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In situ DRIFT study of the reactivity and reaction mechanism of catalysts based on iron–molybdenum oxides encapsulated in Boralite for the selective oxidation of alkylaromatics

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Abstract

An in situ DRIFT investigation of the behavior of iron–molybdenum oxides encapsulated in Boralite (FeMo/Bor) during the oxidation of toluene is reported. The study was carried out to obtain a better understanding of the differences between this catalytic material and (i) V–TiO_2 based catalysts and (ii) bulk $Fe_2(MoO_4)_3$. V–TiO_2 based catalysts show a severe decrease in the selectivity to benzaldehyde with increasing conversion of toluene, in contrast FeMo/Bor samples. The effect was attributed to the presence of stronger Lewis acid sites in vanadium-based catalysts which, activating the carbon atom of the carbonyl groups, facilitate its nucleophilic attack to form benzoate species which further degrade to carbon oxides. FeMo/Bor shows higher selectivity at low conversion than bulk $Fe_2(MoO_4)_3$, probably due to the presence of nanosized iron–molybdate particles inside the zeolite channels, and lower selectivity at high conversion. Due to back-diffusion limitations inside the zeolite pores, the aromatic ring of the alkylaromatic is oxidatively attacked to form maleic anhydride, precursor of the further oxidation to carbon oxides. In FeMo/Bor a different main pathway is responsible for the lowering of selectivity at high conversion with respect to V–TiO_2 based catalysts.

Keywords: Toluene; Benzaldehyde; DRIFT; Infrared; Iron–molybdate

1. Introduction

Although large scale processes such as production of terephthalic acid use a homogeneous selective partial oxidation process to selectively oxidize an alkylaromatic, there is industrial interest in developing heterogeneous selective oxidation processes using gaseous oxygen, when the products cannot be easily recovered from the products stream (e.g., by crystallization as in the case of terephthalic acid). This is the case of various halo-substituted toluenes, for which the development of a solid catalyst capable of selectively converting them to the corresponding aldehydes is industrially attractive, especially when the catalyst can be used in the synthesis of a range of substituted benzaldehydes of commercial interest.

Various solid catalysts have been described in the literature, although focus has principally been on the model reaction of toluene selective oxidation to benzaldehyde [1–10]. Most of these catalysts are based on vanadia supported either on SiO_2 or TiO_2, and further promoted by various additives, such as Te or K_2SO_4 [6]. Although promotion significantly increases selectivity to benzaldehyde, selectivities higher than 50% were obtained only for conversions of toluene below 10% giving rise to a maximum yield of benzaldehyde

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below about 5% [6]. New classes of catalysts capable of maintaining selectivity up to high values of conversion are thus necessary.

Recently zeolites containing iron and molybdenum (indicated as FeMo/DBH) have been reported in the literature to have very interesting reactivity and selectivity characteristics in *p*-xylene selective oxidation to the corresponding aldehydes [11–15]. The synthesis of these catalysts is quite complex, and involves the addition of Fe and Mo by chemical vapor deposition (CVD) to the zeolite [11–15]. Also the nature of the zeolite and its pretreatment to create structural defects are key parameters in the preparation [16,17] to obtain selective catalysts, because specific iron–molybdate nanoparticles within the structure of the host zeolite must be synthesized [16].

Better results have been obtained using partially deboronated zeolites. Using an optimized preparation procedure, maximum yields above 30% in 3-fluoro-benzaldehyde from 3-fluoro-toluene were shown to be possible, which corresponds to an improvement in the productivity to benzaldehyde by a factor of 5–6 with respect to toluene conversion on vanadium-based catalysts [17] — improvement which is even more relevant taking into consideration that a halogen group in the meta-position decreases both activity and selectivity in the oxidation of alkylaromatics [18]. Nevertheless, industrial exploitation of a process of selective oxidation of alkylaromatics requires further improvement of the catalytic performances, which implies a better understanding of the (i) key features of the catalytic behavior and (ii) reasons for the lowering of the selectivity to the aldehyde with increasing conversion of the alkylaromatics.

In order to contribute to this objective, the aim of this study reported in this communication was to analyze by the in situ DRIFT method, the reactivity and reaction mechanism in toluene selective oxidation (chosen as the model reaction for the infrared investigation) of a Fe–Mo oxide encapsulated in a Boralite zeolite (FeMo/Bor) matrix which showed enhanced performances in the selective oxidation of 3-fluoro-toluene [17]. Specifically, the objectives were to:

- analyze the nature and evolution of the adsorbed species on FeMo/Bor during the catalytic reaction and compare them with the known behavior in their interaction with V–TiO_2 based catalysts, in order to understand the differences between the two classes of catalysts;
- understand the differences in the behavior between bulk iron–molybdate and iron–molybdate nanoxides in a zeolite matrix.

