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Catalytic Properties of Metal-containing Polymethylsiloxanes

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Aluminium-, iron-, titanium- and zirconium-containing polymethylsiloxanes were studied as catalysts for acid-catalysed reactions; their surface acidity and the strengths of their acid centres were determined. They appeared to be active for 2-propanol dehydration; the best sample was almost as active as alumina, which is known for its high activity for alcohol dehydration. All metal-containing polymethylsiloxanes (MPS) catalysed double-bond migration and *cis-trans* isomerization of 2-butene. Some of them also catalysed the synthesis of methyl t-butyl ether, but their activity for this reaction was inferior to that of the resin Amberlyst-15 and some of sulphate-ion modified metal oxides. No cumene conversion occurred on the catalysts studied and no pyridinium ion formation was observed by IR spectroscopy, which points to the absence of strong Brönsted acid sites. The MPS are distinguished by quite large surface areas (86–299 $m^2 g^{-1}$) and are capable of chemisorbing pyridine (0.014–0.047 $mmol g^{-1}$) on their Lewis acid centres.

Keywords: metal-containing polymethylsiloxanes; surface acidity; acid strength; acid–base catalysis; alcohol dehydration; olefin isomerization; heteroalkyl ether synthesis; surface area

INTRODUCTION

Polyorganosiloxanes are known for their good thermal stability and chemical resistance which make them promising materials for catalysis. It was reported recently that polyorganosiloxanes with sulphonic groups showed a high catalytic activity for vapour-phase nitration of benzene,[1] while aluminium-containing polymethylsiloxane catalysed dehydration of pinacol in the vapour phase with 100% conversion.[2] The latter observation points to a partial substitution of silicon atoms with atoms of various metals and might be a way of making these organometallic polymers interesting catalysts for reactions proceeding on acid centres.

EXPERIMENTAL

Preparation of catalysts

Methyltrichlorosilane (9 g; >98%, Fluka) and dimethyldichlorosilane (4 g; >99.5%, Fluka) were added to 40 cm^3 of anhydrous ethanol, with cooling during the dissolution of the methylchlorosilanes. The resulting solution was mixed with 400 cm^3 of an aqueous solution prepared by adding a metal chloride ($ZnCl_4$, $TiCl_4$, $FeCl_3$ or $AlCl_3$) to distilled water. The metal content in the latter solutions corresponded to a molar ratio of silicon/metal of 4.5:1 after mixing of the two solutions. Then the pH was increased to 9 by the addition of ammonia. The resulting suspension was stirred overnight at room temperature and later for 5 h at 80 °C. Afterwards the precipitate was filtered, washed with distilled water until the disappearance of chloride anions, heated at 100 °C for 24 h and then at 300 °C for 3 h. Just before the catalytic activity measurements, the polymethylsiloxane catalysts were heated again at 300 °C for 1 h in a microreactor flushed with helium. The resulting samples were labelled as ZrMS, TiMS, AlMS and FeMS. A metal-free polymethylsiloxane sample, designated as MS, was obtained in an analogous way, but no metal chloride was added to the distilled water. Several of the preparation stages of the transition-metal-containing polymethylsiloxanes were analogous to those described by Mishima *et al.*[2] for aluminium-containing polymethylsiloxane. However, our preparation procedure differs from Mishima's in using sodium-free metal chloride solutions instead of solutions obtained by dissolving a metal hydroxide in dilute sodium hydroxide. Aluminium hydroxide, used by Mishima *et al.*,[2] is easily soluble in sodium hydroxide, but difficul-

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ties arise in the case of some other metals (e.g. iron(III) hydroxide is practically alkali-insoluble), and therefore a modified preparation was used. For comparison purposes, however, two additional samples of aluminium-containing polymethylsiloxane were prepared following Mishima's method. The sample rich in sodium (Na^+) cations (an unwashed one) was designated as AlMS-1, and that which was subjected to washing with ammonium chloride (NH_4Cl) solution as AlMS-2. The previously mentioned sample, free of the presence of sodium cations at any stage of preparation, was labelled as AlMS.

Determination of surface acidity

Evacuation of the catalyst sample (10^{-3} Pa) at 300 °C for 1 h was followed by admission of pyridine vapour at room temperature. Then temperature was raised to 150 °C and physisorbed pyridine was pumped off (10^{-3} Pa, 2 h). The amount of pyridine chemisorbed on acid centres was determined in a Perkin–Elmer elemental Analyzer 2400 CHN and was taken as a measure of surface acidity (total acidity including centres of different acid strengths).

