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Journal of Chromatography A, 704 (1995) 45–53

JOURNAL OF
CHROMATOGRAPHY A

Preparation and evaluation of magnesia-coated silica as column packing material for high-performance liquid chromatography

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First received 16 August 1994; revised manuscript received 25 January 1995; accepted 25 January 1995

Abstract

The preparation of a mixed oxide gel composed of silica and magnesia was attempted by a coating method in order to develop a useful column packing material for liquid chromatography. The physical properties of the gels obtained remained almost the same as those of the native silica gel, but the surface silanol groups and the acid strength both changed, depending on the preparation conditions. The chromatographic behaviour of the gels was tested using benzene, dimethyl phthalate, pyridine and phenol as solutes. The magnesia-coated silicas calcined at temperatures between 600 and 800°C exhibited the excellent separation abilities for these compounds.

1. Introduction

Oxides such as silica and alumina have been widely used adsorbents and column packing materials for liquid chromatography. Recently other metal oxides such as titania and zirconia have been studied as alternative column packings material to silica, because these new ceramics have chemical stability and a different separation ability to silica. These interesting surface properties and chromatographic applications have been studied in detail by various workers [1–12].

In our investigations on mixed oxide gels as adsorbents, it has been found that they exhibited different and specific properties from each component of the oxides [13–16]. We have also reported that they could be used as adsorbents

for the recovery of trace and novel elements [17] and for the removal of environmental pollutants [18]. Based on our results on adsorbents, four mixed oxide gels, silica–titania, silica–alumina, silica–zirconia and silica–magnesia, were tested as column packing materials for liquid chromatography. For this purpose, first the four mixed oxide gels, which were prepared by a coprecipitation method, were examined with respect to their surface characteristics and separation abilities. It was found that silica–magnesia had an excellent separation ability for basic solutes such as pyridine, the separation of which is difficult with silica gel [19,20]. However, silica–magnesia obtained by the coprecipitation method was neither spherical nor uniform and had a wide range of particle size distribution. These characteristics are unfavourable for column packing materials.

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In this work, coating for commercially available spherical silica gel with magnesia was attempted in order to avoid the above-mentioned problems with regard to particle morphology and size distribution. The surface characteristics of the magnesia-coated silica gels obtained were evaluated to assess their use as column packing materials for liquid chromatography.

2. Experimental

2.1. Chemicals

The spherical silica gel Super Microbead silica gel 100A-10 (Fuji-Silysia Chemical) was used as a matrix. Magnesium chloride hexahydrate and other reagents (Wako) were of analytical-reagent grade.

2.2. Preparation of magnesia-coated silica gel

To magnesium chloride solution of a given concentration, 10 g of the commercially available spherical silica was added. With stirring, 6 M ammonia solution was added dropwise to adjust the pH to the appropriate value. After stirring for 30 min, the solution was filtered by suction. The resultant gel was washed with 100 ml of distilled water and 100 ml of methanol. The gel was then dried overnight at 110 °C, followed by calcining at 400–1000°C for 2 h.

2.3. Determination of amount of magnesia coated on silica gel

Magnesia-coated silica gel (about 0.1 g) was placed in a platinum vessel that had been accurately weighed. After heating at 1000°C in an electric furnace and cooling to room temperature in a desiccator, the vessel was again weighed accurately to determine the mass loss of the gel. Subsequently, 20 ml of concentrated HF were added to the platinum vessel, then the mixture evaporated to dryness on a heated sand-bath. The same operation was repeated after adding 5 ml of concentrated HF to the residue in the

vessel. The residue was dissolved in 1 M nitric acid and the resulting solution was transferred into a 100-ml calibrated flask and diluted to volume with 1 M nitric acid. An aliquot of the solution was diluted to an appropriate concentration. The final working solution for the determination contained 0.5% of lanthanum. The lanthanum solution was prepared by dissolving lanthanum oxide in hydrochloric acid.

The content of magnesium was determined using a Japan Jarrel-Ash Model AA-880 Mark II atomic absorption spectrometer and converted into magnesia (MgO) concentration.