2. Experimental

2.1. Synthesis of catalysts

A commercial Boralite (HAMS-1B-3 from PQ Company, the same used by Yoo et al. [11–15] for the preparation of the optimal Fe–Mo/zeolite catalysts for *p*-xylene oxidation) having a 10.2% B content was used as the host zeolite. This sample was then partially deboronated by high temperature steaming in a quartz reactor (flow of N_2 (1.2 l/h) up to 650°C using a temperature increase of 30°C/min; once a temperature of 650°C is reached, the flow of N_2 is saturated at room temperature with deionized water and sent to the reactor; the zeolite is treated in these conditions for 16 h). After cooling the reactor to room temperature, the zeolite was then treated with a dilute solution of HCl for 3 h (pH 2.5) to remove extralattice boron. Then the zeolite was washed with double distilled water up to a pH of 7 and finally dried and calcined at 500°C.

After this pretreatment of the Boralite, Fe and Mo were added by CVD using methodology described elsewhere [16,17]. The Mo was added two times by CVD in order to optimize its loading. The solid was finally calcined in air at 300°C (8 h) and then at 650°C (8 h). The content of B in the sample is 5.6 wt.%, the iron content 4.6% and the Mo/Fe ratio about 0.5. The surface area of the final sample is 290 m^2/g. Hereinafter, this sample will be referred to as FeMo/Bor.

The reference bulk $Fe_2(MoO_4)_3$ sample was prepared using the method reported by Carbucicchio and Trifirò [19] to obtain the pure compound. Its surface area is 4 m^2/g and XRD analysis indicates the presence of a $Fe_2(MoO_4)_3$ phase plus weak reflections due to MoO_3.

2.2. Catalytic tests

Catalytic tests were carried out using a quartz continuous flow reactor (5 mm inner diameter) loaded with 0.5 g of catalyst in the form of small pellets (in the range 0.1–0.3 mm). The feed composition was 0.5% 3-fluoro-toluene, 5% O_2 and 94.5% helium. The space-velocity was set at 20 000 h^{-1} to avoid mass transfer limitations on the reaction rate. Tests were made in the range 300–500°C. The catalysts were found to show stable catalytic behavior at least for a timescale of about 20 h of time-on-stream. The axial temperature profile was determined by a thermocouple inserted into the catalytic bed.

Analysis of the feed composition and of the reaction products was carried out using two gas chromatographs (GC), the first being on-line for the analysis of incondensable gases (N_2, O_2, CO, CO_2). All organic products and water were absorbed in two traps containing acetone as the solvent and maintained at about −5°C. The products in the absorption traps were analyzed using a GC equipped with a mass quadrupole detector after adding tridecane as an internal standard. The first GC uses a TCD detector and a 3 m long Carbosphere packed column, and the second a HP-5 5% PhMe Silicone 30 m long capillary column.

2.3. In situ DRIFT experiments

In situ DRIFT (diffuse reflectance infrared fourier transform) measurements were made using a DRIFT cell (Environmental Chamber from Hellma) connected by a heated line to the outlet of a flow reactor apparatus containing the same catalyst mounted in the DRIFT cell and which thus allows the species adsorbed on the catalyst at different levels of conversion to be monitored in the DRIFT cell. The reactor can be by-passed to instead analyze the direct interaction of the feed with the catalyst contained in the DRIFT cell. The DRIFT reaction chamber is made of stainless steel, has a ZnSe window and a total cell volume of about 10 cm^3. The sampling cup containing the undiluted catalyst is at the top of the stainless steel rod, in which both the heating cartridge and the thermocouple are embedded. Gas ports are provided for evacuation, introduction and vents of reactants/products. Circulating water is used to cool the body of the reaction chamber. The temperature limits for the cell are 500°C in vacuum or N_2 flow and about 450°C in helium flow.

Due to its specific geometry, no subtraction for gas phase reactants/products is needed, but the spectra were corrected to consider sample infrared emission by subtracting the spectrum of the catalyst heated at the same temperature in a helium flow. Before the experiments, the catalyst is pretreated at 500°C in air to clean the surface. Then, after cooling to the required temperature, a flow of helium or air (50 cc/min) containing about 2% toluene, benzaldehyde or benzyl alcohol (added by a saturator) is sent to the DRIFT cell and the spectra are recorded progressively up to a time, usually of 3 h. Then, after by-passing the saturator containing the organic, the spectra are recorded for a further 30–60 min to check the stability of the adsorbed species and then the temperature of the DRIFT cell is raised up to its temperature limit (450 or 500°C depending on the use of He or air, respectively).

Spectra were recorded at a 2 cm^{-1} resolution using a Bruker Equinox 50 instrument with an MCT detector.

3. Results and discussion

3.1. Catalytic behavior

Reported in Fig. 1 is the selectivity vs. conversion plot in 3-fluoro-toluene oxidation to 3-fluoro-benzaldehyde (3FBA) of FeMo/Bor and bulk $Fe_2(MoO_4)_3$ samples and for comparison those obtained in comparable reaction conditions by Aguilar Elguézabal and Cortès Corberán [6] for V–TiO_2 based samples, although in toluene oxidation to benzaldehyde. In fact, no literature data are available for 3-fluoro-toluene oxidation, but it is known that the presence of electron withdrawing groups such as F in the meta-position leads to a decrease in both activity and selectivity in alkylaromatic oxidation [18] and thus using 3-fluoro-toluene instead of toluene even worst catalytic results may be obtained. Although various authors have studied toluene oxidation to benzaldehyde on vanadium-based catalysts as cited in the introduction, the catalytic data of Aguilar Elguézabal and Cortès Corberán [6] are among those showing the highest selectivity and thus can be considered representative of the behavior of this class of catalysts. Selected data of Aguilar Elguézabal and Cortès Corberán [6] are for an undoped vanadium on a titania-coated silica support (titania content equivalent to 1.6 theoretical monolayers, and vanadia loading equivalent to 1 theoretical monolayer) and for a potassium sulfate doped sample, because this type of doping was shown to give better catalytic performances [6]. These two

