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Role of preparation parameters on the structure–selectivity properties of MoO_3/Al_2O_3 catalysts for the oxidative dehydrogenation of ethane

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Abstract

Two $MoO_3/\gamma\text{-}Al_2O_3$ catalysts containing 11% (w/w) MoO_3 prepared by equilibrium-deposition-filtration at two different pairs of pH and Mo concentration values (pH $= 3.9$, $C_{Mo} = 1.1 \times 10^{-3}\,mol\,L^{-1}$ and pH $= 6.3$, $C_{Mo} = 2.7 \times 10^{-2}\,mol\,L^{-1}$) were studied for the ethane oxidative dehydrogenation.

The two catalysts demonstrated similar ethane conversions in a temperature range 450–600 °C. Selectivity to ethene was 15% higher for the catalyst prepared at relatively low pH than for the sample prepared at a higher pH. The observed difference in ethylene selectivity was related to the different structural characteristics of the molybdena phase in the two catalysts.

Keywords: Preparation parameters; Structure–selectivity properties; Oxidative dehydrogenation

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1. Introduction

The oxidative dehydrogenation (ODH) of light alkanes is explored as a potential new route to the corresponding alkenes. Since ethane is the second major component of natural gas and also a main product in many methane-coupling reactions, its transformation to ethene at low temperatures is of considerable interest [1].

Most ODH catalysts contain Mo and V oxides as active component [2]. Recent studies performed by the Lemonidou's group on the oxidative dehydrogenation of C_2 and C_3 alkanes have shown that both Mo- and V-supported catalysts are very promising catalytic systems [3–5].

The catalytic performance is greatly influenced by the variation of the support and promotion with alkali metals. Banares [6], in a detailed review article, has discussed the conversion of ethane on supported Mo and V oxide catalysts, stressing the effect of metal oxide and additive loading, as well as the state of the catalyst during working conditions. Recently, Chen et al. [7] have studied alumina-supported molybdenum oxide catalysts with a wide range of Mo surface densities.

Following the equilibrium-deposition-filtration (EDF) method for the preparation of the Al_2O_3-supported MoO_3 catalysts, the amount of the Mo-oxo species deposited on the $\gamma\text{-}Al_2O_3$ surface increases with the Mo concentration in the impregnating solution, whereas it decreases with the impregnation pH [8]. It is, therefore, possible to deposit on the support surface the *same amount* of Mo-oxo species by selecting *different pairs of* (*pH*, *concentration*) *values*. On the other hand, it has been well established that the deposited Mo surface species, following EDF, depend on the particular pair of the (pH, concentration) values selected to carry out the Mo deposition. Thus, in a previous work [9], we succeeded to prepare two $MoO_3/\gamma\text{-}Al_2O_3$ samples with almost the same Mo loading (~11% (w/w) MoO_3) but *different structural characteristics of the molybdena phase*. Characterization of the above catalysts after calcination using UV-Vis diffuse reflectance (DRS) and laser Raman (LRS) spectroscopies revealed that the formation of polymeric octahedral MoO_x species is favored on the sample prepared using relatively low pH, whereas monomeric tetrahedral species are predominant on the sample prepared at higher pH.

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In the present work, and using the above samples, we investigated whether the catalytic properties of the $MoO_3/\gamma\text{-}Al_2O_3$ catalysts with the same Mo content for the ODH of ethane are influenced by the structure of the Mo-phase achieved, and thus by the preparation conditions applied upon deposition of the Mo-oxo species on the support surface.

2. Experimental

Catalyst preparation. Experimental details concerning the preparation of the specimens studied in the present work have been given previously [9]. Thus, they are mentioned here only in brief. Following the EDF methodology, two $MoO_3/\gamma\text{-}Al_2O_3$ samples ($Mo_{3.9}$ and $Mo_{6.3}$) with almost the same MoO_3 loading ($Mo_{3.9}$: 10.5% (w/w) MoO_3 and $Mo_{6.3}$: 11.5% (w/w) MoO_3) were prepared. For the preparation of the $Mo_{3.9}$ sample a Mo solution with relatively low Mo concentration, $C_{Mo} = 1.1 \times 10^{-3}\,mol\,L^{-1}$, and $pH = 3.9$ was used, while for the preparation of the $Mo_{6.3}$ sample another pair of preparation parameters, namely $C_{Mo} = 2.7 \times 10^{-2}\,mol\,L^{-1}$ and $pH = 6.3$, was used. The Mo deposition was followed by drying at 120 °C for 2 h and air calcination at 500 °C for 5 h.

