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Modified main groups metal oxides as potential active fillers for polymers

Summary — The demand for polymers exhibiting special properties has necessitated the modification of metal oxide polymer fillers currently in use to obtain adequate filling characteristics. Recent developments in the literature (also from the authors), in which the advantages of the applications of metal oxides as polymer fillers with special consideration of the dependence of their properties on origin and thermal treatment are presented. The acid-base and donor-acceptor properties of this group of fillers and also the dependence of their properties on electronic parameters is discussed in detail. The use of practical methods of oxide modification, such as precipitation, coprecipitation, gelation and impregnation is further discussed. The importance of defects in the oxide structure and the acidic properties resulting from their activity is presented. The possibility of application of these oxides in synthesizing organic/inorganic hybrid materials is also discussed.

Key words: polymer fillers, metal oxides, methods of preparation, modification, acid-base properties, donor-acceptor properties, structural defects, hybrid materials.

MODYFIKOWANE TLENKI METALI GRUP GŁÓWNYCH UKŁADU OKRESOWEGO JAKO POTENCJALNIE AKTYWNE NAPEŁNIACZE POLIMERÓW

Streszczenie — Zapotrzebowanie na polimery o specjalnych właściwościach spowodowało konieczność modyfikacji tlenków metali obecnie stosowanych do napełniania polimerów w celu uzyskania odpowiedniej ich charakterystyki napełniającej. Przedstawiono przegląd literatury (w tym prac własnych), w których omówiono ogólne zalety wykorzystania tlenków metali w charakterze napełniacza polimerów, uwzględniając zwłaszcza zależność istotnych użytkowych cech tlenków od ich pochodzenia oraz obróbki cieplnej (schemat A, tabela 1). Szczegółowo opisano kwasowo-zasadowe i donorowo-akceptorowe właściwości omawianej grupy związków (rys. 1 i 2), a także zależność ich właściwości od parametrów elektronowych (rys. 3, tabela 2). Scharakteryzowano używane w praktyce sposoby modyfikacji tlenków, mianowicie metodę strącaniową i współstrącaniową, żelowania oraz impregnacji (rys. 4). Dużo miejsca poświęcono też znaczeniu defektów w krystalicznej strukturze tlenków metali oraz ich kwasowości (schematy C i D). Zwrócono uwagę na możliwości wykorzystania tych tlenków w organiczno/nieorganicznych materiałach hybrydowych.

Słowa kluczowe: napełniacze polimerów, tlenki metali, sposoby przygotowywania, modyfikacja, właściwości kwasowo-zasadowe, właściwości donorowo-akceptorowe, defekty strukturalne, materiały hybrydowe.

ADVANTAGES OF METAL OXIDES AS POLYMER FILLERS

Recent advances in technology have necessitated the development of specialty polymers to meet technological, domestic and environmental requirements. This has involved the modification of neat polymers which no longer meet various technological specifications. Namely, the improvement of polymer properties can be achieved in two ways [1]:

- the development of a completely new type of polymer,
- the modification of those already in production.

The first option would involve a considerable amount of work hours and financial resources while the

second would only amount to a fraction of what is required for the first. For this purpose also existing polymers are being modified to achieve properties differing from those of the neat polymer. One of the modification methods is the use of active fillers. These are mainly solid inorganic additives of properties entirely different from the polymer and basically influence the polymer in:

- reducing production costs,
- initiating changes in processing due to a change in the melt viscosity especially when using extruders,
- reducing the overall level of shrinkage after moulding,
- boosting stiffness and heat distortion temperature,
- decreasing flammability,

- improving appearance,
- promoting or inhibiting ageing as may be required,
- boosting toughness.

The growing demand to modify polymers is reflected in the amount of global consumption estimated at 15 million tones annually. The filler market in Europe and NAFTA alone is estimated to be about 7.5 million tones and valued at € 3—4 billion. This market is however dominated by carbon black and calcium carbonate, but the portion of it of high performance fillers is in the 0.5 to 1.0 million ton range and valued at € 400—600 million [2].

The most popular filler today is calcium carbonate (CaCO_3) and a lot of work can be found in the literature on its filling properties [3]. Calcium carbonate however has limitations when the end-product are specialty polymers — especially requiring flame retardant, degradation, conductivity and protective coating properties. It is in this particular field of polymer modification that metal oxides play an important role.

The most popular flame retardant oxide fillers in thermoplastics are aluminum (hydr)oxide [4] (of commercial name aluminum trihydrate) and magnesium (hydr)oxide which are commonly used in the form of their hydroxides. Antimony oxide [5] and molybdenum oxide are also used as flame retardant fillers together with halogens and moreover act as smoke suppressants. Aluminum (hydr)oxide is also known to influence the thermal decomposition of polymers [6, 7].

In the filling process, the interaction that takes place between the filler surface and the monomer or polymer plays the deciding role in the formation of the modified polymer. The surfaces of oxides possess intrinsic properties in relation to the inner phase originating from the significantly reduced coordination of the elements leading to a higher reactivity (*e.g.* in adsorption). This is linked to the tendency to lower the local energy excess referred to as the surface energy as proposed by Krylow [8].

Moreover, the inner structure of main group metal oxides differs in a crucial manner from the band gap model typical of an ideal crystal lattice. This is attributed to the existence of stoichiometric and impurity defects,

which are responsible for the local donor and acceptor levels in the band gap. As a result, the band gap of main group metal oxides possesses properties closer to semi-conducting than to insulating. The defects present in the inner phase can also occur naturally in definite numbers on the surface of the solid and this results in an increase in energy and therefore in reactivity. In other words, the ability to influence the number of defects in the structure of the oxides in a characteristic manner leads to the modification of the reactivity of the surfaces of these oxides.