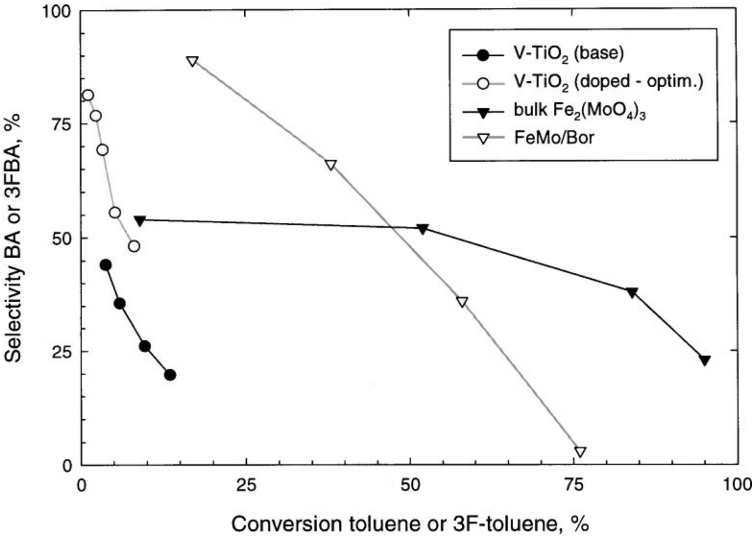

Fig. 1. Behavior in 3-fluoro-toluene conversion to 3-fluoro-benzaldehyde (3FBA) of FeMo/Bor and bulk $Fe_2(MoO_4)_3$ (data obtained at variable reaction temperatures in the range 300–500°C [17]) and for comparison, behavior of doped and undoped (base) V–TiO_2 based catalysts in toluene oxidation to benzaldehyde (data elaborated from [6], see also text).

catalysts are hereinafter referred to as V–TiO_2 (base) and V–TiO_2 (doped — optimized), respectively. Data for iron–molybdenum and vanadium-based catalysts were obtained in comparable reaction conditions and in both cases the selectivity vs. conversion plot was determined at variable reaction temperatures in the range 300–500°C.

Although doping of V–TiO_2 based catalyst can largely increase the selectivity, both doped and undoped V–TiO_2 based catalysts show a drastic decrease in selectivity as conversion increases. It has been suggested that the effect of doping is to inhibit the oxidation of benzaldehyde to benzoic acid [6] which further converts easily to carbon oxides. Using a high steam content in the feed, benzoic acid becomes the main reaction product [20], but there is still a drastic decrease in the selectivity with increasing conversion. It may be concluded that the typical feature of V–TiO_2 based catalysts is the easy oxidation of benzaldehyde to benzoic acid, which, however, is easily converted to carbon oxides.

The behavior of iron–molybdenum based catalysts (Fig. 1) shows instead a much less drastic decrease in selectivity with increasing conversion, which thus results in a considerable increase in productivity. The FeMo/Bor sample shows greater selectivity than bulk $Fe_2(MoO_4)_3$ up to a conversion of about 50%, but lower selectivities for higher conversion values.

The data in Fig. 1 thus raise two main questions about the catalytic behavior of these samples in alkylaromatic oxidation:

1. Why do iron–molybdenum based catalysts show a less dramatic decrease in selectivity with increasing conversion than vanadium-based catalysts?
2. Why does FeMo/Bor show higher selectivity at low conversion than bulk iron–molybdate, but lower selectivity at high conversion?

The answer to these two questions is the core of the in situ DRIFT investigation reported below. Since infrared spectroscopy data (both in transmission and DRIFT mode) of toluene oxidation on vanadium-based catalysts are available in the literature [21–30], further investigation of this type was thought to be unnecessary and thus the present investigation was focused on iron–molybdenum based catalysts.

3.2. In situ DRIFT studies

3.2.1. Low temperature studies

Reported in Fig. 2 are selected in situ DRIFT spectra recorded for the interaction of a flow of 2% toluene in air with the FeMo/Bor catalyst up to reaction

