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THERMAL DECOMPOSITION OF SODIUM NITRITE AND SODIUM NITRATE PRE-ADSORBED ON TiO_2 SURFACES

J. A. Navio, M. Macias, A. Justo and C. Real*

INSTITUTO DE CIENCIA DE MATERIALES, CENTRO COORDINADO DEL CSIC Y
DEPARTIMENTO DE QUÍMICA INORGÁNICA, FACULTAD DE QUÍMICA, UNIVERSIDAD DE
SEVILLA. APDO, 1115, 41080-SEVILLA, SPAIN

The thermal decomposition of sodium nitrite or nitrate pre-adsorbed upon TiO_2 surfaces has been investigated by employing several techniques as infrared spectroscopy (IR) and temperature programmed desorption in conjunction with mass spectrometry analysis (TPD-MS) to study the features observed during these thermal decompositions. Differential thermal analysis (DTA) in combination with X-ray diffraction analysis (XRD) were used to investigate the possibility of a solid state chemical reaction between the solid products originated from the thermal decomposition of the pre-adsorbed species and the TiO_2. On the basis of our results, various characteristic features of these thermal decomposition reactions will be discussed.

Keywords: DTA, pre-adsorbed sodium nitrite/nitrate, solid state chemical reaction, TPD-MS method

Introduction

The thermal decomposition of several metal nitrites and nitrates has been extensively studied. Pure metal nitrates, in general may decompose into either nitrites [1], oxides, or metals, depending upon the relative stability of the final products. In particular, nitrates of pure basic metal as sodium nitrate tend to yield the nitrite as intermediate during the thermal decomposition [2].

The thermal decomposition of pre-adsorbed nitrites and nitrates upon the surface of transition metal oxides has been scarcely studied in spite of this method is a common way for the preparation of composite catalysts based on supported

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* Author to whom all correspondence should be addressed

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Akadémiai Kiadó, Budapest

metals upon the surface of transition metal oxides, or as way to modify the acidity/basicity properties of the surface metal oxides.

Experimental

Preparation of samples

Samples of TiO_2 containing pre-adsorbed amounts (~7 anionic species nm^{-2}) of either NO_3^- or NO_2^- species, were prepared by wet impregnation method; the commercial TiO_2 specimens (Degussa, P-25, S_{BET}=49±1 m^2g^{-1}) were added at room temperature with stirring to aqueous solutions of either sodium nitrate or sodium nitrite (both from Merck) containing the required amounts of anionic species (NO_3^- or NO_2^-) in the minimum volume of bidistilled water and then standing at room temperature for 48 h until the liquid phase had evaporated. After the preparation, samples were carefully stored in a desiccator.

Thermal studies

The analysis of evolved gases produced and/or desorbing during sample heating was performed using temperature programmed desorption linked to continuous monitoring of the gas phase with a quadrupole mass-spectrometer (Hewlett-Packard 5992 A) in its scanning mode of operation (TPD-MS method). Differential thermal analysis (DTA) was recorded in static air atmosphere with a Stanton-Redcroft 673-4 thermal analyser at a heating rate of 10 deg min^{-1} from room temperature to 1000°C. About 20 mg of sample was gently packed in the platinum holder. Calcined alumina used as reference.

X-ray study

The X-ray powder diffractograms (XRD) were recorded at room temperature with a Philips PW 1060 X-ray apparatus using CuK_α radiation, with a Ni filter.

Infrared spectroscopy

The infrared (IR) spectra were recorded on a Perkin-Elmer 883 spectrometer using the same IR cell and thermoevacuation procedure previously described [3].

Results

Figure 1 shows the TPD-MS profiles from the two kind of TiO_2 surfaces containing pre-adsorbed either nitrite or nitrate species. By comparing both thermodesorption spectra, it can be observed that only minor differences exist between the thermodesorption profiles. The TPD products from both surfaces were mainly NO_2(g), O_2(g) and NO(g). The practical similarities between both surfaces tentatively suggest that pre-adsorbed NO_2^- have been partially oxidised to NO_3^- (ads) on TiO_2. In fact, we have proved from XPS study [4] that 'freshly prepared' NO_2^-/TiO_2 are partially transformed into NO_3^-/TiO_2 surfaces.