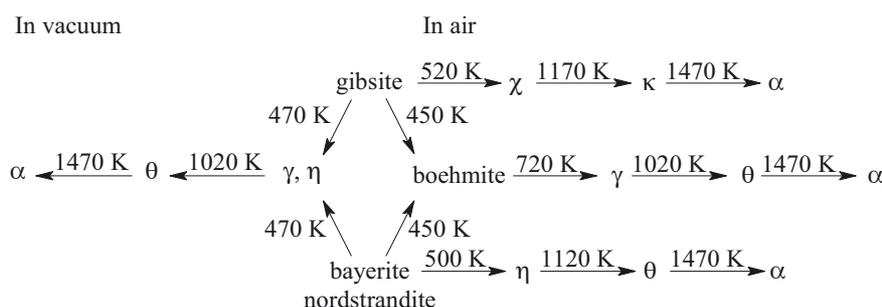
The challenge today in the applicability of metal oxides in their role as fillers is to modify them in order to improve the properties of systems in which they are already in use, and secondly, to open avenues for a wider range of applications in the future [9—11].

The aim of this paper is to shed light on the origin of the different properties which characterize metal oxides and to present methods of their modification which will make them suitable potential fillers for polymers.

PROPERTY DEPENDENCE ON OXIDE ORIGIN AND THERMAL TREATMENT

Metal oxides are different from metals; for instance they differ principally in conductivity. Oxides, in contrast to metals may be insulators, semiconductors, conductors or even superconductors [12]. Research on oxides is in most part, however, focused on their acid-base properties. The elucidation of these properties and the ability to take advantage of them is an invaluable tool in oxide applications.

The properties of metal oxides are, among others, determined by the source of the precursor, method of preparation and thermal treatment. These properties determine also their applicability as fillers in the polymer industry. A number of factors have to be considered before the decision to apply crystalline ore samples of aluminum and magnesium hydroxides over their amorphous synthesized counterparts. The nature of the precursor in precipitated hydroxides and the necessity to work at required temperatures generally below 250 °C in order avoid the dehydration of the hydroxide has been a matter of concern for polymer technologists. The influ-



Scheme A. Transformations of various types of alumina ores



Scheme B. Titania transformations during thermal treatment

ence of precursor and treatment of the various kinds of alumina ores to obtain crystalline species is illustrated in Scheme A [13].

The different forms of alumina obtained are characterized by specific acid and/or basic properties which are a common feature in metal oxides and have to be considered when working with them. Similarly, amorphous titania undergoes structural transformations when subjected to thermal treatment as presented in Scheme B [14].

The differences in the properties of MgO obtained from different synthetic and natural precursors are illustrated in Table 1 [15].

Table 1. Physical properties of MgO powders obtained at 960 °C (40 min) from different precursors *

| Precursors | ρ_{app} , g cm ⁻³ | ρ_{XRD} , g cm ⁻³ | Surface area**, m ² g ⁻¹ | Surface area, m ² g ⁻¹ | G_{BET} , nm | G_{XRD} , nm | $G_{\text{BET}}/G_{\text{XRD}}$ | P_T , % |
|------------|--|--|--|--|-----------------------|-----------------------|---------------------------------|-----------|
| Sulfate | 3.53 | 3.576 | 137.6 | 64.4 | 25.9 | 41.6 | 0.62 | 1.3 |
| Nitrate | 3.46 | 3.584 | 124.2 | 30.8 | 54.2 | 54.9 | 0.99 | 3.46 |
| Acetate | 3.44 | 3.581 | 105.0 | 28.9 | 57.7 | 57.9 | 0.99 | 3.94 |
| Dolomite | 3.42 | 3.585 | 47.3 | 16.5 | 101.1 | 53.1 | 1.90 | 4.60 |

^{*} ρ_{app} — apparent density; ρ_{XRD} — calculated density from X-Ray diffraction; G_{BET} — degree of agglomeration derived from specific surface area; G_{XRD} — degree of agglomeration derived from crystallite size; $P_T(\%)$ — total porosity.

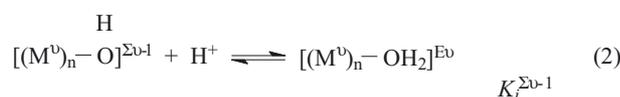
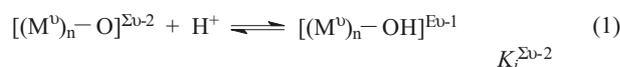
^{**} Values obtained for Mg(OH)₂ at 100 °C, 40 min.

The table shows that Mg(OH)₂ precipitated from different precursors do not share identical physical properties.