To evaluate the acid strength of the centres, benzene solutions of Hammett indicators[3] corresponding to H_0 from 3.3 to −8.2 were contacted with polymethylsiloxane samples activated at 300 °C. Iron-containing polymethylsiloxane was excluded from the indicator tests because of its coloration.

Catalytic activity measurements

Test reactions, except for the synthesis of methyl t-butyl ether (MTBE), were carried out in a microreactor using a pulse technique. The flow rate of helium carrier gas in all pulsed microreactor experiments was 30 $cm^3 min^{-1}$.

Catalytic activity for 2-propanol dehydration was measured at 150 °C, the catalyst weight was 0.05 g, and the isopropanol (liquid) pulse was 0.5 µl. Reaction product separation was performed by gas chromatography at 75 °C on a 1 m column packed with Carbowax 400 (10 wt %) supported on Chromosorb W.

Tests for catalyst performance in butene isomerization were carried out at 200 °C, the catalyst weight was 0.2 g and the 1-butene (gas) pulse was 0.5 cm^3. Reaction product separation was performed at 0 °C on an 8 m column packed with propylene carbonate (25 wt %) supported on firebrick.

Catalyst capability of cumene cracking was examined at 300 °C, the catalyst weight was 0.25 g, and the cumene (liquid) pulse was 0.5 µl. A 1 m GC separation column was packed with Emulphor O (15 wt %) supported on Chromosorb W.

In order to evaluate catalytic activity for MTBE synthesis, isobutene (3.2 $cm^3 min^{-1}$) was mixed with methanol vapour (molar ratio of methanol/isobutene = 1 : 1) diluted with helium (the latter was passed first through a thermostated saturator filled with methanol) and the reactant mixture was introduced into a flow reactor loaded with 0.2 g of catalyst. The reaction was carried out at 90 °C and the products analysed at 170 °C on a 1 m column packed with Porapak Q.

Surface area was measured by low-temperature (−195 °C) nitrogen adsorption using a sorptometer made by Sartorius (Göttingen) and differential thermal analysis was carried out on a Shimadzu DTA 50 instrument with a heating rate of 5 °C min^{-1}.

RESULTS AND DISCUSSION

Surface acidity

Measurements of acid strength using Hammett indicators[3] such as *p*-dimethylaminoazobenzene ($pK_a = 3.3$), benzeneazodiphenylamine ($pK_a = 1.5$), dicinnamalacetone ($pK_a = -3.0$), benzalacetophenone ($pK_a = -5.6$) and anthraquinone ($pK_a = -8.2$) have shown that all metal-containing polymethylsiloxanes, except for AlMS-1 have on their surfaces acid centres capable of converting the base form of the indicators with pK_a values ranging from 1.5 to 3.3 to their conjugated acid form. On the surface of AlMS-1 only weak acid sites ($H_0 \geq 1.5$) were detected and their concentration was small as concluded from the scarcity of red-coloured (i.e. covered by the acidic form of *p*-dimethylaminoazobenzene) particles of AlMS-1. Other aluminium-containing polymethylsiloxanes, namely AlMS and AlMS-2, as well as zirconium-containing polymethylsiloxane, had even higher acid strengths as evidence by the appearance of the acidic form of dicinnamalacetone ($pK_a = -3.0$). One should mention, however, that in the case of AlMS the colour intensity of the acid form of the above indicator was considerably stronger than in the case of AlMS-2 and ZrMS, which suggests that

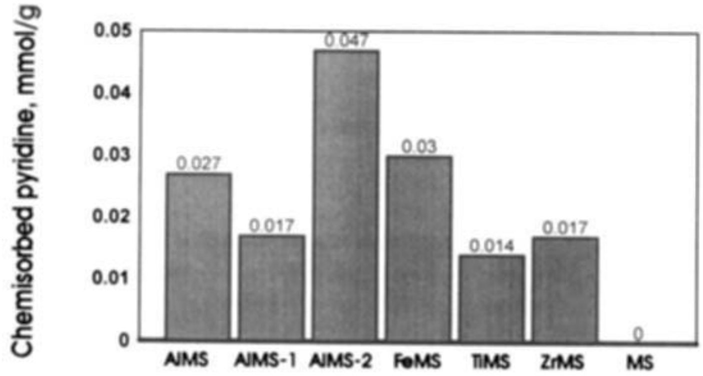

Figure 1 Acidity of metal-containing polymethylsiloxanes.

the concentration of acid sites of strength corresponding to $H_0 = -3.0$ was considerably higher on the surface of AlMS. None of the catalysts had acid centres strong enough to convert benzalacetophenone and anthraquinone into their yellow (i.e. acidic) forms. The metal-free polymethylsiloxane (the MS sample) was unable to react even with *p*-dimethylaminoazobenzene, as shown by the yellow coloration after adsorption of the indicator on the MS surface.

