

TG, FT-IR and NMR characterization of n -C₁₆H₃₄ contaminated alumina and silica after mechanochemical treatment

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Abstract

This paper deals with the application of mechanochemistry to model systems composed of alumina or silica artificially contaminated with n -C₁₆H₃₄. The mechanochemical treatment was carried out by means of a ring mill for times ranging from 10 to 40 h. Thermogravimetry and infrared and nuclear magnetic resonance spectroscopies were used for the characterization of the mechanochemical products. The results have indicated that, in the case of alumina, almost all the contaminant n -C₁₆H₃₄ undergoes a complex oxidative reaction path whose end products are strongly held on the surface. These end products are most likely made of crosslinked, partially oxidized hydrocarbon chains bond to the solid surface via COO⁻ groups. In the case of silica, the hydrocarbon undergoes a different, equally complex reaction path, but to a lower extent. In this case the end products are most probably carbonylic compounds and graphitic carbon. Then, for both solid matrices, the mechanochemical treatment promotes significant modification of the chemical nature of the polluting hydrocarbon with end products much more difficult to remove from the surface. As the systems studied are models of sites contaminated by aliphatic hydrocarbon, the results are worthy of consideration in relation to the mobility of the contaminants in the environment.

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1. Introduction

Mechanochemistry, that is the use of mechanical energy to promote chemical reactions, arises from ancient times, but it was just in the early years of the 20th century that it became of scientific interest (Butyagin, 1990; Boldyrev, 1995; Suryanarayana, 2001; Takacs, 2002). The oldest industrial application of mechanochemistry was in the field of mineral processing, but it was only in the 1960s that innovative applications were developed allowing mechanical alloying in the metallurgical field. Nowadays, some

other applications are currently carried out in high-technology industries for the production of advanced materials characterized by mechanochemically induced highly far-from-equilibrium state (Suryanarayana, 2001).

More recently, mechanochemistry has been applied to the environmental field. Particularly, it proved to be so successful for the treatment of asbestos containing materials that a patented process is now available able to convert toxic asbestos fibres into non-toxic amorphous form (Plescia et al., 2003). Other studies of environmental concern can be found in the pertinent literature for the treatment of polycyclic aromatic hydrocarbons (Field et al., 1997) and organohalide compounds (Rowlands et al., 1994; Hall et al., 1996; Loisel et al., 1997; Cao et al., 1999; Aresta et al., 2003; Tanaka et al.,

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2003). In both cases, the mechanochemical treatment yields non-toxic end products of graphitic nature.

Other studies have also been successfully carried out for alloying polymeric blends to allow recycling of different thermoplastic materials (Cavaliere and Padella, 2002; Cavaliere et al., 2002) and for the remediation of heavy metal contaminated soils (Montinaro et al., 2007).

The scientific interest for the application of mechanochemistry in the environmental field relies on the possibility to achieve waste reclamation by means of a cheap process operating at ambient temperature and pressure. On the contrary, alternative processes (such as incineration) require much more sophisticated equipment and drastic operating conditions. Moreover, the small, if any, volumes of liquid and gaseous effluents with consequent possibility to process them in situ by means of low capacity plants and the strongly reduced volume of the milled reclaimed materials (only small amount of co-reactants are occasionally added) represent other advantageous characteristics of this technology.

The mechanisms responsible for the physical and chemical transformations that take place upon milling are of quite difficult understanding because of their complexity. In addition, the understanding of the mechanisms leading to the destruction of pollutants is even more difficult by the high number of process variables that affect mechanochemical treatments.

Milling time and speed, sample to milling bodies weight ratio (often named charge ratio, CR), type of mill, type of vial and milling bodies material and some other operating conditions represent process variables affecting the chemical and physical properties of the end products. In spite of such complexity, mechanochemistry represents a very attractive alternative to other more common environmental processes because of easy operation and the above mentioned advantages.

In this paper, mechanochemistry has been applied to two model systems made of inorganic matrices, namely alumina and silica, contaminated with an aliphatic hydrocarbon. This is a preliminary study whose scope is the understanding of the interactions that take place, upon mechanochemical treatment, between the hydrocarbon and the two matrices. As these are the most common components of the inorganic fraction of contaminated sites (soils and sediments), this study can be considered the first step for understanding the potentialities that mechanochemistry offers for detoxification in case of aliphatic hydrocarbons mainly responsible for pollution. The proposed remediation technology is innovative inasmuch as no references are found in the literature on this application of mechanochemistry.

2. Materials and methods

The two model systems referred to above were prepared using respectively α -Al₂O₃ and SiO₂ (cristobalite) as inor-

ganic matrices, and *n*-C₁₆H₃₄ as organic pollutant. All these materials were used as received by Fluka.