ACID-BASE PROPERTIES

The acid/base properties are responsible for the suitability of oxide phases in almost all their applications. These are also closely linked to the character (defects) and electronic properties of oxide surfaces. The Brønsted acidity which is dependent on the existence on the oxide surfaces of hydroxyl groups of varying proton affinity is of crucial importance to the sorption (physical and chemical) and catalytic activity of metal oxides [16, 17]. The behavior of hydroxyl groups at the oxide surface depends strongly on the composition of the oxide and the local chemical environment [18]. In a surface coordination around a metal ion as $M^{z+}O_m(OH)_n$ the Brønsted acid strength of -OH bonds increases as m increases and also as z increases. Depending on the type of surrounding metal cations, the accessible oxygen atoms on the surface possess varying properties. This leads to the formation of different types of hydroxyl groups determining the acid-base character of the oxide. The affinity of oxides to the hydroxyl group can be estimated by the constant K . This has been estimated by Heimstra *et al*

[19] as $\log K$ for various types of coordinated hydroxides. A two-stage proton adsorption process whereby the proton is bound first of all by the oxo, and then by the hydroxo group to form -OH and -OH₂ groups has been appropriately proposed and illustrated as [19]:



where n — represents the number of surrounding cations and v — the effective bond valence. The intrinsic affinity constant is therefore dependent on the configuration on the surface [20].

The experimental proton-binding isotherm of alumina and calculated proton affinity distribution $f(\log K)$

of $\gamma\text{-Al}_2\text{O}_3$ is presented in Fig. 1 [18, 21]. This is based on experimental titration calorimetry whereby the proton adsorption enthalpy is dependent on pH and the ionic strength. Three types of surface hydroxyls (I) terminal, (II) bridging and (III) triple-coordinated are identified which is in agreement with similar proposals by Knözin-

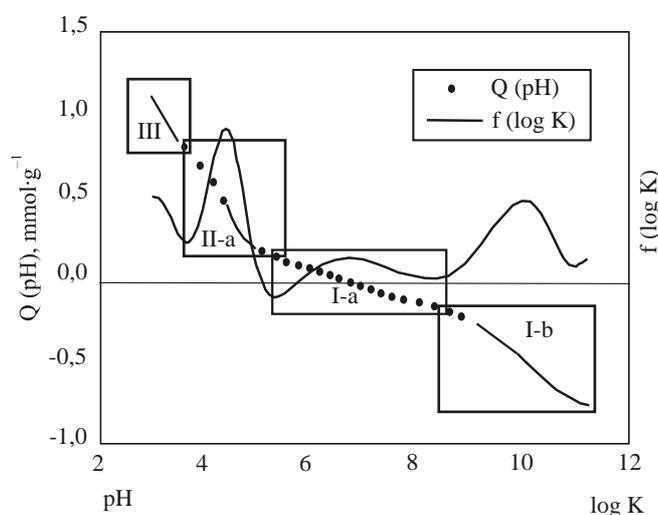


Fig. 1. Experimental proton binding isotherm from potentiometric titration of $\gamma\text{-Al}_2\text{O}_3$ and calculated proton affinity distribution

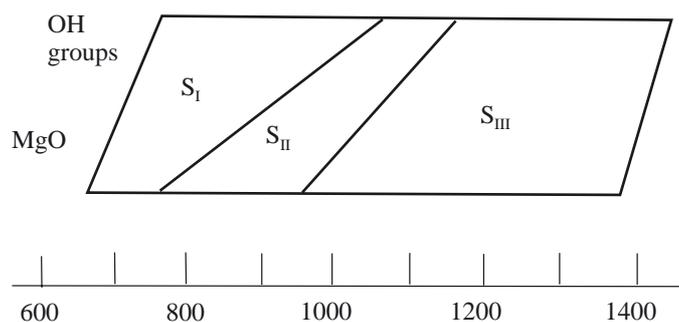


Fig. 2. Appearance of four types of sites (OH groups and S_I – S_{III}) on MgO as a function of temperature

ger and Ratnasamy (γ - Al_2O_3) [22] and Hattori's findings on the occurrence of different sites on MgO surfaces (Fig. 2) dependent on temperature [23].

Sites S_I , S_{II} and S_{III} differ in catalytic activity whereby S_I is generally active in isomerization of olefins, allyl amines and ethers, S_{II} is active in isomerization, H-D exchange and amination while S_{III} is active in hydrogenation reactions. The basicity on oxide surfaces is related to the availability of a pair of 2p electrons associated with oxygen ions. As in the case of acidity, coordination around the oxygen ion is also crucial, but in this case, the function of the charge of the metal ion is opposite to that expected in acidic behavior. Low cation charge and large cation radius lead to weaker bonding and hence more basic O^{2-} ions.

The basic strength of a solid surface is defined as the ability of the surface to convert an adsorbed electrically neutral acid to its conjugate base, i.e. the ability (expressed as the Hammett's function H) of the surface to donate an electron pair to an adsorbed acid. The amount of base is expressed as the number (in mmoles) of basic sites per unit weight or per unit surface area of the solid.

It shows therefore, that not only the nature of the compound, but also the particular crystal plane under consideration are important in determining the acid/base properties.

Particularly large differences might be expected with oxides such as ZnO, where a range of polar (only Zn or O exposed) and nonpolar (charge neutral Zn-O) planes are available.

Lewis acidity/basicity is a crucial parameter when working with metal oxides. Lewis acidity depends on the existence of exposed metal cations at the surface having empty orbitals and positive charges that can interact with the filled orbitals and/or negative charges or dipoles of donor molecules. Lewis acid strength is expected to depend therefore on factors such as the ion charge, degree of coordinating unsaturation and the availability of empty orbitals (the bandgap). The Lewis acid strength of oxides is dependent first and foremost on the charge of the cation, the coordination number and the stereochemical accessibility of vacant orbitals (bandgap).