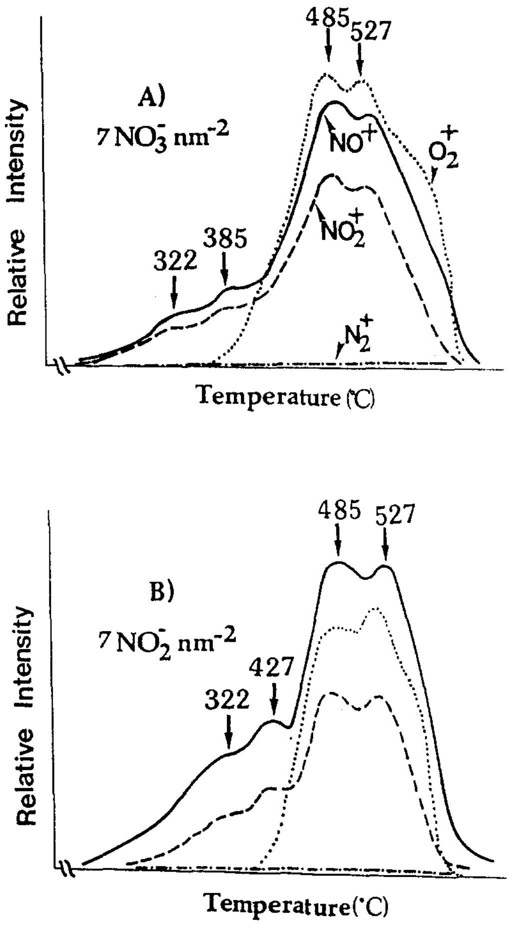


Fig. 1 Thermodesorption from TiO_2 surfaces containing either pre-adsorbed NO_3^- (A) or NO_2^- (B) species (rate 8 deg·min^{-1}). The NO^+ profile is amplified by a factor of 10

In Fig. 2 are given the IR spectra of freshly prepared NO_2^-/TiO_2 (Fig. 2A) and NO_3^-/TiO_2 (Fig. 2B) surfaces and the changes in those spectra with the subsequent thermal evacuation of the specimens.

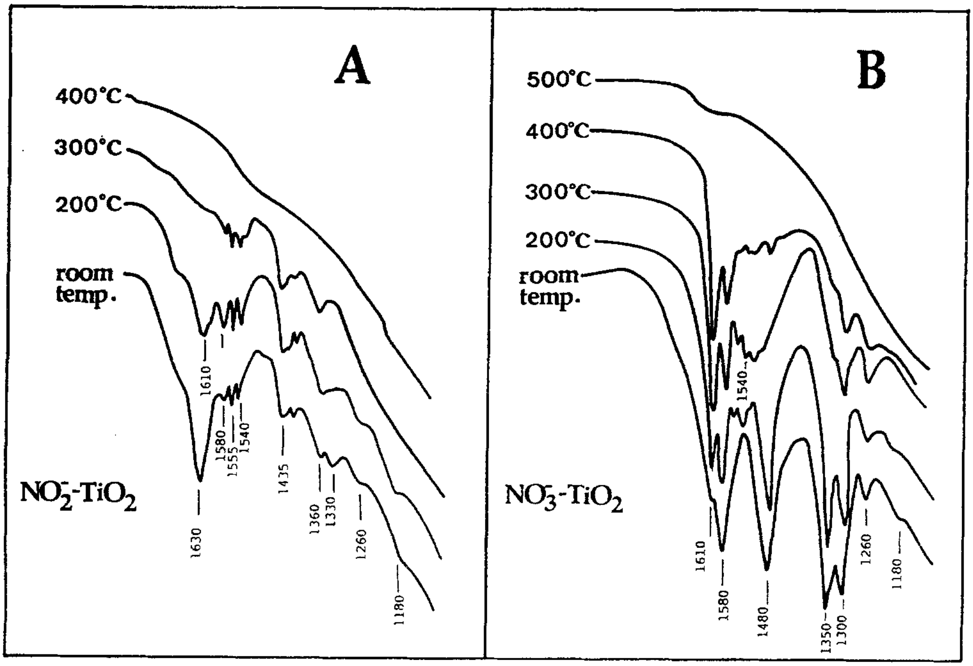


Fig. 2 Infrared spectra from NO_2^-/TiO_2 (A) and NO_3^-/TiO_2 (B) surfaces at various stages of decomposition by thermalevacuation for 30 min at the indicated temperatures

