JOURNAL OF CATALYSIS **178,** 214–225 (1998)
ARTICLE NO. CA982148

Evaluation of γ-MnO_2 as a VOC Removal Catalyst: Comparison with a Noble Metal Catalyst

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Received January 23, 1998; revised April 6, 1998; accepted April 24, 1998

The performances of two very active catalysts for VOC removal (one metal oxide and one noble metal catalyst, namely γ-MnO_2 and Pt/TiO_2) are compared. The comparison takes into account not only the activity but also the sensitivity to competition effects between compounds, the influence of water vapor and the stability. The metal oxide catalyst proves to be more active than the supported noble metal one. Moreover, its performance is less affected by interferences between VOC's than those of the noble metal catalyst. Conversely, the activity of the noble metal appears slightly more stable. Both are affected by water vapor which slightly decreases their efficiency. On the metal oxide catalyst, water shortens the time needed to get a stable catalytic activity. © 1998 Academic Press

INTRODUCTION

Volatile organic compounds (VOC) are pollutants because, in addition of being odorous or toxic sometimes, they almost always contribute to ozone formation (1). Accordingly, when VOC emissions cannot be avoided, they ought to be controlled (2, 3) by an appropriate end-of-pipe device. When there is no interest in recovering VOC's, they are usually destroyed by deep oxidation. However, because the VOC concentration is usually very low (below 1000 ppm), direct combustion may not be appropriate (4). This would require a large amount of extra fuel to maintain the flame temperature and may produce toxic substances (5) and NO_x (6). Catalytic deep oxidation is more selective and, as it requires less heating, is more cost effective than direct combustion when the VOC concentration is lower than 10,000 ppm (1). However, because large gas volumes have to be treated, this has to be performed at very high space velocity (20,000; 80,000 h^{-1}) (5, 1) and thus requires a very active catalyst. An additional difficulty in catalytic VOC removal comes from the fact that the stream generally contains many organic compounds of very different chemical nature. The catalysts have to be able to treat different kinds of substances together simultaneously (5). Finally, the catalyst must keep its activity in the presence of "spectator" species such as water vapor. Indeed, the stream to clean in most cases contains mainly water vapor in air, with a few ppm of VOC (1). In some cases (7), the presence of water vapor is a consequence of the origin of the effluent to treat (e.g., decontamination of waste or ground water by air stripping and VOC oxidation). The cleaning of a printing plant atmosphere also constitutes a typical example: in this case, VOC removal catalysts must often operate on the air in the workplace, namely on atmosphere saturated with water vapor or nearly so.

The various aspects of catalytic VOC removal have been thoroughly reviewed by Catalytica (1). Table 1 gathers the details collected in that study about commercial catalysts and their performances for the removal of the VOC's considered in our work, together with other results from the scientific literature. As shown in this table, two types of catalysts can be used, alone or in combination, to reduce VOC emissions: noble metal catalysts and metal oxide catalysts. Seventy-five percent (8) of the catalysts used for VOC destruction are precious metal catalysts and these are generally supposed to be more active than metal oxide catalysts (5). However, as shown also in Table 1 and demonstrated by some authors (9, 6, 1) metal oxides can sometimes exhibit higher activity than noble metal catalysts. For example, Pope *et al.* (9) have compared the activity of two commercial catalysts, namely a cobalt oxide catalyst and a platinum based catalyst for the oxidation of several components (introducing only one component at a time in the stream). Their work shows that the metal oxide catalyst more efficiently destroys *n*-butanal and *n*-propylamine, whereas the Pt catalyst is more active than Co_3O_4 for the conversion of acrolein, toluene, and butyric acid. The Catalytica study (1) tries to compare the performances of two commercial noble metal catalysts with one commercial metal oxide catalyst (but does not give precisions concerning space velocities and other operation variables). They show, for instance, that 90% of 250–300 ppm of benzene and of methanol are removed at 260°C with the best noble metal catalyst, whereas 300 and 210°C are respectively required to obtain the same

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TABLE 1

Performances of Various Commercial Catalysts

Ref.	Catalyst		Test conditions				Performances	
	Designation	Composition	Reactant nature	Conc. (ppm)	Co-reactant	Space velocity (h^{-1})	Conversion (%)	Temperature (°C)
(20)	UOP Unidox, LTC	precious metal/monolith	*n*-Hexane	500	Methanol, toluene, *n*-butylamine	50,000	99	355
(11)	United Catalyst, G-43A	0.1% Pt/3% Ni/Al_2O_3	*n*-Hexane	410	None	209	90	310
			Benzene	375	None	209	90	215
(7)	United Catalyst, G-43A	0.1% Pt/3% Ni/Al_2O_3	Benzene	5.8	Other hydrocarbons Water	9950	94	400
(12–14)	TORVEX VOC	Pt/monolith	Benzene	1000	None	134,000	60	175
(10)	Precious metal	(Pt, Pd)/monolith	Hexane	1200	None	50,000	90	>300
			Benzene	1200	None	50,000	90	>300
(23)	Allied signal, HDC	?	*n*-Hexane	?	?	15,000	98	345
			Benzene	?	?	72,300	98	345
			Ethylacetate	?	?	34,200	98	345
(24)	Johnson Matthey	Platinum group metal/support	Ethylacetate	?	?	?	90	320–350
(25)	PD-1	0.1% Pt/Al_2O_3	Ethylacetate	2840	None	20,000	75	430
(1)	Platinum catalyst	Platinum catalyst	Benzene	?	?	?	90	250–300
	Metpro	Noble metal catalyst	*n*-Hexane	?	?	?	90	316
			Benzene	?	?	?	90	260
	Haldor Topsoe A/S	Metal oxide catalyst	Benzene	?	?	?	90	300
	ARI Technology	Cr_2O_3/Al_2O_3	Benzene	300	Water	15,000	90	450
	Allied signal, HDC	?	Benzene	300	Water	15,000	90	220

removal with the metal oxides. Their general conclusion is that the metal oxides are not necessarily less active than noble metal catalysts.

Although VOC removal is a new important research topic in catalysis, there is clearly a lack concerning relevant comparisons between metal oxide and noble metal catalysts in the literature. Studies with this objective should however take into account the different aspects of VOC removal, namely not only the catalyst activity or stability, but also the resistance to water vapor or the ability to oxidise simultaneously many different kinds of VOC's.