PROPERTY DEPENDENCE ON ELECTRONIC PARAMETERS

Metal oxides can be classified as acids and bases on the basis of their electronic parameters such as electronegativity, electron affinity, work function and Smith parameter (α) [24]. A schematic representation of the electronic structure of an intrinsic semiconducting oxide in relation to a strong acid and a strong base is presented in Fig. 3. For s and p elements, the gap E_g illustrating the energy difference between the bottom of empty ns^0 me-

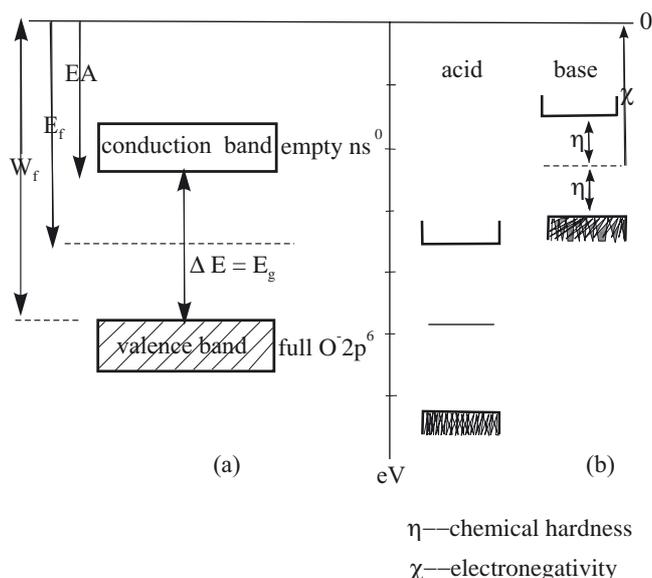


Fig. 3. Schematic representation of the electronic structure of an intrinsic semiconducting oxide (a), and its application to a strong acid and base [24]; η — chemical hardness, χ — electronegativity

tal orbitals (conduction band) and the top of the full $2p^6$ orbitals of the oxygen anions valence band is equivalent to the chemical hardness η . Similarly, the energy at the Fermi level E_f is equivalent to the electronegativity χ .

Examples of some acidic and basic oxides are given in Table 2. The Smith parameter has been derived from thermodynamical data and accounts for the acid-base characteristics of oxides. This is a valuable tool in matching the acid-base properties of an oxide to the filler requirements in polymers.

It can be seen that acidic oxides possess high electronegativity, high electron affinity and positive values of Smith parameter (α). On the other hand basic oxides exhibit low electronegativity, low electron affinity and negative values of the Smith parameter (α).

Apart from the acid-base properties of oxides presented according to the general Lewis or Brönsted definitions, the surfaces of oxides of the main group metals exhibit the single-electron donation or accepting properties. These specific redox properties are responsible for the ability to reduce or oxidize the molecules interacting

T a b l e 2. Examples of acidic and basic oxides illustrating electronegativity* (Pauling unit), work function (Wf in eV), and α Smith parameters [24]

| Oxide | $\chi_{ox}(P.u)$ | EA(eV) | Wf(eV) | α (Smith) | Oxide | $\chi_{ox}(P.u)$ | EA(eV) | Wf(eV) | α (Smith) |
|--------------------------------|------------------|--------|--------|------------------|--------------------------------|------------------|--------|--------|------------------|
| Cs ₂ O | 1.23 | 3.03 | 6.11 | -15.2 | ThO ₂ | 2.58 | 6.19 | 10.38 | -3.8 |
| Rb ₂ O | 1.44 | 3.56 | 6.21 | -15 | Bi ₂ O ₃ | 2.46 | 6.45 | 9.42 | -3.7 |
| K ₂ O | 1.44 | 3.26 | 6.54 | -14.6 | FeO | 2.33 | 6.31 | 8.80 | -3.4 |
| Na ₂ O | 1.49 | 2.64 | 7.47 | -12.5 | Lu ₂ O ₃ | 2.39 | 5.12 | 10.32 | -3.3 |
| BaO | 1.75 | 2.80 | 8.83 | -10.8 | ZnO | 2.36 | 5.78 | 9.52 | -3.2 |
| SrO | 1.88 | 3.52 | 8.93 | -9.4 | CeO ₂ | 2.66 | 6.87 | 10.16 | -2.7 |
| Li ₂ O | 1.531 | 1.28 | 9.05 | -9.2 | CuO | 2.44 | 7.16 | 8.58 | -2.5 |
| Tl ₂ O | 1.58 | 4.85 | 5.78 | -6.8 | In ₂ O ₃ | 2.52 | 6.51 | 9.71 | -2.4 |
| Y ₂ O ₃ | 2.33 | 4.85 | 10.23 | -6.5 | NiO | 2.27 | 5.33 | 9.42 | -2.4 |
| La ₂ O ₃ | 2.31 | 5.10 | 9.87 | -6.1 | BeO | 2.24 | 2.06 | 12.53 | -2.2 |
| Ce ₂ O ₃ | 2.41 | 6.02 | 9.54 | -5.8 | Al ₂ O ₃ | 2.52 | 4.08 | 12.15 | -2 |
| Pr ₂ O ₃ | 2.35 | 5.64 | 9.60 | -5.8 | Fe ₂ O ₃ | 2.65 | 7.12 | 9.91 | -1.7 |
| Eu ₂ O ₃ | 2.34 | 5.18 | 9.99 | -5.1 | Ga ₂ O ₃ | 2.57 | 6.01 | 10.51 | -1.6 |
| Ag ₂ O | 1.99 | 5.58 | 7.50 | -5 | Cu ₂ O | 2.07 | 5.09 | 8.48 | -1 |
| Gd ₂ O ₃ | 2.37 | 5.46 | 9.90 | -5 | H ₂ O | 2.55 | 2.21 | 14.21 | 0 |
| MnO | 2.18 | 5.07 | 9.15 | -4.8 | Sb ₂ O ₃ | 2.39 | 4.91 | 10.54 | 0 |
| Dy ₂ O ₃ | 2.05 | 4.87 | 8.59 | -4.7 | TiO ₂ | 2.81 | 7.28 | 10.66 | 0.7 |
| Ho ₂ O ₃ | 2.43 | 5.67 | 10.0 | -4.5 | SiO ₂ | 2.81 | 4.59 | 13.36 | 0.9 |
| MgO | 2.01 | 3.00 | 10.17 | -4.5 | SnO ₂ | 2.73 | 6.75 | 10.75 | 2.2 |
| PbO | 2.07 | 5.17 | 8.38 | -4.5 | WO ₃ | 3.02 | 8.03 | 11.15 | 4.7 |
| Yb ₂ O ₃ | 2.38 | 5.25 | 10.13 | -4.5 | MoO ₃ | 2.98 | 7.45 | 11.54 | 5.2 |
| CdO | 2.23 | 5.90 | 8.57 | -4.4 | SeO ₂ | 2.77 | 6.17 | 11.55 | 5.2 |
| Er ₂ O ₃ | 2.39 | 5.46 | 10.00 | -4.3 | CrO ₃ | 3.21 | 8.85 | 11.48 | 6.6 |
| Tm ₂ O ₃ | 2.36 | 5.32 | 9.97 | -4.2 | P ₄ O ₁₀ | 3.05 | 5.55 | 13.84 | 7.5 |
| CoO | 2.31 | 5.93 | 9.04 | -3.8 | Mn ₂ O ₇ | 3.27 | 9.38 | 11.32 | 9.6 |

