Sciences & Technologie **A** – **N°38**, Décembre 2013 .15-19.

OBTENTION OF SOLID PHASES ADSORPTIFS BY SYNTHESIS AND TRANSFORMATION

R. NASRI, A. MAGHCHICHE, A. HAOUAM

Laboratoire de Pollution et Traitement des Eaux
Université Mentouri Constantine, ALGERIA

Reçu le 27/03/2012 – Accepté le 23/11/2013

Résumé

L'industrie de la production des métaux et alliages a connu un fort développement durant les dernières décennies, et sous la pression et l'augmentation de la demande mondiale en termes des produits issus de ces procédés de raffinage ceci à engendré un sous produit de raffinage dit, laitier d'aciéries ou scorie de fonte. Ces laitiers sidérurgique sont produits en milliers de tonne à l'usine sidérurgique d'ANNABA Algérie, constituants ainsi un énorme problème environnemental et écologique à l'échelle locale. Le travail de recherche dans cet article rentre dans un vaste projet de valorisation des sous produits, naturels et artificiels, l'agroalimentaire, les plantes à usages domestiques et cosmétiques. L'axe de recherche spécialisé dans le domaine de la préparation des phases solides adsorbantes se situ dans ce grand projet. Le travail actuel se penche sur le laitier sidérurgique de l'aciérie d'El- Hadjar dans le but de valoriser ce sous produit, qui rentre dans le domaine du développement durable.
Mots clés: Haut fourneau, Scories, environnement, écologie, sous-produits

Abstract

The industrial production of metals and metalloids had known a huge development in the last decades. Under the augmentation of world demand on refined products of consumption, things that has been traduced by some sub products, spatially refined iron in high furnaces. The byproducts named scoria, its source is El Hadjar plant, which constitutes an environmental and ecological problem. The work presented is a part of a huge project witch concerns the valorization of natural and artificial sub products, the agro-alimental, local herbs, for medical and cosmeticology uses. The research axe, specialized in preparing adsorbent solid phases is situated in our global project of research in which we are aiming to find a better use for the sub product of the High Furnace, (**H.F**) in order to giveitother values. The memory of this publication spreads on a bibliographic study; followed by experimental works from witch we obtained good results.
Keywords: Blast furnace, slugs, environment, ecology, sub-products

ملخص

الإنتاج الصناعي العالمي عرف في العشريات الأخيرة تطورات ضخمة. وبسبب الطلب العالمي على المنتجات النقية الاستهلاكية وهذا الأمر الذي تطور عنه تكون منتجات تحتية كثيرة. بالنسبة لصناعة الحديد والصلب بالحجار فإن ناتج الخبث صار بكميات كبيرة مما جعله مصدرا لتلوث المحيط و خطرا على البيئة. العمل البحثي المقدم هو جزء من برنامج واسع يهتم بزيادة قيمة المنتجات التحتية للصناعات كالنباتات الطبية والصناعات الزراعية .
محور البحث الخاص بتحضير الأطوار الصلبة المازة متواجدة بمشروعنا البحثي والذي مفاده إيجاد استخدامات جديدة بقصد زيادة قيمته المادية وخاصة خبث الحديد لمصنعبالحجار.

الكلمات المفتاحية، الفرن العالي، خبث الحديد، البيئة، علم البيئة، المنتجات الثانوية.

Introduction :

The wide utilizations of solid phases having organic or inorganic origin in adsorption have been acquired a great importance [1].The importance in many technologic applications like, dying, catalysis, drugs and in medicinal domains [2]. The solid phases of adsorption are applied in the obtaining of crystal fibers; petroleum extraction and in paints also [3].

It is important to distinguish between adsorption and absorption in solids; the first means that concentration on the surface is greater, in the second it means the penetration of the substance in the solid phase. The adsorption is a surface phenomena and this criteria is applied in the description of the phenomena were the concentration of the material on the surface of adsorption is greater than that of the environ ant solution [4].

The adsorption is that operation where the surface of the solid sequestrates the molecules of the fluid on the solid surface. To exprime the quantity of material adsorbed from this solution at a given temperature on unity of surface the following relation is used:

$$X/m = KCn.$$

Inorganic solid phases:

The silicates - the chemistry of silicone is like that of carbon chemistry in many facets. The silicone forms the SiH4 and some higher hydro silicones chains compounds, but the Si-O chains are more important than Si-H and Si-Si bonds. The silicone atom forms single bonds more than multiples bonds. Ex. Si-O-Si; C=O in carbon. The silicon represents the second element spread in nature with 26 % of the earth crust and the SiO2 compound is the most one in nature [5].

