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Synthesis of dimethyl carbonate from methanol and CO_2 on the SnO_2/Al_2O_3 -based catalyst

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The SnO₂/Al₂O₃ catalyst promoted with CuCl₂, ZnCl₂, KF exhibited high activity in the synthesis of dimethyl carbonate from methanol and CO₂ (130 °C, 16 bar, 4 h) providing the 17.8% yield of the product with *ca.* 99% selectivity.

 $2\text{MeOH} + \text{CO}_2 \xrightarrow[\text{SnO}_2(\text{Cu},\text{Zn},\text{K})/\text{Al}_2\text{O}_3]{} \text{(MeO)}_2\text{C=O}$ $\begin{array}{c} \text{Yield 17.8\%} \\ \text{Selectivity >98\%} \end{array}$

Carbon dioxide utilization attracts great interest in view of global warming problem and the environmental protection against waste gases of chemical and power industries. Currently there are several strategies for CO_2 utilization.^{1,2} Among them, a promising approach is the direct synthesis of dimethyl carbonate (DMC) from CO_2 and methanol. DMC is widely used as a methylation agent, a solvent and a fuel additive.^{3–6} In principle, the formation of DMC from methanol and CO_2 can be presented by the equation

 $2 \text{MeOH} + \text{CO}_2 \Rightarrow (\text{MeO})_2 \text{CO} + \text{H}_2 \text{O}.$

However, the equilibrium yield of DMC in this reaction as usual does not exceed 1–1.5%. The main cause of that is the unfavorable thermodynamics of the reaction. The Gibbs energy ΔG for this process at 130 °C is 45.5 kJ mol⁻¹ > 0 that shows that the reaction is not spontaneous.⁷ To increase the yield of DMC, the equilibrium of the reaction can be shifted to the right by removal of water formed in the process.⁸

Both homogeneous and heterogeneous catalysts have been applied to this reaction.^{9–14} Early reports offered Bu₂Sn(OAlk)₂ (Alk = Me, Et, Bu) as the catalysts which provided ~100% selectivity to DMC.¹⁵ The key step in the reaction on these catalysts is supposed to be the insertion of CO₂ into the Sn–OR bonds of the corresponding methoxy precursors. Among heterogeneous systems used in carboxylation of methanol it is worth to note the catalysts on the basis of CeO₂,^{10,13,16,17} ZrO₂,^{10,18,19} TiO₂²⁰ or their mixed compositions.^{21,22} Some promotion effect to the DMC formation was achieved by adding 0.2–0.5% reduced copper to the ceria catalyst.²³ To enhance efficiency of the process, the original membrane reactor which combined the catalytic reaction and separation was developed²⁴ when KF-modified Cu catalyst on MgO–SiO₂ support was employed.

Previously²⁵ the synthesis was carried out over the Cu–Ni bimetal catalysts supported on the molecular sieve, which increased the DMC yield. On using the catalyst with bimetal loading of 20 wt% (123 °C, 1.1 MPa, 5 h) the DMC yield was 5%. Noteworthy, the activity for the DMC synthesis was also raised by employing a supported Cu–Ni/graphite bimetallic catalyst,²⁶ the highest yield of DMC exceeding 9% at 105 °C and 1.2 MPa, and the selectivity was ~88%.

The aim of the present work was to develop the heterogeneous catalyst which could exhibit the higher efficiency in the synthesis of

DMC from CO_2 and MeOH. The catalyst required was prepared on the basis of the supported SnO_2/Al_2O_3 system promoted by $CuCl_2$, $ZnCl_2$, KF additives.[†] The catalyst was investigated by diffuse reflectance infrared Fourier-transform (DRIFT), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and thermogravimetry combined with differential thermal analysis (TG-DTA).