The highest total acidity, as expressed by the proportion of centres capable of chemisorbing pyridine, was found for the AlMS-2 sample, obtained by washing with ammonium chloride according to the procedure described by Mishima,[2] followed by the AlMS sample (Fig. 1). This means that in the case of aluminium-containing polymethylsiloxanes, the preparation conditions which start at a high pH (sodium aluminate[2]), followed by lowering to pH 9 and washing with ammonium chloride, lead to a higher total acidity than those which start from a low pH (addition of metal chloride to distilled water), followed by increase in pH to 9. The advantage of the latter route is, however, the creation of a higher number of stronger acid centres ($H_0 \geq -3.0$) due to the absence of sodium cations at any stage of the sample preparation.

Surface acidity close to that of AlMS is shown by FeMS. It has to be mentioned, however, that some contribution to the acidity of the latter sample can come from iron(III) oxide (which develops acidity after activation at the temperature of these studies, i.e. 300 °C[4,5]), because of the possibility of partial decomposition of the FeMS sample heated at 300 °C (Table 2). The acidity of the unwashed AlMS-1 sample was, as expected,[6] considerably lower (Fig. 1). The acid centres still present on the surface of the latter sample are weak, as already mentioned, and this is reflected in the poor performance of the AlMS-1 sample in the catalytic reactions studied (Figs 2 and 3; Table 1). Tetravalent metal-containing polymethylsiloxanes are characterized by a smaller number of acid centres than trivalent metal-containing ones, provided that the latter do not contain sodium cations. The total acidity of

Table 1 MTBE synthesis from isobutene and methanol on metal-containing polymethylsiloxanes

	Isobutene conversion (%)				
	Time on stream				
Catalyst	10 min	25 min	40 min	55 min	70 min
AlMS	4.3	3.7	3.2	3.1	3.2
AlMS-1	0.0	0.0	0.0	0.0	0.0
AlMS-2	1.4	0.5	0.3	0.3	0.2
FeMS	0.2	0.1	0.04	0.03	0.03
TiMS	Trace	Trace	Trace	Trace	Trace
ZrMS	0.2	0.1	0.1	0.1	0.1
MS	0.0	0.0	0.0	0.0	0.0

Table 2 Surface area and thermal stability of metal-containing polymethylsiloxanes

Sample	Surface area ($m^2 g^{-1}$)	Maxima on DTA curve (°C)	
		In helium	In air
AlMS	145	516	465
AlMS-1	106	283, 467, 542	283, 460, 479
AlMS-2	129	452, 537	422, 500
FeMS	86	338	326
TiMS	129	420, 554	414, 480
ZrMS	299	444, 547	427, 506
MS	14	259, 476, 536	265, 403, 433

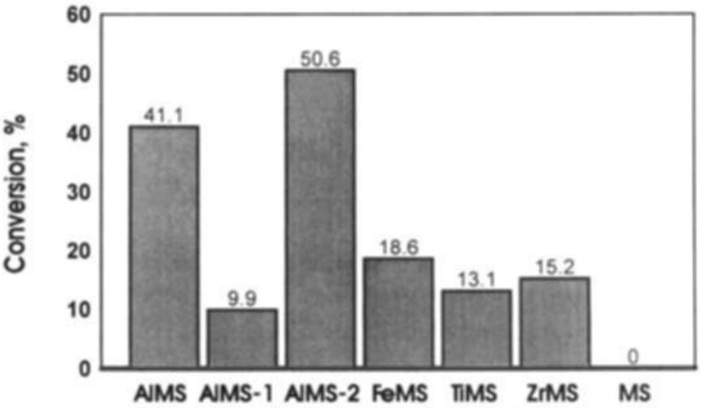

Figure 2 Catalytic activity for 1-butene isomerization.

ZrMS and TiMS is comparable with that of AlMS-1 (Fig. 1), but the acid strength of ZrMS ($H_0 \geq -3.0$) is significantly higher than that of TiMS and AlMS-1.

Summing up, the sequence of total acidity (as determined by chemisorption of pyridine) on surfaces of MPS was found to be:

$$\mathrm{AlMS-2 > AlMS > AlMS-1}$$
$$\mathrm{= ZrMS > TiMS > FeMS}$$

and the polymethylsiloxane sample, which contained no metal, was not acidic at all. On the other hand, sites with the highest acid strength ($H_0 = -3.0$) were found in the case of AlMS and AlMS-2 samples (i.e. ones prepared either in the absence of sodium cations or washed with ammonium chloride to remove sodium cations) and the ZrMS sample.