Analytical grade solvents were used for preparing the model systems (CH₂Cl₂) and in the extraction steps carried out after milling (*n*-C₆H₁₄, CH₂Cl₂, CHCl₃ and CH₃OH). CDCl₃ for ¹H NMR analysis was of the specific grade for spectroscopic analysis. All the solvents were supplied by Carlo Erba.

Mechanochemical treatments were carried out by means of a Pulverisette 9 ring mill from Fritsch. It was equipped with a tungsten carbide grinding set composed by a disk and two rings with a total mass of 3637 g. The rotational rings velocity was 750 rpm, the volumetric capacity 350 cm³ and the electric power 0.6 kW.

Thermal analysis was made with a NETZSCH STA 409 thermal analyser and was carried out by simultaneous thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) in the temperature range 25–950 °C. In one case the gas evolved from thermal analysis was submitted to on-line FT-IR analysis by means of a Perkin–Elmer Spectrum GX apparatus. FT-IR analysis was also carried out on some solid samples, and in this case a Thermo Nicolet Nexus apparatus was used.

Nuclear magnetic resonance (NMR) analysis was carried out on both liquid and solid samples obtained after sequential extraction steps carried out on the various milled samples. The apparatus used for solid state NMR analysis was a Varian 600 MHz NMR spectrometer, while the one for liquid state NMR analyses was a Varian Gemini 200 MHz spectrometer.

The preparation of the model systems started by dissolving the right amount of *n*-C₁₆H₃₄ in CH₂Cl₂ to obtain a diluted solution. This solution was then thoroughly mixed with the solid, and the mixture continuously stirred for 24 h to achieve complete CH₂Cl₂ evaporation. In this way 5% (w/w) of *n*-C₁₆H₃₄ was homogeneously deposited onto the solid matrix. Finally, the artificially contaminated solid samples were air dried for some days and stored in glass bottles closed by screw caps.

In both the cases of the two model systems (contaminated alumina and contaminated silica) the milling operations were carried out with CR equal to 1/91. Milling times ranged from 10 to 40 h with 10-h increments.

After milling, the solid samples were submitted to an extraction process consisting of four consecutive steps using solvents of increasing polarity in the order: *n*-C₆H₁₄, CH₂Cl₂, CHCl₃ and CH₃OH. The extraction steps were carried out by stirring the samples with each solvent for 2 h in 1/20 g cm⁻³ solid/liquid ratio. After each extraction step, the solid–liquid mixtures were vacuum filtered for separation. The solid samples were then vacuum dried and submitted to the planned analyses and further extraction steps.

Samples before and after the mechanochemical treatment, as well as after each extraction step were submitted to thermal analysis as previously pointed out. Liquid samples from the extraction steps were vacuum dried and then

the residue dissolved in CDCl_3 for ^1H NMR analysis. Solid state magic angle spinning (MAS) NMR analysis was carried out by placing about 200 mg sample in a zirconia rotor.

3. Results and discussion

3.1. Alumina samples

Fig. 1 shows the results of TGA carried out in air on $n\text{-C}_{16}\text{H}_{34}$ contaminated alumina samples before and after mechanochemical treatment. The unmilled sample (trace a, dashed) shows a mass loss due to 5% $n\text{-C}_{16}\text{H}_{34}$ contamination which occurs below 220°C with no detectable heat effect (DSC trace not shown). Beyond 220°C no further mass loss takes place.

The TGA behaviour of the samples after mechanochemical treatment changes more and more significantly as the milling time increases. The overall mass loss increases up to about 9% as the milling time increases from 10 to 40 h and takes place over a temperature range that extends up to about 550°C . Although the mass loss is continuous over the above temperature range, at 10-, 20- and 30-h milling time, two distinct steps can be seen in the corresponding thermogravimetric traces b, c and d (Fig. 1). These two mass loss steps take place within contiguous ranges whose common (separation) temperature is about $200\text{--}220^\circ\text{C}$. Traces b, c and d in Fig. 1 also show that the rate at which mass is lost becomes more and more uniform as the milling time increases, making the two mass loss steps less and less distinguishable. At 40-h milling time (trace e), the rate of mass loss is almost constant up to about 550°C and the two steps are hardly seen. In any case, mass loss takes place together with a wide exothermic effect (DSC traces not shown).

