

The synthesis of dimethyl carbonate over different carbon supported catalysts

Thesis of the Ph.D. dissertation

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Szeged

2015

Preliminary and objectives

Green chemistry focuses on the research and production of environmentally friendly materials by sustainable methods on laboratory and industrial scale. Many efforts have been taken to eliminate or decrease the amount of environmentally hazardous substances, and catalytic research is at the forefront of realizing these ambitious purposes.

The production of dimethyl carbonate (DMC), a non-toxic compound that exhibits versatile and tuneable chemical reactivity, depends on the reaction conditions. DMC can be used as a fuel additive; synthesis reagent; a phosgene substituent and as a solvent. The processes for DMC utilization are highly selective allowing the minimization of both waste and unwanted by-products.

Dimethyl carbonate has been produced from phosgene traditionally, later on by using chloride-containing catalysts in different synthesis methods. Due to the hazardous nature of phosgene, it should be avoided nowadays. The use of chlorine derivatives as catalysts results in the undesirable formation of hydrochloric acid. Therefore, the use of these methods does not satisfy the expectations of green chemistry.

Today, activated carbon supported catalysts are frequently used because of the associated low production and purchasing costs. The high specific surface area and the good electrical properties are advantageous for catalytic reactions. The synthesis of DMC is highly effective on carbon supported catalysts but the methods found in the literature still not meet the environmental criteria as chloride containing catalysts are still used.

The aim of my dissertation was to develop an environmentally friendly catalytic synthesis for dimethyl carbonate using low-environmental impact reagents and to minimize subsequent harmful by-products. From the synthesis pathways, the oxidative carbonylation of methanol reaction was studied in detail. The reaction was carried out in a continuous flow system, in a fixed bed reactor, at atmospheric pressure. The complexity of the reaction systems required that several series of parallel experiments had to be performed, such as the characterization of the catalysts and the study of the resulting surface forms.

Experimental

The active carbon supported Cu, Cu–Ni and Ni catalysts were prepared via conventional incipient wetness impregnation technique. The Norit (active carbon) and the MWCNT (multi walled carbon nanotube) supports were impregnated with calculated amount of $\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$ or/ and $\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ solution. In the bimetallic sample the Cu/Ni atomic ratio was 2 and the metal content was 10 wt%. The samples were reduced in situ typically at 873 K in hydrogen flow for 1 h.

The catalytic reactions were carried out in a continuous flow system in a fixed bed quartz reactor at atmospheric pressure. After the reduction, the system was cooled down to given reaction temperatures in He flow.

In the case of DMC synthesis usually 1 g catalyst was pre-treated. The reaction temperature was 393 K. Methanol was introduced into the system by bubbling the mixture of CO and O_2 through it. The ratio of the reactants ($\text{CH}_3\text{OH}/\text{CO}/\text{O}_2$ ratio was 2/1/1) was the same in all experiments. The flow rate was usually 16 ml/min.

For the DMC decomposition usually 0.3 g of catalyst was pre-treated. DMC was introduced to the reactor by bubbling He through it at room temperature ($\text{DMC}/\text{He} = 1/4$). The flow rate was 16 ml/min. In the temperature programmed reactions the system was cooled down to room temperature in He flow, then heated to 873 K in the reaction mixture with 5 K/min heating rate. In isotherm experiments the reaction temperature was set to 473 K. The products were analyzed on-line by gas chromatograph equipped with a mass spectrometer detector.

In order to follow the changes of the surface composition and those of the oxidation states of the catalysts components XPS measurements were performed during the catalytic reaction. Sample treatments were carried out in a high pressure cell directly attached to the analysing chamber which was isolated from that with a gate valve. It was possible to transfer the samples from the analysis chamber into the high pressure cell without the reach of air. After the pre-treatment and the reaction steps XP spectra were taken with a SPECS instrument equipped with a PHOIBOS 150 MCD 9 hemispherical energy analyser.

Infrared spectra were recorded during the catalytic reactions to analyse the surface species with a FTIR spectrometer equipped with diffuse reflectance attachment. During the measurements the kinetic parameters of the catalytic experiments were used

The interaction of DMC and the catalysts was studied by temperature programmed desorption (TPD). DMC was adsorbed on the catalyst at 323 K and then it was heated to 900 K in He flow with the rate of 20 K/min. The desorbed products were analysed by mass spectrometer.