As far as noble metal catalysts are concerned, many studies (10–14) have actually shown that the removal of one VOC can be affected by the presence of other compounds. For example, Tichenor and Palazzolo (10) have studied *n*-hexane conversion in the presence or in the absence of other compounds (namely benzene + isopropanol + methylethylketone + ethylacetate) on a precious metal catalyst. Their results show that 90% of hexane is removed at 305°C (1200 ppm of VOC, 50,000 h^{-1}) when reacted alone, but that its destruction is less than 75% when in the mixture. These authors also compared the reactivity of different classes of compounds. Concerning nonhalogenated VOC, using a noble metal catalyst, they reported that: (1) alcohols were the most easily destroyed, followed by (2) aldehydes, (3) aromatics, (4) ketones, (5) acetates and (6) alkanes. Most other authors (8, 11–15) also detected mutual influences of VOCs on their reactivity while studying their deep oxidation on noble metal or metal oxide catalysts. An explanation of the origin of the "interference" in the case of noble metal catalysts is provided by Barresi *et al.* (12–14). In a series of papers, these authors studied the deep oxidation of aromatic hydrocarbons. They found that the less easily oxidised compound was inhibiting the conversion of the other compounds. They suggested that differences in strength of adsorption were responsible for the inhibition effects observed. Using noble metal catalysts, they concluded that full destruction might occur at a significant increase of the temperature. No such clear explanation and prediction of the effect of interferences between reactants has so far been provided in the case of metal oxides. In that case, the "interferences" are attributed to competition for adsorbed oxygen, competition for adsorption sites (15), or competition for the oxidised part of the catalyst surface (11).

The stability of a representative of the class of metal oxides, namely hopcalite, has been compared to that of noble metals by Musich *et al.* (17) and in tests covering an extended period of time by Agarwal *et al.* (7). These authors reported that the noble metal did not lose activity, although the reaction temperature had to be increased (by 85°C in 297 days by Agarwal *et al.* (7)) with hopcalite in order to maintain more than 99% conversion. These latter authors nevertheless underlined the fact that the final temperature to maintain >99% conversion over the hopcalite was still lower than the initial temperature required for the operation of the noble metal catalyst they tested (450°C).

In these two studies (7, 16) the reactant flow was humidified (saturated with water vapor) in an effort to mimick the stream from a ground water decontamination plant (16). The role played by water in the deactivation and on the catalyst activity was unfortunately not specified. More generally, the effect of water vapor in the oxidation of volatile organic compounds has still to be studied in detail.

Thus, the aim of this paper is:

—first to provide a realistic comparison between two very active catalysts, each of them representative of one category (a metal oxide and a noble metal), namely a comparison taking into account not only the activity but also the stability, the resistance to water vapor, and the sensitivity to interferences between VOCs.

—then to significantly contribute to the description of the behaviour of the less-studied type of catalyst, namely those using metal oxides, notably by better explaining the cause of interferences between reactants using this catalyst and by providing a more comprehensive description of the effect of water.

EXPERIMENTAL

Catalysts

One of the catalysts was a sample of the nsutite (γ) form of MnO_2 provided by SEDEMA-SADACEM, Belgium. This oxide is not specifically developed for catalytic applications (17). Its specific surface area is nevertheless not negligible (100 m^2/g). The supported noble metal catalyst was a 0.3 wt% platinum of high dispersion ($H/Pt = 0.6$) supported on doped TiO_2. Details on its preparation can be found elsewhere (18, 19).

Activity Measurement

Benzene, ethylacetate, and *n*-hexane were chosen as representative VOC reactants; 250 ppm of the three molecules in air were used with a contact time of 60 kg s/cm^3 (which corresponds to a space velocity of 72,000 h^{-1} (NTP) with MnO_2). The catalyst was in the form of $0.2 < \varnothing < 0.315$ mm particles and was diluted in 7 ml of glass beads of the same diameter. For experiments with water vapor, the gas stream was saturated at 25°C with 20,000 ppm of water. The reactants and products of a possible incomplete decomposition were separated by gas chromatography (Chrompack column #773, Wcot fused silica 50 m × 0.32 mm, cdt: 38°C, 1.6 b He) and then quantified using a flame ionisation detector (FID). This type of detector was chosen because it is generally more sensitive, namely more adequate to measure the very low concentration of partially converted VOC, than a thermal conductivity detector.

The contact time, the concentration, the nature of the VOCs and the presence of water vapor are representative of the conditions of VOC removal in printing industries (1, 5). Benzene was chosen to model the oxidation of aromatic compounds and because its removal must be very efficient in order to comply with the very stringent legislation which is aimed at limiting its emission (3, 1); ethylacetate and hexane are very often encountered in the work place atmosphere or the effluents of printing industries. As an alkane, hexane is one of the hardest VOC to oxidise (10). Ethylacetate is expected to be much more reactive, but may give rise to the formation of oxygenated polymer compounds (coke) on the catalyst surface. Hence, these two compounds actually provide some representative information on the catalysts ability to oxidise other VOCs and on their resistance to deactivation by coke formation.

Before measuring the conversion as a function of temperature, the catalysts were first activated, then stabilised. Activation was performed *in situ* at 150°C, during 90 min, under oxygen (50 ml/min). Stabilisation was obtained by letting the reaction proceed for 16 h at 150°C. The conversion was measured during this period, at the end of which it reached an almost constant value. Then, the temperature was decreased to 100°C and subsequently increased by steps of 20 or 10°C until complete combustion was obtained. The conversion was then again measured at 150°C to verify that the conversion at the end of the test was the same as after the preliminary stabilisation period.

In addition, some of the results concerning the noble metal catalyst which will be presented below were obtained on a second apparatus. The reactant concentrations in those experiments were the same, but the space velocity was only 30,000 h^{-1}. The full description of these experiments can be found in earlier papers (18, 19).