When solving the problem of the catalyst composition for the DMC synthesis, we reasoned that the catalyst should generate simultaneously methoxy groups from methanol and carboxylate or carbonate species from CO_2 . Obviously, to meet these requirements, one could include metal oxides of the weak basic or amphoteric nature into the catalyst composition. From this point of view the SnO_2/Al_2O_3 system seemed to be suitable, moreover, it could be easily prepared by the incipient wet impregnation of Al_2O_3 with a solution of $SnCl_4$. To improve basic properties of

Catalyst preparation. The commercial γ -Al₂O₃ (Sasol, Germany, 0.20 mm, 150 m² g⁻¹) was impregnated to incipient wetness with a solution of SnCl₄ and left for 12 h at room temperature. Then the catalyst sample was dried at 100 °C for 2 h and calcined in the dry air flow at 600 °C for 2 h, the heating rate in the range of 20–600 °C was 5 K min⁻¹. The obtained SnO₂/Al₂O₃ sample was sequentially impregnated to incipient wetness with the appropriate solutions of CuCl₂, ZnCl₂ and KF. Between last impregnations the catalyst was dried at 100 °C for 1 h. After supporting of all constituents on the catalyst, the latter was calcined at 400 °C for 2 h. The content of SnO₂, CuCl₂, ZnCl₂, KF in the final catalyst was 14.5, 1.2, 1.2, 6 mol% (or 20, 1.5, 1.5, 3.3 wt%), respectively. Directly before the loading in the reactor the catalyst sample was calcined once more in dry air at 400 °C for 1 h.

[†] The reaction was carried out in the mini 8.5 cm³ autoclave. The catalyst (250 mg, particle size 0.2–0.4 mm) was mixed with crushed quartz (particle size 0.5–1 mm) in the ratio of 1:3 and loaded into the 1.5 cm³ metal gauze basket fixed in the upper part of the autoclave. A layer of calcined B_2O_3 (50 mg, particle size 0.5–1 mm) was placed on the catalyst bed. The function of B_2O_3 was to remove water produced during the reaction. In the middle of the autoclave there was a micro-fan which stirred the gas phase in the reactor with a rate of 500 min⁻¹. Before the run the autoclave was purged with CO₂, then methanol (0.3 ml) was injected by a syringe. The autoclave was closed and filled with CO₂ up to 16 bar (room temperature); the MeOH:CO₂ molar ratio was 1:1.3. The autoclave was heated in the oil bath. The runs were carried out at 130 °C, and the reaction time was varied from 1 to 4 h. The products were analyzed by GLC [Crystal 5000 gas chromatograph (Russia) equipped with FID and the capillary column with SE-30].

Table 1 Results of the DMC synthesis over the $SnO_2(Cu,Z,K)/Al_2O_3$ catalyst.

Time/h	DMC		
	Yield (%)	Selectivity (%)	_
1	3.2	99.1	_
2	12.7	98.6	
4	17.8	98.3	

the catalyst responsible for generating surface carbonate compounds, we modified it with small amounts of $CuCl_2$, $ZnCl_2$ and KF which could serve as the additional promoters for the CO₂ activation. Therefore, the prepared catalyst contained SnO_2 , $CuCl_2$, $ZnCl_2$, KF (14.5, 1.2, 1.2, and 6 mol%, respectively) in the final $SnO_2(Zn,Cu,K)/Al_2O_3$ sample. Table 1 shows the main results obtained in the runs on the DMC synthesis from methanol and CO_2 with such a catalyst. Obviously, this catalyst exhibits rather high activity in the DMC formation, the yield of DMC approaches 18%, with selectivity of 98–99%.

The great assistance in disclosure of the DMC synthesis mechanism on the developed catalyst has been provided by the DRIFT method, mainly due to the identification of the surface compounds formed on the catalyst in the course of adsorption of methanol and CO₂. In our first experiment, carbon dioxide at 1 bar and ~20 °C was adsorbed on the catalyst sample placed in the IR ampoule, after some time the ampoule with the catalyst was evacuated and then filled with the methanol vapor, that is adsorption of methanol was performed on the catalyst with preadsorbed CO₂. The DRIFT spectra obtained in this experiment are shown in Figure 1. One can see that adsorption of CO₂ on the catalyst leads to appearance of a series of intense bands at 1490, 1644, 1772 cm⁻¹ as well few bands of lower intensity, which can be attributed to the stretching vibrations of the chemosorbed carbon dioxide and different types of carbonate structures.^{27–30}

