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Catalytic oxidation of volatile organic compounds (VOCs) mixture (isopropanol/*o*-xylene) on zeolite catalysts

R. Beauchet, P. Magnoux [*], J. Mijoin

Laboratoire de Catalyse en Chimie Organique, UMR CNRS 6503, Faculté des Sciences, Université de Poitiers,
40 av. du Recteur Pineau, 86022 Poitiers Cedex, France

Abstract

The catalytic oxidation of isopropanol and *o*-xylene alone and in mixture was investigated over basic zeolites (CsX and NaX) and an acidic zeolite (HY). For a given temperature, the conversion of VOCs mixture into CO_2 increases with the basicity of the zeolite. Results show that VOCs are oxidized through a basic mechanism over NaX, and through an acidic mechanism over HY. Over HY, the presence of isopropanol increases the oxidation of *o*-xylene, probably because of the formation of isopropyldimethylbenzenes obtained via an acidic mechanism. The addition of platinum over zeolites increases the rate of the VOCs oxidation, this behavior being more pronounced over PtHY maybe because of a higher Pt dispersion.

Keywords: Catalytic oxidation; VOCs mixture; Basic zeolites; Pt/zeolites

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1. Introduction

Among the different emissions contributing to the damage of our environment, volatile organic compounds (VOCs) are a major source of direct (toxicity, odor) or indirect (“smog”) pollution of air [1]. Among VOCs, we can mention aromatic compounds (toluene, xylene), ketones (acetone, methylethylketone), alcohols (methanol, ethanol, propanol), acetates (ethylacetate), and chlorinated compounds (methylene chloride, perchloroethylene).

There are many different techniques for VOCs removal, such as adsorption, absorption, biofiltration, combustion (incineration) and catalytic oxidation. The choice of the technique to use depends on the characteristics of the effluent to be treated, such as VOCs nature and concentration and waste gas flow rate [2]. Catalytic oxidation can be applied effectively and at lower cost in a wide range of VOCs concentrations and waste gas flow rates, and, therefore, presents an interesting solution for VOCs elimination [2]. Recent works showed that basic zeolites were good catalysts for VOCs oxidation [3–6].

If catalytic oxidation of pure VOC has been widely studied, there are, however, few articles about their treatment in mixture, while VOCs are mainly emitted under this form. The different studies agree on the fact that VOC catalytic oxidation in mixture differs from its simple oxidation and, in general, an inhibiting effect can be observed [7–12]. Studies carried out on these mixtures have given rise to competition phenomenon on the catalyst active sites (adsorption competition, reaction competition with the chemisorbed oxygen, . . .) [7]. Over Pt-catalysts, Tsou et al. showed that inhibiting effect of the *o*-xylene on the methyl-isobutyl-ketone should be due to their competition on the active sites and that *o*-xylene adsorption on metallic sites by the π electrons of the aromatics was certainly favored in comparison to the ketone [12]. Promoting effect can be observed when chlorinated compounds are oxidized in presence of non-chlorinated hydrocarbons [13], but also when exothermicity is induced at the surface of a catalyst by the oxidation of one or several VOCs. For example, because of the exothermicity, acetone (isopropanol oxidation product) is oxidized at lower temperature in mixture with methylethylketone, toluene and isopropanol [7]. However, VOCs concentration is also a very important parameter. Indeed, in presence of high quantity of toluene or *n*-hexane the CCl_4

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[*] Corresponding author. Tel.: +33 5 49453498; fax: +33 5 49453779.
E-mail address: patrick.magnoux@univ-poitiers.fr (P. Magnoux).

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conversion decreases [14]. Thus, the degradation of VOCs mixture [11] is very difficult to predict. Typically, the efficiency of a catalyst on the VOC destruction is determined by the reactivity of the most refractory organic compound for oxidation [11,15], especially, when this compound act as an inhibitor of the mixture oxidation. The formation of secondary products present in most of the catalytic oxidation reactions complicates the comprehension of the phenomenon.