* Electronegativity in Pauling units derived as the geometric mean of the atomic electronegativities; for an oxide with the formula M_mO_n will be as follows: $\chi_{oxide} = [(\chi_M)^m(\chi_O)^n]^{1/(m+n)}$.

with them (adsorbed physically and chemically) on their surfaces to the respective anion — or cation-radicals. As we have earlier observed, these centers are capable of generating organic radicals in reactions, in which the initial step is the break-off of a hydrogen atom.

The acid-base and donor acceptor activity of oxide surfaces is influenced by:

- coordination infrastructure of the surface atoms,
- redox properties of the oxide,
- oxidation state of the surface.

To a limited extent the above properties can be controlled (if not specified) by the chemist through various preparation methods.

Surface coordination infrastructure can be controlled by the choice of crystal plane exposed and by the preparation procedure for materials, which permit metastable surface structures to be formed.

OXIDE MODIFICATION

The specification of redox properties is largely a matter of the choice of oxide. As earlier indicated, metal oxides find applications in industry generally as catalysts. The requirements stipulated for oxides in catalysis also corresponds to those which are expected in the polymer industry in their role as potential fillers. These are among others:

- high and stable activity,
- high and stable selectivity,
- controlled surface area and porosity,
- good resistance to poisons,
- good resistance to high temperatures and temperature fluctuations,
- good dispersion of reaction heat around active components,
- high mechanical strength,
- no uncontrollable hazards,
- environmental friendliness.

In synthetically obtained oxides, two preparation routes determine the extremes of traditional procedures used for their preparation:

1. precipitation (with the variant of coprecipitation) and gelation,
2. impregnation (with such variants as ion exchange, deposition, and grafting).

Precipitation

In the precipitation route, a new solid phase is obtained by the “blending” of proper agents (precipitating agents) from a liquid medium. The resulting precipitate is treated in various ways to obtain the final active product. During these transformations, both mechanical properties of the oxide and those intrinsically related to

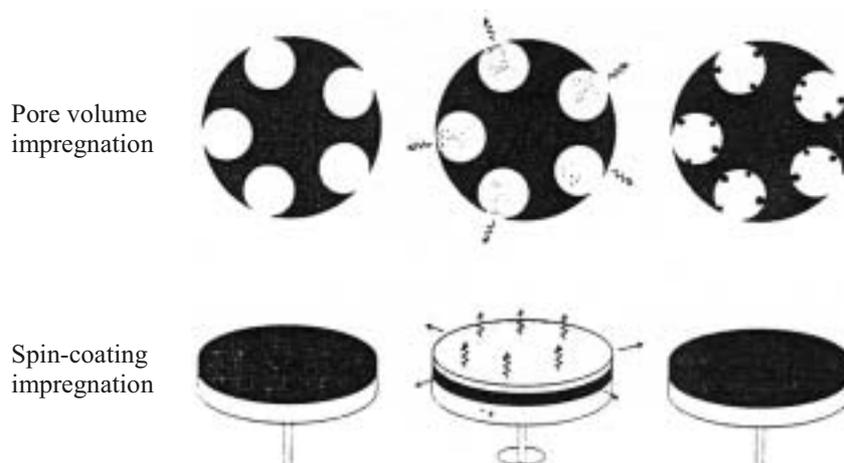


Fig. 4. Analogy of spin coating with incipient wetness impregnation [25]

its performance undergo changes to produce the desired system.

