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Oxidative dehydrogenation of dimethyl ether to 1,2-dimethoxyethane over oxide catalysts

Alexander A. Greish,* Lev M. Glukhov and Leonid M. Kustov

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 499 137 2935; e-mail: greish@ioc.ac.ru

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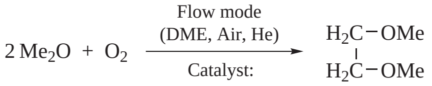
Catalysts based on silica-supported Ga_2O_3, In_2O_3, La_2O_3 possess higher activity in oxidative dehydrogenation of dimethyl ether to dimethoxyethane than co-precipitated CaO–SnO_2, SrO–SnO_2, BaO–SnO_2 catalysts.



$$2\,Me_2O + O_2 \xrightarrow[\text{Catalyst:}]{\text{Flow mode (DME, Air, He)}} \begin{array}{l} H_2C-OMe \\ \;| \\ H_2C-OMe \end{array}$$

CaO–SnO_2 (1:1) 10% Ga_2O_3/SiO_2
SrO–SnO_2 (1:1) 5% In_2O_3/SiO_2
BaO–SnO_2 (1:1) 5% In_2O_3, 5% La_2O_3/SiO_2

Dimethyl ether (DME), a relatively inexpensive product of the large-scale organic synthesis of methanol, is predominately used for production of various organic compounds and may be employed as an additive to diesel fuel. In turn, the product of oxidative dimerization of DME (ODDME), 1,2-dimethoxyethane (DMOE), is a widely popular solvent. Analogously to the catalytic oxidative dimerization of methane and ethane, the ODDME over different catalysts has also been studied.[1–3] In principle, this reaction can be presented as outlined in Scheme 1.

$$2\,Me–O–Me + O_2 \rightarrow Me–O–CH_2–CH_2–O–Me + H_2O$$

Scheme 1

Gas-phase dimerization of DME proceeds on the MgO–SnO_2 catalyst at 200 °C and a pressure of 16 bar to form DMOE in a yield of up to 3.5%,[1] with the low temperatures and high DME/O_2 ratios being beneficial for the DMOE formation. One-step synthesis of DMOE *via* the oxidation of DME on pure silica and silica modified with heteropolyacids was studied, the degree of DME conversion was up to 10–11%.[2] Catalysts CaO/SnO_2 and MgO/SnO_2 prepared by the microemulsion method[3] demonstrated good activity at 275–300 °C providing maximum DME conversion of 21.8% at 300 °C and selectivity to methyl formate and DMOE of 19.1 and 59.0%, respectively, at 275 °C.

Recently, new catalysts based on co-precipitated calcium and tin oxides and exceeding their analogues in activity and selectivity of DMOE formation were proposed.[4] Their IR and ESR spectroscopy study[5] showed that the surface of the CaO–SnO_2 catalyst may generate superoxide species which can be responsible for abstraction of the H atom in DME molecule, which, in turn, leads to recombination of two $MeOCH_2^{\bullet}$ radicals giving a DMOE molecule.

Since ODDME occurs in the presence of oxygen, the process is inevitably accompanied by complete oxidation of DME into carbon dioxide and water. This side reaction is the main cause for the low DMOE yield and poor selectivity of the process.

The present work was aimed at studying the catalysts comprising metal oxides of groups III–IV of the Periodic Table and their activity in the oxidative dehydrogenation of DME to DMOE. For this, a set of various catalysts was prepared and tested in ODDME. The three catalysts were prepared by co-precipitation MO–SnO_2 oxides, where M = Ca, Sr, or Ba, while the three other catalysts were based on silica supported metal oxides of group III, *i.e*. Ga_2O_3, In_2O_3, and La_2O_3 (Table 1). The metal oxides of groups III and IV, in which metals can exhibit variable valence, are regarded as the active phases of the catalysts. To choose the optimal conditions for ODDME, the dependences of the catalyst activity on temperature as well as the content and flow rates of gases were investigated. The catalysts structures were studied by X-ray diffraction (XRD) and thermogravimetry combined with differential thermal analysis (TG-DTA).[†]

To find relationship between the catalyst activity of alkaline-earth metal tinnates, CaO–SnO_2, SrO–SnO_2, BaO–SnO_2, and the basicity of the alkali-earth metal oxide, the dependence of the DMOE yield on the reaction temperature was studied (Figure 1). All the catalysts were truly active in ODDME process. However, the yield of DMOE depended on the nature of the alkaline-earth

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[†] The catalytic tests were carried out in a quartz flow reactor, having 6 mm diameter and 30 cm length. The catalyst fraction of 0.25–0.50 mm was loaded in the middle of the reactor whose free space was filled with quartz chips. The heating of the reactor was performed by an electric furnace equipped with a temperature controller. The temperature was varied in the range of 250–325 °C.