In this study, an evaluation of zeolites performances (CsX, NaX, HY) with or without platinum has been realized for the oxidation of isopropanol (1360 ppm) and *o*-xylene (210 ppm) alone and in mixture. Experiments were carried out in presence of water (11,000 ppm) and at a high gas hourly space velocity (GHSV) of 18,000 h^{-1}.

2. Experimental

X and Y zeolites are aluminosilicates of the faujasite family. Faujasite zeolites are characterized by the presence of one type of large cages (supercages), 13 Å in diameter and ball-shaped, accessible through 12 rings window with a free aperture of 7.4 Å [16], which is larger than the size of *o*-xylene and isopropanol molecules calculated with Cerius^2 software from MSI (respectively 6.6 and 4.7 Å).

Protonic HY zeolite (Si/Al = 5) was supplied by Zeolyst Corporation (CBV 500) and NaX (Si/Al = 1.2) by Axens. CsX was prepared from NaX zeolite by ion exchange with a 0.5 M solution of CsCl (Fluka), at 60 °C with a solution volume/zeolite weight ratio of 10 mL/g. Afterwards, the samples were filtered, washed and dried overnight at 110 °C. Calcination was performed under air flow (9 L h^{-1} g^{-1}) with a heating rate of 1 °C min^{-1} from ambient temperature to 110 °C with a hold of 2 h. Then, a new heating rate of 2 °C min^{-1} was applied, from 110 °C to 450 °C, with a hold of one night.

Acidity of catalysts was characterized by pyridine adsorption followed by IR spectroscopy (Table 1). The adsorption of pyridine results in the appearance of two pyridinium ions, PyH^+ (1545 cm^{-1}), and pyridine bonded to Lewis acid sites, PyL (1450 cm^{-1}). Brønsted and Lewis acid sites were determined and quantified by the subtraction between P_∞ (spectrum of the catalyst before adsorption of pyridine) and P_{150} (spectrum of the catalyst after adsorption and desorption at 150 °C of pyridine). The extinction coefficients of PyH^+ and PyL bands, i.e. respectively 1.13 and 1.28 cm μmol^{-1}, were taken from a previous study [17].

Table 2
Characterization of Pt/catalysts

Catalysts	% Pt[a]	n_{Pt} (10^{18} atoms g^{-1})[b]	Dispersion Pt (%)[b]
0.5PtNaX	0.5	1.89	12
0.5PtHY	0.5	4.95	32

[a] Determined by elemental analysis.
[b] Determined by toluene hydrogenation.

Adsorption–desorption isotherms of nitrogen at −196 °C were carried out with a Micromeritics ASAP 2010 apparatus. Micropores volumes were obtained by the t-plot method and Dubinin–Radushkevich equation was used to calculate the mesoporosity.

The mode of preparation of Pt/zeolites consisted in an cation exchange from the $Pt(NH_3)_4Cl_2$ complex. Zeolite and the appropriate amount of $Pt(NH_3)_4Cl_2$ are introduced in 100 mL of distilled water. The exchange was carried out at room temperature (pH of 6–7) with the addition of NH_4OH ($n(NH_4OH)/n(pt) = 100$). The solution was stirred during 3 h at room temperature. Finally, the catalyst was recovered by filtration and dried at 100 °C during one night. The dispersion of platinum deposited on the catalysts was determined by the toluene hydrogenation reaction (Table 2) [18]. Thus, the Pt dispersion over PtHY was greater than over PtNaX, which suggests that on PtHY a larger part of Pt particles was located in the zeolite pores structure.