2.4. Measurement of physical properties

The nitrogen adsorption isotherms of the gels at 77 K were measured. From the result, the specific surface areas and pore volumes were determined. The specific surface area was calculated from the BET equation. The pore volume was obtained from the liquid nitrogen volume evaluated from the nitrogen adsorption volume at $P/P_0 = 0.97$ [20]. Scanning electron micrographs were taken using a JEOL Model T330A scanning electron microscope.

2.5. Acid strength of gel surface

The surface acid strengths of gels were determined using the visual colour change method as follows [21]. The sample gel (0.1 g) was placed in a 50-ml flask containing 10 ml of dried benzene, then one by one up to seven Hammett's indicators were added successively in order of their pK_a values until the added indicator showed the colour of the acid form. The acid strength of the gel was taken to be between its pK_a value and that of the former. The Hammett's indicators used and their pK_a s were anthraquinone ($pK_a = -8.2$), benzalacetophenone (-5.6), dicinnamalacetone (-3.0), 4-benzazodiphenylamine (1.5), *p*-dimethylaminoazobenzene (3.3), phenylazonaphthylamine (4.0) and methyl red (4.8).

2.6. Chromatographic test

The gel was packed into a stainless-steel column (250 mm × 4.6 mm I.D.) by a slurry method as follows [22]. To a solvent mixture of glycerol and methanol, 3 g of the gel were added, then the slurry was well dispersed by ultrasonic vibration for 20 min in vacuo. The slurry was transferred to a packing reservoir and packed into a column filled using methanol as a solvent under a pressure of 300 kg/cm².

Benzene, dimethyl phthalate, pyridine and phenol as test solutes were used to evaluate the gels as packing materials for HPLC, the concentrations of which were 8.0, 8.0, 3.6 and 18.0 mg/ml, respectively. An aliquot of 10 μl of the methanol solution was injected into a Nippon Bunko LC-800 HPLC system. The mobile phase was *n*-hexane containing 1% methanol at a flow-rate of 1 ml/min at room temperature. Detection was carried out at 254 nm with a UV detector. Using the retention time of benzene as the dead time, the capacity factors of other solutes were estimated.

3. Results and discussion

3.1. Effect of preparation conditions on amount of magnesia coated

The effect of the pH of the solution on the amount of magnesia coated was investigated by adjusting the pH of 100 ml of the solution containing 10 g of silica gel and 0.12 M magnesium chloride with 6 M ammonia solution. The higher the pH, the more magnesia was coated on silica gel (Fig. 1). However, above pH 10 the amount of magnesia coated became almost constant. Also, the amount of magnesia coated increased with increasing concentration of MgCl₂, but above 0.4 M it remained almost constant, as shown in Fig. 2. Generally, the dissociation or ionization of MgCl₂ occurs in a solution of lower pH, but magnesium hydroxide [Mg(OH)₂] precipitates from a solution of higher pH owing to hydrolysis under conditions above

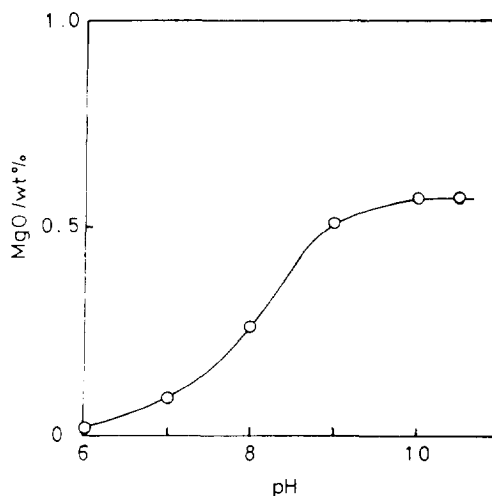


Fig. 1. Effect of pH on amount of magnesia coated on silica. Matrix silica, 10 g; MgCl₂ concentration, 0.12 M.

the solubility product, reported as 10⁻⁹–10⁻¹¹. In fact, a white suspension in addition to silica gel was observed in solutions with higher concentrations of MgCl₂ after adjusting the pH to 9, but the amount of magnesia coated was almost constant. This suggests that magnesia is coated not by the simple deposition of Mg(OH)₂ but by the adsorption of magnesium species on the silica surface.