The initial gas mixture consisted of DME, air and helium as a diluter for the main reagents, DME and oxygen. The gas flow rate was varied in the range of 2 to 40 $cm^3\,min^{-1}$ (GHSV was 150–3000 h^{-1}) and was measured by an electronic flowmeter. The reaction products were analyzed by GLC with the use of two stainless steel packed columns. One column (d = 3 mm, l = 2 m) was packed with Porapak-Q, while the other one (d = 3 mm, l = 4 m) was packed with 8% PEG-2000 on Chromaton N-AW.

Two groups of the catalyst samples were prepared. The first group involved the co-precipitated tin oxide and alkaline-earth metal oxides, CaO–SnO_2, SrO–SnO_2, BaO–SnO_2 with the MO:SnO_2 molar ratio close to 1:1, which corresponds to the composition of the appropriate tinnates. Co-precipitation of hydroxides was carried out by the dropwise addition of NH_4OH to solutions of $SnCl_4$ and $M(NO_3)_2$, (M is Ca, Sr or Ba). In each case, the precipitate was washed with distilled water, dried at 120 °C for 2 h and then calcined at 600 °C for 4 h.

The catalysts of the second group were silica-supported metal oxides of groups IIIa,b of the Periodic Table. Each catalyst from this group was prepared through incipient wetness impregnation of crushed silica (KSK-4, Russia, 230 $m^2\,g^{-1}$), 0.25–0.50 mm fraction, with a solution of the corresponding nitrates. Impregnated silica was kept at ambient temperature for 12 h, then dried at 120 °C for 2 h and calcined at 600 °C for 4 h.

Table 1 Groups of studied catalysts.

Catalyst group	Molecular composition	Catalyst group	Molecular composition
I	CaO–SnO_2 (1 : 1)	II	10% Ga_2O_3/SiO_2
	SrO–SnO_2 (1 : 1)		5% In_2O_3/SiO_2
	BaO–SnO_2 (1 : 1)		5% In_2O_3 + 5% La_2O_3/SiO_2

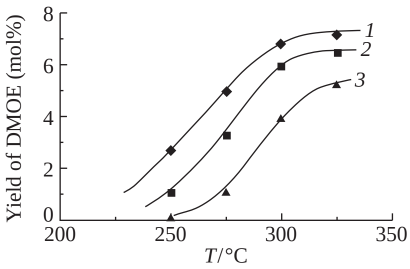

Figure 1 Temperature dependence of the DMOE yield: (*1*) CaO–SnO_2, (*2*) SrO–SnO_2, and (*3*) BaO–SnO_2. Reaction conditions: 1 g of catalyst, GHSV of DME, air and He is 860, 860 and 750 h^{-1}, respectively.

metal in the catalyst, as well as on the reaction temperature. As it was mentioned above, the DMOE formation is accompanied by complete oxidation of DME, so that the yield of CO_2 might be comparable with the yield of DMOE. In addition, minor quantities of methanol, formaldehyde and methyl formate were also detected in the reaction products.

As it can be seen, elevation of the reaction temperature enhances the efficiency of the catalysts, the highest activity being observed at 310–325 °C. The CaO–SnO_2 sample displays the ultimate activity in ODDME among the other tested catalysts, although the activity of each catalyst gets on the temperature plateau when it reaches ~320 °C. On using CaO–SnO_2, the highest yield of DMOE, ~8%, is obtained and raising the temperature from 250 to 320 °C causes increase in selectivity of DMOE formation, from 52% to 61%. This positive effect is probably resulted from the increase in desorption rate of DMOE from the catalyst surface that in turn reduces DMOE subjection to complete oxidation.