The VOCs destruction was carried out in a fixed bed reactor (i.d. = 5 mm, length = 90 cm) at atmospheric pressure and followed as a function of time at constant temperatures, the first point being obtained after 1 min reaction. The catalyst (grain size between 200 and 400 μm; catalyst mass = 0.14 mg; catalyst height = 1.2 cm) was supported in a small plug of glass wool in the vertical glass tubular reactor. The reactor was inserted into an oven, and the temperature was controlled by a Minicor 42. The temperature was measured by a thermocouple inserted near the catalyst bed. The feed gas (20% O_2 in nitrogen + 1.1% water (relative humidity = 33%)) with a concentration of isopropanol of 1360 ppm or/and of *o*-xylene of 210 ppm was introduced in the reactor with a total flow rate of 75 mL min^{-1}, which was controlled by a mass flow controller (Brooks 5850). The desired concentration of VOCs was obtained by passing part of the feed gas through a saturator that was kept at the appropriate temperatures by means of a cryostatic bath (Huber). The space velocity (GHSV) was kept

Table 1
Characterization of catalysts: framework formula, crystallite size, Si/Al, number of Brønsted acid sites (nB) and Lewis sites (nL) able to retain adsorbed pyridine at 150 °C

Zeolites	Formula	Crystallite size (μm)	Si/Al	nB (μmol g^{-1})	nL (μmol g^{-1})	Pore volume (cm^3 g^{-1})	
						Micro	Meso
NaX	$Na_{88}Al_{88}Si_{104}O_{384}$	1	1.2	–	–	0.301	0.009
CsX	$Cs_{52}Na_{36}Al_{88}Si_{104}O_{384}$	1	1.2	–	–	0.174	0.011
HY	$H_{32}Al_{32}Si_{160}O_{384}$	0.5	5	670	248	0.255	0.068

Pore volume determined by nitrogen adsorption isotherm at −196 °C: mesoporous (Meso) and microporous (Micro) volumes.

constant in all the experiments (18,000 h^{-1}, calculated at ambient temperature and pressure).

The analytical system consisted in a gas chromatograph (Varian 3400) equipped with a flame ionization detector for the analysis of the hydrocarbons, and a TCD detector for the analysis of CO_2. The GC was fitted with a 30 m VF-5ms capillary column, with 0.25 mm of internal diameter and 0.25 μm film thickness.

After reaction, catalyst was recovered and the carbon content deposited on the sample was measured by total burning at 1020 °C under helium and oxygen with a Thermoquest analyzer.

3. Results and discussion

3.1. Catalytic oxidation of isopropanol/o-xylene mixture over zeolites

Catalytic oxidation of VOCs mixture was studied for various reaction temperatures over basic zeolites (NaX and CsX) and acidic zeolite (HY). The detected products were CO_2 and by-products: propene and acetone over basic zeolites and propene, isopropyldimethylbenzene over HY. Coke was also formed during reactions. Fig. 1 shows, on NaX, as a function of time-on-stream and for various reaction temperatures, the conversion of isopropanol (Fig. 1a) and *o*-xylene (Fig. 1b), the transformation of VOCs mixture into CO_2 (Fig. 1c), the coke and by-products formation (Fig. 1d). *o*-Xylene and isopropanol were mainly transformed into CO_2 from 250 °C (selectivity into CO_2 was about 95–100%). *o*-Xylene appears as more reactive than isopropanol (total destruction at 250 °C for *o*-xylene against 80% conversion for isopropanol). Identical results were observed when VOCs were destroyed independently.

At 200 °C, after a fast deactivation due to coke formation, activity of NaX was very low, however, by-products, identified by GC–MS as propene and acetone, were formed along with coke components (Fig. 1d). Propene can be formed through a basic mechanism from isopropanol (Scheme 1). Afterwards, propene can be directly oxidized or transformed into acetone and/or aldehyde before oxidation into CO_2 and H_2O (Scheme 2).

Although CsX possesses a smaller pore volume than NaX (Table 1), CsX was slightly more active: it was able to transform 20% of isopropanol and *o*-xylene at 200 °C and by-products (propene + acetone) were only formed at 180 and 200 °C. On this catalyst VOCs mixture was totally transformed into CO_2 at 250 °C.

Over HY zeolite, isopropanol was totally degraded in the 200–300 °C range and *o*-xylene between 250 and 300 °C. At 200 °C, catalyst deactivation was observed after 2 h reaction for *o*-xylene transformation, and coke content was close to 12 wt.% after 5 h reaction. At very low temperature (130 °C) no CO_2 was detected and only by-products (mainly isopropyldimethylbenzenes and propene) were formed. On this catalyst, VOCs mixture was totally oxidized at 300 °C with selectivity into CO_2 close to 98%.