In Table 1 are summarized the assignments of the IR bands from Fig. 2, either for NO_2^- (ads)or NO_3^- (ads) of different structures, based on literature data [5–7]. The progressive thermal evacuation treatments of either NO_2^-/TiO_2 or NO_3^-/TiO_2 specimens leads to a gradual diminution of the intensities of the bands; these changes in the spectra became manifest the different stages of the modified TiO_2 surfaces during the thermal decomposition of the pre-adsorbed nitrites or nitrates species. Note that the total thermal decomposition in vacuum of nitrates pre-adsorbed on TiO_2 surfaces occurs in the temperature range of 400°–500°C whereas for the nitrites pre-adsorbed species the practically total thermal decomposition occurs in the temperature range of 300°–400°C leading then to a clean TiO_2 surface. These results suggest a lesser thermal stability for the pre-adsorbed nitrites on TiO_2 if compared with the pre-adsorbed nitrates species.

Table 1 Frequencies of stretching vibrations of NO$_2^-$ /TiO$_2$ and NO$_3^-$ /TiO$_2$ of the IR spectra from Fig. 2

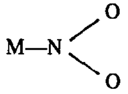
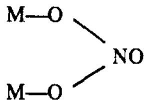
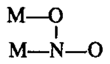
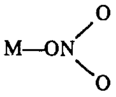
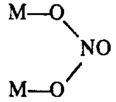
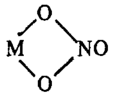
Surface	ν / cm^{-1}	Structure
NO$_2^-$ / TiO$_2$	1260–1330	uncoordinated NO$_2^-$ ions
	1445; 1360	
	1630; 1180	
	1540; 1260	
NO$_3^-$ / TiO$_2$	1350	uncoordinated NO$_3^-$ ions
	1480; 1260	
	1540; 1260	
	1610; 1180	
	1555; 1300	
	1580; 1300	

Figure 3 shows the DTA traces of the TiO$_2$, NO$_2^-$ /TiO$_2$, and NO$_3^-$ /TiO$_2$ specimens. The first endothermic effect at ~100°C is ascribed to the elimination of adsorbed molecular water from the surface of the powder. As the thermal treatment increses, the remaining water strongly bonded inside the pores of the particles can then be eliminated giving thus the second overlapping endothermic effect at ~180°C. After the main loss of water, below 200°C, very complex thermal effects are developing for both NO$_2^-$ /TiO$_2$ and NO$_3^-$ /TiO$_2$ samples, between 300° and 650°C, which is difficult to ascertain if they are corresponding to endothermic or exothermic effects. Note, however, that differences on the DTA profiles are observed for the three studied samples in the temperature range of 300°–650°C.

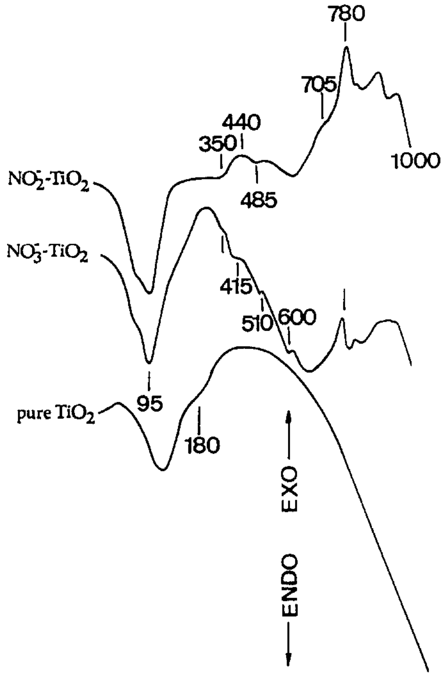


Fig. 3 DTA curves of the TiO_2, NO_2^- /TiO_2 and NO_3^- /TiO_2 samples. β=10 deg·min^{-1}

In the case of TiO_2, a continuous sinterization process is observed by DTA from 350°C. The loss of water from the condensation of surface hydroxyl groups [8] at higher temperatures than 400°C must be account of the commencement of the sinterization process. However, according with DTA results, the sinterization process observed in TiO_2 seems to be retarded by the presence of pre-adsorbed nitrite species and accelerated by pre-adsorbed nitrate species. At present we have not a plausible explanation for this observation although results are reproducible.