The oxide compounds of silicone can be obtained by two ways: the first is its extraction from mines, beaches and streams; the second is by synthesis [6].

Experimental part:

Synthesis of silicates - The synthesis of silicates begins with the etherification of the tetra-halo silicone, especially SiCl4 with low molecular alcohols (C5) as follows:

$$SiCl4 + 4\ ROH \longrightarrow Si\text{-}(OR)\ 4 + 4\ HCl \quad (1)$$

R = (CH3), C2H5 .... ECT n = 1.....5

The tetra alcoxy silicone after treatment with alcohol in basic medium (NH3 or NH4OH) at low temperature (- 8° ⟶ + 5°C) will give silicates as follows:

$$Si\ (RO)4 + R'OH \longrightarrow (SiO2)n + H2O \quad (2)$$

The solid particulate obtained varies in diameter with the variation of molecular masse of the alcohol.

We began the synthesis of silicates by the synthesis of esters by the reaction of the tetrachloro silicone with alcohol in presence of sodium methoxyde.

1 - The alcoxy silicone is prepared by adding freshly distilled SiCl4, (Te = 329 K), drop by drop to the absolute alcohol on agitation. When all equivalent of SiCl4 is added, a quantity of NaOCH3 is auditioned to the reaction in order to equilibrate the HCl gas produced by the reaction. The product of the reaction was washed rapidly by distilled water and alcohol mixture, separated from the fluid wash, and distilled under reduced pressure (vacuum). By this way we prepared the methoxy; ethoxy; butoxy and pentoxy tetra esters of silicone.

2 - Methoxy-silicone: Methoxy silicone was prepared by adding tetra chloro silane (TCSi) to methyl alcohol in presence of sodium methoxyde:

$$SiCl4 + 4\ CH3OH + NaOCH\ 3 \longrightarrow Si\ (OCH3)4 + 4\ CH3OH + 4\ Na\ Cl \quad (5)$$

To 162 ml methanol absolute in three necked round bottomed flask (V = 250 ml) in a bath at a temperature of 35 °C; the balloon was supplied with a refrigerant and mechanical sheerer. 115 ml of SiCl4 are added drop by drop under steering, time of 40 min, in that time a current of dry air is bubbled in the reactor. The bubbling of air was stopped and agitation continued for other 15 min. After that the solution is heated for 30 min. For eliminating the residual HCl gas. The liquid is distilled under vacuum.

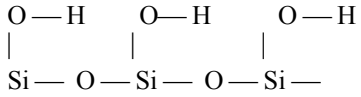
3 - Ethoxy silicone- The tetra ethoxy and tetra pentoxy silicones are prepared in the same manner like methoxy ester by respecting the molar concentration:

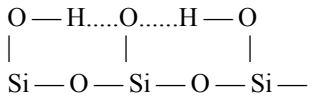
$$SiCl4 + 4\ C5H11OH \longrightarrow Si\ (OC5H11)4 + HCl \quad (6)$$

4 - The ethoxy ester was prepared under low temperature condition by putting 130 ml absolute methanol in a three necked flask with a refrigerant, mechanically steered in a freezing bath. 57 ml of SiCl4 are added slowly from a dropping funnel supplied with tubing, ranging to the bottom of the flask; steering is continued during the time of reaction. Dry air is bubbled in the solution in order to evacuate (in water) the HCl produced as a byproduct. The solution was treated in the same manner as above to obtain the ester.

Preparation of the solid phase of adsorption:

The surface of silicate is formed of hydroxyls groups linked to siliceous atoms by covalent bonds. The hydrogen groups appear free or bounded by hydrogen as follows:

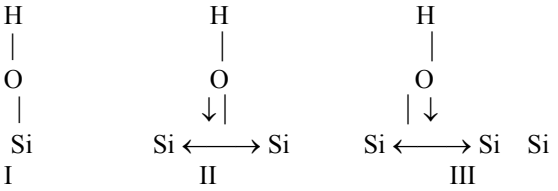




This description is supported by physical and chemical an experience which indicates that, in silanols group (SiOH); the proton has a marked positive character than in carbonyl group (C-OH). The important charge on the proton may be the result of the formation of a π bond, between one of the pair of electrons none associated to the oxygen and none occupied d orbital of the siliceous atom.