According to the classification,^{27,31} the band at 1772 cm⁻¹ can be attributed to the stretching vibration v_{as} C=O which is typical of the organic carbonate (O–CO₂). The bands v_{as} 1644 and v_s 1490 cm⁻¹ evidently correspond to the stretching vibrations $v_{C=O}$ in the bidentate and monodentate carbonates, respectively. Smaller in the intensity bands at 1668 and 1695 cm⁻¹ can be attributed to bicarbonate (HOCO₂). The spectrum also contains an intense band at 2348 cm⁻¹ which can be ascribed to the stretching vibrations of C–O bonds of chemisorbed CO₂.

Introduction of methanol into the ampoule containing the catalyst with preadsorbed CO_2 leads to remarkable changes in the DRIFT spectra. First of all, appearance of two pairs of the bands in the region of CH vibrations occurs, which correspond to the asymmetric and symmetric stretching vibrations of C–H



Figure 1 DRIFT spectra of adsorbed CO₂ and MeOH on the sample $SnO_2(Cu, Zn, K)/Al_2O_3$: (1) after introduction of CO₂ at 1 bar and 20°C; (2) 10 min after short evacuation of the sample and introduction of MeOH at saturated vapor pressure at 20°C; (3) after 17 h; (4) after evacuation of the sample at 400°C for 1 h.

bonds in two forms of the methanol adsorption complexes. The bands at 2954, 2830 cm⁻¹ are related to the CH vibrations in the Me groups of adsorbed methanol, while the bands at 2904, 2778 cm⁻¹ can be attributed to the CH vibrations of methoxy groups, which may appear when methanol adsorbs on the cationic sites of the catalyst.²⁷

Some changes are observed in the region of the C–O vibrations, in particular, a decrease in the intensity of the band at 1772 cm^{-1} which corresponds to the stretching vibration v_{as} C=O in the covalently bound carbonate (O–CO₂). Probably when methanol is adsorbed on the catalyst the quantity of sites containing OH groups of basic nature, which interact with adsorbed CO₂, can increase.

In the Me region there are two types of vibration: the bands at 2778 and 2904 cm⁻¹ are associated with the symmetric and asymmetric modes of Me groups of chemisorbed methoxy groups; the bands at 2954 and 2830 cm⁻¹ are attributed to symmetric and asymmetric Me stretching modes of physisorbed methanol.

A sharp decrease and then almost disappearance of the band at 2348 cm⁻¹ indicate that next to nothing of chemisorbed CO₂ remains. It can be supposed that CO₂ previously adsorbed on the catalyst either takes part in any chemical transformations, or converts to another adsorption form. Moreover, one can note a small band at 1533 cm⁻¹ which can attributed to the carbonate anions $CO_3^{2-,27}$ After 17 h exposure of the catalyst under the methanol vapor, a band at 1373 cm⁻¹ appears, which can be ascribed to the stretching vibrations v_s of carboxylate anion COO^{-,27}

It is known that chemisorption of alcohols occurring on the catalyst comprising transition metal oxides may cause formation of the corresponding alkoxides from alcohols under the action of coordinatively unsaturated cations or the oxygen anions.²⁷ Two possible mechanisms for the formation of methoxy groups during adsorption of methanol on SnO₂ are proposed: (1) through the formation of ester; (2) due to the dissociation of methanol on the ion pairs.³² It has been shown that methanol being adsorbed at ambient temperature on Al₂O₃ did not dissociate on the oxide surface but formed a strong hydrogen bond with the cation–anion pair, which had strong basic character.³³