Above 650°C there are several exothermic peaks with a DTA profile which is more or less identical for both NO_2^- /TiO_2 and NO_3^- /TiO_2 specimens. These results indicate that after thermal heating in air up to 650°C, both NO_2^- /TiO_2 and NO_3^- /TiO_2 specimens leads to the same surface and possibly structural characteristics.

In order to add to the DTA and for a better understanding of the thermoevolution of studied samples, XRD patterns were taken for the NO$_2^-$ /TiO$_2$ and NO$_3^-$ /TiO$_2$ samples after cut off the DTA experiments at several temperatures. Figure 4 shows XRD patterns for NO$_2^-$ /TiO$_2$ (Fig. 4A) and for NO$_3^-$ /TiO$_2$ (Fig. 4B) as representative results of this study. In both case, below 600°C, both samples gave only anatase and rutile patterns, although the anatase fraction *vs.* the rutile one is progressively decreasing when the thermal treatment increasing as corresponding to the transformation of anatase phase into the rutile phase. This process seems to be independent of the presence of either sodium nitrite or nitrate adsorbed on the TiO$_2$.

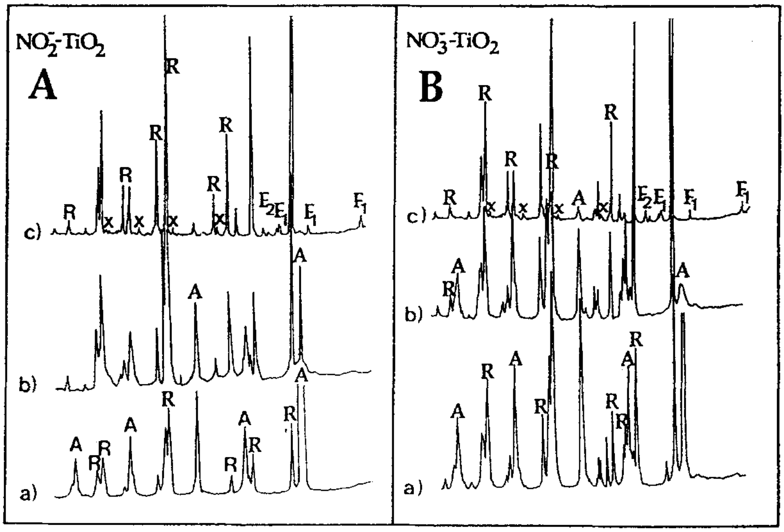


Fig. 4 X-ray diffraction diagrams of NO$_2^-$ /TiO$_2$ (A) and NO$_3^-$ /TiO$_2$ (B) specimens: (a) freshly prepared' samples; (b) after cut off the DTA at 600°C; (c) after cut off the DTA at 1000°C. *R*=rutile; *A*=anatase; *F*$_1$=Na$_2$Ti$_5$O$_{11}$; *F*$_2$=NaO$_2$; *X*=reflections of small amounts of non identified phases (possibly, disordered phases of sodium titanates)

On the other hand for both NO$_2^-$ /TiO$_2$ and NO$_3^-$ /TiO$_2$ specimens thermal treatments in air at ~1000°C causes the appearence, on the XRD patterns, reflections of small amounts of new phases some of them have been identified as sodium superoxide NaO$_2$ and other disordered phases of sodium titanates Na$_2$Ti$_5$O$_{11}$ and Na$_{0.23}$TiO$_2$ which are not observed for the same specimens heated in air below 600°C. Thus, according with XRD results the formation of these solid phases (sodium titanates and sodium superoxide) must be account of the exothermic effects observed in the DTA experiments above 650°C.