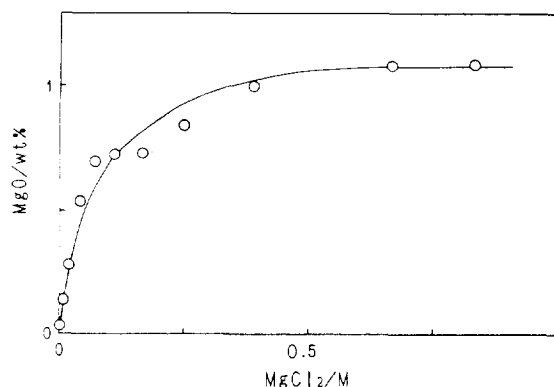


Fig. 2. Effect of concentration of magnesium chloride. Preparation pH = 9.

Table 1
Relationship between surface characteristics and amount of magnesia coated

Gel	Amount of magnesia (ppm)	Specific surface area (m ² /g)	Pore volume (ml/g)
Silica (untreated)	–	344	1.14
Magnesia-coated silica ^a	1400	322	1.15
	2800	327	1.16
	5400	322	1.16
	7400	317	1.14
	11000	319	1.13

^a Dried at 110°C.

3.2. Physical properties of the surface of gels

The specific surface areas and the pore volumes of untreated and magnesia-coated silicas are given in Tables 1 and 2, respectively. The specific surface areas have a tendency to decrease only slightly with increase in the amount of magnesia coated, but the pore volumes were constant, independent on the magnesia coating. The calcining temperature did not influence the specific surface area and the pore volume of magnesia-coated silica. Fig. 3 shows that the morphology and grain size of untreated silica were very close to those of magnesia-coated silica.

The FT-IR spectra of untreated and magnesia-coated silicas are shown in Fig. 4. The isolated silanol group was assigned from the spectrum and was observed at around 3750 cm⁻¹ in both gels [23]. The hydrogen-bonded silanol group, which was assigned from the spectrum observed at around 3400 cm⁻¹, existed only on untreated

silica. Stout and DeStefano [24] reported a similar observation on a zirconia-treated silica surface by means of NMR. Neither the specific surface area nor the pore volume was influenced, but the surface silanol groups changed in quality with the magnesia coating.

3.3. Surface acid strength

Using the visual colour change method [21], the acid strength of the gels was investigated (Table 3). The introduction of basic magnesia on silica by coating had a tendency to weaken the surface acid strength; the untreated silica had the strongest acid strength. Further, the effect of calcining on the surface acid strength of the gels is summarized in Table 4. Magnesia-coated silicas dried at 110°C and calcined at 400°C showed weaker acid strengths than untreated silica. The acid strengths of the gels calcined at 600 and 800°C were the same as that of untreated silica. The gel calcined at the highest temperature of

Table 2
Relationship between surface characteristics and calcining temperature

Gel	Drying or calcining temperature (°C)	Specific surface area (m ² /g)	Pore volume (ml/g)
Silica (untreated)	–	344	1.14
Magnesia-coated silica ^a	110	322	1.16
	400	327	1.15
	600	330	1.16
	800	330	1.15

^a Coated with 5400 ppm magnesia.

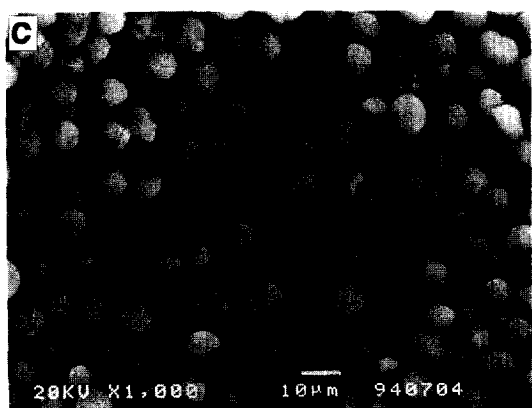
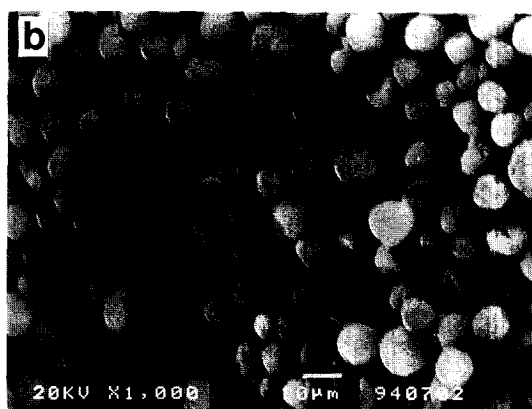
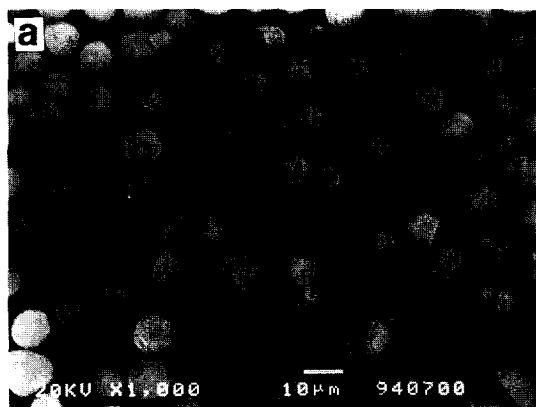