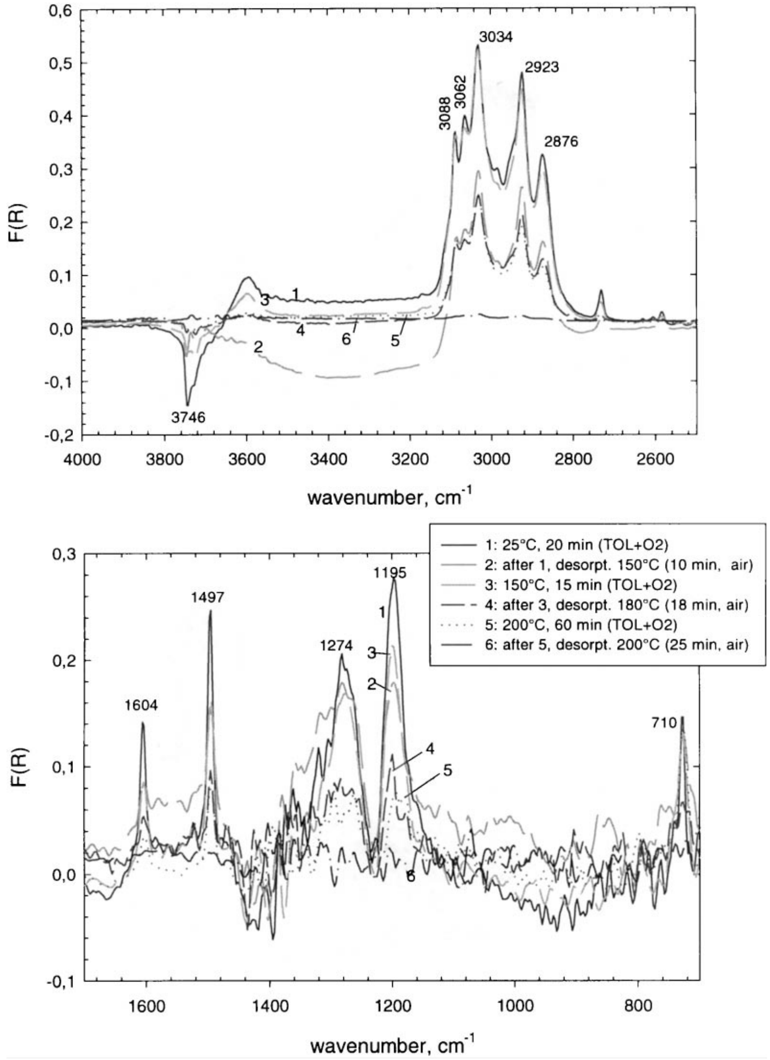

Fig. 2. In situ DRIFT studies of the interaction of toluene in the presence of air with the FeMo/Bor catalyst at 25°C for 20 min (1), at 150°C for 15 min (3) and at 200°C for 60 min (5). Spectra (2), (4) and (6) refer to the spectra detected after treatment in an air flow at 150°C for 10 min (2), 180°C for 18 min (4) and 200°C for 25 min (6) after having recorded spectra (1), (3) and (5), respectively.

temperatures of 200°C (spectrum 1: 25°C for 20 min; spectrum 3: 150°C for 15 min; spectrum 5: 200°C for 60 min) as well as selected spectra after consecutive desorption up to 200°C in an air only flow. The upper graph in Fig. 2 reports the spectra in the 4000–2500 cm^{-1} region (ν_{OH} and ν_{CH} region). At 25°C (spectrum 1) toluene interacts weakly with the external silanol groups of the zeolite as shown by the disappearance of the band at 3746 cm^{-1} and the appearance of the new band at 3600 cm^{-1} (ν_{OH} group interacting with the methyl group of toluene). The bands in the 2800–3200 cm^{-1} region are characteristic of the stretching frequencies of C–H groups in weakly perturbed toluene. The bands in the 700–1800 cm^{-1} region (ring in-plane and out-of-plane deformations) confirm the weak interaction of toluene mainly through the methyl group and indicate that no products of partial oxidation of toluene form by interaction of toluene with the catalyst in the presence of air, in contrast V–TiO$_2$ based catalysts [24,31] which show the formation of carboxylate by contacting toluene at room temperature even in the absence of gaseous oxygen. In agreement, when the temperature is increased up to 150°C in an air only flow, the intensity of the spectrum decreases, but no new bands appear to be detectable. With respect to V–TiO_2 based catalysts [24,25,31], it should also be noted that no bands in the 1340–1370 cm^{-1} region, assigned to a CH_2 deformation mode and indicating the formation of benzyl species, can be detected. Furthermore, the band near 1450 cm^{-1} (19b vibration of the aromatic ring) is absent or very weak, whereas the bands at 1274 and 1195 cm^{-1} ($\nu_{Ar\text{–}C}$ and 9a vibration of the aromatic ring, respectively [24]) are significantly more intense (with respect to the 1497 cm^{-1} band; 19a vibration of the aromatic ring) than those observed on V–TiO_2 catalysts. This is consistent with the presence of a nearly unperturbed toluene adsorbed on FeMo/Bor and activated toluene species (benzyl radical) on V–TiO_2 catalysts.

It should be noted that the same conclusions about the species which form by interaction of toluene with V–TiO_2 catalysts were obtained using transmission [25] and DRIFT [24] modes and thus, reasonably they, do not depend on the specific modalities of the infrared study. Therefore, toluene interaction at room temperature with FeMo/Bor, in contrast V–TiO_2 catalysts, does not give evidence of the formation of partial oxidation products of toluene, nor of its activation (benzyl radical).

