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Stability of a cryptomelane catalyst in the oxidation of toluene

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ABSTRACT

The oxidation of toluene over a cryptomelane (K-OMS-2) catalyst was investigated at temperatures between 100 and 300 °C. The catalyst was tested both in temperature-programmed experiments (light-off curves) and in isothermal tests.

The carbonaceous deposits retained in the porous structure after the isothermal tests were evaluated by temperature-programmed oxidation. The results show that gradual deactivation occurs at temperatures below 268 °C (which corresponds to the peak maximum in the TPO curves). Furthermore, in a restricted temperature range (252–258 °C), the catalyst shows an unstable behaviour, and oscillations in the conversion into CO_2 occur.

TPD experiments after adsorption of toluene at room temperature show that this compound is strongly retained in the porous structure up to high temperatures, which can explain the deactivation and the unstable behaviour. For comparative purposes, TPD after adsorption of ethyl acetate was also carried out, and it was observed that this compound was not retained as much as toluene, no oscillations being detected.

1. Introduction

Manganese oxides with octahedral molecular sieve structure (OMS-2) are considered very active catalysts for the oxidation of volatile organic compounds [1–4]. Their catalytic properties are related to the mixed valence of manganese into the framework of the catalyst and to the high mobility of oxygen species [4,5].

In industrial applications, catalyst stability and durability are as important as activity and selectivity. Therefore, catalyst deactivation must be prevented as much as possible. An overview of catalyst deactivation was presented by Butt and co-worker [6]. In the case of catalytic oxidation, several mechanisms can lead to deactivation: (i) volatilization of catalyst species; (ii) poisoning; (iii) formation of coke deposits and (iv) thermal degradation.

The formation of carbonaceous deposits (coke) inside the pores or on the outer surface is the main cause of deactivation during transformation of organic reactants in molecular sieves [7,8]. When the coke precursors are strongly retained in the porous structure, besides deactivation, the catalyst may also become unstable, showing an oscillatory behaviour. Tsou et al. [9,10] have studied in detail the origin of this oscillatory behaviour in the oxidation of some VOC compounds over zeolite-based catalysts. Accumulation of coke was found to be at the origin of oscillations; on the other hand, this was found to be related to the adsorption properties of the support. In particular, a support which is capable of retaining the VOC at temperatures higher than the reaction temperature may lead to oscillations in the apparent conversion into CO_2. In this context, it is also interesting to refer the work of Paulis et al. [11]. These authors studied the influence of adsorption and desorption processes in the oxidation of toluene and acetone over Pd/Al_2O_3, Mn_2O_3/Al_2O_3 and Mn_2O_3/SiO_2 catalysts. The corresponding light-off curves show apparent conversions into CO_2 which are higher than 100%. These results were also explained in terms of the accumulation of coke at low temperatures. It may be concluded that the oscillations observed in isothermal tests and the CO_2 peak (conversions higher than 100%) in the light-off curves are different manifestations of the same phenomenon.

The aim of the present report is to study the stability of the cryptomelane catalyst in the oxidation of toluene. For that purpose, isothermal tests at selected temperatures were carried out. TPD and TPO after adsorption of toluene were also performed in order to assess the strength of the adsorption. For comparative purposes, similar experiments were carried out with ethyl acetate.

2. Experimental

2.1. Preparation and characterization of the catalyst

Cryptomelane-type manganese oxide (K-OMS-2) was synthesized by the reflux method developed by Luo et al. [3]. The

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Table 1
Properties of K-OMS-2.

Sample	Mn 3s ΔE_s (eV)	AOS	S (m^2/g)[a]	V_p (cm^3/g)[a]	Chemical composition (ICP/AES)
K-OMS-2	4.50	3.89	50	0.141	$K_{0.13}MnO_2$

[a] Calculated by the BJH method.

structure, morphology, composition and texture were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), inductively coupled plasma/atomic emission spectroscopy (ICP-AES) and nitrogen adsorption, respectively. The average oxidation state (AOS) of manganese was determined by X-ray photoelectron spectroscopy (XPS) based on a correlation between the binding energies of the doublet separation of Mn3s (ΔE_s) and the AOS proposed by Galakhov et al. [12]. Catalyst synthesis and characterization are explained in detail elsewhere [2].

