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Deactivation of V_2O_5/TiO_2 catalysts during the oxidation of *meta*-dichlorobenzene in the presence of methyl-naphthalene

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Abstract

Kinetic and in situ infrared spectroscopic studies were conducted during the investigation of the effect of methyl-naphthalene (mNpht) on the oxidation of *meta*-dichlorobenzene (*m*-DCB) over a 3.6 wt.% V_2O_5/TiO_2 catalyst. A gradual decrease in the conversion of *m*-DCB was observed with time on stream in the presence of mNpht. This deactivation was more pronounced at lower temperatures and higher mNpht inlet concentrations. The results of in situ FTIR studies indicate the accumulation of carbonaceous species on the catalyst surface. The catalyst can regain its activity towards the oxidation of *m*-DCB upon removal of mNpht from the reaction gas mixture. The rate of regeneration depends on temperature and the amount of carbon accumulated on the catalyst surface.

Keywords: Polychlorinated dibenzodioxins; Polychlorinated dibenzofurans; FTIR

1. Introduction

The incineration of municipal and medical waste produces trace amounts of chlorinated volatile organic compounds including highly toxic polychlorinated dibenzodioxins (PCDD) and dibenzofurans (PCDF). Stringent regulations are in place regarding the emissions of PCDD/PCDFs [1], due to the major health problems associated with exposure to these compounds [2]. Catalytic oxidation represents the current state of the art technique used commercially for the destruction for PCDD/PCDFs. In particular, V_2O_5/TiO_2-based catalysts, employed in most incinerators for the control of NO_x emissions via the selective catalytic reduction with NH_3, are also active for the oxidation of PCDD/PCDFs [3–7]. In addition to PCDD/PCDFs and NO_x, incinerator flue gas streams also contain complex mixtures of both halogenated and non-halogenated volatile organic compounds (i.e., biphenyls and polyaromatic hydrocarbons [8]). V_2O_5/TiO_2 catalysts used commercially for the selective oxidation of xylene to phthalic anhydride are known to undergo deactivation under similar conditions due to carbon deposition [9–11]. Furthermore, it was reported recently that vanadia/titania-based catalytic filters used commercially for the oxidation of PCDD/PCDFs in secondary copper and alumina plants undergo deactivation due to the presence of incomplete combustion products and coke on the catalyst surface [12].

Kinetic studies of the oxidation of chlorinated aromatic compounds (i.e., PCDD/PCDFs and/or model compounds) over V_2O_5/TiO_2 systems have been performed by several groups [1,13–16]. A combination of kinetic and in situ FTIR spectroscopic studies of V_2O_5/TiO_2 catalysts utilizing several different chlorinated aromatic compounds has been also conducted in our group in an effort to gain a better understanding of the reaction mechanism involved [17–21]. In this paper we investigate the effect of the presence of 1-methyl-naphthalene (mNpht) on the catalytic oxidation of *m*-dichlorobenzene (*m*-DCB) over a V_2O_5/TiO_2 catalyst. MNpht was chosen for these studies as a representative of the polyaromatic compounds present in the flue gas streams of incinerators. Furthermore, mNpht is known to be a coke precursor and has been extensively used in coking studies over zeolites [22,23]. Similarly, *m*-DCB has been previously used in our group, as a model compound for PCDD/PCDFs [21].

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2. Experimental

2.1. Catalyst preparation

The 3.6 wt.% V_2O_5/TiO_2 catalyst used in this study was prepared by an impregnation procedure. Prior to impregnation the TiO_2 support was calcined at 500 °C for 3 h. Ammonium metavanadate (NH_4VO_3) was used as the V_2O_5 precursor. An aqueous solution of ammonium metavanadate was prepared and heated slowly until the entire precursor was completely dissolved. This solution was then added to an aqueous TiO_2 slurry. The resulting solution was stirred and heated until all the water was evaporated. Samples thus obtained were dried overnight in a vacuum oven at 80 °C, and then slowly heated to 520 °C in 8 h and calcined in air at this temperature for 2 h. During the calcination the ammonium metavanadate precursor was decomposed to yield vanadium oxide. The final vanadia loading of the catalyst was obtained through ICP measurements (Galbraight), while its surface area (69 m^2/g) was obtained through a BET measurement.