The interaction up to 200°C of FeMo/Bor with toluene in the presence of air does not change the spectrum significantly, apart from the fact that interaction with the silanol groups external to the zeolite crystals is not more evident. This indicates that at room temperature, possibly due to diffusion limitations, toluene interacts mainly with sites on the external zeolite crystals, whereas at higher temperatures adsorption occurs predominantly inside the zeolite channels. Other features of the spectra, however, remain nearly unchanged. Desorption at 200°C for 25 min (spectrum 6 in Fig. 2) after interaction at the same temperature with toluene/air for 1 h (spectrum 5) leads to the complete disappearance of all adsorbed species, confirming their weak interaction and the complete absence of formation of carboxylate type species which desorb at much higher temperatures (400°C or above). DRIFT experiments with V–TiO_2 have shown that at 150°C toluene is instead nearly completely transformed to benzoate and benzoquinone species [24].

3.2.2. Higher temperature studies

Above a temperature of about 230°C the in situ DRIFT spectra during the interaction of toluene/air with the FeMo/Bor catalyst change considerably. Reported in Figs. 3 and 4 are the spectra recorded at 250°C (Fig. 3), 300°C (Fig. 4a) and 400°C (Fig. 4b). At 250°C new bands appear at 1708, 1663, 1450 and 1386 cm^{-1}, plus a series of new weak bands in the 1150–750 cm^{-1} region which, however, do not provide useful information because they are influenced by the effect of toluene adsorption/transformation on the skeletal catalyst vibrations. The other new bands grow in intensity with increasing time in contact of the toluene/air flow with the catalyst (from 1 to 72 min in the 1→4 spectra of Fig. 3) . The spectrum is consistent with that detected in DRIFT experiments on V–TiO_2 at 150°C [24], apart from the absence of broad bands indicating the presence of carboxylate species. Sanati and Andersson [24] observed bands at 1705 and 1662 cm^{-1} (the first rather weak) and assigned them to $\nu_{C=O}$ in benzaldehyde and benzoquinone, respectively, whereas Busca et al. [25,31] in transmission mode experiments found $\nu_{C=O}$ in benzaldehyde at 1635 cm^{-1} due to interaction of carbonyl groups with Lewis acid sites (coordinatively unsaturated V centers). Our observation on benzaldehyde adsorption (see later) is consistent with this second interpretation, and thus the bands at 1708 and 1663 cm^{-1} indicate the presence of two types of adsorbed benzaldehyde with carbonyl groups weakly or more strongly interacting with surface Lewis acid sites of the catalyst. Other new bands at 1450 and 1386 cm^{-1} are consistent with ring and CHO deformations, respectively, of adsorbed benzaldehyde.

Desorption at 250°C in a flow of air (spectra 5 and 6 in Fig. 3 for 10 and 30 min of desorption time, respectively) does not change the spectra significantly. However, immediately after the switching off of the toluene feed, new bands appear at 1316 and 1386 cm^{-1} (see spectrum 5 in the expansion of the 1600–1200 cm^{-1} region in Fig. 3), which disappear after a longer desorption time at 250°C (spectrum 6) thus indicating that they are associated with a transient species which becomes detectable after stopping the toluene feed. Other

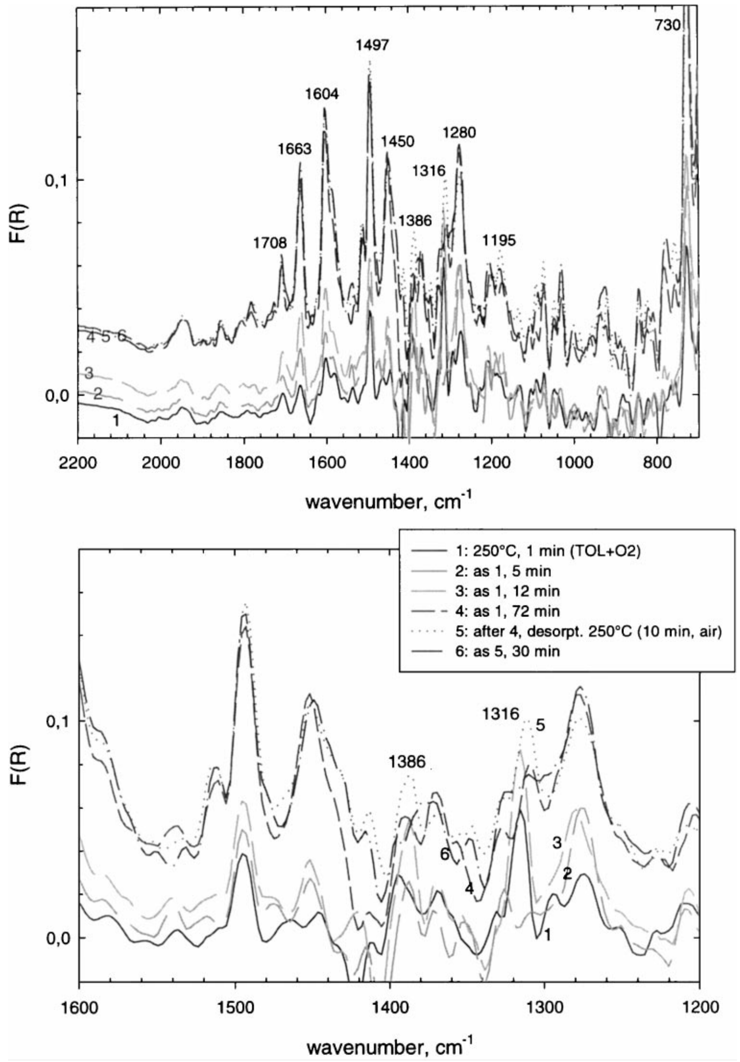

Fig. 3. In situ DRIFT studies of the interaction of toluene in the presence of air with the FeMo/Bor catalyst at 250°C for 1 min (1), 5 min (2), 12 min (3) and 72 min (4). Spectra (5) and (6) refer to the spectra detected after treatment in an air flow at 250°C for 10 min (5) and 30 min (6) after having recorded spectrum (4).