The behaviour of the contaminated, unmilled sample is due to $n\text{-C}_{16}\text{H}_{34}$ desorption from the alumina surface. The low temperature range over which this phenomenon occurs and the lack of heat effect implies that, once the hydrocarbon is deposited on the alumina surface, its interactions with the solid surface are weak. After 10-, 20- and 30-h milling, the hydrocarbon partially undergoes some transformation (true chemical reactions, as will be seen later). The unreacted fraction of the hydrocarbon is lost during TGA at temperature below 220°C , while the reaction products not only require higher temperature up to about 550°C , but also are lost due to an air oxidation process. Evidence of this is the exothermic effect observed in DSC. Then, the reaction products can be either much more tightly held on the alumina surface, or of such nature to be very scarcely volatile (much higher molecular weight). After 40-h milling, the hydrocarbon conversion is almost complete, as the initial steep portion of TGA disappears. Of course, it cannot be excluded that mass loss is partially due to water desorption. In fact, water might be adsorbed during the long-lasting milling process which causes a strong reduction of particle size (surface area correspondingly increases) and loss of crystalline structure (more active centres are formed on the surface) with consequent possible strong increase of adsorption capacity. However, TGA carried out on a 40-h milled uncontaminated alumina sample only showed negligible mass loss, and then, the hypothesis of significant water adsorption during milling proves to be unreliable. Furthermore, in case of significant water uptake during milling, its desorption during TGA would be endothermic (Della Gatta et al., 1982), and then detectable by TG/DSC, at least at lower temperature, below $200\text{--}250^\circ\text{C}$, where the oxidation rate is low.

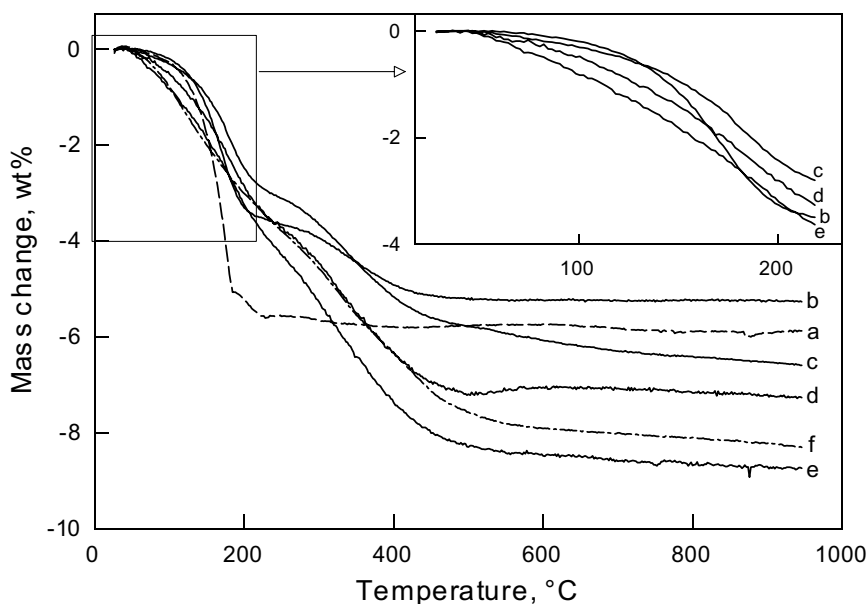


Fig. 1. Results of thermogravimetric analysis carried out on contaminated alumina samples: (a) unmilled; (b) after 10-h milling time (c) after 20-h milling time; (d) after 30-h milling time; (e) after 40-h milling time and (f) extracted after 40-h milling time.

After milling, the samples were submitted to the sequential extraction process previously described, and then to TGA. The results are shown in Fig. 1 for the 40-h milled sample (trace f, dash-dotted). The comparison with the unextracted sample (trace e) shows that the two traces are overlapped up to about 200 °C and that very little of the mechanochemical products are extracted, as the overall mass loss is reduced of less than 1%. This proves that these products are either very tightly held on the alumina surface or of such nature not to be soluble in the increasing polarity solvents employed in the extraction steps. In the two cases e and f of Fig. 1, the DSC traces (not shown) were almost the same.

To get a better understanding of the processes induced by the milling treatment and the nature of the products obtained, the TGA output was connected on-line to an FT-IR gas analyser. The combined TGA/FT-IR analysis (in air) was carried out on the 40-h milled sample as obtained at the end of the sequential multiple extraction referred to above. The results are reported in Fig. 2, where traces a, b and c are relative to the gas evolved from the sample at 120, 350 and 900 °C. It is clearly seen that significant IR absorption only takes place in the range 2223–2397 cm^{-1} , due to the presence of CO_2 . Even if the results of Fig. 2 are not quantitative, it is clear that relatively high CO_2 evolution rate is obtained at intermediate tempera-