$\text{Mg}(\text{OH})_2$ used in various applications is obtained through this method. The hydroxide is precipitated from a diluted (10 %) solution of magnesium nitrate with concentrated ammonia (25 %). The ammonium nitrate obtained to be further used as raw material in the fertilizer industry. MgO is obtained through the thermal dehydration of the hydroxide at temperatures at or above 450°C . This fraction has the advantage over ore-derived MgO species by virtue of the minimal impurity level and is the first choice for catalysis and as fillers for polymers.

Coprecipitation

In the coprecipitation method, two solid phases are precipitated from an aqueous solution. The phases can act as a dual-support oxide system or as a support-active phase oxide system. In coprecipitation, many factors which lead to the characteristics of the final system have to be considered. These are: the concentration of each salt content in relation to the precipitating solution, the salt-salt interaction before coprecipitation, effective mixing and precipitation rate — all contribute to the morphology of the obtained oxide-oxide system.

Gelation

The gelation method generally referred to as the sol-gel method involves the continuous transformation of the solution into a hydrated solid precursor. This is a much slower process than precipitation or coprecipitation (which takes place instantly), but provides a greater possibility of modification during preparation.

Impregnation

This is the modification of oxides by the deposition on them of active phases dissolved in the aqueous solutions of their precursors. This is achieved either through

wet or dry impregnation routes. In the wet method, the support is immersed in the solution of the active phase precursor and then removed and dried. This is sometimes necessary whenever only a monolayer coverage is required. In the dry impregnation method, an accurate volume corresponding to the liquid absorbing capacity of the support oxide is applied. The dry impregnation method is preferred for it ensures an accurate deposition of the required amount of the active phase. These methods allow for the deposition of oxides from their salts (generally nitrates), as well as metals (Pt, Pd, Rh) which are deposited from their acidic solutions (*e.g.* H_3PtCl_6). A graphic illustration of deposition on oxides by impregnation methods is illustrated in Fig 4. As use is made of hydrodynamic forces to immobilize the solvent, these methods can be applied when there is not sufficient chemical interaction between support and precursor [25].

Impregnation methods are used also to deposit multiple layers and/or different types of active phases. It allows for the deposition of metals on monolayer oxides and *vice versa* on supports and the possibility of coimpregnation of two active phases from a single solution.

The obtained active phase/support system is dried and later calcined at higher temperatures in order to initiate an appropriate interaction between them. The interaction that takes place between a deposited active phase and support has been reported by us recently [26].

The modification of oxides leads to systems whose properties reflect a change in the properties of the deposited or mixed medium, those of the support oxide, or the formation of an entirely different system. The changes caused in oxide-oxide systems is attributed to the strong oxide-oxide interaction (SOOI) [27]. This interaction has paved the way for the application of oxide systems in catalysis.

Temperature-Programmed Reduction (TPR) with a H_2 /carrier gas stream is a differential thermal analysis method used to evaluate the extent of interaction between a reducible deposited oxide and its support. This

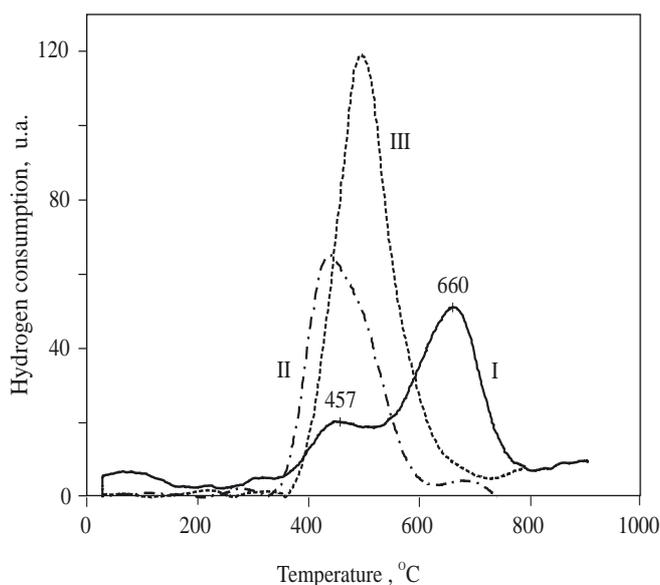


Fig. 5. TPR profiles of $Ni_xO_y/Co_mO_n/SiO_2$ [28]: I — Ni_xO_y/SiO_2 , II — Co_mO_n , III — $Ni_xO_y/Co_mO_n/SiO_2$

is reflected in changes in the reduction temperature peak and the amount of hydrogen consumed during reduction. This phenomenon is illustrated in Fig. 5 where the TPR of $Ni_xO_y/Co_mO_n/SiO_2$ multiple phase oxide system produces a single reduction peak after preparation and thermal treatment. Monooxide deposited Ni_xO_y and Co_mO_n phases on SiO_2 produced reduction peaks at 457 and 660 °C for Ni_xO_y and at 441 °C for Co_mO_n . A deposition by dry impregnation method of both phases on SiO_2 , first CoO followed by the NiO species and thermal treatment at 550 °C produced a single reduction peak. This is attributed to the strong interaction that has taken place between oxide phases and support.

The inability of metals (Pt, Pd) deposited on Al_2O_3 to adsorb hydrogen after high temperature treatment is attributed to the strong metal support interaction (SMSI) [28].

These interactions are a result of electron transfer from the deposited medium to the support and open up a wide variety of systems whose properties can be explored as potential fillers for polymers.