2.2. Activity measurements

Activity measurements were carried out in a quartz, single-pass, fixed-bed reactor. A K-type thermocouple was placed into the catalyst bed to monitor the reaction temperature. Liquid organic reactants (i.e., *m*-DCB and mNpht) were introduced to the reactor system by passage of a He stream through saturators maintained at the appropriate temperatures. The saturated He streams were further mixed with He and O_2 so that the desired inlet concentrations were achieved. The concentrations of the organic reactants in the reactor inlet and exit streams were determined online with a gas chromatograph (SRI 8610) equipped with a 1/8″ packed silica gel column and a flame ionization detector.

Each run utilized approximately 250 mg of catalyst in the form of 80–120 mesh (125–177 μm) particles. The volumetric flow rate through the catalyst bed was held constant at 222 ml/min measured at atmospheric pressure and room temperature (corresponding space velocity of 53,000 cc/g h). Prior to each experiment, the catalyst was pretreated in oxygen for 2 h at 500 °C. An inlet concentration of approximately 500 ppmv *m*-DCB was used in all experiments, while the concentration of mNpht was either 20 or 200 ppmv.

Small amounts of by-products condensed at the reactor outlet were analyzed off-line using GC–MS. Finally, the carbon content of a deactivated catalyst was measured using ICP (Galbraight Laboratories).

2.3. In situ FTIR studies

FTIR spectra were collected with a Nicolet 740 spectrometer and a homemade in situ flow cell. The spectrometer was equipped with a MCT-B detector cooled by liquid nitrogen. The cell had a path length of 10 cm and both ends were "capped" by IR-transparent NaCl crystal windows. Approximately 18–20 mg of the catalyst sample were pressed into a self-supported disc of approximately 1 cm in diameter. This disc was placed in a sample holder located at the center of the cell. The cell was wrapped with heating tape, and the temperature was measured with a thermocouple, placed close to the catalyst sample. Transmission spectra were collected in a single beam mode with a resolution of 2 cm^{-1}.

Prior to each experiment the catalyst was oxidized at 350 °C for 2 h. Spectra of the clean catalyst surface were collected at the temperature of the particular experiment and utilized as the background. Subsequently, a mixture of He, O_2 and the organic reactant (i.e., mNpht) was introduced into the cell, and in situ spectra were collected at different time intervals.

3. Results and discussion

3.1. Deactivation

3.1.1. Activity measurements

The effect of mNpht on the conversion of *m*-DCB over the 3.6 wt.% V_2O_5/TiO_2 catalyst studied is demonstrated in Fig. 1 for three different temperatures. The results show that the catalyst activity for the oxidation of *m*-DCB decreases with time on stream. The observed decrease is substantially more pronounced at the lower temperatures. During these experiments the concentration of mNpht was kept constant at 20 ppmv but no mNpht was detected at the reactor outlet, indicating that mNpht is reacting and/or accumulating on the catalyst surface.

No loss of activity is observed for the oxidation of *m*-DCB at 250 °C over the same catalyst in the absence of mNpht after 15 h on stream (Fig. 2). Similarly, no

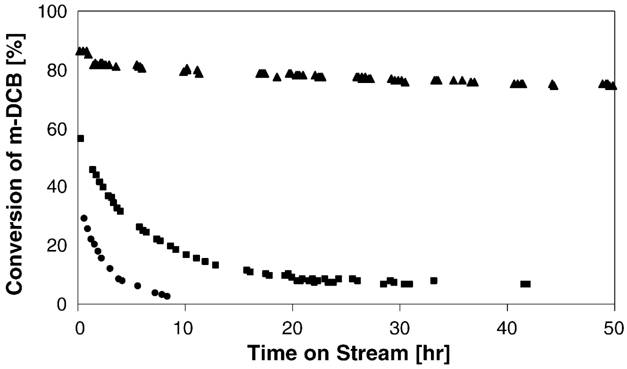

Fig. 1. Oxidation of *m*-DCB in the presence of mNpht over a 3.6 wt.% V_2O_5/TiO_2 catalyst at: (▲) 350 °C, (■) 275 °C, and (●) 250 °C (500 ppmv *m*-DCB, 20 ppmv mNpht, 10% O_2, balance He, space velocity of 53,000 cc/g h).