In this manner, electron displacement is produced from the O-H bond to the O atom. The calculus of integral orbital overlaps indicate that the probability of existence of this type of bonds, especially when the orbital d is the ultimate, so as in the case of siliceous molecule.

This situation is described by the following resonance structure.



Concerning molecular silanols, only structures I and II are important; meanwhile in surfaces I and II structures, exist one possible contribution of structure III. This confers to silanol groups of surface, one more acid character than molecular silanols.

The solid particulates of $(SiO_2)_n$ are synthesized in different shapes (volumes) according to the ester utilized. The diameter of the particulate differs in function of the alcohol utilized as follows; methanol, ethanol, and propanol ECT.....

These solid phases are produced with different ways:

1 - In a round bottom flask of one liter we put 600 ml of absolute ethanol; the reactor is dotted with a refrigerant, a mechanically steered. The dispositive of reaction is put in a freezing bath, below - 5 °C, in which we added dry NH_3 for a time of two hours, to liquefy the ammoniac. Conserving the temperature we add 40 ml of the $Si(OC_2H_5)_4$ ester, drop by drop from a dropping funnel with a gentle steering at first; when the solution begins to be opaque the steering is augmented. The steering is continued 10 min. after the complete addition of the ester. The agitation is stopped and after settling, the solid phase is faltered, washed which distilled water till neutral pH and dried at 40°C sub reduced pressure; with a product of ≅ 85%.

2 - In the same manner as above and in the same conditions, we take 200 ml of absolute ethanol to which we added 70 ml of NH_4OH 25%. To the solution we added another solution of 100 ml ethanol absolute and 12 ml ethoxy ester drop by drop. A solid phase is obtained which differs in size in function of the ester utilized.

Analysis of the products:

The products are analyzed chemically and by IR spectroscopy. The chemical analysis proving the origin of that solid phase is by dissolution / precipitation in conc. NaOH and dissolution in HF acid. The analysis of IR was conducted in a PERKIN ELMER N° 577 in a solid phase using dry KBr as eluant (1:300). We found the following bands for the methoxy ester and for the propyloxy ester for examples; the bands are listed in the following tables:

N° 1 use of methanol

ν (Cm-1)	Bands
1120 - 1200 Cm-1	Si-O-Si
3200 - 3800 Cm-1	Si-OH

N° 1 use ethanol

ν (Cm-1)	Bands
920 - 950 Cm-1	Si-O
1000 - 1200 Cm-1	Si-O-Si
3000 - 3600 Cm-1	Si-OH

N° 3 use propane alcohol

ν (Cm-1)	Bands
1020 - 1250 Cm-1	Si-O-Si (25), (29)
3100 - 3600 Cm-1	Si-OH (25), (29)

N° 4 use butanol

ν (Cm-1)	Bands
900 - 970 Cm-1	Si-OR
1000 - 1250 Cm-1	Si-O-Si
3100 - 3600 Cm-1	Si-OH

Preparation of solid phase from the score of the high furnace:

The score of the high furnace (H.F), (Laitier), was graciously supplied by the siderurgical Plant of «El- Hadjar ANNABA, ALGERIA" as a row material. The row material was ground and washed many times with cold and hot distilled water, to eliminate soluble dusts and salts.

After filtration and rinsing with hot distilled water, the quantity of the spelled score was agitated magnetically in water to eliminate the residual pig iron. When the material of iron is excluded it was treated with boiling conc. HCl for 2 hours minimum to discard iron and FeSO4. The material was washed with distilled water till neutral pH. By this treatment we eliminate the surface charges and transform the siloxanes surface groups in silanols. The product, after filtration, was dried in an oven at 105 °C. After drying the score was grounded again in a porcelain mortar, sieved to sort the granules.