Fig. 3. Scanning electron micrographs of matrix silica and magnesia-coated silicas: (a) untreated silica; (b) 5400 ppm magnesia-coated silica dried at 110°C; (c) 5400 ppm magnesia-coated silica calcined at 800°C.

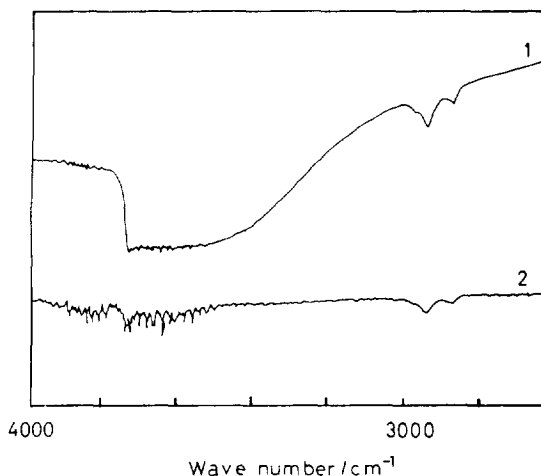


Fig. 4. FT-IR spectra. 1 = Untreated silica; 2 = magnesia-coated silica (5400 ppm).

Table 3
Acid strength of magnesia-coated silica

Gel	Amount of magnesia (ppm)	Acid strength (H_0)
Silica (untreated)	–	$1.5 < H_0 < 3.3$
Magnesia-coated silica ^a	1400	$1.5 < H_0 < 3.3$
	2800	$3.3 < H_0 < 4.0$
	5400	$3.3 < H_0 < 4.0$
	7400	$4.0 < H_0 < 4.8$
	11000	$4.0 < H_0 < 4.8$

^a Dried at 110°C.

1000°C exhibited the greatest strength in the gels examined.

From Fig. 4 and Table 5, it is suggested that the magnesia coating contributes to weakening the surface acid strength by diminishing the hydrogen-bonding silanol groups. However, the effect of the thermal treatment on the surface acid strength was not clearly explained from the above results, because it is considered that the surface silanol groups are decreased by calcining, resulting in the lowering of the acid strength. As an example, the investigation of Okamoto et al. [25] made it clear that the number of the hydrogen-bonded silanol groups was decreased on thermal treatment of silica, but the number of isolated silanol groups unchanged. Mause and

Table 4
Acid strength of magnesia-coated silica

Gel	Drying or calcining temperature (°C)	Acid strength (H_0)
Silica (untreated)	–	$1.5 < H_0 < 3.3$
Magnesia-coated silica ^a	110	$3.3 < H_0 < 4.0$
	400	$3.3 < H_0 < 4.0$
	600	$1.5 < H_0 < 3.3$
	800	$1.5 < H_0 < 3.3$
	1000	$-3.0 < H_0 < 1.5$

^a Coated with 5400 ppm of magnesia.

Engelhardt [26] also reported that the hydrogen-bonded silanol groups were removed by thermal treatment, whereas the number of the isolated silanol group increased. In addition, Malinowski et al. [27] demonstrated that the acid strength of magnesia increased as the heat treatment temperature was raised. Hence the increase in the acid strength of the magnesia-coated silica by thermal treatment may be caused not by silica but magnesia. The relationship between the surface acid strength and the thermal treatment must be clarified by further investigations on the type and amount of the surface acid and base sites.