spectral features remain nearly unchanged, and thus an unequivocal attribution is not possible. However, the position of the bands corresponds to that indicated as the particular spectroscopic feature for the benzyl radical. Tentatively, the 1316 and 1386 cm^{-1} bands may be attributed to wagging and scissoring modes of perturbed methylene groups in the benzyl radical. This species is reasonably present during the catalytic reaction at 250°C, but becomes more evident during the transient situation after stopping the toluene feed. These bands resulting from enhanced relative intensity during the transient situation after stopping the toluene feed also occur at higher reaction temperatures (spectrum 5 in Fig. 4a and b), confirming that the phenomenon is common over the entire temperature range 250–400°C.

At higher reaction temperatures (300 and 400°C as shown in Fig. 4a and b, respectively) the main spectral features remain similar to those discussed before, but new bands become evident at 1775 and 1852 cm^{-1}.

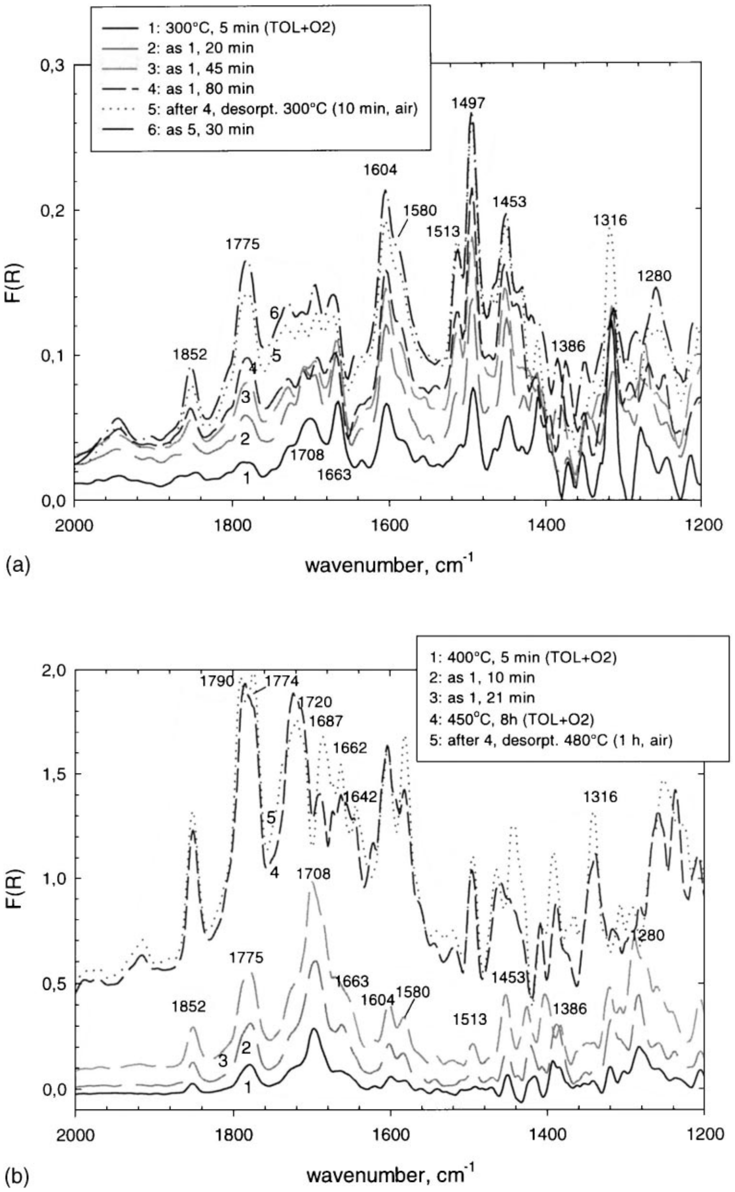

Fig. 4. In situ DRIFT studies of the interaction of toluene in the presence of air with the FeMo/Bor catalyst at 300°C (a) and 400°C (b): (a) interaction at 300°C for 5 min (1), 20 min (2), 45 min (3) and 80 min (4). Spectra (5) and (6) refer to the spectra detected after treatment in an air flow at 300°C for 10 min (5) and 30 min (6) after having recorded spectrum (4); (b) interaction at 400°C for 5 min (1), 10 min (2) and 21 min (3); interaction at 450°C for 8 h (4) and consecutive desorption in an air flow at 480°C for 1 h (5).