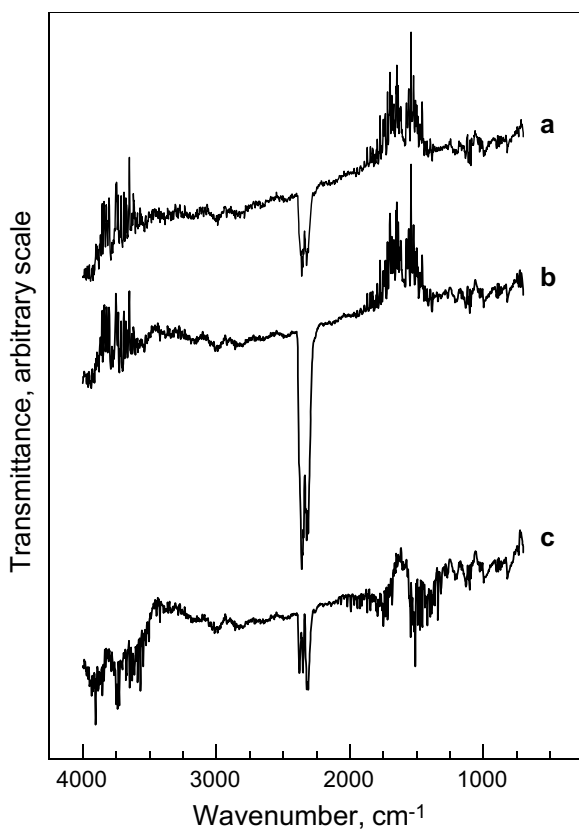


Fig. 2. Results of on-line FT-IR analysis carried out on gas evolved during thermal analysis of the 40-h milled sample after sequential extraction: (a) at 120 °C; (b) at 350 °C and (c) at 900 °C.

ture. Also, it is important to observe that no detectable H_2O evolution takes place (H_2O IR absorption is located around 3652 and 3756 cm^{-1} for symmetric and asymmetric stretching, respectively). Then, as air oxidation of the mechanochemical products only yields CO_2 in significant amount, H_2O being below the detection limit of the instrument, the conclusion is reached that the $n\text{-C}_{16}\text{H}_{34}$ originally present on the alumina surface is mechanochemically converted into an organic product with a much higher carbon/hydrogen ratio.

Suggestions on the nature of the mechanochemical products can be drawn from the pertinent literature and must take into account the strong increase of carbon/hydrogen ratio induced by the mechanochemical treatment.

Aromatic hydrocarbons deposited on alumina and silica were found by Field et al. (1997) to be largely converted into graphitic carbon after 24-h ball milling. The formation of a similar product in the system under investigation would explain the TG/FT-IR results, but, although the mechanochemical formation of graphitic carbon starting from an aliphatic hydrocarbon is thought to be quite improbable, it cannot be excluded, as mechanochemistry is often surprising.

The mechanochemical formation of higher molecular weight products was also found by Cavalieri and Padella (2002) and Cavalieri et al. (2002). These authors submitted a blend of polypropylene and low density polyethylene to a milling process under liquid CO_2 to assess the feasibility of mechanochemistry as a process for the compatibilization of waste plastics of different types. They found that mechanochemically induced crosslinking took place as high-energy milling caused breaking of the polypropylene chains with subsequent recombination with the neighbouring polyethylene ones. The resulting product was a polymeric network with higher carbon/hydrogen ratio and much better mechanical properties than the starting blend. Based on these findings, it could be considered that crosslinking may take place in the system under consideration, too. This would give rise to hydrogen evolution during milling and yield mechanochemical products with a higher carbon/hydrogen ratio.

The above considerations, on their own, obviously do not allow to say that the formation of graphitic carbon and/or crosslinking among the alkyl chains take place in our system, and, if so, the occurrence of other mechanochemically induced processes cannot be excluded. Evidently, other experimental evidence is required to better understand the processes that take place in our system. To this scope, NMR and FT-IR characterization of the products of the sequential extraction was undertaken.

The liquid extracts obtained from the various extraction steps were submitted to ^1H NMR analysis. Some difficulties were encountered in this phase of the experiments because the amount of extractable organic material was found to decrease with milling time and also because most of it was extracted during the first step. Then, not always the NMR analysis of the liquid extracts was reliable.

In general, the results obtained with the different milled samples for which the analysis was judged to be reliable (not shown for the sake of brevity) can be summarized as follows. The *n*-hexane extract (first step) spectrum only shows the presence of unreacted $n\text{-C}_{16}\text{H}_{34}$, while those relative to the successive steps show the presence of oxidized organic compounds. Specifically, evidence of the presence of geminal hydroxyl hydrogens and hydrogen atoms adjacent to carbonyl groups was found.

These observations must be correlated to the results of solid state NMR carried out on the residue after the complete sequential extraction step. This is helpful for the identification of the unextractable products permanently held on the solid matrix.

To this scope, ^{13}C MAS NMR analysis did not give significant results, differently from cross polarization (CP) analysis. The $^1\text{H}\text{-}^{13}\text{C}$ CP MAS NMR spectrum for the 40-h milled sample is shown in Fig. 3. Two different groups of signals can be surely identified: the first one at about 30 ppm is due to the presence of aliphatic chain methyl and methylene groups, while the second one, placed at about 180 ppm, can be related to the presence of carbonyl groups (Loiseau et al., 2005).