Catalytic activity measurements. The catalytic performance of the samples was measured in a fixed-bed quartz reactor. First, the activity of the catalysts was measured as a function of reaction temperature. The experiments were run at a temperature range of 450–600 °C, with a constant gas flow ($55\,cm^3$/min, $C_2H_6/O_2/He = 5/5/45$) and weight of catalyst (0.3 g). In a second series of experiments, the W/F ratio was varied from 0.1 to $0.85\,g\,s\,cm^{-3}$, in order to obtain various ethane conversion levels at constant temperature (550 °C). Prior to experiments, samples were pretreated in O_2 at 500 °C for 30 min. The reaction products were analyzed on line by a Varian 3700 gas chromatograph equipped with a thermal conductivity detector (TCD). Two columns in a series-bypass configuration were used in the analysis: a Porapak Q and an MS 5A.

3. Results and discussion

Fig. 1 illustrates the ethane conversion achieved over the prepared catalysts as a function of reaction temperature. It is clearly demonstrated that in all temperatures studied the activity of both samples is almost the same. This implies that even though the two samples exhibit differences in their structure and/or coordination of surface Mo-oxo species, the main factor that probably determines catalytic activity is the total active area of each sample. This area is expected to be the same as the EDF methodology brings about a very high dispersion of the molybdena phase, whereas the Mo loading of the catalysts, as well as their BET surface areas ($Mo_{3.9}$: $236\,m^2\,g^{-1}$; $Mo_{6.3}$: $233\,m^2\,g^{-1}$), are almost the same [9].

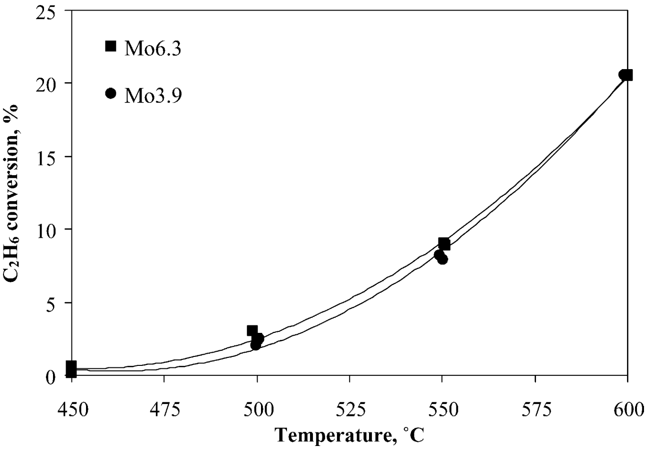

Fig. 1. Ethane conversion in the temperature range between 450 and 600 °C over the MoO_3/Al_2O_3 catalysts (reaction conditions: $W/F = 0.33\,g\,s\,cm^{-3}$, $C_2H_6/O_2 = 1/1$).

The selective reaction of the ODH of ethane leading to the formation of ethene is accompanied by the total oxidation of the hydrocarbons, leading to the formation of CO and CO_2. The inverse relation between conversion and selectivity, typical of the oxidative dehydrogenation reactions, implies a parallel-consecutive reaction network. The produced carbon oxides can be formed either in a parallel reaction directly from ethane or/and from the consecutive over-oxidation of the produced olefin.

The ethene selectivity as a function of conversion attained at various W/F ratios and constant temperature is depicted in Fig. 2. An inspection of this figure shows that selectivity decreases slightly over both samples as the conversion increases. However, the $Mo_{3.9}$ catalyst proved to be 15% more selective than the $Mo_{6.3}$ one in all range of conversion values studied. In order to get a clearer picture, the CO_2 and CO selectivities are plotted as a function of the ethane conversion in Figs. 3 and 4. It is evident that the initial CO_2 selectivity at zero conversion, originating from

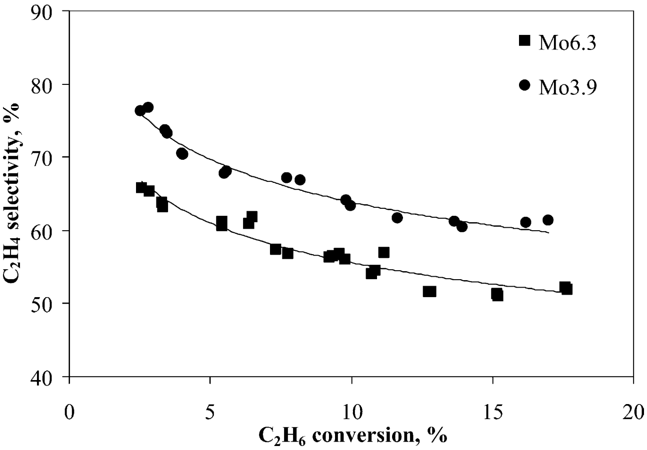

Fig. 2. Selectivity of ethane ODH to ethene over the MoO_3/Al_2O_3 catalysts for various conversion values (reaction conditions: $T = 550\,°C$, $C_2H_6/O_2 = 1/1$).