A summary of the catalyst characterization results is presented in Table 1.

2.2. Catalytic experiments

The catalytic oxidation of toluene was performed under atmospheric pressure, using a VOC concentration of 2000 ppmv and a space velocity of 20,000 h^{-1}. Prior to the reaction, the catalyst is activated "in situ" under air at 400 °C for 1 h, and then cooled to room temperature.

The light-off curves were obtained in a fixed-bed reactor, consisting of an U-shaped quartz tube of 6 mm internal diameter, placed inside a temperature controlled electrical furnace. The temperature in the reactor zone was measured by a thermocouple placed in the middle of the catalyst bed. The gas mixture at the reactor outlet was analysed by a CO_2 non-dispersive infrared (NDIR) sensor and a total volatile organic compounds analyser. In these experiments, the temperature was increased at 2.5 °C/min between room temperature and 300 °C. In order to test the stability of the catalyst, the reaction was performed in two cycles of increasing and decreasing temperature.

The isothermal experiments were carried out in a fixed-bed reactor (BTRS Jr Autoclave Engineers) at atmospheric pressure. The catalyst was supported in a small plug of glass wool in a vertical stainless steel tubular reactor. The reactor was placed into an oven, and the temperature controlled by a thermocouple that was inserted into the middle of the catalyst bed. The analytical system consisted of a gas chromatograph equipped with a flame ionization detector (FID) for the analysis of the organic compounds, and an online non-dispersive infrared (NDIR) analyser for CO_2.

The conversion of toluene (X) and the conversion into CO_2 (X_{CO_2}) were respectively calculated as $X = 1 - (F_{VOC}/F_{VOC,in})$ and $X_{CO_2} = F_{CO_2}/\nu F_{VOC,in}$, where F_{VOC} is the outlet molar flow rate of VOC, $F_{VOC,in}$ is the inlet molar flow rate of VOC, F_{CO_2} is the outlet molar flow rate of CO_2 and ν is the number of carbon atoms in the VOC molecule (for toluene, $\nu = 7$).

The total amount of carbon retained in the porous structure of the catalyst after reaction was measured by temperature-programmed oxidation in air (TPO). After the reaction, the catalyst was cooled in nitrogen to 100 °C. Then, a stream of air was passed and the temperature increased at 10 °C min^{-1} up to 450 °C.

Temperature-programmed desorption (TPD) was also studied after pre-adsorption of the VOC at room temperature. The reactant was adsorbed on the catalysts from an air stream, using the same concentration as in the reaction study. After saturation, the lines were purged with nitrogen and the TPD started. The reactant was analysed using a total volatile organic compounds analyser.

3. Results and discussion

3.1. Light-off curves

The light-off curves for complete oxidation of toluene over K-OMS-2 are shown in Fig. 1. A large hysteresis was observed both in the conversion of toluene and in the conversion into CO_2 when performing heating (1) and cooling (2) cycles. In the heating ramp, the toluene conversion starts to increase at 220 °C, reaching 100% at about 270 °C. Decreasing the temperature to 205 °C resulted in a small drop in toluene conversion to 98%. When the temperature was further decreased to 190 °C, the catalyst became inactive. The hysteresis and the characteristic steep increase in the conversion can be in part attributed to the increase of the bed temperature during the highly exothermic oxidation of toluene ($\Delta H^{\circ}_{298\,K} = -4163$ kJ/mol). Furthermore, the gap between these two curves may also be a function of the amount and strength of the adsorbed molecules (reactant and products) on the catalyst surface. The reactant remains adsorbed when the temperature is increased up to 260 °C. As the temperature increases, below the ignition point, there is no desorption of VOC and products, and a considerable amount of molecules can be retained by the catalyst. On the other hand, during cooling, in the temperature range mentioned, the catalyst surface is clean and toluene is oxidised at lower temperatures. Our results suggest that retained toluene and eventually some of its oxidation products could deactivate the catalyst.