Discussion

According to literature [9] $NaNO_2(s)$ is unstable above 330°C. The first step in the decomposition is probably:

$$2NaNO_2 \xrightarrow{\Delta} Na_2O + NO_2 + NO$$

Between 330° and 380°C the reaction sequence seems to be as follows:

$$2NaNO_2 \xrightarrow{\Delta} Na_2O + NO_2 + NO \tag{1}$$

The NO produced in (1) reacts with $NaNO_2$ according with Eq. (2)

$$2NaNO_2 + 2NO \xrightarrow{\Delta} 2NaNO_3 + N_2 \tag{2}$$

The NO_2 produced in (1) reacts further [10]

$$Na_2O + 2NO_2 \xrightarrow{\Delta} NaNO_2 + NaNO_3 \tag{3}$$

$$NaNO_2 + NO_2 \xrightarrow{\Delta} NaNO_3 + NO \tag{4}$$

Because $NaNO_3$ is stable in this temperature range [11] and N_2 is unreactive the net result of reactions (1)–(4) is the production of $NaNO_3$ and N_2. If the gas phase is continuosly removed (this is the case for our TPD experiments) then, only reaction (1) will occur.

According to literature [11] at higher temperatures, 600°–750°C, $NaNO_2$ can reacts with O_2 to establish the equilibrium:

$$NaNO_2 + 1/2O_2 \rightleftarrows NaNO_3 \tag{5}$$

Since the DTA experiments are carried out in static air atmosphere we do not exclude the possibility that the adsorbed NO_2^- species on TiO_2 may undergo further oxidation to NO_3^- adsorbed species. Thus the exothermic peak at 705°C which is observed during the ATD experiments for NO_2^-/TiO_2 specimen could be associated to this thermal oxidation process.

If the thermal decomposition is carried out in an inert atmosphere the first decomposition product is N_2, accompanied by an increasing in the concentration of O_2 [11]. Freeman [11] attributes the evolution of N_2 to the formation of a superoxide which later decomposes to Na_2O and O_2

$$2NaO_2 \xrightarrow{\Delta} Na_2O + 3/2O_2 \tag{6}$$

This view is also supported by Bond and Jacobs [12] who report that the reaction (7) also proceed in air.

$$2NaNO_2 \xrightarrow{\Delta} Na_2O + N_2 + 3/2O_2 \tag{7}$$

However according with our XRD results for those either NO_2^-/TiO_2 or NO_3^-/TiO_2 after the DTA experiments we have not detected the formation of Na_2O but the formation of sodium superoxide and substoichiometric sodium titanates have been detected.

In conclusion the thermal decomposition of sodium nitrite or sodium nitrate when they are pre-adsorbed on TiO_2 surfaces seems to follows the same sequences observed for pure solid specimens [1] with relative slight differences produced by the presence of the TiO_2 support which interact with the thermal decomposition products giving sodium titanates and stabilizing sodium superoxide. In addition, it must be noted that when metal/TiO_2 catalysts are prepared by thermal decomposition of metal nitrites or nitrates pre-adsorbed on TiO_2 surfaces, the calcination temperature must be not higher than 500°C in order to prevent the solid state reactions described above.

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Zusammenfassung — Mittels verschiedenen Techniken, wie z.B. IR-Spektroskopie oder temperaturprogrammierte Desorption in Verbindung mit massenspektrometrischer Analyse wurde die thermische Zersetzung von Natriumnitrit oder Natriumnitrat, welches zuvor an der Oberfläche von TiO_2 absorbiert wurde, untersucht, um die Eigenschaften bei dieser thermischen Zersetzung zu beobachten. DTA in Verbindung mit Röntgendiffraktionsanalyse wurde eingesetzt, um die Möglichkeit einer chemischen Feststoffreaktion zwischen den bei der thermischen Zersetzung der voradsorbierten Proben entstehenden Produkten und TiO_2 zu untersuchen. Anhand der Ergebnisse werden zahlreiche verschiedene charakteristische Wesenszüge dieser thermischen Zersetzung diskutiert.