RESULTS

Results on MnO_2

Behavior in the absence of added water vapor. Figure 1 presents the variation of the conversion of the three model VOC's as a function of the reaction temperature on the nsutite-MnO_2 catalyst. In the absence of water vapor and when there is only one VOC per experiment in the stream, complete combustion of ethylacetate, *n*-hexane, and benzene is obtained below respectively 160, 200, and 220°C. No incomplete oxidation products were detected.

Figure 1 also presents ethylacetate and hexane conversion when these are introduced together in the stream. The presence of hexane in the stream does not significantly modify the ethylacetate conversion. But, the presence of ethylacetate deeply affects the hexane conversion. The hexane conversion remains below 10% as long as some ethylacetate

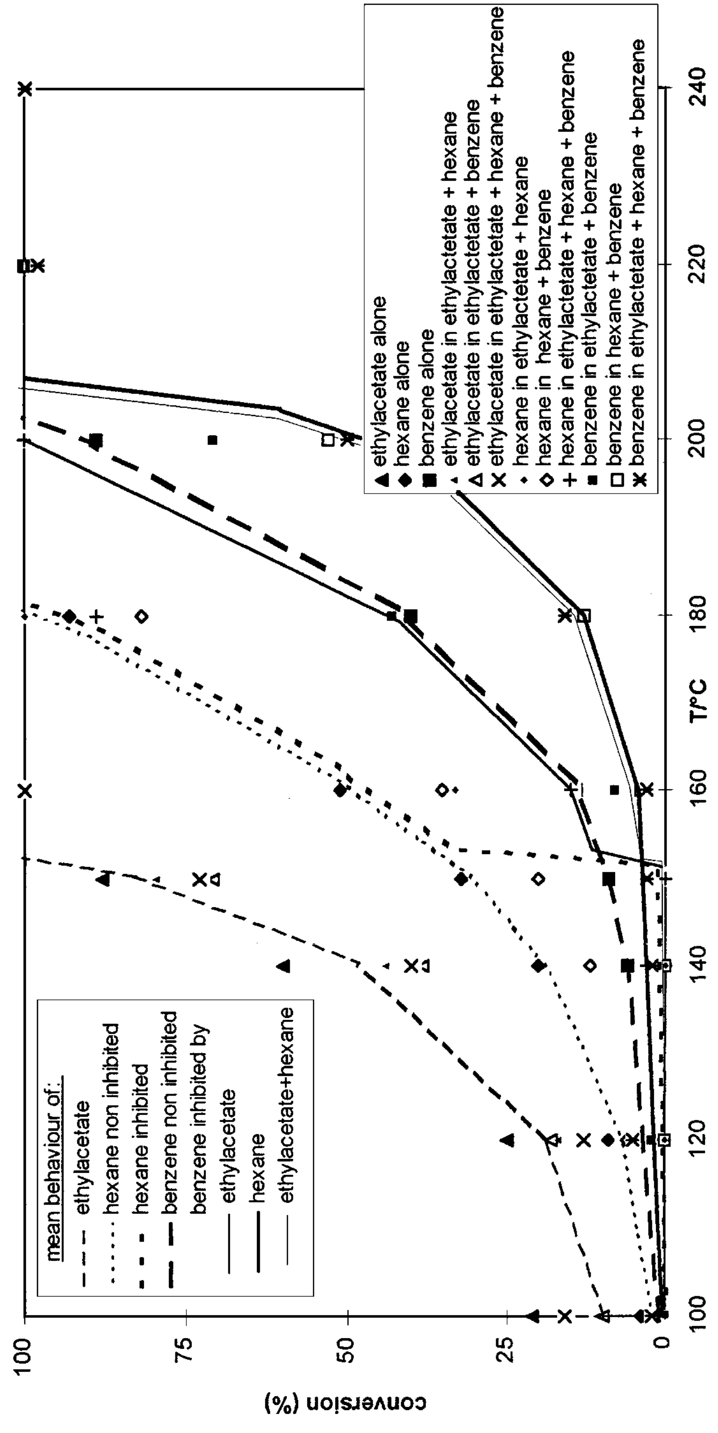

FIG. 1. Conversion of ethylacetate, hexane, and benzene on MnO_2 for each possible combination the three VOC as a function of the reaction temperature.

remains. Above the temperature at which all ethylacetate is removed, the conversion obtained for *n*-hexane is the same as when it is introduced alone. Ethylacetate seems to strongly inhibit hexane conversion. However, as ethylacetate is completely removed at a lower temperature than hexane, the temperature at which hexane is totally removed remains unchanged.

Similar conclusions can be reached with respect to benzene and ethylacetate. The presence of benzene does not influence ethylacetate conversion whereas a strong inhibition of benzene conversion by ethylacetate is detected to the point that practically no conversion of benzene is observed as long as ethylacetate is not completely converted; benzene conversion then increases to its expected value. The easy removal of ethylactetate allows the temperature of complete removal of benzene to remain unchanged.

As far as benzene and hexane are concerned, Fig. 1 shows that hexane conversion is slightly decreased in the presence of benzene and an important loss of benzene conversion is recorded. But, unlike ethylacetate, hexane does not completely inhibit the benzene. As the temperature at which the complete removal of hexane and benzene are close, it is not possible to specify the behavior of benzene in benzene + hexane mixture above the temperature of hexane complete conversion. The temperature at which all the benzene is oxidised remains below 220°C.

The observation made on the binary mixture is confirmed by the results obtained when introducing the three VOC together. Ethylacetate conversion remains unchanged in all cases. Ethylacetate limits hexane conversion in the ethylacetate + hexane + benzene experiment like in the ethylacetate + hexane case, as long as it is not completely converted. As far as benzene conversion is concerned, in accordance with the behaviour observed in the mixture of two VOC, the removal of ethylacetate should suppress part of the benzene conversion inhibition. However, hexane remains present and as shown by Fig. 1, the conversion of benzene in the presence of hexane at the temperature of ethylacetate complete removal is very small. Thus, it is not actually possible to observe a sudden recovery of benzene conversion linked to the complete removal of ethylacetate. To summarise, using MnO_2, the conversion of one VOC is modified by the presence of a second VOC (there are "interferences"), but the temperature at which each compound is completely removed is the same when the compound is alone or in the presence of other VOCs.