For the characterisation of the catalysts acid-base properties NH_3 and CO_2 TPD profiles were registered. The NH_3 or CO_2 flow was passed through the reduced sample at 373 K, after it was purged with He. Finally, the system was heated to 873 K in He flow and the desorbed products were analysed by thermal conductivity detector (BELCAT A).

Novel scientific results

T 1.

During the oxidative carbonylation of methanol the carbon supported copper catalysts showed remarkable catalytic properties. The DMC yield at atmospheric pressure on Cu/MWCNT in the nearly steady state was 0.99%. The highest DMC yield was obtained on Cu/Norit, it was 13.2%. Both results are higher than the data reported in the literature at high pressure. Unlike the published data, the activity of carbon-supported Cu-Ni catalysts was much lower than the results obtained on Cu/Norit. In these cases Cu-Ni alloy was formed, which could be responsible for the inferior activity of these catalysts.

T 2.

On Cu/MWCNT the DMC and the MF (methyl formate) production increased, however, the amount of CO₂ decreased in the first part of the reaction. According to the XPS results registered during this time the surface Cu was oxidized, Cu⁺ and Cu²⁺ were formed. From these observations, it can be concluded that the formation of DMC and MF was catalysed by the oxidized Cu while the CO₂ production was stronger on the metallic copper.

T 3.

On Cu/Norit during the DMC synthesis CO₂ formation rate increased steadily, the curves of MF and DMC formation rates had a maximum as a function of temperature. We have found that the optimum reaction temperature is 393 K for DMC synthesis. In the experiments on Cu/Norit the formation rate of CO₂ and DMC increased linearly as a function of contact time, while the MF formation rate curve went through a maximum in the oxidative carbonylation of methanol.

T 4.

Considering the activation energies obtained in the isothermal decomposition of DMC on Cu/MWCNT and Cu/Norit samples, the calculated DMC conversions (for the reaction temperature used in the methanol oxidative carbonylation) showed that the rate of decomposition is not significant during the synthesis.

T 5.

The number of acidic sites was more and the BET surface area was greater in the case of Norit support, but Cu/MWCNT was more active during the decomposition of DMC. The

conversion was higher on the reoxidized sample than on the reduced catalyst and on Cu/Norit the product distribution also changed. On the reduced sample mainly DME, on the reoxidized sample methanol was the main product. On the reduced sample DMC decarbonylation occurs while on the reoxidized sample the hydrolysis of it.

T 6.

According to the temperature programmed decomposition of DMC (registered on Cu/MWCNT and Cu/Norit) on the reduced samples only a few acidic sites were found. During the decomposition of DMC their amount increased significantly regardless of the DMC decomposition, whether it was constant or decreasing in time. The acidic character of the support is not the determining factor in the case of Cu/MWCNT and Cu/Norit catalysts.

T 7.

The results of XPS measurements on active carbon supported Cu catalysts showed that Cu was oxidized during the DMC synthesis. In the first minutes of the reaction only metallic surface Cu was detected, then Cu^+ was formed. In these cases no DMC formation was observed. The amount of Cu^+ , later the amount of Cu^{2+} increased with time. Eventually, when the amount of Cu^{2+} started to increase, the DMC formation began and the rate of it also increased in time. The fully oxidized sample was completely inactive in the DMC synthesis. From these results it can be concluded that both Cu^+ and Cu^{2+} are required for DMC synthesis.

T 8.

On Cu/Norit the DMC formation started after an extended induction period. The different pre-treatment of the catalysts had diverse impact on the DMC synthesis in case of Cu/Norit. Reduction at lower temperature resulted in the extension of the induction period for the DMC formation and DMC selectivity was also less at the initial state. When, the catalyst was oxidized after the pre-treatment, prior to the reaction, the period of DMC formation induction slightly decreased. XP spectra registered during the induction period showed changes in the ratio of the surface Cu^+ and Cu^{2+} . From these results, we can conclude that in the DMC synthesis not only the formation of the appropriate oxidation state of Cu was the determining factor but also the amount and ratio of the surface Cu^+ and Cu^{2+} as well.

T 9.

In the case of the pure supports the XP spectra revealed that no significant change was measurable on the surface, although the O 1s spectra showed a change in the oxygen content of the catalyst.