Another aspect, which is related to these processes, is the observation of a CO_2 peak with 196% of conversion in the light-off curve at about 235 °C. Furthermore, below this temperature an important disagreement was found between the conversion of VOC and the CO_2 released. This phenomenon was observed in the oxidation of many VOCs in several catalytic systems and according to some authors is the result of adsorption/desorption processes on the catalyst surface [11]. The catalyst adsorbs the VOC and, as the reaction temperature increases, CO_2 starts to be produced, and part of the VOC can also stay adsorbed on the catalyst surface. Since the oxidation reaction is highly exothermic, the bed temperature increases rapidly and the VOC is oxidised into CO_2, leading to instantaneous CO_2 conversions higher than 100%. The CO_2 peak appears in the ignition curves whenever the activity of the catalyst is high enough to start the oxidation of VOC at low temperatures, which are close to the temperatures for which the adsorption–desorption of the VOC take place [11].

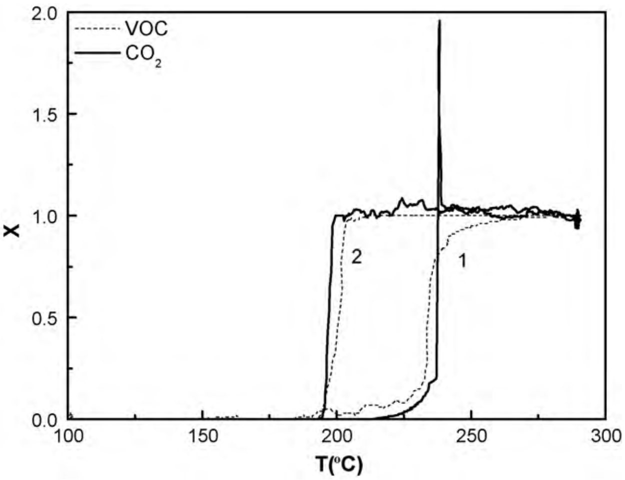

Fig. 1. Light-off curves for toluene oxidation over K-OMS-2 (1: heating; 2: cooling).

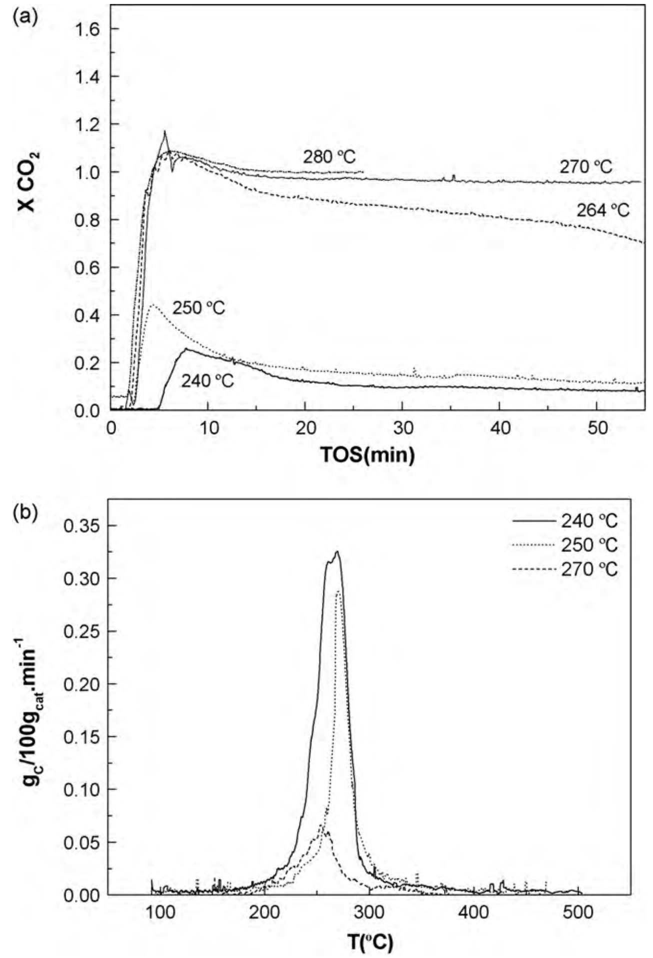

Fig. 2. Isothermal tests at selected temperatures as a function of time on stream (TOS) (a) and some of the corresponding TPO curves (b).

3.2. Isothermal tests

To get a closer insight into the effect of adsorption/desorption processes in the stability and activity of the catalyst, isothermal experiments were performed at selected temperatures. The conversions into CO_2 obtained over K-OMS-2 catalyst at 240, 250, 264, 270 and 280 °C as a function of time on stream (TOS) are compared in Fig. 2a. The catalytic behaviour at temperatures between 250 and 264 °C will be further discussed.