A novel method of the preparation of oxides has also been recently proposed by Gedanken [29]. This involves the sonification of the carbonyl compounds of metals in solvents to obtain nanosized particles of oxides. The oxides obtained through this method are generally characterized by a uniform morphology although agglomeration is a cause of concern. The precipitated oxides are generally used as supports or catalysts in their pure forms.

ROLE OF DEFECTS

The origin of surface defects in the crystal lattice containing metal cations and oxygen anions of lowered co-

ordination, and also hydroxyl groups of specific properties is the intensive dehydration process of the oxide surfaces commencing at about 350–450 °C, and terminating at temperatures as high as even 1500 °C (MgO).

A classical dehydration mechanism of MgO was proposed by Freud *et al.* [30].

The reaction pathway proposed by the authors of [30] leads to a decrease in the cation coordination of magnesium (in the vicinity of anion vacancies) which in addition leads to a decrease in the coordination number of oxygen atoms.

As has been shown by us [31], thermal treatment has a significant influence on MgO species regarding ionic properties (basicity) and radical (single-electron donation) properties. Thermal treatment of MgO in the 450–550 °C temperature range leads to species possessing dominant ionic properties, while MgO species treated at temperatures between 700 and 800 °C possess dominant radical character.

The chemistry of metal oxides is closely linked to the occurrence of defect equilibrium present in every oxide [32]. The reason for this is that first and foremost defects are responsible for the properties of oxides in many processes. Secondly, the concentration of defects (especially in modifications) is associated with the variability of the valence or oxidation state. Defects primarily occur in the form of lattice vacancies, interstitials, impurities or dopants and it is regarded that the overall effect of their interactions leads to an equilibrium in the solid.

Two types of defects have been identified in MgO for instance. These are the O vacancies or Fermi centers (F centers) and the cation vacancies. An O vacancy is neutral and possesses two remaining electrons which may be trapped by the unbalanced coulomb potential linked to the vacancy. Removing one of these electrons gives the F^+ center. The V^- centers are Mg^{2+} vacancies and are associated with electronic holes which may be regarded as an O^- ion. In the modification of MgO by cations Li^+ , Na^+ , K^+ , a substitution of Mg^{2+} takes place whereby one electron is removed from the neutral solid thereby creating a hole and the dependence in charge substituted by and O^- from a neighbouring site.

In the case of SnO_2 , this type of doping can be performed by replacing Sn with Sb (in the form of Sb^{5+}) or some O^{2-} by F^- . At doping modification levels exceeding $5 \cdot 10^{18}$ ions per cm^3 an overlapping takes place leading to the semiconductor-to-metal transition. The introduced electrons can be regarded as occupying a free-electron-like conduction band based on the Sn 5s atomic orbitals. These conduction electrons give rise to a plasma excitation which, unusual for a metal, lies in the infrared. This phenomenon together with the 3,6 eV band gap lying outside the visible spectrum characterizes modified SnO_2 with its transparent metal properties which has led to its various applications [33].

The last paper by Prof. S. Malinowski [34] seems to be of great interest from the point of view of the interactions

between oxide defects in the earth's crust and polymers. A hypothesis was formulated in this work of the alternative inorganic origin of natural gas and crude oil on earth as a result of the reaction between carbon dioxide molecules and water. This reaction is reported to be able to proceed over lattice defects in the earth's crust, similar to those occurring during the calcination of alkali metal oxides, according to the reaction scheme:



ROLE OF ACIDITY OF METAL OXIDES

The acidity of pure main group metal oxides does not exceed the value of an 80% concentration of sulphuric acid while the basicity of the strongest solid base is equivalent to a fraction of a molar concentration of a hydroxide solution.

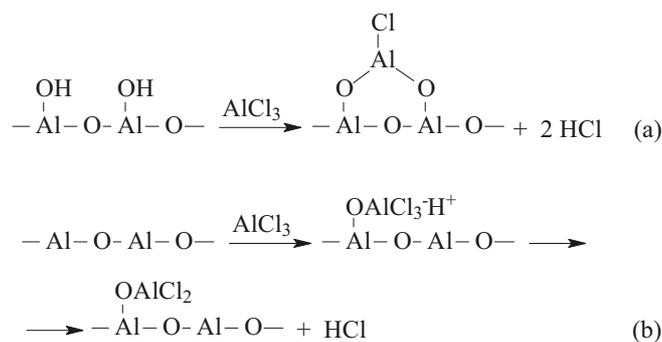
The acid strength of a solid oxide system can be modified chemically to higher values in a crucial manner.

The first, on the basis of natural minerals, modification method of the acidity of oxides is the preparation of mixtures comprising of two oxides — silica-alumina, mixed gels $\text{SiO}_2\text{-TiO}_2$, $\text{SiO}_2\text{-MgO}$, $\text{SiO}_2\text{-B}_2\text{O}_3$ etc. The origin of the increase in acidity of these mixed systems as compared to their single oxide counterparts has always been a topic of controversy and the acid strength of synthetic systems obtained in this manner is equivalent to a 100% concentration of sulphuric acid.