Catalytic activity

The high acidity of AlMS-2 is reflected in its leading position in the butene isomerization activity series (Fig. 2). It is followed by AlMS and FeMS catalysts, while tetravalent-metal containing polymethylsiloxanes and AlMS-1 are in the lower part of the isomerization activity series (Fig. 2). Ratios of *cis*-2-butene to *trans*-2-butene were in all cases close to unity, which suggests that butene isomerization on metal-containing polymethylsiloxanes proceeds according to an acid-centred mechanism involving 2-butyl carbenium ions rather than through a base-centred route requiring formation of π-alkyl carbanions as an intermediate.[7] It is interesting that even in the case of AlMS-1, which contains sodium ions, the *cis*/*trans* ratio is not much higher than unity (1.41 : 1).

It is worth adding that the activity of MPS

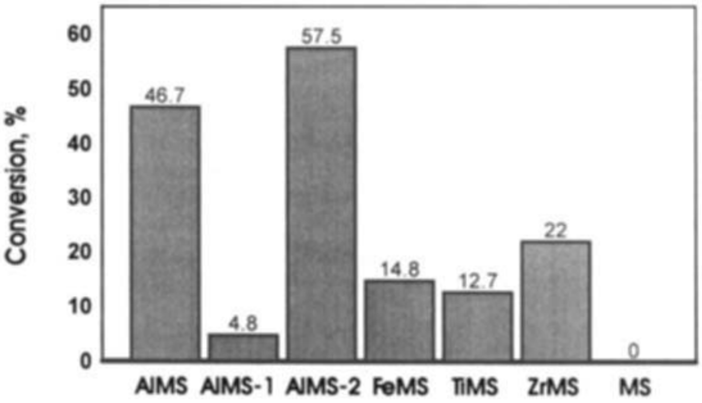

Figure 3 Catalytic activity for 2-propanol dehydration.

catalysts for double-bond migration in butenes can be boosted by increasing the catalyst activation (heating) temperature within the temperature range in which the catalyst is thermally stable. For instance, heating of ZrMS at 335 and 350 °C (i.e. below its decomposition temperature—Table 2) results in a spectacular rise in isomerization activity to 47.4% and 78.5%, respectively. This seems to originate from an increase in the number and/or strength of acid sites on the ZrMS surface rather than from a change in the reaction mechanism; since the ratio of 2-butene geometrical isomers remains close to 1:1.

Although the order of isomerization activity (Fig. 2) is similar to that of total acidity (Fig. 1), there is no direct proportional relationship between catalytic activity and surface acidity. The latter fact may be caused by differences in strengths of acid centres between the polymethylsiloxanes studied. The same can be said about the activity series for 2-propanol dehydration (Fig. 3), since olefin isomerization requires stronger acid centres than alcohol dehydration. Moreover, the AlMS-1 sample (i.e. that with unwashed sodium cations) catalysed, to a small extent, isopropyl alcohol dehydrogenation to acetone. The conversion to acetone was, however, an order of magnitude lower than that to propene. All the other catalysts studied have shown 100% selectivity to propene. It is somewhat surprising that no acetone was found also in the products of 2-propanol decomposition over FeMS, although differential thermal analysis (DTA) curves suggest that the above catalyst can undergo a partial decomposition when heated at 300 °C. Perhaps the thermal effects observed on the DTA curves reflect only the beginning of pyrolysis of the methyl groups, and not a complete decomposition of the catalyst with the formation of iron(III) oxide. (The latter can catalyse dehydrogenation of isopropyl alcohol to acetone). It is worth noting that the alcohol dehydration activity (Fig. 3) of some of the MPS studied is comparable with that of alumina, which is known for its excellent dehydrating performance. For instance, alumina prepared by hydrolysis of aluminium isopropoxide, activated at 300 and 600 °C and tested for its dehydration activity under the same conditions as the MPS catalysts, showed conversion of 28.1% and 59.6%, respectively. The high dehydration activity of MPS (particularly aluminium-containing ones) may lead to a suspicion that we are dealing with oxides formed as a result of thermal decomposition of polymethylsiloxanes. We have prepared physical mixtures of metal oxides with MS at the same silicon/metal ratio as that used in the preparation of catalysts. The mixtures were used as catalysts for 2-propanol dehydration at 150 °C and their activity appeared to be close to zero, except for a mixture of MS with alumina (prepared by hydrolysis of aluminium isopropoxide and then calcined at 300 °C) which catalysed the above reaction with 11.2% conversion, i.e. lower than that when AlMS or AlMS-2 was used.