Thus, the obtained results show that the nature of the alkaline-earth metal in the catalyst affects the rate of ODDME. The higher basicity of the oxide, the lower the catalyst efficiency in the ODDME reaction. In this respect, the greatest difference between the catalysts is observed when the reaction temperature does not exceed 300 °C. In fact, only traces of DMOE are detected over BaO–SnO_2 catalyst at 250 °C, while the yield of DMOE reaches ~3% over CaO–SnO_2 catalyst under similar reaction conditions.

It was revealed that catalyst efficiency in the ODDME reaction, in particular over CaO–SnO_2, depended on the concentration of oxygen in the initial gas mixture (see Online Supplementary Materials). Apparently, there should be an optimal concentration of oxygen in the inlet gas flow providing the catalyst best performance. Indeed, the increase of the air flow rate leads, on the one hand, to the growth of oxygen concentration on the catalyst surface, which should be beneficial for ODDME. On the other hand, this should decrease the contact time, which diminishes the yield of DMOE. In our experiments, when air flow rate is less than 8–10 ml min^{-1} the selectivity is at the 65–67% level, whereas the selectivity falls to the 40% level and even lower at the air flow rates higher than 10 ml min^{-1} (GHSV = 750 h^{-1}).

To evaluate the role of the gas-phase reactions in DME conversion, several experiments were carried out with the no-load reactor. For this purpose a small quantity of DMOE was added to the initial gas mixture. It was found that DMOE can also participate in the free space complete oxidation, with this reaction rate being higher than the rate of DME complete oxidation. Obviously, slow desorption of DMOE from the catalyst into the gas phase is favourable for complete oxidation. Therefore, to reduce an undesired DMOE complete oxidation, this product should be removed from the reactor as quickly as possible. Dilution of the initial mixture with inert gas (He) and filling the free space of the reactor with quartz can be a good solution of the problem.

Similar plots displaying dependences of the ODDME efficiency on oxygen concentration in the feed gas were obtained for the SrO–SnO_2 and BaO–SnO_2 catalysts. The highest selectivity to DMOE for these catalysts was ~63–65%, and the highest yields of DMOE on BaO–SnO_2 and SrO–SnO_2 were 5.5% and 6.5%, respectively. Sufficiently high efficiency in ODDME was obtained with the DME : air ratio close to 1 : 1, which corresponded to the DME : O_2 molar ratio of 4.6 : 1. This value appeared to be optimal for ODDME under the applied reaction conditions. Calculations show that this ratio corresponds to 70% conversion of oxygen.

We also studied the dependence of the ODDME reaction on the contact time, which was changed by variation of flow rates of DME, air and He, whereas the molar ratios between gases were maintained constant (see Online Supplementary Materials). The results show that the plot for the yield of DME has extreme character, while the selectivity to DMOE sharply diminishes with the increase of the contact time. The optimal contact time of 1–1.5 s provides the highest yield of DMOE, which most likely is caused by the occurrence of two competing reactions, ODDME and complete oxidation. Indeed, the higher contact time, the higher probability for both reactant DME and product DMOE to undergo complete oxidation. On the contrary, low contact times shorten the interaction of DME and DMOE with molecular oxygen preventing their complete oxidation.

The conversion of DME into DMOE on using the catalysts containing the variable valence metal oxides of group III was evaluated. These oxides are often used in catalytic systems destined for various oxidation reactions, in particular for methane oxidative dehydrogenation.[6] We tested the following catalysts on the basis of the silica supported metal oxides of group III: 10% Ga_2O_3/SiO_2, 5% In_2O_3/SiO_2, 5% In_2O_3, 5% La_2O_3/SiO_2. In all the cases, the experiments were carried out under optimal conditions found above. All these catalysts are capable of catalyzing ODDME. However, their specific activity in ODDME and selectivity for DMOE formation differ (Figure 2).

According to Figure 2, the catalyst activity decreases in the order: 5% In_2O_3, 5% La_2O_3/SiO_2 > 5% In_2O_3/SiO_2 > 10% Ga_2O_3/SiO_2 > CaO–SnO_2 > SrO–SnO_2 > BaO–SnO_2. Activity of the supported catalysts is much higher than those of co-precipitated ones. The highest activity was exhibited by 5% In_2O_3, 5% La_2O_3/SiO_2 catalyst, which makes it possible to suppose a synergism between indium and lanthanum oxides at their equal content in the catalyst. Moreover, the increase in the catalyst activity is accompanied by the increase in selectivity of the reaction. Apparently, it is caused by the competition between two reactions occurring