Analysis of the product:

The product was analyzed by IR spectroscopy; the bands of adsorption are given in the following tables:

The no treated score of the high furnace

ν (Cm-1)	Bands
1150 Cm-1	Si-O-Si
1655 Cm-1	band of water or deformation of adsorbed of water molecules
3700 Cm-1	Si-OH hydroxyl groups germinal

The score of the high furnace treated with conc. HCl

ν (Cm-1)	Bands
1180 Cm-1	Si-O-Si
3700 Cm-1	Si-OH germinal hydroxyle groups

The score of the high furnace treated with conc. hydrogen fluoride acid (H.F)

ν (Cm-1)	Bands
1200 Cm-1	states of siliceous non crystallized
1655 Cm-1	band of water or deformation of adsorbed water molecules
3750 Cm-1	Si-OH of isolated hydroxyl groups

The score of the high furnace treated with conc. H2SO4

ν (Cm-1)	Bands
1050 - 1200 Cm-1	Si-O-Si
1640 Cm-1	OH of water
3400 Cm-1	germinal hydroxyl groups or silanols linked by the hydrogen of the water molecule

Conclusion

The solid phases produced chemically or prepared from iron slag can be used an many purposes especially as adsorbant phases because theses surfaces are active.

Synthesis of silicates

We began the synthesis of silicates by the synthesis of esters by the reaction of the tetrachloro silicone with alcohol in presence of sodium methoxyde.

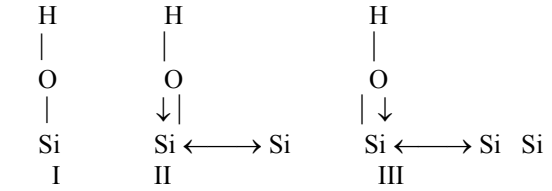
The alcoxy silicone is prepared by adding freshly distilled SiCl4, (Te = 329 K), drop by drop to the absolute alcohol on agitation.

By this way we prepared the methoxy; ethoxy; butoxy and pentoxy tetra esters of silicone.

II- Preparation of silanols

The calculus of integral orbital overlaps indicate that the probability of existence of this type of bonds, especially when the orbital d is the ultimate, so as in the case of siliceous molecule.

This situation is described by the following resonance structure.



Concerning molecular silanols, only structures I and II are important; meanwhile in surfaces I and II structures, exist one possible contribution of structure III. This confers to silanol groups of surface, one more acid character than molecular silanols.

The methyl groups along the chain can be substituted by many other groups (e.g., phenyl, vinyl or trifluoropropyl). The simultaneous presence of “organic” groups attached to an “inorganic” backbone gives silicones a combination of unique properties and allows their use in fields as different as aerospace (low and high temperature performance), electronics (electrical insulation), health care (excellent biocompatibility) or in the building industries (resistance to weathering).

The solid particulates of (SiO2)n are synthesized in different shapes (volumes) according to the ester utilized. The diameter of the particulate differs in

function of the alcohol utilized as follows; methanol, ethanol, and propanol ECT.....

The solid phases were prepared by two means: in dry and in humid mediums

The products are analyzed chemically and by IR spectroscopy. The chemical analysis proving the origin of that solid phase is by dissolution / precipitation in conc. NaOH and dissolution in HF acid. The analysis of IR was conducted in a PERKIN ELMER N° 577 in a solid phase using dry KBr as solid eluant medium (1:300).

The IR Analysis proved the existence of the adsorption bands of methyl, ethyl, silanol and ester groups.

Preparation of solid phase from the score of the high furnace:

The row material was ground and washed many times with cold and hot distilled water, to eliminate soluble dusts and salts. After analysis of the scores or iron slag provided by El Hadjar plant proves that the solid material is constituted essentially as follows: SIO2 : (25-30%), AlO3: 14%, Cao: 55%, with other compounds. These compounds can bi reactive with some other salts and be used in purifying fluids, as active resins.

RÉFÉRENCES

[1] Peter Jutzi, Ulrich Schubert, (2003), Silicon chemistry: from the atom to extended systems,

[2] Sunggyu Lee (2006) Encyclopedia of chemical processing , CRC Press, ISBN 0824755634

[3] Maoudian, R. Surf, Sci. Rep. 1998, 30, 207

[4] Ulman, A. Chem Rev. 1996, 96, 1553.

[5] Stenger, D. A.; Georger et al. J. Am. Chem. Soc. 1992, 114, 8435-42.

[6] Tuoli et Col. Langmuir 1999, 15, 4328-34.