused by more strongly bound chemisorbed gas or cracked products (β-peak).

At present there are two differing trains of thought in the literature as to the significance of the β-peak temperature, depending on the structure of the probe gas employed. The traditional view is that a base adsorbed onto a strong acid site is more stable than one adsorbed on a weak site, and therefore requires more elevated temperatures for removal from the catalyst surface. This theory would suggest that increased desorption temperature would indicate stronger acid site strength [2].

Recently the work by McCormick et al. [6] has suggested that this in fact may not be the case for more complicated nitrogen bases such as TBA. They found using field ionisation mass spectroscopy (FIMS) analysis that the major desorp-

$$(CH_3)_3C\text{-}NH_2 + H^+B^- \longrightarrow (CH_3)_2C{=}CH_2 + NH_3 + H^+B^-$$

Fig. 2. Hofmann-type elimination reaction for isobutylene formation over a Brønsted acid site.

tion product at temperatures characteristic of the β-peak was isobutylene, formed via a "Hofmann-type" elimination mechanism from the adsorbed TBA (fig. 2). As a result of this acid-catalysed cracking reaction taking place, they argued that lower desorption temperatures indicates increased acid site strength when using TBA, regardless of the acid site type (i.e., Brønsted or Lewis).

The results of a study using a similar technique to determine the surface acidity of a number of blank Al_2O_3 supports as well as a range of Ni-Mo/Al_2O_3 catalysts of differing surface areas and active species loadings, used in the upgrading of Australian coal-derived liquids are reported herein. It was not the purpose of this work to differentiate between Brønsted and Lewis acid sites, but rather to study the total detectable acidity of these catalytic materials.

2. Experimental

CATALYST SURFACE AREA INVESTIGATION

A number of Al_2O_3 supports of varying surface areas were obtained from the catalyst suppliers, Norton and Strem. Details of the supports are listed in table 1, along with their surface areas, as measured by the BET method with nitrogen adsorption. Upgrading catalysts were prepared by impregnating these same supports to a loading of 3 wt% Ni/13 wt% Mo. This loading is the same as that employed by Shell in the production of their 424 catalyst, a common commercial

Table 1
Acidity of supports and calcined catalysts of varying surface areas

Support type	Purity (%)	Surface areas (m^2/g)		RAD values		β-Peak T (°C)	
		Supp. [a]	Cat. [b]	Supp.	Cat.	Supp.	Cat.
Norton SA5151	99.3	< 1	< 1	–	–	–	–
Norton SA3232	80.3 [c]	23	39	< 0.0001	0.0008	–	243
Strem 132550	99	97	83	0.0001	0.0014	305	251
Norton SA6275	99.8	204	198	0.0003	0.0012	296	256
Norton SA6173	99.8	229	222	0.0004	0.0011	320	275
Strem 132500	92 [d]	279	154	0.0001	0.0012	300	255
Shell 424 reference		–	166	–	0.0017	–	263

[a] Data for Al_2O_3 support materials.

[b] Data for catalysts of loading 3 wt% Ni/13 wt% Mo.

[c] The major impurity was given as 17.9% SiO_2 by Norton catalogue.

[d] The major impurity present in 132500 was not stated.

Table 2
Acidity of calcined and sulphided catalysts of varying metal loading

Catalyst type [a]	Surface areas (m^2/g)		RAD values		β-Peak T (°C)	
	Calcined	Sulphided	Calcined	Sulphided	Calcined	Sulphided
Blank SA6275	204	161	0.0003	0.0006	296	297
1 wt% Ni/4.1 wt% Mo	205	144	0.0008	0.0012	264	277
2 wt% Ni/8.3 wt% Mo	181	145	0.0013	0.0011	250	263
3 wt% Ni/12.4 wt% Mo	173	133	0.0014	0.0017	255	253
4 wt% Ni/16.5 wt% Mo	162	128	0.0017	0.0018	251	248
5 wt% Ni/20.6 wt% Mo	136	102	0.0019	0.0023	249	257
6 wt% Ni/24.8 wt% Mo	118	91	0.0020	0.0025	250	247
8 wt% Ni/33.0 wt% Mo	79	68	0.0023	0.0024	249	250
10 wt% Ni/41.2 wt% Mo	55	57	0.0022	0.0021	243	260
12 wt% Ni/49.5 wt% Mo	48	45	0.0019	0.0015	243	242
15 wt% Ni/61.9 wt% Mo	25	35	0.0019	0.0009	243	249

[a] All catalysts were supported on Al_2O_3 (Norton SA6275).

hydrotreating catalyst. Further details on catalyst preparation have been given elsewhere [13,14]. Surface areas for the prepared catalysts are also given in table 1.