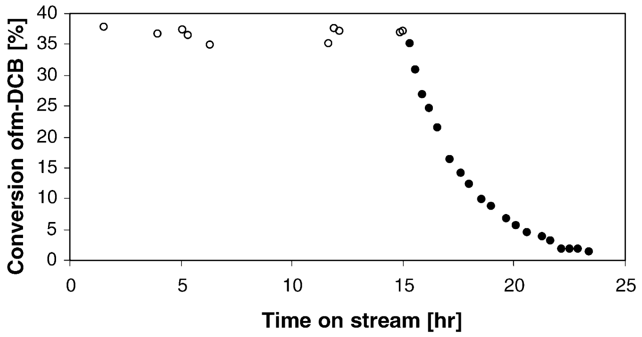

Fig. 2. Oxidation of *m*-DCB over a 3.6 wt.% V_2O_5/TiO_2 catalyst at 250 °C in the absence (○) and presence (●) of mNpht (500 ppmv *m*-DCB, 0 or 20 ppmv mNpht, 10% O_2, balance He, space velocity of 53,000 cc/g h).

deactivation was observed for the oxidation of *o*-DCB at 350 °C after 100 h on stream [17].

Finally, the effect of the concentration of mNpht on the oxidation of *m*-DCB is demonstrated for two different temperatures in Fig. 3a. Both at 250 and 275 °C an increase in the mNpht concentration results in a significantly faster deactivation of the V_2O_5/TiO_2 catalyst. The removal of the mNpht by the V_2O_5/TiO_2 catalyst during the same experiments is shown in Fig. 3b. While no mNpht was detected at the reactor outlet during the experiments in the presence of 20 ppmv mNpht, the conversion of mNpht decreases with time on stream if 200 ppmv mNpht is used. Nevertheless, substantial amounts of mNpht are still removed by the V_2O_5/TiO_2 catalyst even after the catalyst has been completely deactivated for the oxidation of *m*-DCB (i.e., after 5 h on stream). These results indicate that after poisoning selectively the vanadia active sites, mNpht continues to accumulate on the surface, presumably on the titania support.