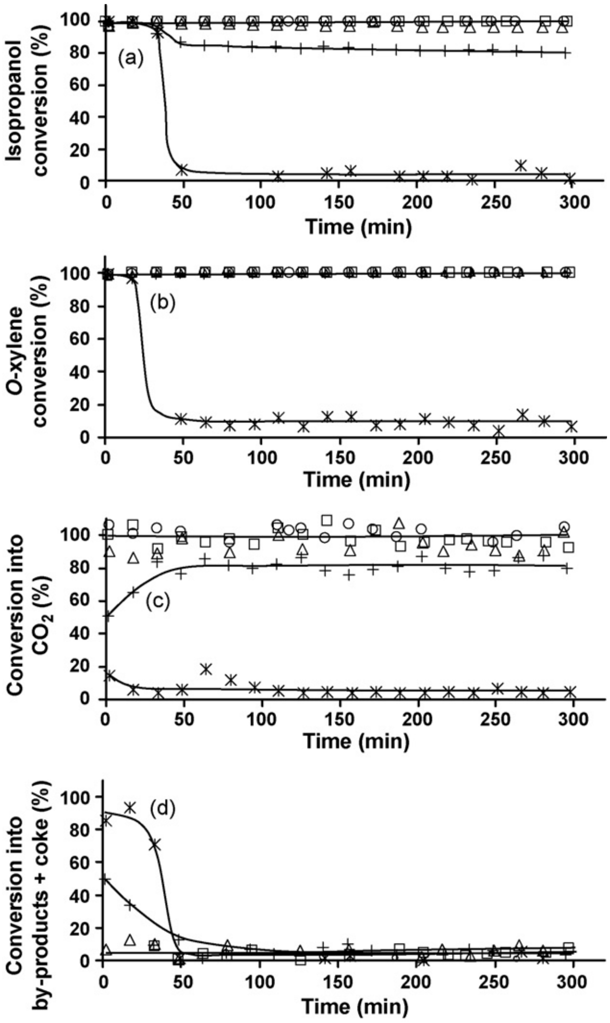
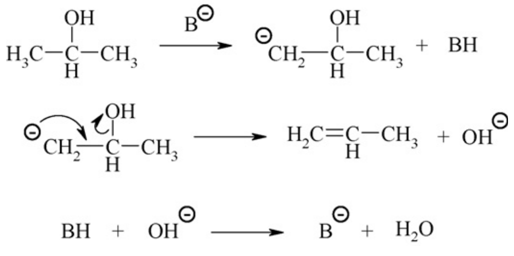


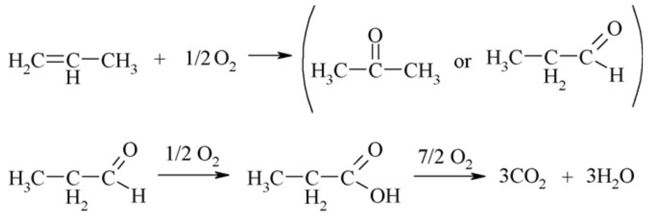
Fig. 1. Catalytic destruction of isopropanol/*o*-xylene mixture over NaX. Isopropanol conversion (a), *o*-xylene conversion (b), conversion of VOCs mixture into CO_2 (c) and by-products + coke (d) at 200 °C (*), 250 °C (+), 350 °C (○), 300 °C (△), 450 °C (□).

The formation of isopropyldimethylbenzene can come from the alkylation of *o*-xylene by propene, resulting from the dehydration of isopropanol via an acidic mechanism (Scheme 3).