CATALYST METAL LOADING INVESTIGATION

A second suite of catalysts was prepared with varying metal oxide loadings on an Al_2O_3 support of surface area approximately 200 m^2/g (Norton SA6275). The atomic ratio of Ni to Mo was kept constant at approximately 1:4.1, the same as that used for the Shell 424 reference material. Further catalyst information is given in table 2.

Before use upgrading catalysts are usually sulphided, as it has been well established that sulphided catalysts possess superior activity over their calcined counterparts for the upgrading of coal-derived liquids [15]. The catalysts were sulphided under a H_2S (10%) and H_2 (90%) mixture at a total flow rate of 120 ml/min at 350°C for 4 hours, to determine what effect this had on catalyst acidity. The sulphided catalyst data is also noted in table 2.

ACIDITY DETERMINATION

The method of McCormick [6] was used for the acidity determinations and the reader is referred there for further elaboration. The temperature-programmed desorption of TBA was carried out using a modified laboratory built TPR apparatus. Samples (0.1 g) were placed in a 9 mm diameter quartz heating tube and dried under a flowing stream of He (10 mls/min) at 350°C until the evolution of moisture was complete (as monitored by a TCD). After cooling to below 100°C, the He was flowed through TBA (kept at 0°C in an ice/water bath) until the sample surface was saturated with the nitrogen base. Excess TBA was flushed from the reaction chamber with pure He. Heating was then commenced at 12°C/min until desorption products were observed.

3. Results and discussion

The major β-peak desorption product was found by GCMS analysis to be isobutylene, supporting the Hofmann elimination mechanism proposed by McCormick et al. [6]. Therefore it was assumed that the inverse relationship between β-peak maximum temperature and acid site strength proposed by McCormick could be applied to the catalysts used in this study.

The Hofmann elimination reaction has ammonia produced as a reaction product along with isobutylene (fig. 2). However no mention as to the fate of this gas is made by the previous authors in their analysis. Complications in the technique may arise if this species was readsorbed onto the catalyst surface after the cracking of TBA. No desorption peak due to ammonia was found by the current authors when the temperature was ramped to 800°C, indicating that this gas is flushed free of the reactor system, avoiding any interference with the catalyst.

Prior to investigating the prepared catalysts the reproducibility of the method was tested using a Shell 424 catalyst. The β-peak area was found to differ by $\pm 6\%$ for five acidity determinations using this catalyst, while the β-peak temperature was found to be accurate to $\pm 5\%$. These values were deemed to be suitable for the analysis of further catalyst/support samples.

The alumina supports of varying surface areas were found to possess low RAD values (table 1). These values were less than 0.0004, with the support of lowest surface area, SA5151, not exhibiting any detectable desorption peak. This support was principally α-Al_2O_3, known to have lower intrinsic acidity than γ-Al_2O_3 supports [8], of which the higher surface area materials are typical. The acidic nature of these supports is under some debate, with some authors considering them to be Brønsted in character (resulting from surface adsorbed water providing donatable protons [1]), while others have found the acid sites to be Lewis in character [9]. No correlation between the RAD values and surface area was found for the blank alumina supports. The desorption temperature was found to be near 300°C for these supports.

The acidity of the impregnated catalysts prepared from the various aluminas was markedly increased relative to the supports themselves (table 1). Relatively constant RAD values were observed for the catalysts, being between 0.0008 and 0.0014. This is not surprising as each catalyst had a similar loading of active species. Both Co-Mo and Ni-Mo catalysts supported on Al_2O_3 were found to have both Brønsted and Lewis acid sites in a previous work by Kiviat and Petrakis [9].

The RAD value of 0.0008 for the catalyst supported on SA3232 appears slightly lower than those found for the other catalysts. Using real estimates of the percentage errors involved for the peak mass and catalyst surface area, the absolute maximum error associated with this RAD value was calculated to be ±15%, not large enough to raise the RAD value to be similar to the others. This would suggest that the value of 0.0008 found represents a small drop in RAD with lower surface area, rather than a drop due to experimental error. The catalyst supported on SA5151 did not display any detectable desorption peak, as was similarly found for the blank support material alone. This finding may result from the very low surface area of this Al_2O_3 material.

From the peak temperatures noted in table 1, it can be seen that increasing catalyst surface area results in a slight decrease in acid site strength (i.e. increasing β-peak temperature). In general these desorption temperatures (up to 275°C) fall well below that observed for the blank supports (up to 320°C). None of the prepared catalysts of constant metal loading possessed a RAD value greater than the Shell 424 reference catalyst, of 0.0017.