The NMR results clearly indicate that an air-oxidation mechanochemically induced process takes place. The non extractable end products are strongly held on the surface due to the formation of bonds whose nature should be understood. To this scope, the work of other authors on similar systems can be taken into consideration.

Tripathy et al. (1995) studied the wear mechanism involved when an alumina ball slides on an alumina disk in a pin-on-disk machine using $n\text{-C}_{16}\text{H}_{34}$ as lubricant. They observed partial oxidation of $n\text{-C}_{16}\text{H}_{34}$ due to the transfer of mechanical energy from the sliding ball to the hydrocar-

bon, which resulted in the formation of a like alumina soap compound. This, in turn, was able to interact more strongly with the support thanks to the presence of COO^- groups. Despite this more strong interactions, the like alumina soap compound was extractable with acetone. When a small amount (1 wt.%) of an unsaturated esteric monomer was added to $n\text{-C}_{16}\text{H}_{34}$, an oligomerization/polymerization process (also said tribopolymerization) occurred yielding the formation of a polymeric film on the alumina surface. The presence of several COO^- groups inside each oligomer/polymer molecule resulted in so strong interactions with the alumina matrix that the product was not extractable by acetone.

On the basis of our experiments and all the above literature results (Tripathy et al., 1995; Cavalieri and Padella, 2002; Cavalieri et al., 2002; Loiseau et al., 2005), it is possible to infer that the milling treatment of the model system under investigation promotes similar mechanochemical reaction leading to a product made of highly crosslinked, partially oxidized hydrocarbon chains directly bond to the alumina surface via the detected COO^- groups. Furthermore, this consideration can be supported by the observation that in a ring mill (like the one used in our experiments) the energy transfer from the milling bodies to the milled material is mainly due to shearing forces. This makes our milling system closely similar to the sliding system referred to above (Tripathy et al., 1995) from the point of view of the reaction mechanism involved.

A support to the above consideration comes from the work by Rong et al. (2002) who studied the properties of alumina–polymer composites made of polystyrene and polyacrylamide grafted on the surface of alumina nanoparticles. In this work, the alumina surface was firstly treated with silane, followed by radical grafting polymerization to

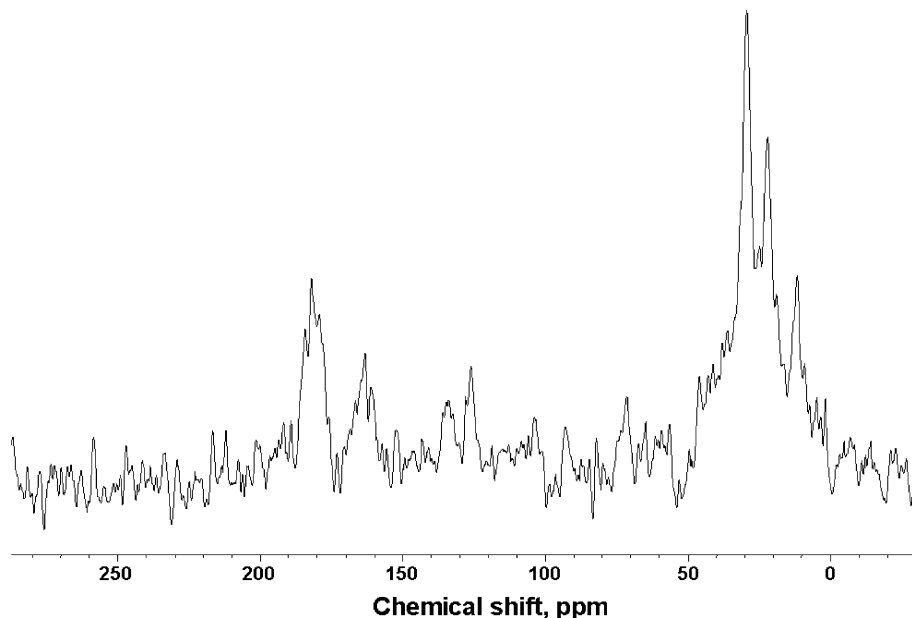


Fig. 3. Results of $^1\text{H}\text{-}^{13}\text{C}$ CP MAS NMR analysis carried out on alumina 40-h milled sample after sequential extraction.

get polymer chains covalently bonded to the surface. The thermoanalytical behaviour of these systems was exactly the same as that of those studied in the present work, that is the mass loss was found to extend over a temperature range up to about 600 °C with maximum rate at about 400 °C, in contrast to the thermoanalytical behaviour of simple mixtures of alumina and the free unbound polymers which showed lower thermal stability.

