Available online at www.sciencedirect.com

ScienceDirect

Mendeleev Commun., 2008, **18**, 268–269

Mendeleev
Communications

Dynamics of ethane transformation under redox conditions over Pt/M_xO_y/Al_2O_3: effect of an oxygen storage component (M_xO_y)

Viktor V. Sinel'nikov, Galina O. Bragina, Nataliya S. Telegina,
Galina N. Baeva and Aleksandr Yu. Stakheev*

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation.
Fax: +7 499 135 5328; e-mail: st@ioc.ac.ru

DOI: 10.1016/j.mencom.2008.09.014

Selectivity in ethylene was significantly improved by introduction of ZnO as an oxygen storage component into Pt/Al_2O_3 catalyst and alloying of Pt with Sn.

Oxidative transformation of light alkanes (C_1–C_3) to valuable products is one of the most important directions of research. The process of ethane oxidative dehydrogenation (ODH) to ethylene is of significant industrial interest.[1] However, there are a number of problems, which limit application of this process. On one hand, hydrocarbon (ethane or ethylene)–air feed is explosive. On the other hand, there is a considerable decrease in selectivity at high ethane conversions due to a total oxidation of ethane and ethylene by gas phase oxygen.

One of the promising approaches for improving selectivity of ethane ODH consists in performing reaction under alternating supply of an oxidant (air) and a hydrocarbon to a catalyst (redox conditions). At the first stage, oxygen is accumulated on a catalyst surface, and at the second stage the hydrocarbon interacts with catalyst active sites and accumulated oxygen. Previously, we observed the considerable decrease in total oxidation products amount during propane ODH under redox conditions.[2] Hence, this method allows increasing selectivity of ethane oxidative dehydrogenation due to a suppression of undesirable total oxidation process in gas phase. Besides, the alternating supply of oxygen and hydrocarbon eliminates danger of explosion of the feed gas.

However, two main problems arise: (i) low efficiency due to small oxygen storage capacity of the catalyst and (ii) low activity in hydrocarbon oxidation of catalytic systems studied so far. These drawbacks can be overcome by designing a dual-function catalyst containing oxygen storage component (OSC)[3] and highly active dehydrogenation component (*e.g.*, Pt).[2]

The main focus of this research consisted in elucidating dynamics of ethane ODH and formation of the reaction products under conditions of alternating supply of reagents over a catalyst. The catalysts studied contained Pt as dehydrogenation component and a series of different metal oxides as oxygen storage components (OSCs). The effect of OSC and alloying Pt with Sn on the catalyst performances was evaluated.

The 1% Pt/15% M_xO_y/Al_2O_3 catalysts (where M_xO_y is CeO_2, ZnO, TiO_2, *i.e.* oxides of various metal types as an oxygen storage component) were studied. Additionally, 1% Pt/Al_2O_3 and 1% Pt–7% Sn/15% ZnO/Al_2O_3 were studied. The parent Al_2O_3 (Sasol, Puralox NWa155) was used as received. Al_2O_3 was loaded with 1 wt% Pt (from H_2PtCl_6) and 15 wt% CeO_2 or ZnO [from $Ce(NO_3)_3 \cdot 6H_2O$ or $Zn(NO_3)_2 \cdot 6H_2O$ aqueous solution, respectively] by incipient–wetness coimpregnation. To produce 1% Pt/15% TiO_2/Al_2O_3 the $Ti(OPr^i)_4$ was diluted with Pr^iOH. Thus prepared solution was used for incipient–wetness impregnation. Then, the TiO_2 loaded carrier was impregnated with aqueous H_2PtCl_6. The resulting materials were calcined at 600 °C (2 h) in air (300 ml min^{-1}). Further, the samples were reduced at 400 °C (2 h) in H_2 flow (100 ml min^{-1}).

Before catalytic tests, we evaluated the oxygen storage capacity of the catalysts by CO titration at 300, 350 and 400 °C. CO titration experiments consisted of three stages. At the first stage, the air was supplied and oxygen was accumulated on a catalyst surface. On the next stage, the feed was replaced by nitrogen for removing oxygen from gas phase. And, finally, the CO was supplied. On this stage, the CO reacts with accumulated oxygen and a catalyst OSC was measured on the basis of the amount of CO_2 formed.