These bands are typical of cyclic anhydrides such as maleic anhydride [31] deriving from the degradation of the phenyl ring. They have also been observed on V–TiO_2 catalysts [24], although they were relatively much less intense. Comparing the spectra obtained at 300–400°C (Fig. 4) with those obtained at 250°C (Fig. 3) broader bands centered at about 1600–1550 and 1450 cm^{-1} can be observed which indicate the probable presence of benzoate or carboxylate species also, but in relatively smaller amounts than those observed on V–TiO_2 catalysts for which bands of carboxylate species are the dominant features of spectra recorded after interaction at temperatures above 200°C, even in the absence of gaseous oxygen.

It may be thus concluded that on the FeMo/Bor catalyst the general oxidation pathways of transformation are similar to those indicated for V–TiO_2 catalysts [31], e.g., toluene is activated through the formation of benzyl radicals and further transformed, possibly via a benzyloxo intermediate, to benzaldehyde and further to benzoate species, with a parallel pathway leading to degradation of the phenyl ring via maleic anhydride. However, with respect to V–TiO_2 catalysts, the following differences can be noted:

1. The benzaldehyde interacts weakly through the carbonyl group with surface Lewis acid sites.
2. Adsorbed benzaldehyde is less easily transformed to benzoate species, tentatively as a consequence of the first observation, as discussed in more detail later.
3. The oxidative attack of the aromatic ring via maleic anhydride intermediate is enhanced.

After prolonged interaction of the toluene/air feed with the FeMo/Bor catalyst at high temperature (spectrum 4 in Fig. 4b) the bands indicating the presence of maleic anhydride (1852 and 1780 cm^{-1} bands assigned to $\nu_{C=O_{sym}}$ and $\nu_{C=O_{as}}$) become the dominant bands, but a range of new bands in the 1550–1650 cm^{-1} region also appear which indicates the coexistence of a number of adsorbed products (possibly, benzoic acid $-1720\,cm^{-1}$, benzaldehyde $-1708\,cm^{-1}$, and benzoquinone $-1662\,cm^{-1}$, although the complexity of the spectrum does not allow clear conclusions). However, bands indicating the presence of carboxylate species (1550 and 1430 cm^{-1}) remain rather weak in comparison with other bands, in clear contrast with the usual finding for a range of oxide catalysts in the interaction with alkylaromatics [31]. This indicates the lower tendency of this catalyst to form such a type of species.

After the interaction of toluene/air feed with the catalyst, the consecutive desorption in an air only flow (spectrum 6 in Fig. 4a and spectrum 5 in Fig. 4b) does not change significantly the features of the spectrum. This indicates that such a type of species is rather stable and does not desorb after switching off the toluene feed. It may be noted that the bands in the 1700–1720 cm^{-1} region, assigned to $\nu_{C=O}$ in weakly coordinated benzaldehyde and benzoic acid species and which become rather intense especially in the spectra recorded at 400°C (Fig. 4b), indicate a rather weak interaction of these products with the surface. Therefore, their easier desorption upon switching off the toluene feed may be expected. The fact that instead they are not removed when the toluene feed is stopped suggests that they are trapped inside the zeolite channels. It must be noted that in DRIFT cell the catalyst powder is pressed to form a nearly flat surface to reflect the infrared radiation. The reactant feed passes tangentially over this flat catalyst surface with a nearly laminar flow. Therefore, diffusion limitations on the desorption of the products can be expected, but reasonably the diffusion limitations should be comparable to those for adsorption of the reactants in the absence of additional effects. Instead, the growth in intensity of the bands of the products is faster than their decrease upon switching off the toluene feed, as shown in Figs. 3 and 4. Therefore, desorption of the products is slower than product adsorption, although the infrared spectrum indicates a rather weak coordination with the catalyst surface, at least for some of them. It may be concluded that desorption is slower due to steric constraints, since these products are formed inside the zeolite channels. This confirms that the iron–molybdenum active sites are predominantly located inside the zeolite channels, but also indicates that a reasonable limitation in obtaining high selectivities at high conversion is the low desorption rate of the products from the zeolite channels. This is in agreement with the observation of the enhanced rate of oxidative degradation of the aromatic ring to form maleic anhydride and then carbon oxides with respect to V–TiO_2 catalysts. In fact, it is reasonable that the oxidative addition of oxygen to the π system of toluene is enhanced in the confined environment of the zeolite.

3.2.3. Benzyl alcohol and benzaldehyde interaction

In situ DRIFT spectra recorded by interaction of a feed of benzyl alcohol or benzaldehyde in air with the FeMo/Bor catalyst are shown in Fig. 5. The spectra support the previously discussed assignments of adsorbed species. Two bands are observed for benzaldehyde in the 1600–1750 cm^{-1} region, namely at 1665 and 1706 cm^{-1}, with the latter the more intense even after desorption at 100°C. This confirms the presence of a weakly coordinated benzaldehyde species