Further evidence that the milling treatment can promote the formation of carboxylate groups able to link the mechanochemical products to the alumina surface comes from the work by Greenler (1962), Kagel (1967) and Datka et al. (1994). These authors studied the nature of the adsorbed surface species which results when alumina is exposed to alcohols and unsaturated hydrocarbons. They found that at temperature ranging from 170 to 250 °C the catalytic activity of alumina results in the formation of carboxylate species chemisorbed on the alumina surface. These carboxylate species can be detected via infrared analysis as they produce absorption bands at 1580 and 1460 cm^{-1} , due to asymmetric and symmetric COO stretching, respectively. Fig. 4 shows that these two bands are completely absent in the FT-IR spectrum of both the unmilled mixture of alumina and $n\text{-C}_{16}\text{H}_{34}$ (trace a) and the 40-h milled uncontaminated alumina (trace d), while

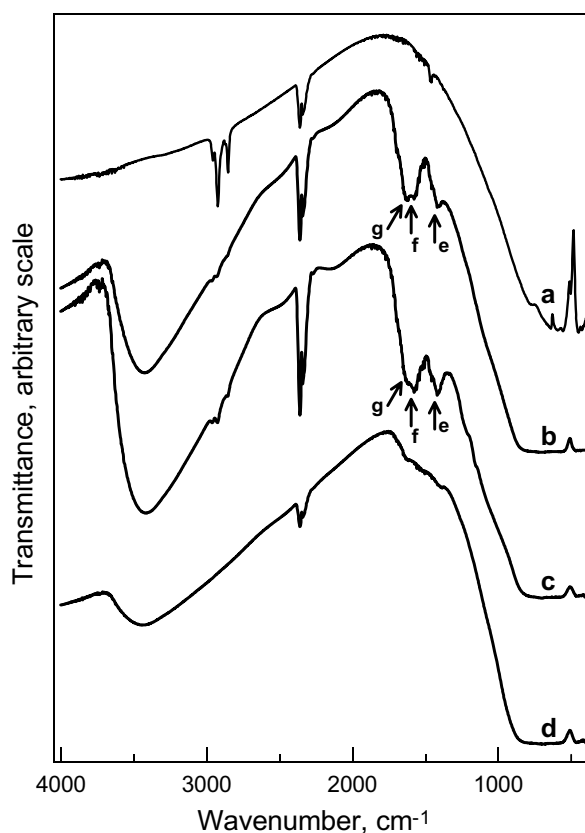


Fig. 4. Results of FT-IR analysis carried out on alumina samples: (a) contaminated unmilled; (b) contaminated after 20-h milling time; (c) contaminated after 40-h milling time and (d) uncontaminated after 40-h milling time.

are present in the spectra of the milled samples (bands e and f in traces b and c for 20- and 40-h milling time, respectively) and increase in intensity with milling time. In our case the above bands are shifted to 1577 and 1419 cm^{-1} , respectively. The former shift is obviously not significant at all, while the latter is due to the fact that the symmetric COO stretching frequency decreases as the mass of the attached groups increases, and this is our case in comparison to the work referred to above (Greenler, 1962; Kagel, 1967; Datka et al., 1994) which dealt with low molecular weight alcohols and unsaturated hydrocarbons. All these considerations lead to the conclusion that, owing to the temperature increase locally due to mechanical energy conversion into heat, carboxylate species are formed and they are able to bind the mechanochemical product to the alumina surface. This process takes place on the alumina surface due to its catalytic activity. To this regard, Datka et al. (1994) evidenced that the formation of carboxylate species is not detected on zeolite.

The formation of carboxylate species bonded on alumina surface, often called “alumoxanes”, has been reported by other authors in studies dealing with the different technological applications of alumina (Silverstein et al., 1981; Vogelsson and Barron, 2001). Again, these compounds proved to be very stable, being removed from the surface only at high temperature, 600 °C or more.

Finally, band g centred around 1620 cm^{-1} in Fig. 4 could be due to carboxyl groups not bonded on the alumina surface (Vogelsson and Barron, 2001) or to ester groups linking different $n\text{-C}_{16}\text{H}_{34}$ molecules (Tripathy et al., 1995). Actually, the absorption band related to these groups should be located at higher wavenumbers (about 1700 cm^{-1}), but the observed shift could be due to intramolecular hydrogen bonds (Vogelsson and Barron, 2001).

Traces b and c in Fig. 4 also show wide bands centred at about 3400 cm^{-1} . It is thought that these bands are due to the stretching of organic OH formed after partial hydrocarbon oxidation. On the other hand, water contribution is considered of minor importance. In fact, trace d shows that this band is much less intense in the case of the 40-h milled pure alumina sample, when IR absorption can only be ascribed to water surface adsorption. However, the extent to which this process takes place onto the milled contaminated alumina is believed to be quite lower, as the contamination makes the alumina surface acquire hydrophobic character.