It is interesting that in the proposed method, without changing the favourable physical characteristics as a column packing material, the species of silanol groups and the surface acid strength of silica can be changed.

3.4. Chromatographic behaviour

Chromatographic tests were carried out by using neutral dimethyl phthalate, acidic phenol and basic pyridine as solutes, and benzene for the dead time determination. The chromatograms obtained with magnesia-coated silica gels are shown in Fig. 5. The neutral dimethyl phthalate was not influenced by the magnesia coating and was separated successfully with a sharp and symmetrical peak, because the material had adequate physical characteristics for this separation such as a specific surface area and pore volume much the same as those of untreated silica. In contrast, the elution behaviours of

pyridine and phenol changed considerably after the magnesia coating. Pyridine was not eluted at all using untreated silica because of the specific interaction with surface silanol groups, but it could be separated successfully without tailing on magnesia-coated silica. The capacity factors decreased slightly depending on the amount of magnesia coated. Hence, it is evident that the separation ability for pyridine is changed con-

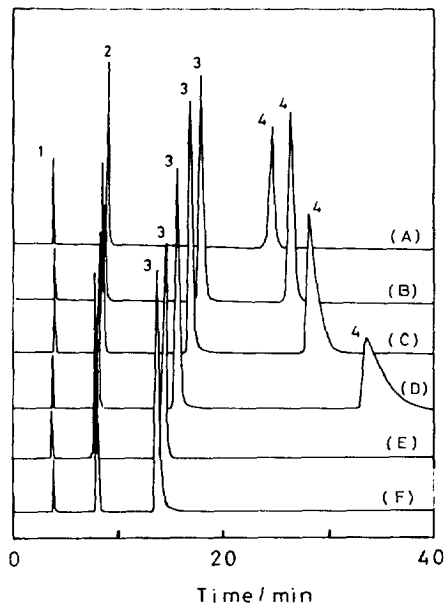


Fig. 5. Chromatograms obtained with magnesia-coated silica. Amount of magnesia coated on silica by drying at 110°C: (A) 0 (untreated silica); (B) 1400; (C) 2800; (D) 5400; (E) 7400; (F) 11 000 ppm. Solutes: 1 = benzene; 2 = dimethyl phthalate; 3 = pyridine; 4 = phenol. Mobile phase, 1% methanol-n-hexane; flow-rate, 1 ml/min; detection at 254 nm.

siderably by the magnesia coating. The elution behaviour of phenol was different to that of pyridine. The magnesia coating caused a strong retention of phenol, although the untreated silica exhibited a good separation ability. The 1400 ppm gel-coated magnesia still retained a good separation ability, but other gels lost this ability with increase in the amount of magnesia and caused distinct peak tailing. With the 7400 ppm coated gel, phenol could not be eluted at all within 60 min.

The effect of calcining on the separation behaviour of the magnesia-coated silica gels for these four solutes is shown in Fig. 6. The retention of dimethyl phthalate on the gels increased with increase in calcination temperature. This tendency has also been shown on silica [25]. The calcining of the magnesia-coated gels considerably affected the elution of pyridine and phenol. The retention of pyridine, which could be improved by the magnesia coating, had a tendency also to be strengthened with calcining, whereas, the elution of phenol was facilitated.

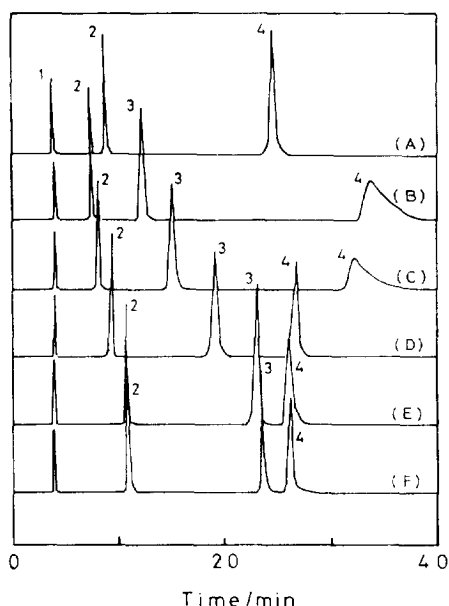


Fig. 6. Chromatograms obtained with calcined magnesia-coated silica. Treated silicas contained 5400 ppm of magnesia. Calcining temperature; (A) untreated; (B) 110; (C) 400; (D) 600; (E) 800; (F) 1000°C. Solutes and conditions are the same in Fig. 5.