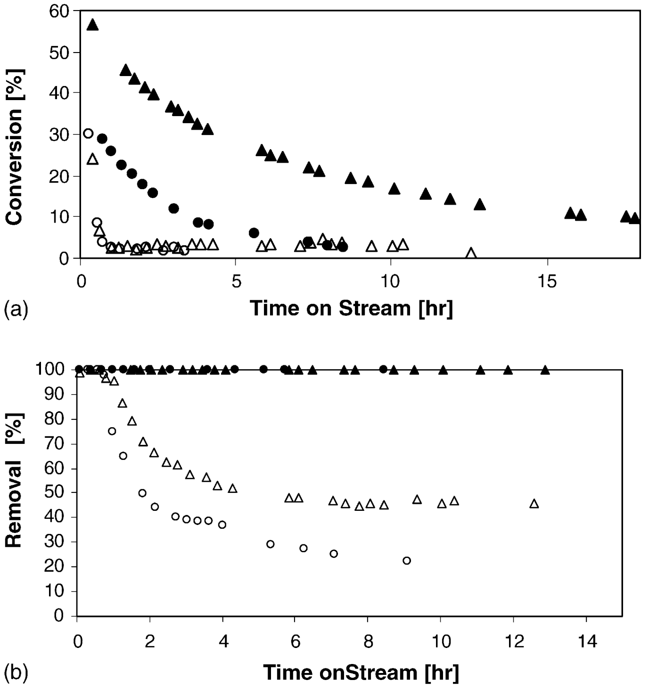

Fig. 3. (a) Oxidation of *m*-DCB over a 3.6 wt.% V_2O_5/TiO_2 catalyst at: (▲) 275 °C and 20 ppmv mNpht, (●) 250 °C and 20 ppmv mNpht, (△) 275 °C and 200 ppmv mNpht and (○) 250 °C and 200 ppmv mNpht (500 ppmv *m*-DCB, 20 or 200 ppmv mNpht, 10% O_2, balance He, space velocity of 53,000 cc/g h). (b) Removal of mNpht over a 3.6 wt.% V_2O_5/TiO_2 catalyst at: (▲) 275 °C and 20 ppmv mNpht, (●) 250 °C and 20 ppmv mNpht, (△) 275 °C and 200 ppmv mNpht and (○) 250 °C and 200 ppmv mNpht (500 ppmv *m*-DCB, 20 or 200 ppmv mNpht, 10% O_2, balance He, space velocity of 53,000 cc/g h).

An elemental analysis (Galbraight laboratories) performed on a spent catalyst (i.e., a catalyst deactivated at 250 °C) revealed the presence of 10 wt.% carbon on the catalyst surface. This suggests that the deactivation observed in the present study may be attributed to the formation of carbonaceous surface species. In agreement with these results, Bond and König [11] also observed a deactivation of vanadia/titania catalysts during the oxidation of *o*-xylene. The loss of activity in that case was also attributed to the formation of surface carbonaceous deposits and was more pronounced at lower temperatures. Similar results were also reported by Mongkhonsi and Kershenbaum [9], who ruled out the possibility of vanadia reduction during deactivation, based on the results of XPS measurements.

The pure titania support was also exposed to a mixture of *m*-DCB and mNpht at 250 °C (Fig. 4). Previous studies of the oxidation of *o*-DCB indicated that the TiO_2 support exhibits some activity for the oxidation of this compound [17]. However, TiO_2 also deactivates very quickly when mNpht is present in the reaction gas stream. In contrast, no mNpht was detected at the reactor outlet during the first 5 h on stream. Even after 24 h approximately 25% of mNpht was removed, indicating that the mNpht continues to react and/or accumulate on the titania.

3.1.2. Reaction by-products

The only observable products of the catalytic oxidation of chlorobenzenes (i.e., *o*- or *m*-DCB) over a V_2O_5/TiO_2 catalyst are CO, CO_2 and HCl. In fact, the carbon balance can be closed within ±5% in this case [17]. However, when mNpht was added to the reaction mixture heavier compounds condensed at the reactor outlet at room

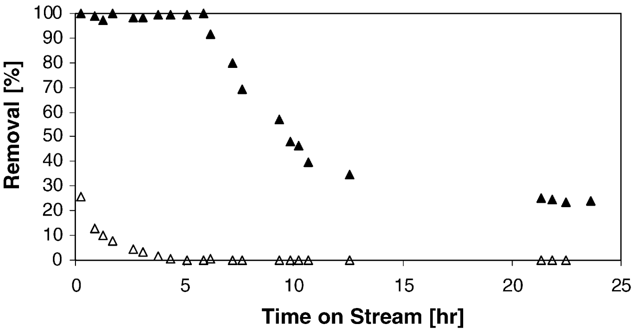

Fig. 4. Removal of *m*-DCB and mNpht over TiO_2 at 250 °C (△), *m*-DCB (▲): mNpht (500 ppmv *m*-DCB, 20 ppmv mNpht, 10% O_2, balance He, space velocity of 53,000 cc/g h).