As mentioned in the experimental part, the activity is stabilised by letting the reaction proceed for 16 h at 150°C. The conversion of ethylacetate and hexane as a function of time during this period is given in Table 2. In these conditions, the activity first decreases rapidly. The decrease becomes increasingly slower as time on stream increases. At the end of the stabilisation period, no further decrease is measurable within the duration of the experiment. Such long stabilisation periods are observed any time the conversion is lowered (e.g., when decreasing the temperature) but not when it is raised. The conversion decreases slowly but increases rapidly.

Figure 2 presents the ethylacetate and hexane conversion at 180°C when time on stream is extended to two days. In this experiment, the VOCs concentration is suddenly dramatically increased in order to check the catalyst ability to stand "accidents" (to sustain an important increase of VOC concentration and to recover its activity afterwards). In these conditions, ethylacetate conversion is complete. The conversion of hexane slowly decreases during the two days of the experiment; in our experimental conditions, the stabilisation is very long. The increase of the two VOC concentrations does not impair the catalyst performance. Indeed, the conversion recovered after the perturbation are those which would be expected by extrapolating the data concerning conversion versus time on stream before the perturbation of the feed flow. The conclusion is that MnO_2 can stand "accidents."

Effect of water vapor. Figure 3 displays the curves of conversion versus temperature for ethylacetate and hexane alone or together, with or without water vapor. Water causes a decrease in the conversion of each VOC. Actually, the complete combustion of hexane is only obtained at 240°C, while 180°C is now required for ethylacetate complete oxidation. The presence of water thus results in a diminution of the performances, namely an increase by 10°C for ethylacetate and 40°C for hexane of the temperature required to obtain the same conversion.

Figure 3 also enables us to evaluate the effect of water on the "interferences" between reactants. Hexane conversion was strongly inhibited by ethylacetate and very much affected by the presence of water vapor. The curves of Fig. 3 show that as long as some ethylacetate remains, hexane conversion in the presence of the two inhibitors is similar to that observed with ethylacetate only. Above the temperature of complete removal of ethylacetate, hexane conversion is the same as that recorded with water only. Thus there seems to be no cumulation of the inhibition effects. The result is simply that the more important inhibition rules the behaviour of hexane conversion. As far as ethylacetate conversion is concerned, the curves presented in Fig. 3 show that ethylacetate conversion in the presence of hexane and water is the same as in the absence of hexane (namely with water vapor only). The presence of water does not strengthen interferences.

Table 2 presents the conversion versus time on stream curves at 150°C for ethylacetate and hexane, alone or together, with or without water. A dramatic shortening of the stabilisation period is observed (45 min instead of more than 12 h). Figure 4 shows the conversions of ethylacetate, obtained during 7 days, at 150°C, in the presence of 250 ppm

TABLE 2

Variation of the Conversion of Each Reactant with Different Flow Compositions, on the Two Types of Catalyst, as a Function of Time

Catalyst	Reactant studied	Flow components	Conversion (%) after										
			5 min	1 h	2 h	3 h	4 h	5 h	6 h	8 h	10 h	12 h	15 h
MnO_2	Ethylacetate	Ethylacetate alone	100	100	100	99	98	98	97	96	94	93	91
MnO_2	Ethylacetate	Ethylacetate + hexane	100	99	97	95	93	94	91	90	89	88	86
MnO_2	Ethylacetate	Ethylacetate + H_2O	100	96	83	72	68	65	68	64	61	59	59
MnO_2	Ethylacetate	Ethylacetate + hexane + H_2O	100	100	98	92	85	78	74	72	69	63	60
MnO_2	Hexane	Hexane alone	100	86	74	66	61	55	51	45	41	37	34
MnO_2	Hexane	Ethylacetate + hexane	85	51	32	22	15	16	10	8	7	6	8
MnO_2	Hexane	Hexane + H_2O	94	23	21	24	23	23	23	23	22	20	21
MnO_2	Hexane	Ethylacetate + hexane + H_2O	99	28	16	14	14	13	13	9	10	7	7
Pt/TiO_2	Ethylacetate	Ethylacetate alone	85	25	21	20	20	20	21	21	19	19	19
Pt/TiO_2	Ethylacetate	Ethylacetate + hexane	86	23	23	21	23	20	20	20	19	19	20

hexane and 20,000 ppm of water. In "humid" atmosphere, the catalytic activity of MnO_2 gets stabilised very rapidly. Unlike what happens without water, almost no stabilisation period can be detected in this case. In the experiment reported in Fig. 4, the catalytic activity of γ-MnO_2 has been recorded during 7 days, and, during this interval, less than 2% of conversion was lost. This loss of activity could be balanced by an increase of temperature of 0.6°C. Under these reaction conditions, the catalyst activity is very stable. In this experiment also, the flow was willingly modified in order to study the catalyst ability to stand "accidents." The results show that the catalyst recovers its activity rapidly. These results suggest that the catalyst activity should be very stable in conditions similar to those existing in a real industrial plant, where the operation conditions may fluctuate.

Results on Pt/TiO_2

Behaviour in the absence of added water vapor. Figure 5 shows the ethylacetate and hexane conversions, when tested alone or together, with or without water vapor, as a function of the reaction temperature on the Pt/TiO_2 catalyst. In the experiments involving one single VOC and in the absence of water vapor, ethylacetate is completely removed at 240°C and 90% is converted at 200°C and more than 220 or 280°C are required to obtain 90 or 100% hexane conversion, respectively. Benzene conversion was measured in slightly different conditions (space velocity 30,000 h^{-1}). As shown in Fig. 6, benzene (alone) is completely removed above 200°C in these conditions and is already extensively (90%) converted at 160°C. In the same conditions, 90% of ethylacetate is removed at 220°C. The noble metal catalyst is less active than the metal oxide but, compared to usual commercial catalysts, it is nevertheless a very active catalyst.