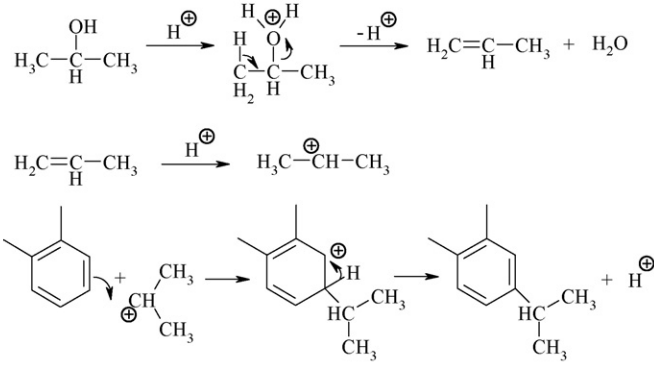
Afterwards, isopropyldimethylbenzene can be oxidized into dimethylphenol and acetone (Scheme 4) in a similar way of cumene for the industrial production of phenol and acetone [19]. When the reaction temperature increases (from 300 °C), acetone and dimethylphenol were totally oxidized into CO_2 and



Scheme 1.



Scheme 2.



Scheme 3.

H_2O. At 300 °C, the coke content after 5 h reaction was only of 0.8 wt.%.

3.2. Formation of CO_2 from VOCs mixture

Fig. 2 compares the conversion of VOCs mixture into CO_2 as a function of temperature, for various zeolites and after 5 h reaction. The activity order is the following: CsX > NaX > HY.

Basic zeolites (CsX and NaX) appear more active in CO_2 formation than acidic zeolite (HY). As it was the case for the catalytic oxidation of methyl-isobutyl-ketone [4], this greater activity of basic zeolite can be the result of a stronger adsorption of VOC molecule on the cations and framework oxygen of the zeolite. When isopropanol is adsorbed on a zeolite with alkali cations, it is probable that the OH group of isopropanol will adsorb on the cation (acting as a Lewis acid site), and that hydrogen of molecule will adsorb on the basic framework oxygen (Scheme 5). Therefore, the greater the basicity of the zeolite, the higher the adsorption strength and the greater the oxidation of VOC molecule. Isopropanol, which possesses an OH group, will be certainly more strongly adsorbed on dual function of zeolite (cation and framework oxygen) than *o*-xylene, which does not possess functional group.

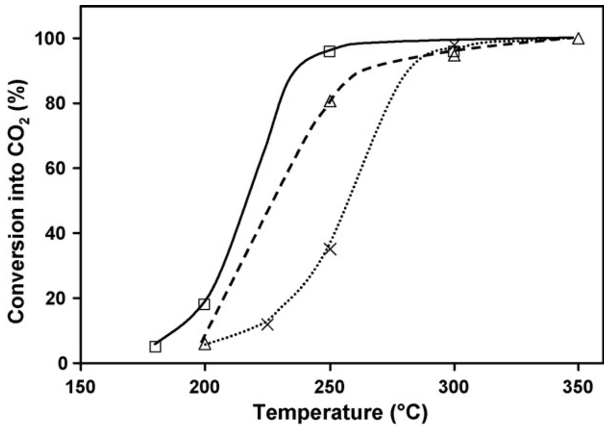
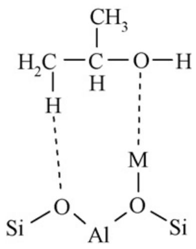
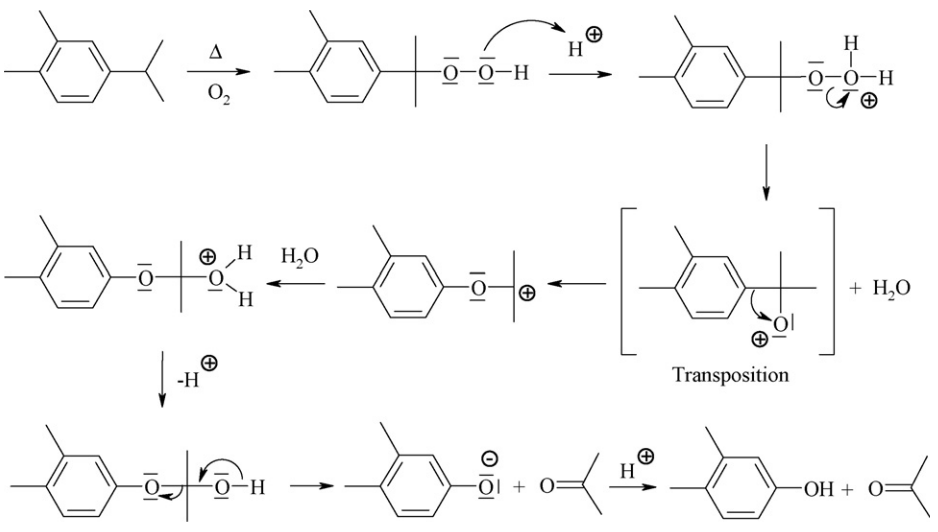