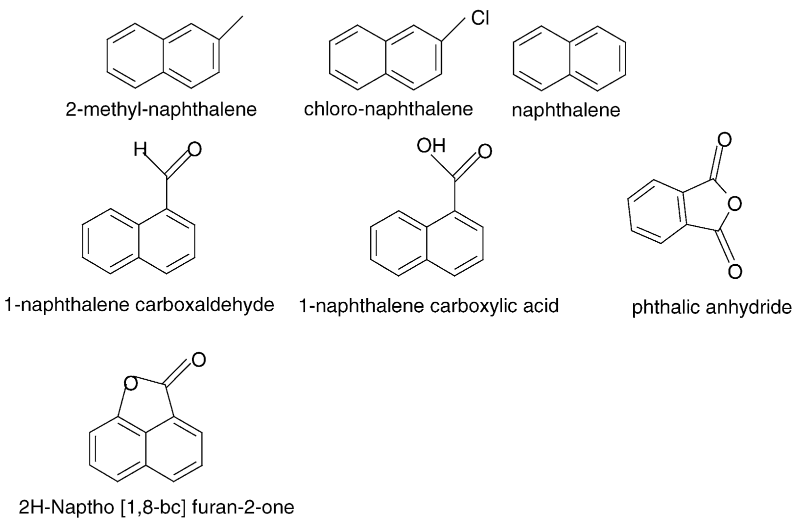

Fig. 5. Reaction by-products formed during the oxidation of *m*-DCB in the presence of mNpht.

temperature. A GC–MS analysis of these by-products revealed the presence of trace amounts of isomerization (i.e., 2-methyl-naphthalene), partial oxidation (i.e., 1-naphthalene carboxaldehyde, 1-naphthalene carboxylic acid, phthalic anhydride and 2H-naphtho[1,8]furan-2-one), cracking (i.e., naphthalene) and chlorination (i.e., chloronaphthalene) products (Fig. 5).

3.1.3. FTIR studies

FTIR spectra collected at different time intervals during exposure of the 3.6 wt.% V_2O_5/TiO_2 catalyst to mNpht at 250 °C are shown in Fig. 6. Several bands were observed in the 1850–1650 cm^{-1} region characteristic of C=O stretching vibrations. In particular, the bands at 1850 and 1783 cm^{-1} can be assigned to the symmetric and asymmetric C=O

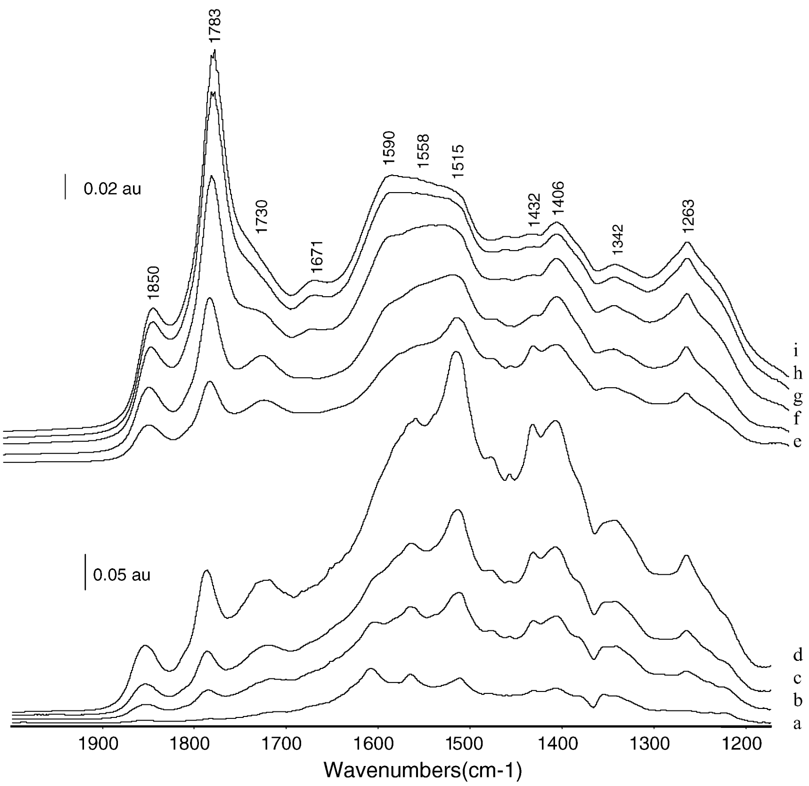

Fig. 6. In situ FTIR spectra of a 3.6 wt.% V_2O_5/TiO_2 catalyst collected in a 20 ppmv mNpht/10% O_2/balance He stream at 250 °C after (a) 10 min, (b) 20 min, (c) 30 min, (d) 50 min, (e) 2 h, (f) 4 h, (g) 10 h, (h) 17 h and (i) 20 h.