Polymers having acid sites, e.g. Amberlyst-15, are known for their activity for synthesis of octane boosters such as methyl t-butyl ether (MTBE) and t-amyl methyl ether (TAME), which are valued for their capability of increasing gasoline octane number with no addition of tetraethyllead. The presence of acid centres on the surfaces of MPS has encouraged us to examine their behaviour in MTBE synthesis. As shown in Table 1, the AlMS sample, which was prepared in a sodium-free medium, appeared to be the best of the MPS catalysts investigated, from the point of view of both isobutene conversion and the rate of activity loss with time on stream. It was followed by AlMS-2 (washed with ammonium chloride), which underwent a faster deactivation than the AlMS catalyst, and poorly active ZrMS and FeMS catalysts. MPS catalysts which had acid centres weaker than those required to convert dicinnamalacetone to its acid form were inactive for the above reaction. The activity of MPS for MTBE synthesis appears to be low when compared with that of Amberlyst-15 (a sulphonated styrene–divinylbenzene copolymer) and some sulphate-ion-modified metal oxides. Under analogous catalyst testing conditions, conversions of isobutene to MTBE after 10 min on stream were 23.3% on Amberlyst-15, 17.1% on sulphate-containing (5 wt %) zirconia and 16.8% on sulphate-containing (5 wt %) tin dioxide.[8] The reason for this fact is probably concerned with the number and strength of acid centres, which are more abundant and much stronger on the latter catalysts.[9]

The last test reaction studied was cumene cracking, for which all MPS failed to show any activity. This proves the absence of strong Brönsted acidity which is essential to the occurrence of the above reaction. In order to verify this observation by an independent method, we have recorded IR spectra of the AlMS sample on a Bruker FTS 113V spectrometer before and after chemisorption of pyridine. The disc made of compressed AlMS was heated and evacuated in an IR cell: this *in situ* pretreatment prevented contact with atmospheric moisture at any stage of the measurement. The admission of pyridine vapour to the IR cell resulted in the appearance of bands originating from pyridine coordinatively bonded on Lewis centres, whereas the band at about 1545 cm^{-1}, which is typical of the pyridinium ion formed by chemisorption on Brönsted acid sites, was absent from the spectrum.

To make sure that materials pretreated at 300 °C, which we have used as catalysts for the test reactions, were MPS rather than the products of their thermal decomposition, we carried out DTA in inert gas (helium) and air. Results of the analysis, which are listed in Table 2, reveal that maxima on DTA curves of AlMS, AlMS-2, TiMS and ZrMS are located at temperatures exceeding 400 °C and all the thermal effects begin at well above 300 °C. As a rule, the maxima recorded in air appear at temperatures lower than in helium and thermal effects in the former gas are larger, most likely due to evolution of heat during oxidation of methyl groups. AlMS-1 and MS samples are characterized by a maximum below 300 °C, in addition to high-temperature maxima above 400 °C. In the case of iron-containing polymethylsiloxane, the maximum on the DTA curve is situated above 300 °C, but the thermal effect begins below 300 °C which, as was already mentioned, throws doubt upon the chemical homogeneity of the FeMS sample heated at 300 °C.

CONCLUSIONS

A replacement of a proportion of the silicon atoms in polymethylsiloxanes by aluminium as well as by some transition metals results in the appearance of acid centres capable of efficiently catalysing alcohol dehydration and olefin double-bond migration. The MPS can also catalyse MTBE synthesis, but should be considered poor catalysts for the latter reaction.

The MPS chemisorb pyridine on their Lewis acid sites and/or weak Brönsted acid centres. Strong proton-donor sites are absent on their surfaces because all the MPS investigated show no activity for cumene cracking. We believe that the presence of a band at 1548 cm^{-1} in the spectrum of pyridine chemisorbed on aluminium-containing polyethylsiloxane, presented in Mishima's paper,[2] was an artefact caused by reaction between Lewis acid centres and water vapour due to easy access of the latter under the conditions of their experiment (most likely during compression and transfer of the disc).

The results of our study suggest that MPS make interesting materials for prospective catalysts. Their hydrophobicity could extend the use of MPS for reactions requiring hydrophobic catalysts. Although Mishima *et al.*[2] found them inactive for hydrolysis of methyl acetate and explained this fact by insufficient hydrophobic properties of aluminium polymethylsiloxane, sucessful application of other silicon-containing hydrophobic catalysts in a number of reactions[10–12] allows us to expect that MPS will find their use in reactions for which the catalyst's hydrophobicity, chemical resistance and thermal stability are essential.

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