Fig. 2. Conversion of VOCs mixture in CO_2 as a function of reaction temperature over basic (CsX (□) and NaX (△)) and acid (HY (×)) zeolites.



Scheme 5.



Scheme 4.

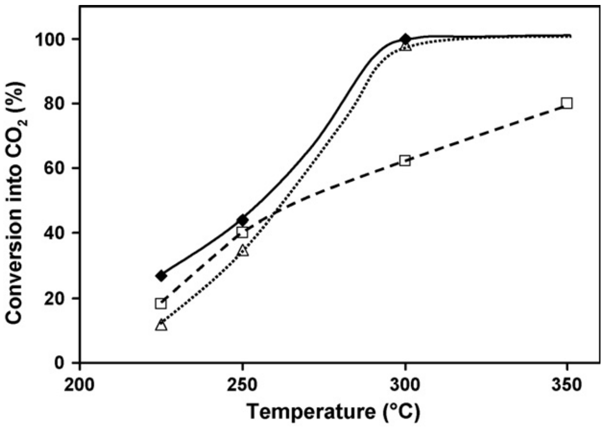


Fig. 3. Conversion into CO_2 of *o*-xylene alone (□), *o*-xylene in mixture with isopropanol (△) and isopropylbenzene alone (◆) as a function of reaction temperature over HY.

Usually, the relative easiness of destruction of VOCs by catalytic oxidation follows the general order: alcohols > aldehydes > aromatics > ketones > alkenes > alkanes [20–22]. Isopropanol, the more reactive VOC, can initiate the oxidation reaction and lead by a local exothermicity to the oxidation of *o*-xylene, which is in low concentration in the mixture (1360 ppm isopropanol/210 ppm *o*-xylene). However, over basic zeolites, when isopropanol and *o*-xylene were oxidized separately, no differences in oxidation temperatures were observed. The only difference was the easier transformation of isopropanol into by-product at 180 °C. The low concentration of *o*-xylene in this mixture (210 ppm) would be responsible to the slight effect on the isopropanol conversion while the presence of *o*-xylene (1500 ppm) inhibited the methyl-isobutyl-ketone oxidation [12].

For HY, it seems that the presence of isopropanol increases the oxidation of *o*-xylene, especially for a reaction temperature higher than 250 °C (Fig. 3). Knowing that formation of isopropyldimethylbenzene occurs during the reaction, the higher conversion of *o*-xylene in mixture could be the result of a fast alkylation rate of *o*-xylene by propene and an easier destruction of isopropyldimethylbenzene than *o*-xylene. To confirm this hypothesis, oxidation of isopropylbenzene (cumene), a close commercially available analogue of isopropyldimethylbenzene, was achieved over HY zeolite in the same operating conditions ($[C_9H_{12}] = 210$ ppm, relative humidity = 33% and GHSV = 18,000 h^{-1}). Results obtained with the isopropylbenzene oxidation show the easier conversion of isopropylbenzene, and therefore probably of isopropyldimethylbenzene, than *o*-xylene. It seems that the lightoff curves of isopropylbenzene follow the one of the mixture, which leads to think that the formation and the easier destruction of isopropyldimethylbenzene can be responsible for this promoting mixture effect.

