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Mixture effects during the oxidation of toluene, ethyl acetate and ethanol over a cryptomelane catalyst

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ABSTRACT

The catalytic oxidation of two-component VOC mixtures (ethanol, ethyl acetate and toluene) was studied over cryptomelane.

Remarkable mixture effects were observed on the activity and the selectivity. Toluene inhibits both ethyl acetate and ethanol oxidation, this effect being more evident in the case of ethyl acetate. For instance, the temperature for 100% conversion is about 210 °C when ethyl acetate is oxidised alone, and 250 °C or higher, when it is oxidised in mixtures with toluene.

On the contrary, toluene oxidation is only slightly inhibited by the presence of ethyl acetate, while the presence of ethanol has a promoting effect.

Concerning the mixtures of ethyl acetate and ethanol, both compounds have a mutual inhibitory effect, which is more evident in the case of ethyl acetate (the temperature for 100% conversion of ethyl acetate is about 45 °C higher when ethyl acetate is oxidised in mixtures with ethanol, while in the case of ethanol the corresponding increase is only 10 °C).

1. Introduction

Air pollution is both a local and a trans-boundary problem caused by the emission of certain pollutants that, either alone or by chemical reactions, have negative environmental and health impacts [1].

Volatile organic compounds (VOC) are an important class of air pollutants which covers a wide range of compounds that differ in their properties and chemistry, but display similar behaviour in the atmosphere. The release of VOC into the atmosphere has widespread environmental implications and has been linked to stratospheric ozone depletion, formation of ground level ozone (photochemical smog) and enhancement of the global greenhouse effect [1–3]. Moreover, these compounds require special attention due to their toxicity (human health effects), high stability and persistence in the environment.

The environmental and human health issues have led to a variety of standards and legislation [4]. One of the most important for the European Union is the directive 2001/81/EC (NECD), which establishes ceilings for the emission of certain atmospheric pollutants (SO_2, NO_x, VOC and NH_3) for the different countries, which should be reached by 2010 [4,5]. The aim is to minimize the adverse effects from acidification, soil eutrophication and ground level ozone.

Catalytic oxidation is a promising technology to control the emissions of volatile organic compounds (VOC) [6]. The key parameter of this process is the type of catalyst used, which is always a function of the VOC and its concentration, the presence of poisons or/and inhibitors, and any inlet temperature constraints.

Industrial emissions usually contain a mixture of VOC with variable composition. The “mixture effect” is very difficult to predict *a priori* [7], as either an inhibition effect [8–10] or (more rarely) a promoting effect [11] can be observed when the components of the mixture are oxidised. In addition, changes in selectivity to by-products have also been observed [8,12–14].

Some authors have pointed out that the inhibition effect can be due to competition between the compounds for adsorption onto the active sites [10,13,15–17]. For example, Tsou et al. [10] observed that the oxidation of methyl-isobutyl-ketone (MIBK) on zeolite supported platinum catalysts was strongly inhibited by the presence of o-xylene, which adsorbs strongly onto the active sites. Moreover, the oxidation of 2-propanol over platinum supported on a monolith was negatively affected by the presence of toluene and methyl-ethyl-ketone (MEK) [8]. This inhibition effect was found to be related to the competition for the oxygen atoms chemisorbed on Pt, and not due to competition for the adsorption sites on the support.

On the other hand, the oxidation of certain compounds can also be independent of the presence of other VOC. For example, the

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Table 1
Properties of the catalyst: structure (obtained by XRD), surface area (obtained by nitrogen adsorption), average oxidation state (AOS) and relative amount of Mn(IV) surface species (obtained by XPS).

Phase	S_{BET} (m^2/g)	AOS	% Mn(IV)
KMn_8O_{16}	71	3.89	83

presence of n-hexane does not affect the oxidation of benzene and toluene over a Pt/Al_2O_3 catalyst [18]. It was concluded that the addition of a compound that is more weakly adsorbed on the catalyst than the original one does not affect the reaction rate significantly.

A promoting effect has also been observed in the oxidation of mixtures [11,19,20]. Generally, this effect is a consequence of the higher exothermicity of the process [20]. However, in some systems this effect cannot be explained by heat generation during the reaction. For example, the oxidation of chlorobenzene over a Pt/γ-Al_2O_3 catalyst [19] is enhanced by the addition of aliphatic hydrocarbons, such as pentane, heptane or decane. Alkanes have the ability to remove Cl from the Pt surface (at the same time reducing the metal), which otherwise would only be removed at higher temperatures, explaining the promoting effect.

The aim of the present work is to study the performance of cryptomelane (KMn_8O_{16}) in the oxidation of VOC binary mixtures. Three binary mixtures are studied: ethyl acetate/toluene, ethyl acetate/ethanol and ethanol/toluene.