3.2. Silica samples

The results of TGA for the contaminated silica samples before and after the mechanochemical treatment are shown in Fig. 5. Similarly to the alumina- $\text{C}_{16}\text{H}_{34}$ system, the mass change for the unmilled sample (trace a, dashed) occurs below 220 °C without any detectable thermal effect (DSC trace not shown) and is due to the loss of the contaminating hydrocarbon. From the quantitative point of view, this

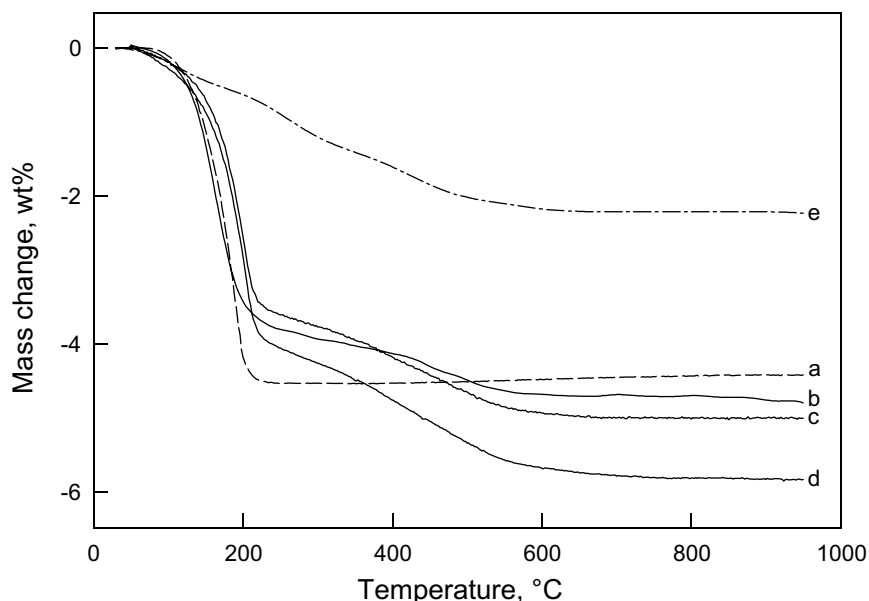


Fig. 5. Results of thermogravimetric analysis carried out on contaminated silica samples: (a) unmilled; (b) after 20-h milling time; (c) after 30-h milling time; (d) after 40-h milling time and (e) extracted after 40-h milling time.

mass loss is comparable to the initial contamination (about 5%).

The thermogravimetric behaviour of the 20-, 30- and 40-h milled samples (traces b, c and d, solid) is similar to that of the unmilled one below 220 °C, again in relation with the presence of $n\text{-C}_{16}\text{H}_{34}$. In these three cases, compared to the unmilled sample, only little decrease of mass loss is observed within the temperature range up to 220 °C. This remarkably makes the silica- $\text{C}_{16}\text{H}_{34}$ system different from the alumina- $\text{C}_{16}\text{H}_{34}$ one and has the meaning that in the former case the hydrocarbon mechanochemical conversion takes place to a much lower extent. Beyond 220 °C, a further, less steep mass loss is observed in traces b, c and d. This loss extends up to about 600 °C and increases with milling time, but not as much as for the alumina- $\text{C}_{16}\text{H}_{34}$ system. A wide exothermic effect was observed in the associated DSC traces (not shown), meaning that the mechanochemical products removal takes place via air oxidation in the temperature range 220–600 °C.

The milled samples were submitted to the same sequential extraction steps as the alumina- $\text{C}_{16}\text{H}_{34}$ system and the result of thermal analysis carried out on the solid residue of the 40-h milled sample is shown in Fig. 5 (trace e, dot-dashed). By comparing traces d and e in Fig. 5, it is seen that mass loss is reduced to about one third after the sequential extraction process; particularly, the initial steep portion of the thermogram below 220 °C disappears. In the two cases d and e of Fig. 5, the DSC traces (not shown) were almost the same. These results prove that the behaviour of the silica- $\text{C}_{16}\text{H}_{34}$ system remarkably differs from that of the alumina- $\text{C}_{16}\text{H}_{34}$ system, as in the former case the hydrocarbon conversion into non-extractable products proceeds to a much lower extent. What is similar for the two systems is that the mechanochemical products removal

takes place via exothermic air oxidation. Then, even for the silica- $\text{C}_{16}\text{H}_{34}$ system, the reaction products can be either much more tightly held on the solid surface, or of such nature to be much less volatile (much higher molecular weight).

The extracts obtained at the end of each step of the sequential extraction process were analyzed via ^1H NMR spectroscopy (results not shown for the sake of brevity). The resulting spectra again show the presence of unreacted $n\text{-C}_{16}\text{H}_{34}$ in the $n\text{-C}_6\text{H}_{14}$ extracts, while those relative to the other, more polar solvent extracts show the presence of two different classes of compounds: aromatic compounds and hydrogen atoms adjacent to carbonylic groups.