T 10.

Infrared measurements proved that methoxy groups were formed only on oxidized copper surface. Accordingly, the first step of the reaction was the oxidation of copper, followed by the formation of the methoxy groups.

In addition, CO absorption was more favourable on Cu^+ than on Cu^{2+} .

The activation of methanol took place on Cu^+ .

Practical application of results

Dimethyl carbonate can be used in organic synthesis as reagent, as phosgene substituent in aromatic polycarbonate preparation or it can be used instead of a ketone as a solvent. To use as a high oxygen containing additive in gasoline and diesel is promising for reducing the emissions. Because of the high oxygen content it can be used as an octane improver additive. Due to the increasing demands of the use of DMC, the development of production techniques is important. Developing an economical and environmentally friendly technology is beneficial for the industry and the society for which my thesis can serve as a good basis.

Publications

Publications related to the Thesis

1. **G. Merza**, B. László, A. Oszkó, G. Pótári, K. Baán, A. Erdőhelyi
The direct synthesis of dimethyl carbonate by the oxycarbonylation of methanol over Cu supported on carbon nanotube
J. Mol. Catal.: A Chem. 393 (2014) 117-124. IF: 3.651
2. **G. Merza**, B. László, A. Oszkó, G. Pótári, E. Varga, A. Erdőhelyi
The Synthesis of Dimethyl Carbonate by the Oxycarbonylation of Methanol over Cu Supported on Carbon Norit
Catal. Lett. 145 (2015) 881-892. IF: 2.307
3. **G. Merza**, B. László, A. Oszkó, K. Baán, A. Erdőhelyi
The decomposition of dimethyl carbonate over carbon supported Cu catalysts
React. Kinet. Mech. Cat. (In press) IF: 1.170

Cumulative Impact factor: 7.128

Lectures and poster presentations

1. G. Merza, B. László, A. Oszkó, A. Erdőhelyi
The decomposition and production of dimethyl carbonate on different carbon supported Cu, Ni and Cu-Ni catalysts (poster)
12th Pannonian Symposium on Catalysis, Trest, Czech Republic, 2014.
2. G. Merza, B. László, A. Oszkó, A. Erdőhelyi
The synthesis and decomposition of dimethyl carbonate on different carbon supported Cu catalysts (presentation)
International Conference on Green Chemistry and Sustainable Engineering, Barcelona, Spain, 2014.
3. G. Merza, B. László, A. Oszkó, K. Baán, A. Erdőhelyi
Dimethyl carbonate synthesis on different carbon supported Cu catalysts (presentation)
Spring wind 2013 Conference, Sopron, Hungary, 2013.

4. G. Merza, B. László, A. Oszkó, G. Pótári, A. Erdőhelyi
The synthesis of dimethyl carbonate by oxidative carbonylation of methanol on different supported Cu catalysts (presentation and poster)
XIth European Congress on Catalysis, Lyon, France, 2013.
5. G. Merza, B. László, A. Oszkó, G. Pótári, A. Erdőhelyi
Dimethyl carbonate synthesis on different carbon supported catalysts (presentation)
Carbocat – V (ICC 2012 pre-Conference), Brixen, Italy, 2012.
6. G. Merza, G. Pótári, K. Baán, B. László, A. Erdőhelyi
Dimethyl carbonate synthesis – oxidative carbonylation of methanol (presentation)
Cross Border Cooperation Programme 2007-2013, Catalysts for Bio-Ethanol and Bio-Methane Conversion Conference, Szeged, Hungary, 2012.
7. J. Kiss, P. Pusztai, L. Óvári, K. Baán, **G. Merza**, A. Erdőhelyi, A. Kukovecz, Z. Kónya
Decoration of Titanate Nanowires and Nanotubes by Gold Nanoparticles: XPS, LEIS, HRTEM and XRD Characterization (presentation)
ACSIN-12 Conference, Tsukuba, Japan, 2013.

Other publications:

1. J. Kiss, P. Pusztai, L. Óvári, K. Baán, **G. Merza**, A. Erdőhelyi, A. Kukovecz, Z. Kónya
Decoration of Titanate Nanowires and Nanotubes by Gold Nanoparticles: XPS, HRTEM and XRD Characterization
e-J. Surf. Sci. Nanotech. 12 (2014) 252-258. IF: -