The RAD values for the calcined catalysts of increasing active species loading are given in table 2. An increase in RAD is observed with loading to 8 wt% Ni/33 wt% Mo, reaching a peak value of 0.0023. At higher loadings the RAD decreased, being 0.0019 at the maximum metal level considered in this study. It is thought that this decrease does not result from lower RAD, but rather is caused by steric factors of the adsorbed TBA. At low loadings the TBA is able to successfully "see" all the acid sites of the sample. However as the loading increases a point is reached when the surface is saturated with TBA. At higher loadings still, the number of acidic sites may increase, but these extra sites would not be seen by the adsorbing TBA, due to steric reasons. Therefore a lower RAD value is observed than is actually present on the sample. At higher loadings monolayer coverage by the active catalyst species will be exceeded, so that not every acid site may be accessible, regardless of the steric effects of the TBA. This may also contribute to the drop in RAD values observed. The steric considerations of using TBA had not been discussed in any detail by previous authors [4,6]. This is clearly a limitation of the technique.

The β-peak temperatures were found to generally decrease with increased loading, indicating that slightly stronger acidic sites are formed at high metal loadings, although this difference is small. The temperature values are typical of what was observed for the catalysts of varying surface area previously.

For ease of comparison, the RAD results for the sulphided catalysts are shown with the RAD values for the calcined catalysts in fig. 3. As before, a RAD maximum is observed, this time at a lower loading. This results from the sulphided catalysts generally having a lower surface area than the calcined catalysts, particularly at low loadings. The lower surface areas of these catalysts

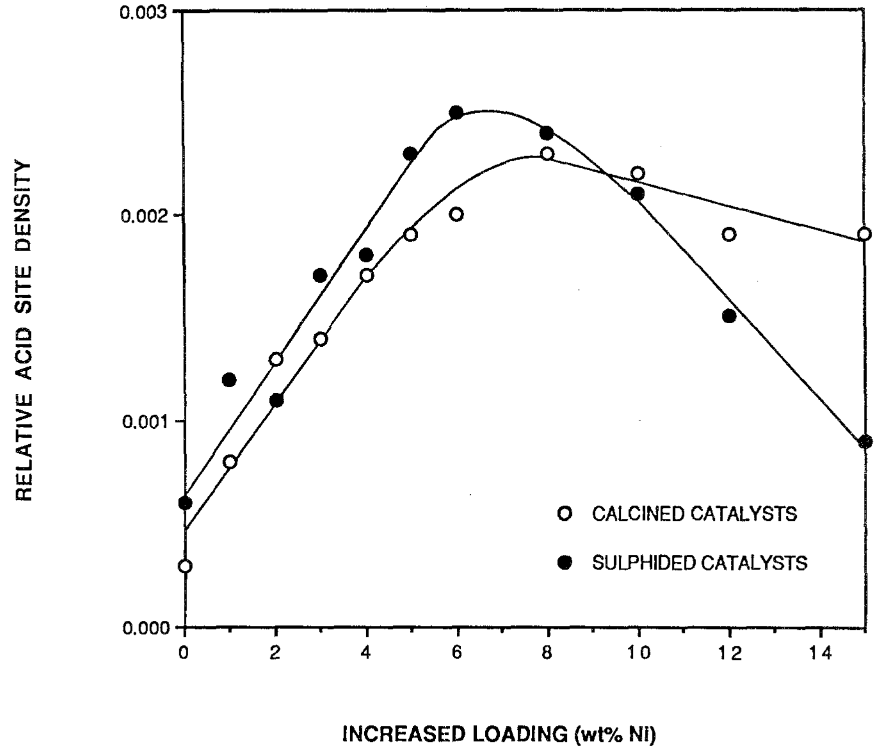

Fig. 3. RAD values for the suite of calcined and sulphided catalysts of varying active species loading. The loading values refer to the wt% Ni content of the catalysts with the Ni:Mo weight ratio held constant at 1:4.1.

were thought to be caused by the conversion of the metal oxides to sulphides. However the blank alumina support similarly displayed a drop in surface area, disproving this theory. It is now thought that the lower surface area of the sulphided catalysts was caused by the deposition of a sulphur containing layer onto the catalyst surface during sulphiding, with the adsorbing N_2 gas having a lower affinity for such surfaces. The presence of such a layer was confirmed by X-ray photoelectron analysis (XPA). As a result of the difference in surface areas, the largest RAD value seen in this study was found for the sulphided 6 wt% Ni/24.8 wt% Mo catalyst, having a value of 0.0025. Once again steric factors are thought to cause the drop in RAD values observed.

Unlike the calcined catalysts, no correlation between metal loading and β-peak maximum temperature was observed for the sulphided catalysts.

In conclusion, the determination of the relative acid site density of a series of alumina based supports and catalysts can be carried out using TBA as a probe molecule. Unlike traditional TPD methods, a lower desorption peak temperature indicates increased acid site strength, resulting from a Hofmann elimination mechanism. In agreement with previous authors, the major desorption product was found to be isobutylene, confirming this fact. A limitation of the technique is exposed when catalysts of high loadings (i.e. very low active species dispersions) are considered. In such cases steric factors due to the size of the adsorbed TBA molecule, coupled with low catalyst surface areas, prevent the total number of acid sites from being detected.

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