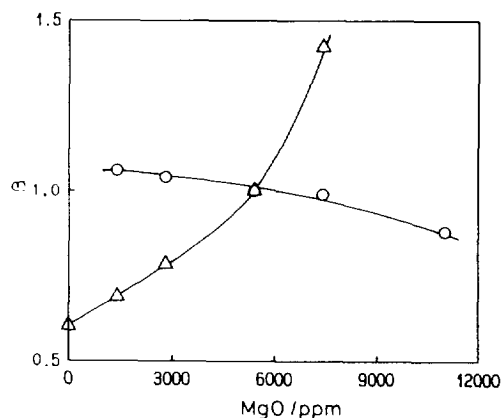


Fig. 7. Effect of amount of magnesia coated on capacity factor. \circ = Pyridine; \triangle = phenol.

Figs. 7 and 8 show the effects of the magnesia coating of silica and the calcining of magnesia-coated silica on the retention. The ratio of the capacity factor of pyridine or phenol to that of dimethyl-phthalate ($k'_{\text{pyridine}}/k'_{\text{DMP}} = \alpha_{\text{pyridine}}$ or $k'_{\text{phenol}}/k'_{\text{DMP}} = \alpha_{\text{phenol}}$) can be regarded as a measure of the interaction between the solute and the stationary phase. In Figs. 7 and 8, β is estimated as the relative value of α in each gel when α in the gel with 5400 ppm magnesia and dried at 110°C is defined as unity. These two graphs illustrate more clearly than the chromatograms the effects of magnesia coating and calcining on the retention behaviour of pyridine and

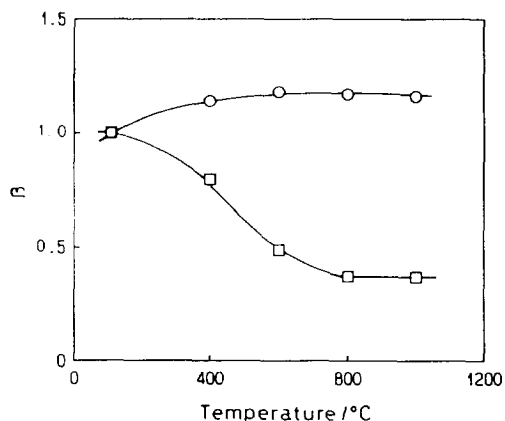


Fig. 8. Effect of calcining temperature on capacity factor. \circ = Pyridine; \square = phenol.

phenol. From these results, it is considered that (1) the specific interaction between silica and basic solutes such as pyridine is considerably improved by coating magnesia on the silica surface, but the dependence on the amount of magnesia coated is not very great, (2) coating with magnesia has a tendency lead to the loss of the excellent separation ability of silica for acidic compounds such as phenol, depending on the amount coated, (3) the lost separation ability for acidic compounds on coating can be recovered by calcining without a great influence on the separation of other solutes and (4), the separation of pyridine is not affected as much as that of phenol by the calcining.

The elution behaviour of pyridine and phenol is related to the surface acid strength. As described above, the coating of magnesia on silica diminishes the surface silanol groups, and consequently the acid strength of the gel is weakened. This would result in a better separation for pyridine, because of the lowering of both the solid acid–base interactions and the interactions between the surface silanol groups and pyridine. Conversely, the gel with a weakened surface acid strength would interact more strongly with phenol by acid–base interaction. The effect of calcining on the chromatographic behaviour can also be explained by the same interactions as those of coating. The relationship may be made clearer by the measurement of total acid and base amounts of the gel.

4. Conclusion

Magnesia-coated silica could be easily obtained by the proposed method, and retained the same physical properties as the commercially available silica used as the silica matrix. However, the separation ability of magnesia-coated silica was very different from that of the silica matrix, depending on both the amount of magnesia coated and the thermal treatment. The difference in the separation ability for the basic solute pyridine is noticeable. The separation ability for phenol was improved by calcining the

gel, although the retention of the acidic phenol was unfavourably influenced by the magnesia coating.

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