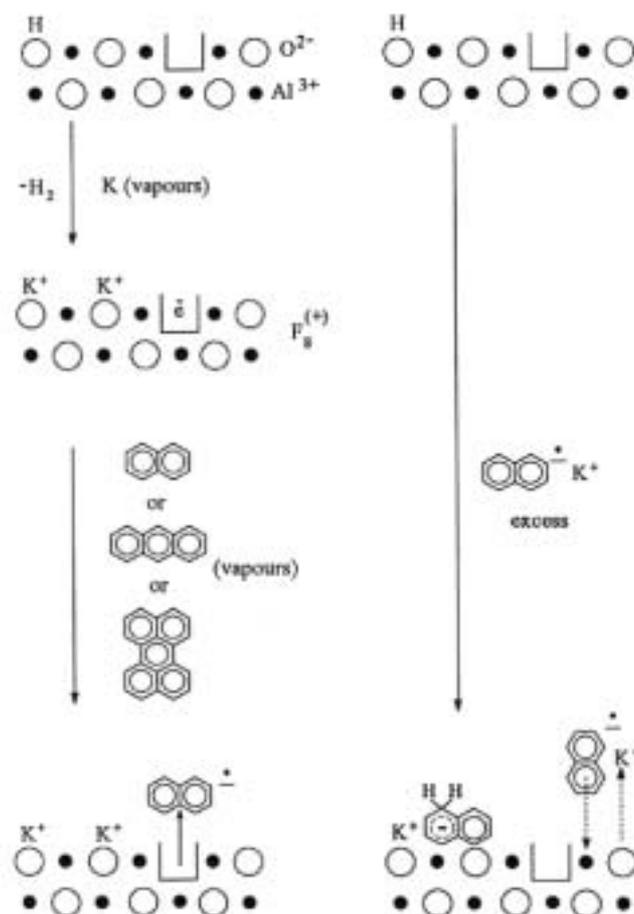
A dramatic increase in the surface acidity of main group oxides can be achieved through the selective reaction with vaporized Lewis acids (e.g. AlCl_3 , BF_3 , SbCl_5) or by impregnation with 100% sulphuric acid [35, 36]. These reactions lead to the formation of surface groups of strength referred to as superacid and proceed according to Scheme C.

Oxide systems capable of possessing strong acidic and basic properties (an impossible phenomenon with solutions) have been successfully synthesized by the impregnation of MgO with 100% H_2SO_4 or 80% H_3PO_4 .

The vapor deposition of alkaline metals on the surfaces of MgO and $\gamma\text{-Al}_2\text{O}_3$ leads to systems of superbasic



Scheme C. Mechanism of acidity enhancement of $\gamma\text{-Al}_2\text{O}_3$ with AlCl_3



Scheme D. Synthesis of ion radical species on $\gamma\text{-alumina}$ surface [33]

properties capable of removing a proton from a toluene molecule ($\text{pK}_A = 35$). These systems also possess remarkable single-electron donor properties [37]. These single-electron properties are particularly important when considering metal oxides as potential polymer fillers. Various forms of radical modifications of main group oxides are presented in Scheme D with $\gamma\text{-Al}_2\text{O}_3$ as example. The left column represents the synthesis by adsorption of polyaromatic hydrocarbons (naphthalene, anthracene or phenanthrene) on the surface of $\gamma\text{-Al}_2\text{O}_3$ -potassium system rich in F_s^+ centers and the right one — radical modification of this oxide by the chemical immobilization of naphthalene anion radical salt (potassium naphthalenide) on the surface of $\gamma\text{-Al}_2\text{O}_3$.

Systems possessing remarkable single-electron properties exhibit extraordinary activity in hydrogenation, dehydrogenation and isomerization reactions of alkenes as well as in Fischer-Tropsch reactions with CO or CO_2 . They are also known to be active in the polymerization of alkenes. The relation between acid-base reactions in the structure and conductivity has been presented by Wiczorek and coworkers. The addition of species containing Lewis acid centers AlCl_3 [38] and AlBr_3 [39] have been found to enhance the ambient temperature conductivities of ethylene-based polymers.

HYBRID MATERIALS

A similar concept to the modification of oxides and their applications in polymer filling is the synthesis of organic/inorganic hybrid materials. Nanocomposite hybrid materials are high value materials with potential applications, among others, in optics [40], electronics, catalysis and protective coatings. Reviews on the synthesis of these novel nanocomposite materials have been presented by Matyjaszewski (radical polymerization) [41], Sanchez [42] and Kickelbick [43]. The integration into inorganic particles of polymers and *vice versa* are based on the similar principles of preparation (*e.g.* sol-gel) and modifications (*e.g.* impregnation) of metal oxides. The properties of the final hybrid material is closely linked to the properties of the starting materials and the interactions which take place between them. A simple classification of hybrid systems into two types was given by Sanchez *et al.* Type I is characterised by the fact that no covalent or iono-covalent bonds exist between the organic and inorganic components but only weak interactions. This is an analogical situation to deposited phase/SiO₂ system in oxide modification. In type II hybrid networks, the inorganic and organic components are bond by stronger chemical bonds which could be of the covalent, iono-covalent or of Lewis acid-base interaction. The modification of oxides such as γ -Al₂O₃, TiO₂ and MgO and the resulting post interaction strong chemical bonds are also based on analogical principles.

The possibility of application of a wide range of precursors (metal alkoxides and organo-functional metal alkoxides) provides the opportunity to synthesize innumerable species of hybrid materials.

CONCLUSIONS

The modification of oxide fillers has proved to be an essential and cheap route to obtaining specialty polymers. It has been shown that modification possibilities are immense and can only be limited by the researcher's imagination. Modifications are means of tailoring oxides to meet specific needs and this is achieved one way or the other by taking advantage of the acid/base, redox and defect properties of both the support and the deposited modifier. Modified oxides therefore possess the potential of a wide range of future applications in the chemistry of polymers.

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