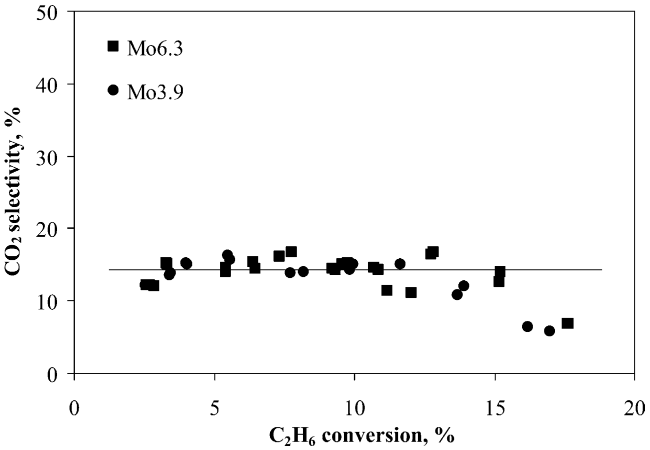

Fig. 3. CO_2 selectivity as a function of ethane conversion (reaction conditions: $T = 550\,^{\circ}C$, $C_2H_6/O_2 = 1/1$).

the primary unselective oxidation of ethane, is the same for the two catalysts (~14%) and remains almost constant for up to 15% ethane conversion. The decline from linearity observed at higher conversion levels is possibly due to the participation of CO_2 in the ODH reaction as an oxidant, promoting the conversion of ethane to ethene.

On the contrary, the initial CO selectivity, produced by primary unselective oxidation of ethane, is significantly higher for the $Mo_{6.3}$ catalyst. The increase of the CO selectivity with conversion, accompanied by parallel decrease of the C_2H_4 selectivity, shows that CO is also produced from consecutive secondary reactions of the formed ethylene. We can observe that the trend of the CO increase with conversion is the same for both samples, indicating the same extent of secondary reactions of ethylene to CO over the two catalysts. In view of the above, the inferior ethene selectivity of the $Mo_{6.3}$ catalyst can be attributed almost exclusively to the higher extent of the unselective primary oxidation of ethane to carbon monoxide observed over this catalyst.

At relatively low temperatures (<600 °C) and over reducible metal oxides, the partial oxidation reactions are considered to proceed via a classical redox cycle [10]. The redox mechanism of ethane ODH is generally accepted to occur by a Mars–van Krevelen mechanism [11]. The rate-determining step is the abstraction of one H from a C–H bond by lattice oxygen, though no differentiation can be always achieved concerning the nature of the oxygen species involved in the C–H bond activation. The relative ease in the removal of lattice oxygen, which presumably leads to high activity, is frequently characterized by the ease of catalyst reduction with hydrogen. TPR experiments have shown that larger amounts of loosely bonded and more easily reducible Mo-oxo species are formed in the $Mo_{3.9}$ sample than those formed in the $Mo_{6.3}$ sample [9]. Although the reduction behavior of the catalysts under study is different, their ability to activate ethane appears to be the same, since both samples demonstrate the same activity. Contradictory results appear in literature concerning the reducibility-activity relationship in ODH reactions [7,12]. According to Banares [6], these disagreements arise from the fact that some reports correlate activity with the bulk reducibility of the catalyst, which may differ significantly from that of the surface sites and lead to different conclusions.

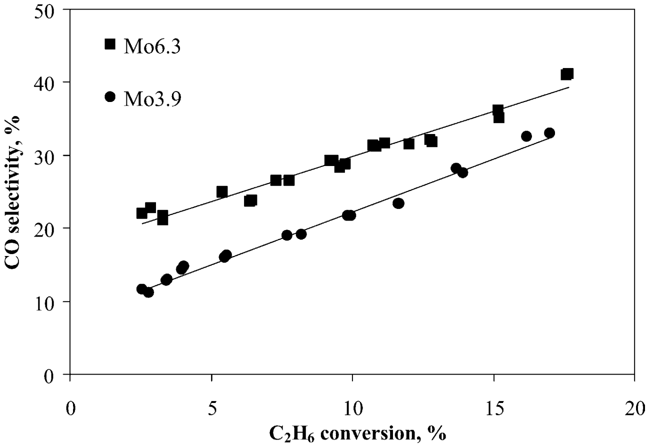

Fig. 4. CO selectivity as a function of ethane conversion (reaction conditions: $T = 550\,^{\circ}C$, $C_2H_6/O_2 = 1/1$).