2. Experimental

2.1. Catalyst synthesis and characterization

Cryptomelane was prepared by the reflux method according to [21]. Briefly, a solution of $KMnO_4$ (Vaz Pereira, 99% purity) was added to $Mn(CH_3COO)_2$ (Fluka, 99% purity) in acidic medium. The initial pH was adjusted to 3.5, using HNO_3 (Panreac, 65% purity). Further details can be found elsewhere [22]. The structure, morphology, composition, manganese average oxidation state (AOS), BET surface area and stability of the prepared samples were fully characterized by X-ray diffraction (XRD), scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDS), X-ray photoelectron spectroscopy (XPS), N_2 adsorption at −196 °C, thermogravimetric analysis (TGA) and temperature programmed desorption (TPD) [22,23]. A summary of the main catalyst properties is presented in Table 1.

2.2. Catalytic activity measurements

Ethyl acetate, ethanol and toluene were the VOC chosen for this study. The catalytic oxidation of VOC was performed under atmospheric pressure in a fixed-bed reactor from Autoclave Engineers (BTRS Jr), which consists of a stainless steel tube of 6 mm internal diameter, placed inside a temperature-controlled electric furnace. A feed gas with selected VOC inlet concentrations and a space velocity of 16,000 h^{-1} was used. The catalyst sample (50 mg) was diluted with glass spheres of the same size as the catalyst particles (0.2–0.5 mm), in order to minimize temperature gradients.

Conversions were measured over the range 100–350 °C by incremental steps (10–20 °C), the temperature being measured by a thermocouple placed in the middle of the catalyst bed. To ensure that steady state data were measured, the reactor was maintained at each temperature for 30 min. The conversion of VOC (X) was calculated as

$$X = 1 - \frac{F_{VOC}}{F_{VOC,in}}$$

where F_{VOC} is the outlet molar flow rate of VOC at steady state and $F_{VOC,in}$ is the inlet molar flow rate of VOC. Further details can be found elsewhere [22].

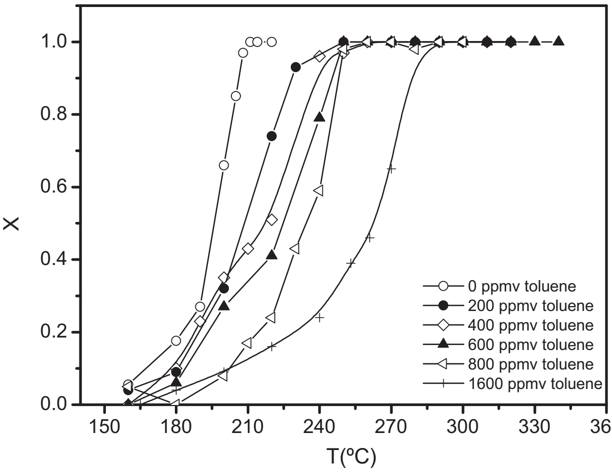

Fig. 1. Conversion of ethyl acetate alone (1600 ppmv), and in binary mixtures with toluene.

3. Results and discussion

The catalytic performance of cryptomelane in the single oxidation of ethanol, ethyl acetate and toluene was previously studied [22–25]. Cryptomelane was found to be very active, promoting the oxidation of these VOC at relatively low temperatures. The conversion level was influenced by the type of VOC, the reactivity into CO_2 increasing in the following order: toluene < ethanol < ethyl acetate.

The oxidation process of the oxy-derivative compounds was found to be more complex than that of toluene, yielding not only CO_2 and H_2O, but also partially oxidised intermediates (namely acetaldehyde). On the other hand, it was established that lattice oxygen is involved in the oxidation process of all VOC studied, suggesting a Mars and van Krevelen mechanism [23]. In this context, the type of VOC is particularly important, as it dictates the reduction of the catalyst and, consequently, the rate of oxygen incorporation in the lattice, which explains the lower reactivity observed with toluene.

In the present work, the performance of cryptomelane in the oxidation of three binary mixtures was evaluated.

3.1. Ethyl acetate/toluene mixtures

The activity of cryptomelane in the oxidation of ethyl acetate/toluene mixtures was evaluated by performing two sets of experiments. In the first one, the concentration of one of the components was kept constant, while the concentration of the other component was changed within a pre-established range (see Figs. 1 and 2). The second type of experiment was carried out by changing the relative proportions of toluene and ethyl acetate in the mixture, while keeping the concentration of carbon in the feed constant (see Fig. 3).

Fig. 1 shows the effect of toluene on ethyl acetate oxidation. It can be observed that the presence of toluene strongly inhibits the oxidation of ethyl acetate, and this effect increases with the toluene concentration, being particularly important for 1600 ppmv. For instance, the temperature for 100% conversion is about 210 °C when ethyl acetate is oxidised alone, and 250 °C or higher, when it is oxidised in mixtures with toluene. On the other hand, it can be observed (see Fig. 2) that ethyl acetate does not have a significant effect in the oxidation of toluene. This result was already expected,