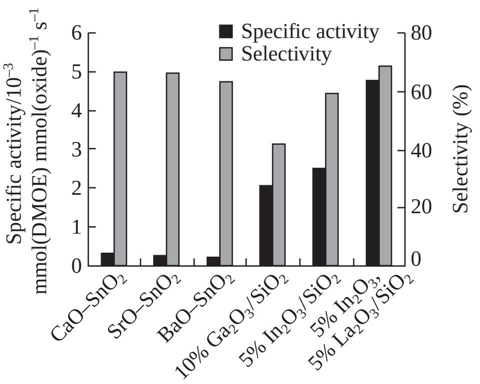

Figure 2 Specific activity in ODDME and selectivity to DMOE under optimal conditions for the catalysts.

over the catalyst, ODDME and complete oxidation. Indeed, reasonable processing should be based on stoichiometry since the complete oxidation of DME requires much more oxygen than ODDME. Therefore, oxygen consumption in the ODDME reaction reduces to some extent the rate of complete oxidation. This effect is noticeable for most active catalysts, *i.e.* containing Ga_2O_3, In_2O_3 and La_2O_3. For another group of catalysts based on SnO_2 and alkaline-earth metal oxides, such a phenomenon is also observed but to a significantly lesser extent.

It is worth noting that CaO–SnO_2, SrO–SnO_2 and BaO–SnO_2 catalysts are strongly inferior to the silica supported catalysts containing variable valence metal oxides of group III. This may be regarded as the evidence that the ODDME reaction occurs mainly on the surface of the heterogeneous catalyst and the internal part of the catalyst does not participate in the reaction due to a relatively low internal diffusion of DME in the solid catalyst. The selectivity of DMOE formation for the majority of the studied catalysts is about 60–69%, while the highest selectivity (69%) is achieved for the 5% In_2O_3, 5% La_2O_3/SiO_2 catalyst.

The mechanisms of DME partial oxidation on the studied catalysts can be different due to existence of various pathways of oxygen activation required for transformation of DME to DMOE. In the case of the catalysts based on tin and alkaline-earth metal oxides, oxidation activity can be provided by participation of peroxide anion O_2^- generated from O_2 on the catalyst surface.[5] High activity of peroxide species can be responsible for removal of hydrogen atom from DME giving $MeOCH_2^\bullet$ radicals.

As for catalysts containing In_2O_3, La_2O_3 oxides, the partial oxidation can occur with participation of the lattice oxygen of these metal oxides. The reaction pathway can be similar to the redox mechanism which was postulated earlier for oxidative dimerization of methane[7–9] (Scheme 2).

$$MO_x + 2\,Me_2O \rightarrow MO_{x-1} + MeO\text{–}CH_2CH_2\text{–}OMe + H_2O,$$

$$MO_{x-1} + {}^1\!/_2\,O_2 \rightarrow MO_x.$$

Scheme 2

In case of Ga_2O_3-containing catalysts, the partial oxidation of DME is most likely promoted by dissociative adsorption of the reactant on the acid–base pair incorporating the low-coordinated Ga^{3+} cation and the adjacent oxygen atom.[10]

The XRD patterns obtained for the catalyst on the basis of SnO_2 and alkaline-earth metal oxides are very typical of the dispersed phase of SnO_2 with very small peaks related to the phases of alkaline-earth metal oxides. In all patterns obtained for the catalysts on the basis of group III metal oxides, the hallo picture characteristic of amorphous SiO_2 was observed.

The TG-DTA analysis of the catalysts showed the absence of any serious structural or phase changes upon their heating in an inert gas from 20 to 600 °C. This fact corroborates that all oxides in the catalyst composition are essentially stable and do not undergo any chemical or phase transformations.

In conclusion, we have demonstrated that the catalysts based on SnO_2 and the alkaline-earth metal oxides as well as on the silica-supported group III metal oxides promote conversion of DME to DMOE. The specific activity of the supported catalysts is much higher than that of co-precipitated catalysts, with the best activity belonging to 5% In_2O_3, 5% La_2O_3/SiO_2 sample in which In and La, most probably, demonstrate synergism. Selectivity of the DMOE formation was 60–69%. In the process, not only DME but also the reaction product DMOE partially undergo complete oxidation, which decreases both the yield of DMOE and the selectivity.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2017.01.023.

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