Furthermore, our results imply that the polymerization degree and/or coordination of the surface molybdena species are not the predominant factors that affect the reactivity of the two catalysts under study in ethane ODH. Both catalysts exhibit the same activity, although the (polymerized/isolated) species ratio in the two samples is different, as indicated by characterization with Raman spectroscopy [9]. It may be inferred that the activation of the C–H bond, which is the rate-determining step, proceeds on only one Mo site. This is in agreement with recent studies examining the dynamic behavior of supported metal oxides in ethane and propane ODH by in situ Raman spectroscopy [13–15]. According to these studies, the Mo–O-support oxygen is the kinetically critical active site during oxidation reactions, while the terminal Mo=O and bridging Mo–O–Mo bonds do not appear to have a significant role in reactivity.

On the other hand, the selectivity to ethene seems to be sensitive to the structure of the Mo-oxo species deposited on the surface of alumina, since the $Mo_{3.9}$ catalyst appears to be 15% more selective to ethene than the $Mo_{6.3}$ catalyst at isoconversion. The Mo deposition at relatively low pH (pH = 3.9) favors the deposition of a polymeric Mo-phase loosely bounded with the support surface. This phase, in which molybdenum is found in an octahedral environment, has one Mo=O terminal bond per Mo atom and bonds bridging Mo to the oxide support (Mo–O–Al) and to adjacent surface MoO_x species (Mo–O–Mo). One possible reason responsible for the observed surface structure sensitivity may be the different strength of the Mo=O bonds in the octahedral and tetrahedral molybdena species. The vibration of the Mo=O bond in the laser Raman spectra shifts from $940\,cm^{-1}$ for the tetrahedral to $970\,cm^{-1}$ for the octahedral MoO_x species, indicating stronger bonds in the $Mo_{3.9}$ sample [9]. The stronger the Mo=O bond, the more basic is its functionality. It could be possible that the ethane C–H bond is more selectively activated on the nucleophilic Mo=O bonds of the octahedral species that are present on the surface of the $Mo_{3.9}$ catalyst, thus preventing its oxidation to carbon oxides. Chen et al. have also related higher selectivity in the propane ODH over Mo/ZrO_2 catalysts to the increased strength of the Mo=O bonds [16]. In another work [7], they have also shown that the selectivity over MoO_3/Al_2O_3 catalysts increases with the concentration of *the polymeric Mo-oxo species* formed on the catalyst surfaces.

In the case of the $Mo_{6.3}$ catalyst, the monomeric tetrahedral Mo-oxo species are predominant. The diffuse reflectance spectrum obtained for this sample exhibits higher absorption at 244 nm, attributed to tetrahedral species, than absorption at 305 nm, corresponding to species in octahedral coordination [9]. For tetrahedrally coordinated species on the alumina surface, the most likely structure is that possessing two terminal Mo=O bonds and two bridging Mo–O–Al bonds [17]. The lower selectivity of this sample could suggest that it may be easier to abstract oxygen from the terminal Mo=O bonds of the tetrahedral species. This greater facility of oxygen abstraction leads to an over-oxidation of ethane to carbon monoxide. Raman studies of surface species on Mo/SiO_2 catalysts, in regard to their role in the partial oxidation of methane, have also shown that tetrahedral species are responsible for the non-selective oxidation of methane to CO [18].

The above results show that using EDF, one could presumably regulate the selectivity of the prepared $MoO_3/\gamma\text{-}Al_2O_3$ catalysts for the ODH of ethane by selecting the suitable pair of impregnation parameters (pH and concentration). This clearly shows the importance of the conditions (pH, concentration) under which the Mo-oxo species are deposited on the support surface for the achievement of a desired final speciation and thus catalytic behavior.

4. Conclusions

Testing of the two 11% (w/w) $MoO_3/\gamma\text{-}Al_2O_3$ catalysts prepared by EDF in the ethane ODH reaction showed that the activity of the catalysts is similar implying that the amount of the molybdenum phase present on the catalytic surface is the determinant factor for ethane conversion.

Selectivity to ethene proved to be surface structure sensitive increasing over the catalyst prepared at relatively low pH, in which molybdenum is found in an octahedral environment, and decreasing over the catalyst prepared at relatively high pH, in which the monomeric tetrahedral Mo-oxo species are predominant. One possible reason responsible for the observed surface structure sensitivity may be the different strength of the Mo=O bonds in the octahedral and tetrahedral molybdena species.

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