Figure 5 compares the ethylacetate and hexane conversions obtained with only one VOC in the feed to the conversions obtained in the presence of the second VOC. The presence of hexane seems to have no effect on ethylacetate conversion. But, the presence of ethylacetate inhibits hex-

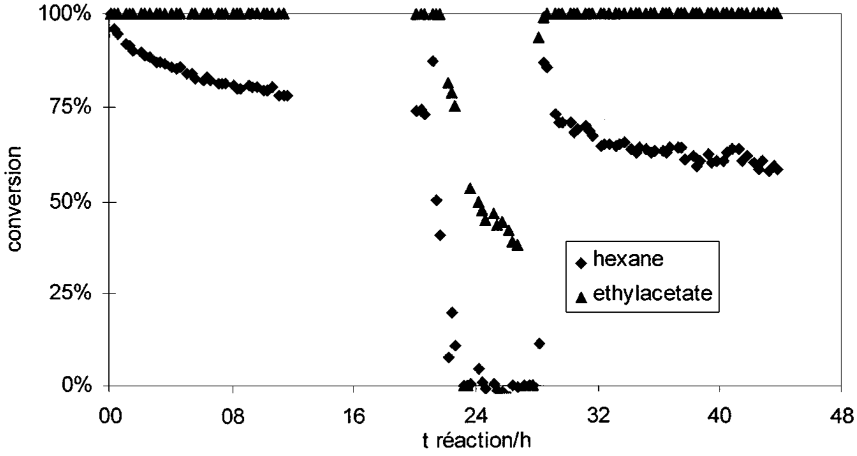

FIG. 2. Ethylacetate and hexane conversion on MnO_2 at 180°C as functions of time on stream.

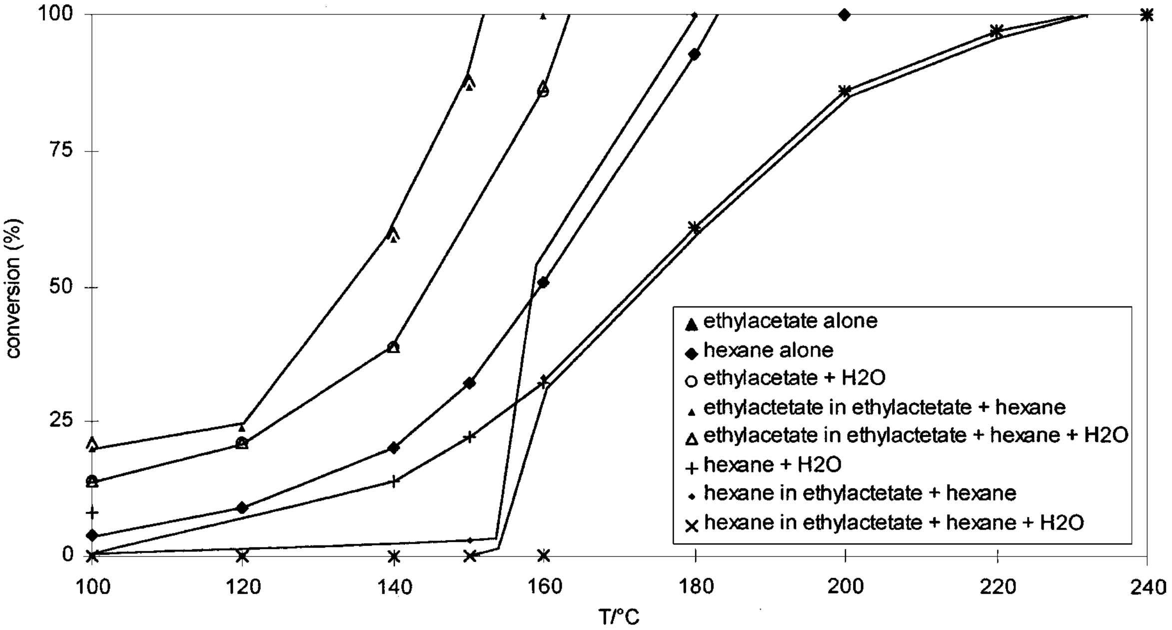

FIG. 3. Hexane or ethylacetate conversion on MnO_2 in the presence or in the absence of the second VOC and/or water as a function of the reaction temperature.

ane since the temperature required to achieve the same conversion of hexane is increased by 35°C. Actually, the conversion of hexane in the presence of ethylacetate remains lower than when alone, until the last of the ethylacetate is removed. Fortunately, ethylacetate completely disappears before hexane and the temperature at which 100% conversion of both VOCs is obtained remains the same.

As shown in Fig. 6, the "interference" between benzene and ethylacetate does not lead to the same result. Indeed, if benzene has no effect on ethylacetate conversion, benzene conversion in the presence of ethylacetate is strongly decreased. Unfortunately, an unfavourable effect is observed in this case, because benzene is normally oxidised more rapidly than ethylacetate: the presence of ethylacetate modifies the temperature at which all the benzene is removed (temperature increases between +60 and +80°C). With the noble metal catalyst, interferences between the VOC affect the overall performance of the catalyst.

The conversion measured during the stabilisation period is presented in Table 2 for ethylacetate alone or in the presence of hexane. (In these conditions only 2% hexane conversion is measured when using this VOC alone. At 150°C,

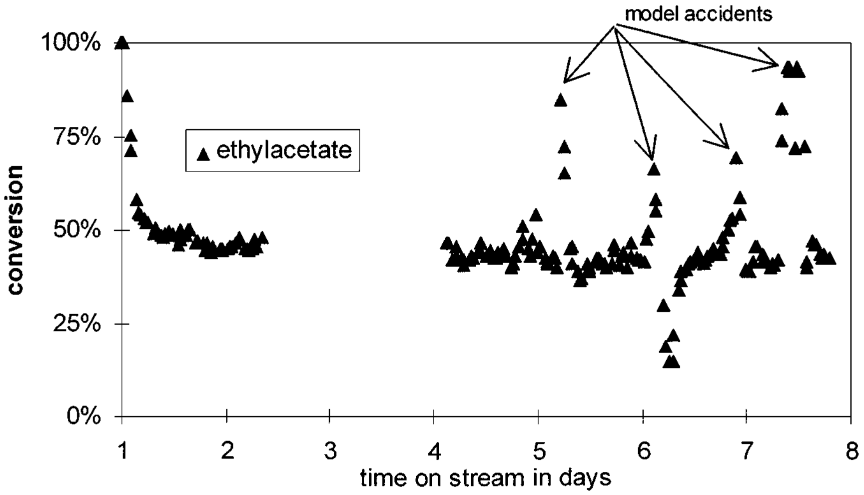

FIG. 4. Ethylacetate conversion on MnO_2 at 150°C in the presence of 250 ppm of hexane and of 20,000 ppm of water vapour, as a function of time on stream.