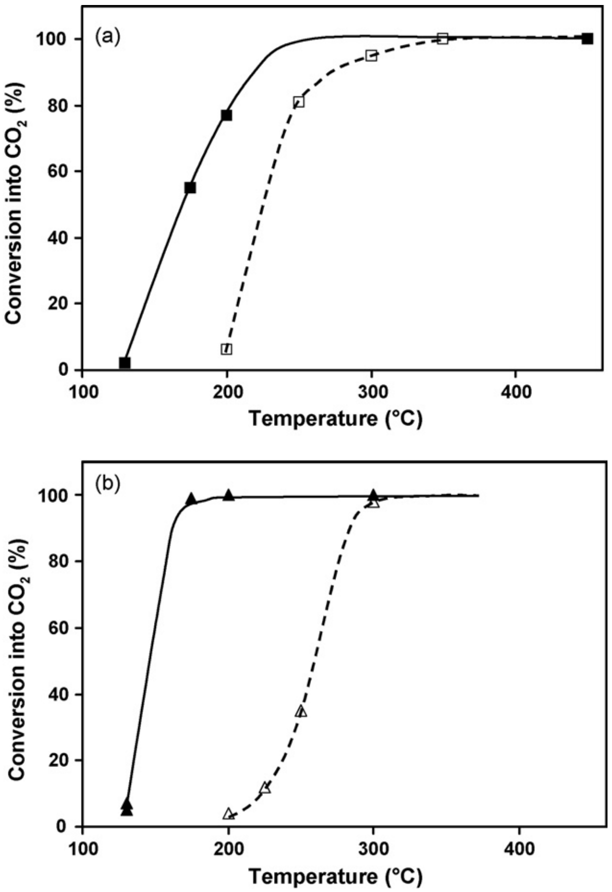


Fig. 4. Conversion into CO_2 of VOCs mixture as a function of reaction temperature over NaX (□) and 0.5PtNaX (■) (a) and over HY (△) and 0.5PtHY (▲) (b).

3.3. Effect of platinum on the VOCs mixture oxidation

The oxidation of VOCs mixture was compared over NaX and 0.5PtNaX (0.5 wt.% Pt). Fig. 4a reports the conversion of VOCs mixture into CO_2 as a function of reaction temperature after 5 h of reaction. The introduction of platinum in NaX zeolite increases the oxidizing activity. Thus, the T50 (the necessary temperature to oxidize 50% of VOCs) was about 50 °C lower when the reaction was carried out over PtNaX catalyst, and VOCs mixture could be totally oxidized at 200 °C over PtNaX. The effect of Pt was certainly to increase the rate of propene oxidation formed over zeolite and the oxidation rate of *o*-xylene. Indeed, in the case of *o*-xylene oxidation, a great effect of Pt was shown [23,24]. In our case, the effect of Pt was more pronounced over HY since the mixture was almost totally oxidized at 175 °C over 0.5PtHY (Fig. 4b). The higher activity of 0.5PtHY compared to 0.5PtNaX could be the result of a better dispersion of platinum on HY with 32% against 12% over PtNaX (Table 2).

4. Conclusions

Basic zeolites such as CsX and NaX zeolites appear as promising catalysts for the catalytic oxidation of isopropanol/*o*-xylene mixture. It was shown over NaX zeolite that isopropanol can be transformed via a basic mechanism into propene, which can be afterwards oxidized into aldehyde and ketone before complete oxidation in CO_2. NaX was able to transform these VOCs with a good selectivity in CO_2 from 250 °C. The strong adsorption of isopropanol, the main VOCs in the mixture, was the determining parameter to the oxidation rate and *o*-xylene in low concentration was easily transformed when isopropanol begins its oxidation.

In the case of acidic zeolite, the behavior is more complex: alkylation of *o*-xylene by propene follows to the formation of isopropyldimethylbenzene, which can be more easily oxidized than *o*-xylene. Lastly, the introduction of Pt over NaX and HY, increases the rate of VOCs oxidation.

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