These results could be due to a mechanism involving, in the case of silica samples, two different competitive reactions: these would lead to the formation of highly unsaturated products and, as for alumina samples, oxidized compounds strongly bond onto the solid matrix.

The 40-h milled silica sample as obtained at the end of the sequential extraction process was submitted to ^1H - ^{13}C CP MAS NMR analysis. The resulting spectrum is reported in Fig. 6 and shows the presence of a peak placed around 30 ppm due to methyl and methylenic aliphatic carbons and a broad band placed around 145 ppm due to aromatic compounds characterized by a low H/C ratio. More specifically, the latter signal was found by Holmes et al. (1997) and Callejas et al. (2001) to be characteristic of coke formation on different catalysts and was used by Hall and co-workers as a proof of the formation of graphitic compounds in the mechanochemical treatment of DDT with CaO (Hall et al., 1996). Furthermore, the formation of graphitic carbon is in agreement with the literature results concerning the application of mechanochemistry to the treatment of other organic pollutants (Field et al., 1997).

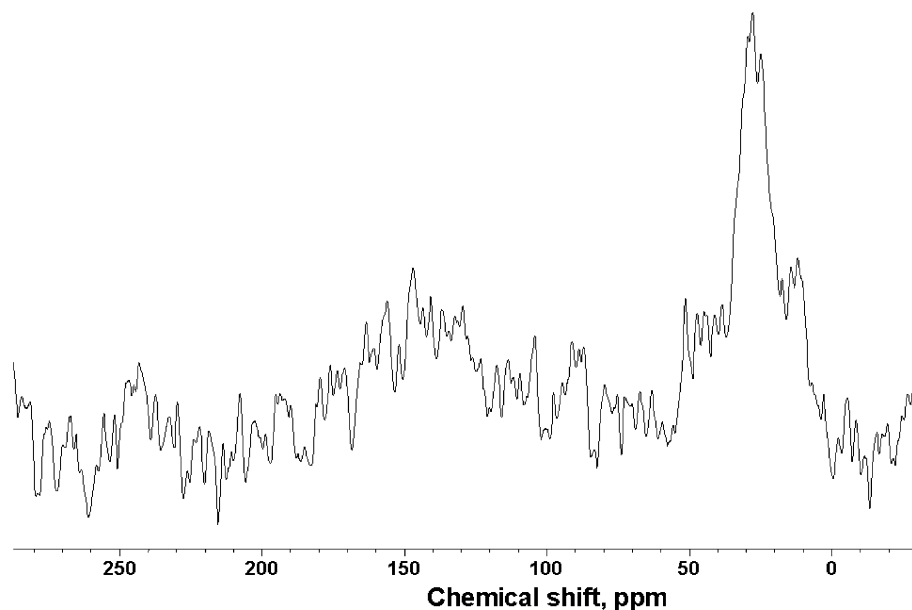


Fig. 6. Results of ^1H - ^{13}C CP MAS NMR analysis carried out on silica 40-h milled sample after sequential extraction.

The carbonylic compounds are surely more strongly bonded to the silica surface than the starting hydrocarbon, but there is no evidence that they are not removed during the sequential extraction process. On the other hand, the graphitic product is permanently held on the same surface. In the case of the silica- $\text{C}_{16}\text{H}_{34}$ system the hydrocarbon conversion is much lower than in the case of the alumina- $\text{C}_{16}\text{H}_{34}$ system.

4. Conclusions

The experiments have shown that the hydrocarbon n - $\text{C}_{16}\text{H}_{34}$ undergoes different mechanochemical reaction paths in the two model systems studied.

In the case of the alumina system, it has been possible to conclude that the milling treatment promotes the formation of a product made of highly crosslinked, partially oxidized hydrocarbon chains directly bond to the alumina surface via COO^- groups.

In the case of the silica system, two competitive mechanochemically induced processes appear to take place. The hydrocarbon is partially oxidized to carbonylic compounds and partially converted into graphitic carbon.

These findings demonstrate the relevant role of the inorganic substrate whose effect can be very different from case to case. This may be a weakness in mechanochemical processes, inasmuch as their effectiveness will not only depend on the nature of the polluting organics, but also on that of the substrate.

Sites where aliphatic hydrocarbons are responsible for pollution are frequently encountered all over the world, especially where oil refineries are currently or were in the past in operation, as in the eastern industrial area of the city of Naples, Italy. Other sources of such type of pollution are accidental leakages and illegal waste landfill. Then,

aliphatic hydrocarbons can be among the common contaminants of soils and sediments. In these cases, the mechanochemical processes studied in this paper can well be taken into account for remediation.

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