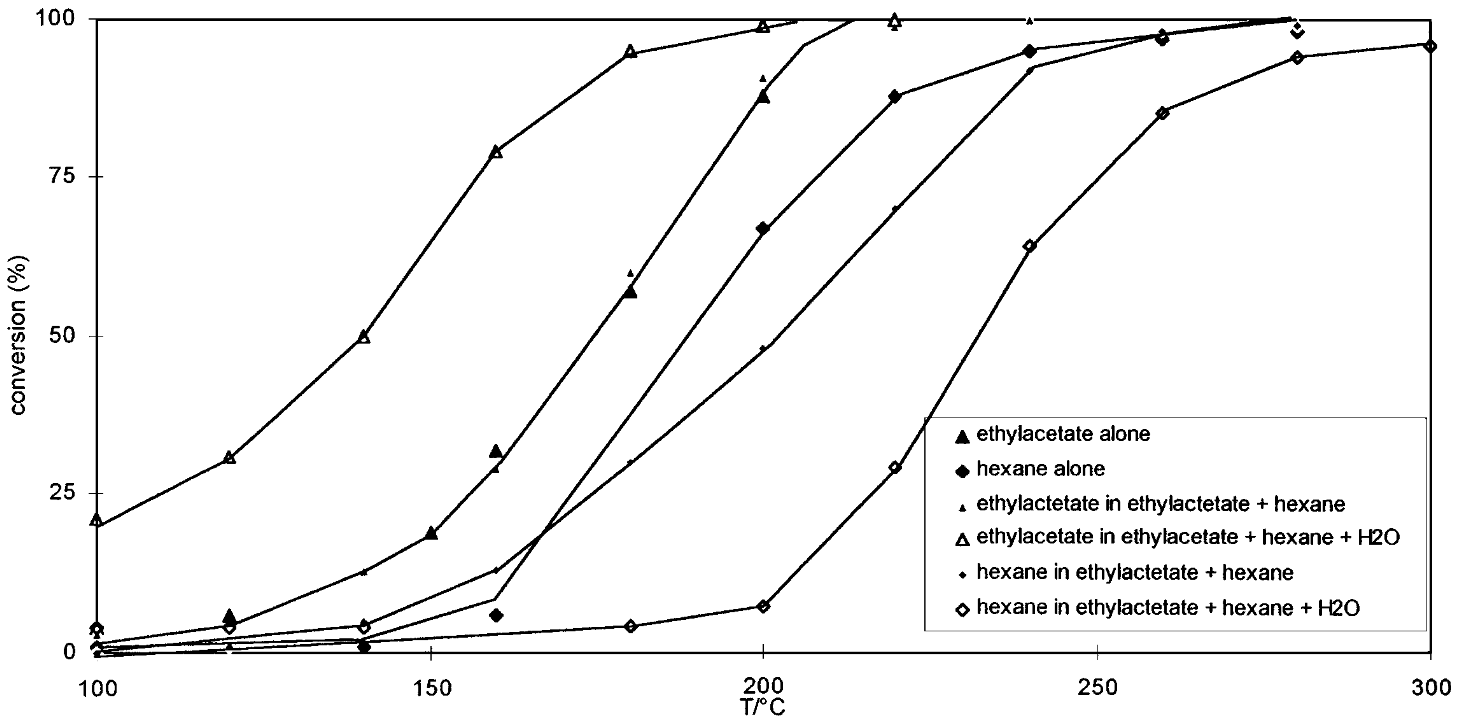

FIG. 5. Hexane or ethylacetate conversion on Pt/TiO_2 in the presence or in the absence of the second VOC and/or water as a function of the reaction temperature.

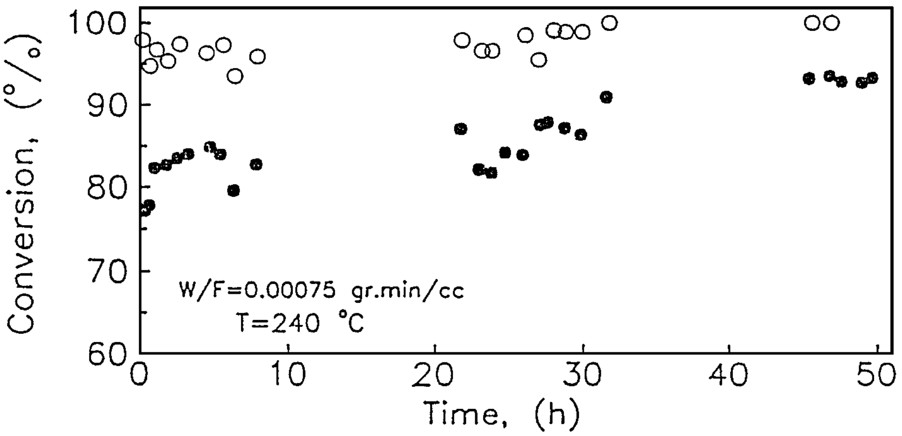

FIG. 6. Conversion to CO_2 of ethylacetate and benzene on Pt/TiO_2 in the presence or in the absence of a second VOC as a function of the reaction temperature (space velocity = 30,000 h^{-1}).

no conversion is detectable for hexane when ethylacetate is present in the stream.)

The ethylacetate conversion is stabilised within 4 h at the 20% level. The stability of catalyst activity versus time on stream is remarkable. However, in previous works (18, 19), the formation of acetic acid, and to a smaller extend acetaldehyde, had been observed with this catalyst. Under these conditions of test, the presence of incomplete decomposition products is also detected by chromatography and some heavy compound deposition can be observed on the coolest part of the glass reactor. The characterisation of the catalyst shows that some of these by-products accumulate on the catalyst. Figure 7 presents the ethylacetate conversion measured at 240°C during 2 days with a space velocity of 30,000 h^{-1}, using a device able to quantify CO_2 production (TCD). The amount of CO_2 produced does not correspond to the quantity of VOC that disappeared. The yield in CO_2 remains, nevertheless, remarkably stable. This shows that the small accumulation of by-products does not induce an immediate deactivation of the catalyst. Other results, which are not in the scope of this article, have shown that these by-products can be removed by raising the reaction temperature above 300°C. Provided such periodic reactivations are performed, the stability of the activity of the noble metal catalyst seems ensured and is excellent.