stretching vibrations of the O=C–O–C=O system of a cyclic anhydride. A similar assignment was also made during the adsorption of maleic anhydride on vanadia/titania [24,25] and on alumina-supported V_2O_5-P_2O_5 [26] catalysts. Furthermore, the band at 1263 cm^{-1} also shows the same changes in intensity with time on stream as the bands assigned to the C=O stretching vibrations of this anhydride species and can be assigned to the C–O–C bridge of the same molecule [26]. This cyclic anhydride formed is probably the same phthalic anhydride species detected as a reaction by-product.

The lower intensity features at 1730 and 1671 cm^{-1} can be assigned to the C=O stretching vibrations of a lactone [25] and a quinone type [21,24] species, respectively. A band at 1342 cm^{-1} shows the same increase in intensity as the band at 1730 cm^{-1} and can be assigned to the C–O vibration of this lactonic structure [27]. The lactone-type surface species observed may be similar to the 2H-naphtho[1,8]-furan-2-one species detected during the offline MS analysis. Quinones have been reported as reaction intermediates during the oxidation of toluene to phthalic anhydride [28]. Finally, the presence of several surface species containing carbonyl groups was also detected by FTIR during the oxidation of *o*-xylene to phthalic anhydride over vanadia/titania catalysts [29], although their exact nature was not determined.

The spectra of Fig. 6 further include two bands at 1515 and 1432 cm^{-1}, which are in the typical region of the asymmetric and symmetric stretching vibrations of carboxylates. Similar bands were previously assigned to surface maleate species [21,24,25]. In the present study however, the carboxylate species formed is probably a phthaleate, since methyl naphthalene was used as the reactant. Furthermore, additional bands at 1558 and 1406 cm^{-1} are in the region characteristic for the asymmetric and symmetric vibrations of surface benzoates [30] and hence, can be assigned to naphthoates in the present study. These species are probably precursors for the further oxidized phthaleates.

Finally, a band appears to grow slowly with time on stream in the spectra of Fig. 6 at 1590 cm^{-1}. This is believed to be a vibration of polyaromatic systems and similar bands were previously assigned to surface "coke" on zeolites [27]. The intensity of this polyaromatic "coke" band appears to increase together in the spectra of Fig. 6 with the intensity of bands at 1850 and 1783 cm^{-1} (C=O bond) even after exposure of the catalyst to mNpht for several hours, suggesting the formation and surface accumulation of polyaromatic compounds containing carbonyl groups. Similar polyaromatic compounds, containing oxygenated fragments were also observed on zeolites during the oxidation of benzene [27].

Spectra of both the 3.6 wt.% V_2O_5/TiO_2 catalyst and the pure TiO_2 support after a 20 h exposure to mNpht under reaction conditions (i.e., 20 ppmv mNpht, 10% O_2, balance He) are shown in Fig. 7. As expected from the kinetic results, TiO_2 also shows some activity for the oxidation of mNpht. In particular, surface phthaleates and naphthoates (characteristic bands at 1515, 1432 and at 1558, 1406 cm^{-1}, respectively) accumulate on the catalyst surface with time on stream. However, the bands corresponding to carbonyl bonds are much weaker than the corresponding bands in the spectra of the V_2O_5/TiO_2 catalyst, indicating that vanadia catalyzed the formation of these species. Furthermore, the intensity of the band at 1590 cm^{-1} corresponding to polyaromatic "coke" compounds, is lower on the TiO_2 support than on the V_2O_5/TiO_2 catalyst after 20 h on stream.