Typical reaction cycle consisted of four stages: (i) catalyst treatment in air for 200 s for surface oxygen accumulation; (ii) purging in nitrogen for 50 s for removing gas phase oxygen; (iii) ethane oxidation by accumulated oxygen for 400 s; (iv) purging in nitrogen for 50 s for removing unreacted ethane and reaction products from gas phase. Gas feed composition on the ethane conversion stage was 17% C_2H_6 in N_2. The catalyst sample (0.5 g) was held in place between two plugs of quartz wool. Gas flow rate and GHSV were constant at all cycle stages and equal to 200 ml min^{-1} and 12000 h^{-1}, respectively. Reaction temperature was 500 °C. Dynamics of variations of C_2H_6 concentrations and reaction products (CH_4, C_2H_4, CO, CO_2) formation were monitored by on-line FTIR gas analyzer (GASMET Dx-4000n).

The results of the OSC measurements by CO titration are displayed in Table 1. The values allow us to rank samples in the following order: Pt/CeO_2/Al_2O_3 > Pt/ZnO/Al_2O_3 > Pt/TiO_2/Al_2O_3 > > Pt/Al_2O_3.

Introduction of a metal oxide in Pt/Al_2O_3 considerably increases OSC of a system. Among the catalysts tested, the sample with the CeO_2 exhibited highest oxygen storage capacity (147 μmol O_2 per gramm of catalyst at 400 °C). The catalysts containing ZnO and TiO_2 are also promising since OSC for these systems is relatively high (> 70 μmol O_2 per gram of catalyst).

Table 1 Effect of oxygen storage component on catalyst OSC.

Catalyst	Oxygen storage capacity/ μmol O_2 per gram of catalyst		
	300 °C	350 °C	400 °C
1% Pt/Al_2O_3	35	40	40
1% Pt/15% CeO_2/Al_2O_3	137	137	147
1% Pt/15% ZnO/Al_2O_3	80	94	100
1% Pt/15% TiO_2/Al_2O_3	61	68	72

© 2008 Mendeleev Communications. All rights reserved.

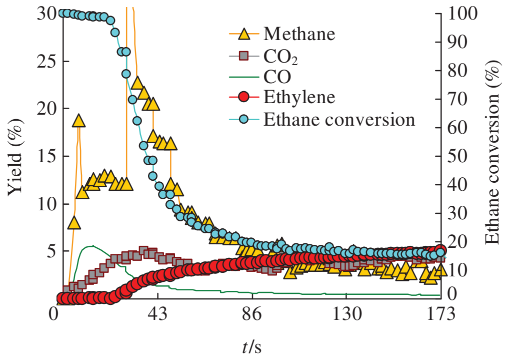

Figure 1 Dynamics of ethane conversion and reaction products formation over Pt/Al_2O_3 at 500 °C.

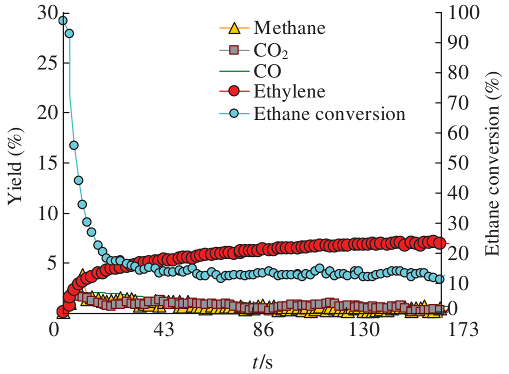

Figure 2 Dynamics of ethane conversion and reaction products formation over $Pt/ZnO/Al_2O_3$ at 500 °C.

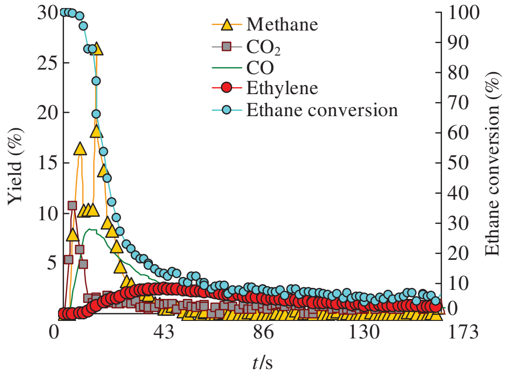

Figure 3 Dynamics of ethane conversion and reaction products formation over $Pt/CeO_2/Al_2O_3$ at 500 °C.

Variations of ethane conversion and reaction products (ethylene, methane, CO, CO_2) yields over Pt/Al_2O_3, $Pt/ZnO/Al_2O_3$ and $Pt/CeO_2/Al_2O_3$ at 500 °C are displayed in Figures 1–3, respectively. Comparison of these data brings us to a conclusion that oxygen storage component is crucial for overall catalysts performance. The main reaction products over Pt/Al_2O_3 (without OSC) were methane and CO (Figure 1). For ~50 s of ethane pulse a maximum formation of methane (yield up to 35%) and CO was observed. The following air pulse resulted in an intensive (up to 50%) CO_x evolution, presumably due to oxidation of carbon deposits accumulated on the catalyst surface during C_2H_6 ODH (is not presented in the figure).