Effect of water vapor on the behaviour of noble metal catalysts. The effect of water on noble metal catalyst performance was first evaluated in the conditions used for γ-MnO_2, namely with a flow composition of 20,000 ppm water and 250 ppm of ethylacetate and hexane in air. The curves are presented in Fig. 5. The effect is different for the two VOCs; namely, water enhances the conversion of ethylacetate and inhibits that of hexane. On the average, a loss (an increase of the temperature required to obtained the same conversion) of 30°C is observed for hexane. In these conditions the complete removal of hexane is not yet obtained at 360°C. On the other hand, a gain of 40°C is evidenced for ethylacetate. But, the amount of products resulting from partial oxidation reactions detected by chromatography significantly increases. In particular, traces of ethanol and acetic acid suggest that hydrolysis of ethylacetate could occur.

Figure 8 presents the yield in CO_2 obtained from ethylacetate as a function of the reaction temperature in the presence or in the absence of water vapor, measured in the same conditions as the results presented in Fig. 6. An inhibition of the ethylacetate combustion by water is clearly observed. An increase of 50°C is required to obtain the same degree of elimination of ethylacetate in the presence of water.

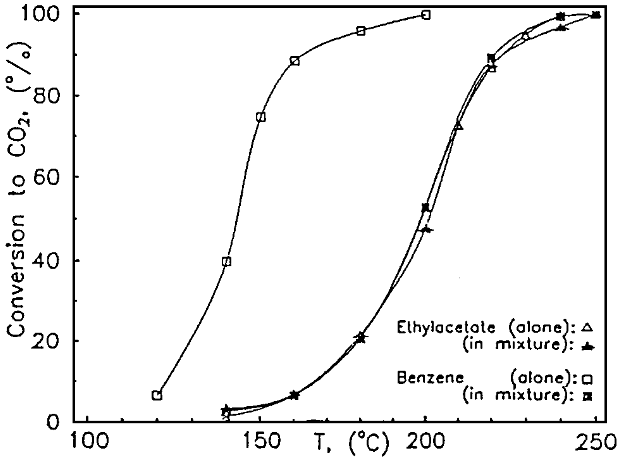

FIG. 7. Conversion of ethylacetate (open symbols) and yield in CO_2 (filled symbols) on Pt/TiO_2 as a function of time.

DISCUSSION

The comparison with the data of Table 1 show that both catalysts tested in the present work give better results than the existing commercial catalysts. Actually, the tempera-

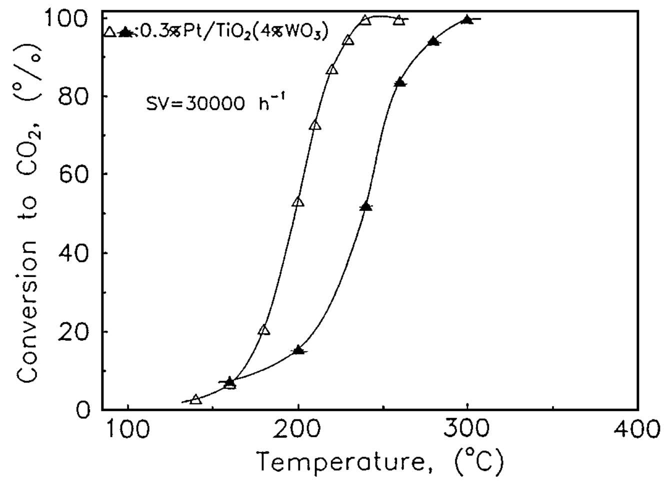

FIG. 8. Ethylacetate conversion to CO_2 as a function of temperature over Pt/TiO_2 (open symbols, ethylacetate; filled symbols, ethylacetate plus 20,000 ppm H_2O).

tures at which all *n*-hexane is removed, in our conditions (72,000 h^{-1}, VOC concentration = 250 ppm), are 200°C with MnO_2 and 280°C with the Pt supported on doped TiO_2, whereas for example, in conditions equivalent to ours (space velocity of 50,000 h^{-1}, VOC concentration = 500 ppm) 355°C is needed to achieve 99% conversion of *n*-hexane with the UOP Unidox low-temperature catalyst (20). The work presented here thus constitutes a comparison of two very active catalysts.

Noble metal catalysts are considered to be more active than metal oxide catalysts (5). Our work shows that some metal oxides can exhibit higher activity than the most active noble metal catalysts. For instance, 100% conversion of ethylacetate into CO_2 and H_2O is obtained at 180°C with MnO_2, while at the same temperature only 60% of the ethylacetate is removed by the Pt supported catalyst. The same comparison can be made for hexane (alone) since 100% conversion is reached at 200°C with MnO_2, while the noble metal catalyst gives a conversion of only 67% in the same conditions. The fact shown in this work that metal oxide can be more active than a very active noble metal catalyst upsets the commonly accepted ideas. Metal oxides also make easier the treatment of VOC which are difficult to remove with noble metal catalysts. In fact, as shown by our results, the scale of reactivity between VOCs (when reacted alone), is different using the two kinds of catalyst. The order of removal is (1) ethylacetate, (2) hexane, (3) benzene on the metal oxide, while, with supported noble metal catalysts, benzene reacts first, then ethylacetate, and still later, the oxidation of hexane begins.

The results presented here are representative of those obtained in the frame of a broader work performed in our laboratories on VOC oxidation using metal oxide or supported noble metal as catalysts. Other VOCs (e.g., butanol) and other catalysts have been considered and the behaviour of each catalyst has been examined in detail (17–19). On the basis of this relatively rich amount of data, some rules for determining the easiness of destruction of the different VOC and the impact of interferences on the overall catalyst performance can be provisionally established.