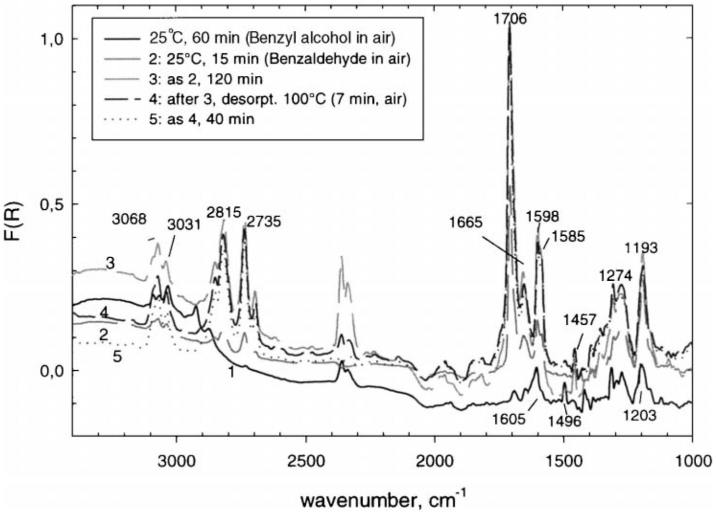

Fig. 5. In situ DRIFT studies of the interaction of benzyl alcohol (spectrum 1) and benzaldehyde (spectra 2→5) in the presence of air with the FeMo/Bor catalyst at 25°C for 60 min (1), and 15 min (2) or 120 min (3). Spectra (4) and (5) refer to the spectra detected after treatment in an air flow at 100°C for 7 min (4) and 40 min (5) after having recorded spectrum (3).

(1706 cm^{-1} band $-\nu_{C=O}$) and of a more strongly coordinated species (1665 cm^{-1} band $-\nu_{C=O}$ interacting with weak surface Lewis acid sites). Benzyl alcohol adsorbs as such with no or minimal transformation to benzaldehyde, and benzaldehyde also does not give evidence of transformation to benzoate species up to a temperature of 100°C, in contrast to that observed on V–TiO_2 catalysts [24,31]. This further confirms the previous indication of a lower rate of transformation of these products to benzoate species with respect to V–TiO_2 catalysts.

3.3. Relationship between catalyst properties and catalytic behavior

The comparison of the catalytic behavior of V–TiO_2 and iron–molybdate based catalysts (Fig. 1) shows that in the latter the decrease in selectivity with increasing conversion is significantly reduced. Infrared data show that on the FeMo/Bor catalyst the general pathway of transformation of toluene is comparable with that of V–TiO_2 based catalysts, but (i) the interaction of carbonyl groups of benzaldehyde with surface Lewis acid sites is weaker and (ii) the rate of oxidation to benzoate species is lower. The interaction of the carbonyl group with Lewis acid sites makes easier the nucleophilic attack of surface oxygens on the carbon atom of the carbonyl group and thus it is reasonable that a weaker interaction should correspond to a lower rate of oxidation to benzoate species. In the presence of a high steam concentration the benzoate species transforms to benzoic acid which then desorbs, in agreement with the observed effect of steam in enhancing the selectivity to benzoic acid on vanadium-based catalysts [20]. Otherwise, coordination of benzoate species with surface vanadium sites is quite strong to avoid desorption, favoring instead its unselective degradation to carbon oxides. This explains the drastic decrease in the selectivity to benzaldehyde of vanadium-based catalysts with increasing conversion. The slower rate of benzaldehyde to benzoate transformation on iron–molybdenum based catalysts instead makes easier benzaldehyde desorption to the gas phase and the presence of only weaker Lewis acid sites reduces the rate of its readsorption with a consequent lower decrease in selectivity with increasing conversion and higher productivity to benzaldehyde.

The Lewis acidity of molybdenum-based catalysts is related to the presence of reduced molybdenum sites which, on the other hand, form during the catalytic reaction as a consequence of the oxidation of the organic substrate. Fast reoxidation of reduced molybdenum sites is therefore necessary to avoid the formation of strong Lewis acid sites which can favor degradation of the alkylaromatic according to the mechanism discussed above.

In situ DRIFT studies on FeMo/Bor also showed the presence of diffusion limitations on the desorption of toluene oxidation products from the zeolite channels and the enhanced rate of oxidative degradation of the aromatic ring to form maleic anhydride from these toluene oxidation products, presumably due to the enhanced rate of oxygen attack to the π system of toluene in the confined environment of the zeolite. This explains why FeMo/Bor shows a lower selectivity to benzaldehyde at high conversion with respect to bulk iron–molybdate (Fig. 1), notwithstanding the higher selectivity at low conversion probably due to the presence of iron–molybdate nanocrystals encapsulated in the zeolite which show a different catalytic behavior with respect to bulk iron molybdate. In fact, Raman data [16] indicate a similar iron–molybdate phase in bulk iron–molybdate and FeMo/zeolite catalysts, but the presence of a more disordered structure in the latter due to the constraints related to the inclusion of iron–molybdate inside the zeolite pore structure.

Therefore, the encapsulation of the iron–molybdate inside the Boralite pore structure results in a benefit due to the possibility of having nanosized particles showing enhanced selectivity, but also leads to back-diffusion problems on the oxidation products responsible for lowering the selectivity at high conversion. In this case the main pathway responsible for the formation of carbon oxides (oxidative degradation of the aromatic ring) is different from that shown by vanadium-based catalysts (further oxidation of benzoate species).

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