The results of these in situ FTIR studies in combination with the activity measurements indicate that the deposition of carbonaceous surface species is the main cause for the observed deactivation for the oxidation of *m*-DCB in the

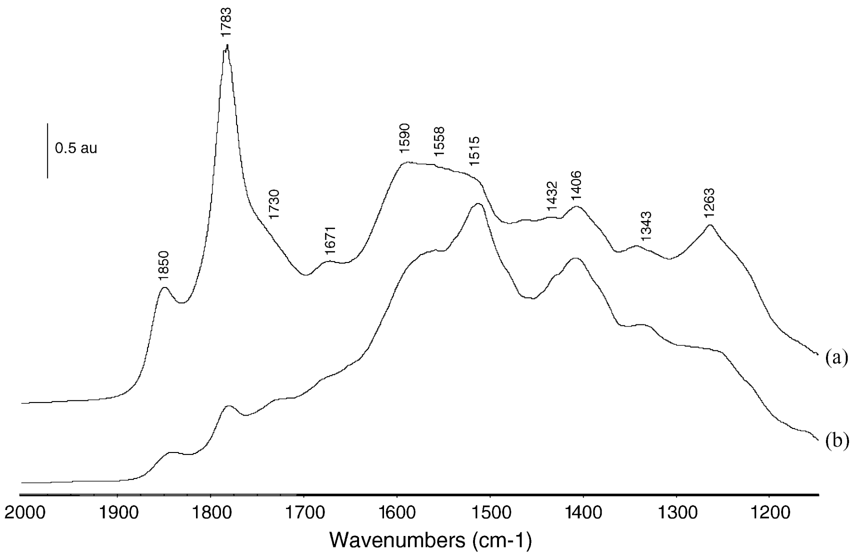

Fig. 7. In situ FTIR spectra collected at 250 °C after exposure of (a) the 3.6 wt.% V_2O_5/TiO_2 catalyst and (b) the TiO_2 support to a 20 ppm mNpht/10% O_2/balance He stream for 20 h.

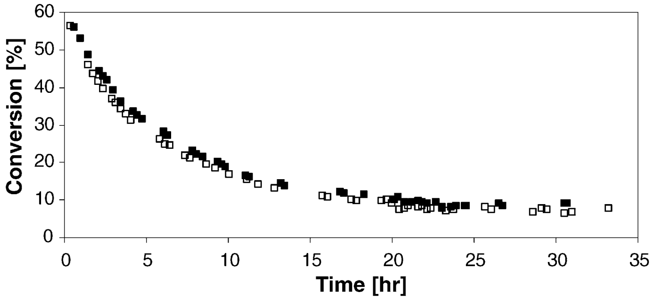

Fig. 8. Oxidation of *m*-DCB in the presence of mNpht over (■) a fresh and (□) a regenerated 3.6 wt.% V_2O_5/TiO_2 catalyst at 275 °C (500 ppmv *m*-DCB, 20 ppmv mNpht, 10% O_2, balance He, space velocity of 53,000 cc/g h).

presence of mNpht. Furthermore, the deactivation proceeds faster at lower temperatures indicating that the carbon deposits react to form total combustion products at higher temperatures.

3.2. Regeneration

The conversion of *m*-DCB as a function of time on stream over a fresh 3.6 wt.% V_2O_5/TiO_2 sample and a deactivated sample, that was subsequently exposed to a 10% O_2/He mixture for 5 h at 350 °C is shown in Fig. 8. Identical results were obtained in both cases, indicating that the deactivation is fully reversible when the deactivated sample is oxidized at elevated temperatures. The regeneration process is relatively fast at 350 °C and is completed within a few hours.

Once mNpht is removed from the reacting gas mixture, the catalyst can be regenerated even in the presence of *m*-DCB. The rate of regeneration in this case depends both on the temperature used and the amount of carbon accumulated on the catalyst. As can be seen in Fig. 9 for example, upon removal of mNpht the catalyst regains its activity faster at 275 than at 250 °C (12 versus 30 h). Furthermore, a sample deactivated using an inlet concentration of 200 ppmv mNpht requires a substantially longer period to reach its original activity upon removal of mNpht than a sample deactivated using 20 ppmv (mNpht 30 versus 12 h). These results are consistent with the gasification of the accumulated surface "coke" through a slow oxidation process.