At temperatures below 270 °C the conversion increases to a maximum and decreases afterwards. The strong adsorption of toluene and other high molecular weight carbonaceous compounds on the catalyst surface could be responsible for deactivation. To elucidate this question, TPO analyses were carried out after reaction at selected temperatures (see Fig. 2b). It was observed that at temperatures higher than 268 °C (peak maximum in the TPO curves), deactivation does not occur, in agreement with smaller amounts of "coke". Moreover, TPD experiments after pre-adsorption of toluene at 30 °C (see Fig. 3a) were also carried out. For comparative purposes, the adsorption strength of ethyl acetate was also studied in the same conditions, because in a previous study it was shown that there is no deactivation at low temperatures [2]. In both experiments, there is no desorption of VOC and only CO_2 is detected, which suggests that lattice oxygen is involved in the oxidation mechanism of ethyl acetate and toluene. This result is in agreement with previous studies [13,14]. However, lattice oxygen was not able to oxidise all adsorbed toluene. For this reason, a TPO experiment after TPD (see Fig. 3b) shows a CO_2 peak at 250 °C, which is absent in the case of ethyl acetate.

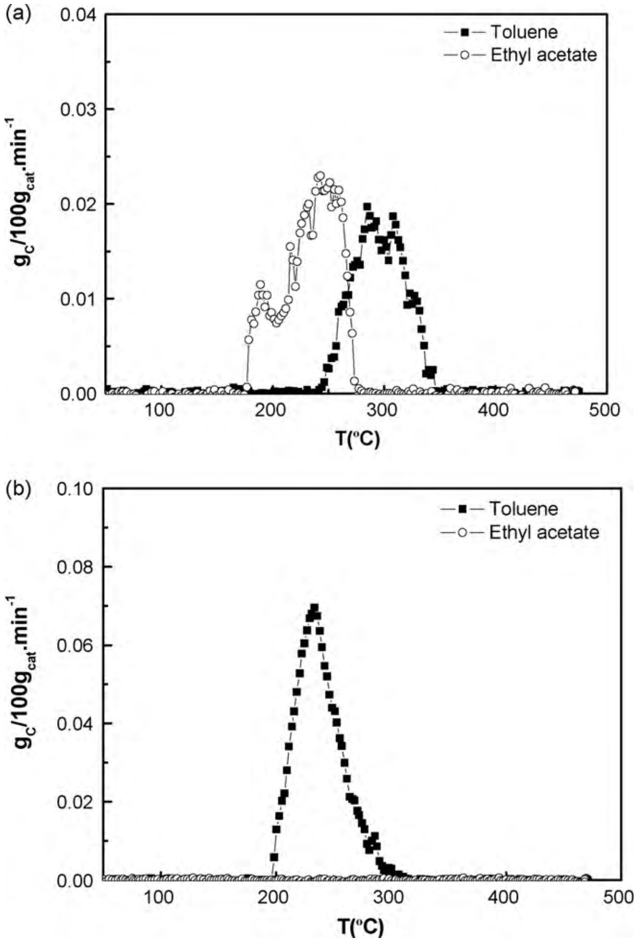

Fig. 3. TPD after pre-adsorption of toluene or ethyl acetate at room temperature (a) and TPO of toluene and ethyl acetate after TPD (b).

The TPD experiments show that there is a large difference in the adsorption strength of toluene and ethyl acetate on the cryptomelane catalyst. In the case of toluene, CO_2 starts to appear at 246 °C and presents a broad peak with a maximum at around 300 °C. So, if the reaction takes place at temperatures below 300 °C, the oxidation reaction will be coupled with adsorption processes, and the catalyst will keep the reactant adsorbed at higher temperatures. On the contrary, in the case of ethyl acetate, CO_2 is evolved at much lower temperatures and presents two peaks with maxima at 180 and 240 °C. It is then clear that ethyl acetate is less strongly adsorbed on cryptomelane than toluene, and that cryptomelane is able to keep the reactant adsorbed up to higher temperatures.