As regards scales of activity, it seems that polar compounds such as ethylacetate are comparatively more difficult to oxidise on noble metal than on metal oxide catalysts. For example, the oxidation of ethylacetate occurs at higher temperatures than the one of benzene alone on the Pt/TiO_2, whereas on MnO_2, ethylacetate is oxidised first.

Unfortunately, as shown in our results, this type of compounds often acts as the inhibitor of the conversion of other compounds. As far as metal oxides are concerned, all the results collected so far about interferences between the reactions of different VOCs can be understood according to a competition for adsorption. The component which is adsorbed preferentially is oxidised first. For instance, ethylacetate, which is certainly rapidly and efficiently adsorbed, strongly inhibits both hexane and benzene conversion; hexane competes with benzene adsorption and thus decreases benzene conversion. In the case of the metal oxide catalyst and for all the VOCs considered in our works, the compound which inhibits the reaction of the others, namely which is preferentially adsorbed, is also the most easily oxidised one. Thus, the temperature at which each VOC is completely removed has never been affected by the competition phenomena. To generalise, it seems that, on the metal oxide, the easiness of adsorption and the easiness of reaction vary in a parallel way. As a result, the inhibition is rapidly lifted by destruction of the inhibitor and there is no impact on the overall performance of the catalyst.

Competitive adsorption certainly also plays an important role in the inhibitions detected with the noble metal catalyst. The effects observed are qualitatively similar to those recorded on metal oxide. (ethylacetate inhibits hexane and benzene conversion.) The VOC which controls the oxidation of another VOC is the same. Nevertheless, when using noble metals, unlike what happens with MnO_2, the competition and interference between reactants usually result in an increase of the temperature at which complete removal of each VOC is achieved. With this type of catalyst, polar compounds such as ethylacetate are difficult to remove. The more strongly adsorbed VOC is no longer the easiest to oxidise. The consequence for a noble metal catalyst is that the most difficultly oxidised compound very often controls the overall oxidation, and the complete conversion of all components is achieved at temperatures which are higher, although close to that corresponding to the most refractory VOC, as measured with that compound alone.

Summarising, there are interferences with both types of catalysts, but their effect on the catalyst performance is different. The inhibitions change the temperature of complete removal of the VOC only in the case of the noble metal catalyst. Metal oxides are thus less sensitive to the effect of interferences between compounds.

Another point considered in this study is the effect of water vapor. As shown, water has two effects on the metal oxide catalyst: it decreases the conversions obtained (slightly that of ethylacetate, a little more strongly that of hexane) and it dramatically shortens the time needed to obtain a stable conversion.

The MnO_2 catalyst was thoroughly characterised after use. The results of this study will be presented in a future communication (21). It is possible to conclude that the stabilisation period observed is a transient period. As suggested by the results presented here, it is the time needed to get a constant coverage of the catalyst surface by the reactants and by the products, and more especially by water. The surprisingly long period observed in the present experiments is undoubtedly related to the very low concentrations in the mixture that we used.

In a recent communication (17), we compared the activity of various crystallographic forms of MnO_2 in the presence or in the absence of added water vapor. The structure of the sites which are the most sensitive to water vapor was identified. The adsorption of water on the sites decreases the catalyst activity. Thus the decrease of hexane and ethylacetate conversion can be explained by a competition of the VOCs and water for specific sites. Our results show that hexane is more affected by this competition than ethylacetate. As the controlling VOC (ethylacetate) is less affected than the controlled one (hexane), the interference effect is not strengthened by water. On MnO_2, water slightly decreases the conversion, but it does not dramatically affect the catalyst performance. Therefore, γ-MnO_2 appears as a very promising VOC removal catalyst.

The noble metal catalyst is a little more affected by the presence of water vapor. An increase of 10 or 40°C is actually enough to offset the water effect on respectively ethylacetate or hexane conversion with MnO_2, whereas the reaction temperature must be raised by 40 or 30°C respectively to obtain the same efficiency of the noble metal catalyst for ethylacetate and hexane removal. In addition, water affects the selectivity of the supported noble metal catalyst and by-products are formed.

On the whole, the effect of water on the performance of the two catalysts nevertheless remains limited. The controlling VOC (ethylacetate) is more affected in the case of Pt/TiO_2 than with MnO_2.

The long-term stability of these catalysts was also evaluated (as far as this is possible in an academic laboratory). Both catalysts seem quite stable. No decrease of the catalytic activity of the noble metal has been detected after 2 days. The stability of the metal oxide is more dependent of the conditions of VOC removal. In the presence of water vapor, the time stability is excellent. With low VOC concentration, in "dry" atmosphere, very long transient periods can be found. In these conditions, it seems that the steady-state coverage of the catalyst surface by each species, and especially water, has not been reached yet after 2 days of operation. But, the activity is still superior to what is measured in the presence of water vapor. Many VOC emissions are not continuous (22, 1). In dry conditions, with fluctuating emissions, the conversions obtained with γ-MnO_2 could always stay above their stable level, namely above the level of conversion obtained on a fully hydrated surface. There is, with this catalyst, a reserve of activity for the treatment of fluctuating emissions. This catalyst seems particularly well adapted to the treatment of such emissions since, as demonstrated with and without water, it sustains "accidents."

To summarise, whatever the catalyst, the stability of the activity seems excellent. However, at a longer term, it seems that the preservation of the catalytic activity might be easier with the metal oxide.

CONCLUSION

The aim of this study was to make a precise comparison of noble metal and metal oxide catalysts for VOC removal. Two very active catalysts were selected. Account was taken of all the main specific aspects of VOC removal (low concentration, complex composition of the stream, effect of water). Although other studies will probably find other advantages and disadvantages of these two families of catalysts, this study shows that the representative of the family of the oxide catalysts, namely γ-MnO_2 can present several properties which make it very suitable for VOC removal. This catalyst can be more active than noble metal catalysts. It is able to treat representative compounds of the main classes of polluting VOCs. The removal of one type of molecules is not sensitive to the presence of another type of VOC. This catalyst selectively converts every VOC into CO_2 and H_2O and is stable. But both the noble metal and γ-MnO_2 can certainly be improved and they will probably both remain excellent candidates as high performance catalysts.

ACKNOWLEDGMENT

Financial support by the commission of the European Union Contract No. EV5V-CT93-0253 is gratefully acknowledged.

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