In another experiment, methanol was first adsorbed on the catalyst, and then CO₂ was introduced into the ampoule. Figure 2 shows that introduction of CO₂ leads to remarkable changes in the DRIFT spectra, especially in the region of $1800-1300 \text{ cm}^{-1}$. First of all, the high intensity band at 1670 cm⁻¹ appears, which can be attributed to the stretching vibrations of the C=O bonds in the acid carbonate $HOCO_2$, while a small shoulder at 1630 cm⁻¹ can belong to stretching vibrations of C=O (COO⁻) in the bidentate carbonate.²⁷ The bands of small intensity at 1469 and 1371 cm⁻¹ are likely related with the stretching vibrations of the C=O bond in monodentate carboxylate COO-, although they also can be attributed to monodentate methyl carbonate.³⁴ Note that after evacuation of the catalyst, the DRIFT spectrum contained the band at 1606 cm⁻¹, which can characterize the stretching vibrations in the bidentate carbonate bonded with the on-top metal cations.

We also studied the joint adsorption of CO_2 and MeOH on the catalyst at room temperature. Adsorption of the MeOH/ CO_2 mixture results in appearance of bands at 4837, 5140 cm⁻¹, which can be ascribed to the vibrations of the methyl groups of adsorbed methanol and the composite vibrations of water, respectively. The latter can be regarded as an evidence of methanol carboxylation which really occurs on the catalyst, with water being formed as a secondary product of this reaction.

To get the information on elemental composition, chemical and electronic state of the elements of the $SnO_2(Cu,Zn,K)/Al_2O_3$ catalyst, we investigated it by XPS method (see Online Supplementary Materials). According to the obtained XPS data, the active



Figure 2 DRIFT spectra of adsorbed MeOH and CO₂ on the sample of $SnO_2(Cu,Zn,K)/Al_2O_3$: (1) 17 h after introduction of MeOH at saturated vapor pressure at 20 °C; (2) 10 min after introduction of CO₂ at 1 bar and 20 °C; (3) after 75 h; (4) after evacuation of the sample at 400 °C for 2 h.

surface of the catalyst sample was little enriched with Sn compared with the calculated concentration of Sn in the catalyst, the atomic Sn/Al ratio in the surface and subsurface layers of a thickness of ~30 Å is 0.134 *vs*. 0.100. The atomic Cl/Al ratio in the catalyst is close to the content of Cl in ZnCl₂ and CuCl₂. The XPS data point out that copper exists in two electronic states, Cu²⁺ and Cu⁺, on the catalyst surface.

The X-ray diffraction data for the $SnO_2(Cu,Zn,K)/Al_2O_3$ catalyst obtained show that the XRD pattern contains only two peaks at 45 and 66°, which are attributed to alumina. No other peaks were detected, including peaks from SnO_2 . This points out to amorphous state of the supported SnO_2 .

The thermogravimetry analysis of the SnO₂(Cu,Zn,K)/Al₂O₃ catalyst has revealed that during its heating in the inert gas from 20 to 600 °C any remarkable structural or phase changes in the catalyst do not occur. This proves that all oxides and salts comprised in the catalyst are quite stable and have the constant composition.

The data obtained allow us to suggest the mechanism for the DMC synthesis from methanol and CO_2 on the catalyst prepared in the work (Figure 3).

In our opinion, the reaction proceeds through two alternative paths, that depends on what substance, methanol or CO_2 , is adsorbed on the catalyst at first. If it is methanol, the reaction starts from the formation of methoxy groups bonded with the metal cations (path a). Alternatively, if CO_2 is the first to chemosorb, one can expect the generation of the carbonyl or carboxyl compounds (path b). The further stages of the reaction may consist of the interaction of the surface compounds with the second reactant, MeOH or CO_2 , coming from the gas phase. Note that for both pathways the key intermediate is considered to be



Figure 3 Postulated mechanism for the DMC formation from methanol and CO_2 .

the hemicarbonate bonded with the coordinatively unsaturated metal cation. The final stage of the reaction, obviously, is the interaction of the hemicarbonate with the second methanol molecule that should afford the target product, DMC.

In conclusion, we prepared a new catalyst on the basis of the supported SnO_2/Al_2O_3 system promoted with $CuCl_2$, $ZnCl_2$, KF, which showed the high efficiency in the direct synthesis of DMC from methanol and CO_2 .

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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.2016.11.012.

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