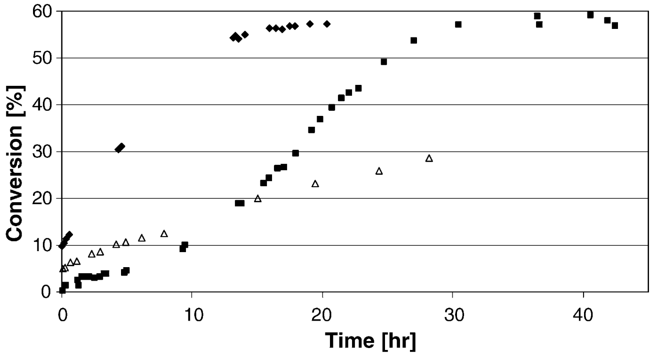

Fig. 9. Oxidation of *m*-DCB over a 3.6 wt.% V_2O_5/TiO_2 catalyst after deactivation at (◆) 275 °C with 20 ppmv mNpht, (■) 275 °C with 200 ppmv mNpht and (△) 250 °C with 20 ppmv mNpht and removal of mNpht from the reaction gas stream (500 ppmv *m*-DCB, 10% O_2, balance He, space velocity of 53,000 cc/g h).

This hypothesis is further supported by in situ FTIR spectra collected during treatment of a deactivated V_2O_5/TiO_2 sample with a 10% O_2/He mixture (Fig. 10). The spectra of Fig. 10 indicate that all bands associated with the different types of surface organic fragments discussed above – including the "coke" band at 1590 cm^{-1} – decrease in intensity upon exposure to the O_2/He mixture at 275 °C. However, this is a very slow process and several hours are required for the complete elimination of these bands from the spectra.

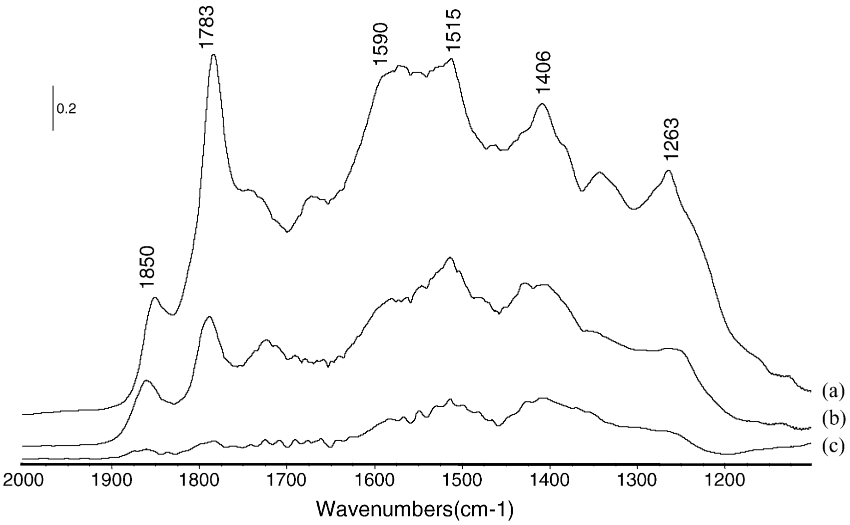

Fig. 10. In situ FTIR spectra of a 3.6 wt. % V_2O_5/TiO_2 catalyst collected after (a) exposure to a 20 ppm mNpht/10% O_2/balance He stream for 29 h, followed by exposure to a 10% O_2/He stream for (b) 3 h and (c) 18 h.

4. Conclusion

We have investigated the effect of mNpht, a known coke-precursor, on the oxidation of *m*-DCB over a 3.6 wt.% V_2O_5/TiO_2 catalyst. Complete deactivation of the catalyst was observed in the presence of mNpht. The rate of deactivation was higher at lower temperatures and higher mNpht concentrations. Results of in situ FTIR studies confirm that carbon deposition in the form of coke is responsible for the observed loss of activity. The catalyst activity can be fully restored upon removal of mNpht from the reaction gas mixture. The rate of regeneration depends on the amount of carbon accumulated on the catalyst surface and the regeneration temperature.

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