Loading of ZnO (or TiO_2) as an oxygen storage component increased ethylene yield and selectivity (Figure 4). The yield of undesirable side products (CO, CO_2, CH_4) over $Pt/ZnO/Al_2O_3$ did not exceed 4% and dominant product of C_2H_6 conversion was ethylene (Figure 2). Ethylene yield passes through the maximum after 2–3 min of the reaction (Figure 4). Presumably during this period, easily accessible oxygen is consumed, and further ethylene formation proceeds *via* a combination of a non-oxidative dehydrogenation and oxidative dehydrogenation by oxygen diffused from the catalyst bulk. CO_x evolution during the following air pulse was considerably lower over $Pt/ZnO/Al_2O_3$ and $Pt/TiO_2/Al_2O_3$, as compared to Pt/Al_2O_3.

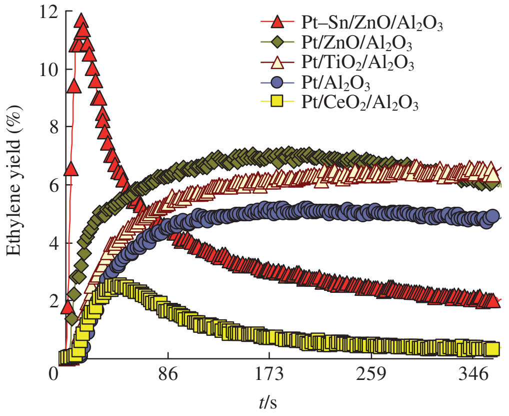

Figure 4 Ethylene formation over $Pt/M_xO_y/Al_2O_3$ catalysts (where M_xO_y is CeO_2, ZnO or TiO_2).

On the other hand, CO, CO_2 and methane were the main products of the reaction over $Pt/CeO_2/Al_2O_3$ (Figure 3). During the first ~50 s of ethane pulse maximum formation of CO_2 (yield up to 11%), CO (yield up to 8.5%) and methane was observed. Carbon oxides were formed presumably *via* reaction of ethane and ethylene with highly reactive oxygen stored by cerium oxide. Ethylene selectivity over $Pt/CeO_2/Al_2O_3$ was low (see Online Supplementary Materials).

The most promising selectivity toward ethane ODH under conditions of alternating supply of reagents was demonstrated by $Pt/ZnO/Al_2O_3$. However, analysis of the reaction products indicated that one of the main factors limiting the process selectivity was CH_4 formation during the first stage of ODH, and carbon deposition on the catalyst surface (probably, coke formation). A possible route of carbon deposition (coking of the catalyst) can be the carbon-filament growth over the metal surface. Modification of Pt by alloying it with Sn in $Pt–Sn/ZnO/Al_2O_3$ suppresses undesirable side reactions and significantly increases ethylene yield (Figure 4) and selectivity. CO_x evolution during the following air pulse did not exceed 5%.

The data obtained allow us to conclude that the oxygen storage component (M_xO_y) nature considerably affects the catalysts performance. Over $Pt/ZnO/Al_2O_3$ and $Pt/TiO_2/Al_2O_3$ ethylene predominates, while the main products over $Pt/CeO_2/Al_2O_3$ are CO, CO_2 and methane.

The main factors limiting selectivity of ethylene ODH are CH_4 formation and carbon deposition. Modification of Pt with Sn allows us to increase significantly selectivity in ethylene by suppressing side reactions.

This work was supported by the Russian Academy of Sciences (programme no. 7).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2008.09.014.

References

1 F. Cavani, N. Ballarini and A. Cericola, *Catalysis Today*, 2007, **127**, 113.
2 V. V. Sinel'nikov, N. N. Tolkachev, S. S. Goryashchenko, N. S. Telegina and A. Yu. Stakheev, *Kinet. Katal.*, 2006, **47**, 103 [*Kinet. Catal.* (*Engl. Transl.*), 2006, **47**, 98].
3 V. V. Sinel'nikov, N. N. Tolkachev and A. Yu. Stakheev, *Kinet. Katal.*, 2005, **46**, 585 [*Kinet. Catal.* (*Engl. Transl.*), 2005, **46**, 550].

Received: 22nd February 2008; Com. 08/3087