3.3. Oscillatory behaviour

At temperatures between 250 and 264 °C, oscillations in the CO_2 conversion were observed. Tsou et al. [9,10] studied in detail the oscillatory behaviour in the oxidation of methyl-isobutyl-ketone and xylene, and found that the oscillations result from cycles of accumulation and oxidation of the so-called "reactive coke", which includes adsorbed VOC and heavier products. The accumulation of reactive coke was found to be related to the adsorption properties of the catalyst. In particular, the catalyst must be able to retain the VOC at temperatures higher than the reaction temperature. As demonstrated by TPD experiments,

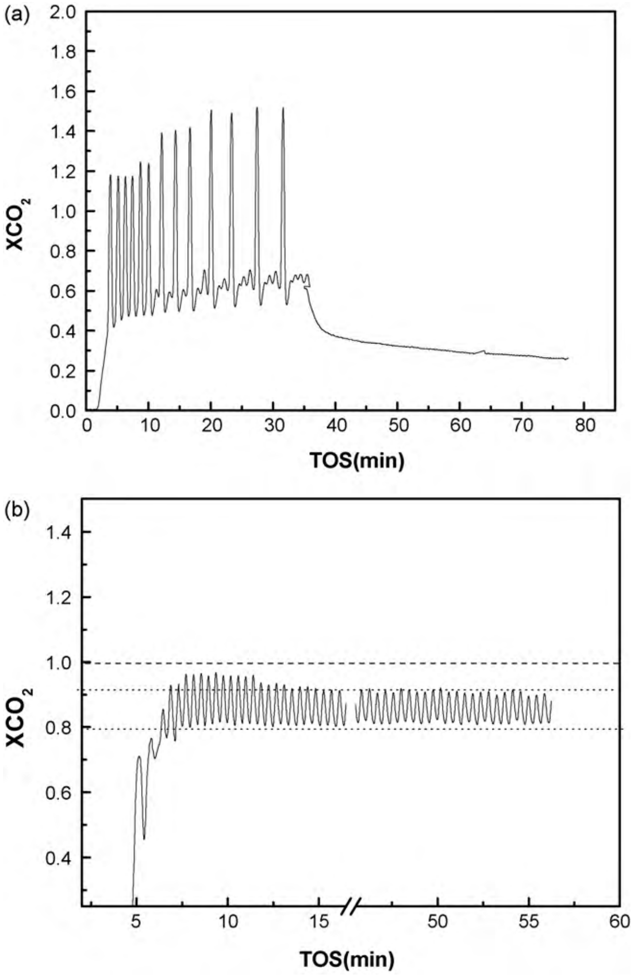

Fig. 4. Effect of TOS and temperature on the oscillatory behaviour: (a) 252 °C; (b) 258 °C.

cryptomelane is able to retain toluene at higher temperatures, explaining why there are oscillations in this system and not in the case of ethyl acetate oxidation.

The effect of TOS on the oscillatory behaviour at 252 and 258 °C is shown in Fig. 4. It was observed that at temperatures near 250 °C, the amplitude and frequency of the oscillations are not constant with time (Fig. 4a), and after 30 min of reaction the system stops to oscillate and deactivation occurs. The measured temperature follows the same cyclic behaviour as the conversion into CO_2: it increases initially up to about 260 °C, and then it starts to oscillate between 252 and 268 °C during the first 10 min; then there is a period up to about 30 min where the amplitude is higher; afterwards, the temperature stabilizes at 249 °C, and the system stops to oscillate. At higher temperatures (e.g. 258 °C) the frequency and amplitude of oscillations are constant with time (the temperature ranges between 258 and 262 °C), and deactivation does not occur (Fig. 4b). It is important to notice that the frequency of oscillations increases with rising temperature, while the amplitude was larger at low temperatures. In both cases, there was a clear synchronization between the oscillations in X_{CO_2} and the temperatures measured in the catalyst bed.

4. Conclusions

The effect of the adsorption/desorption processes on the activity and stability of the catalyst were evaluated in this study. The following conclusions can be drawn:

- Cryptomelane is able to retain toluene up to high temperatures (until 300 °C).
- At lower temperatures ($T < 270$ °C) accumulation of toluene and products occurs, and the activity of cryptomelane decays.
- In a restricted temperature range (252–258 °C), oscillations in the apparent conversion into CO_2 occur, which result from cycles of accumulation and oxidation of adsorbed reactant and products. The frequency and amplitude of the oscillations are synchronized with the measured temperatures.

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