# КАТАЛИЗ В ПРОМЫШЛЕННОСТИ

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CATALYSIS IN INDUSTRY


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# СОДЕРЖАНИЕ

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A template-free sol-gel technique was developed for synthesis of micro-mesoporous and mesoporous titanosilicates using commercially available raw materials such as mixture of oligomer esters of orthosilicic acid (ethylsilicate-40) and an aqueous-alcoholic solution of tetraethoxysilane. The influence of pH of the reaction mixture on the characteristics of the porous structure of titanosilicates prepared by the sol-gel technique was investigated. pH was varied between 3 and 10 to prepare samples of the amorphous structure with different textural parameters: specific surface area 320–740 $m^2/g$, micropore volume 0,04–0,15 $cm^3/g$, mesopore volume 0–0,92 $cm^3/g$. The mesoporous titanosilicate prepared at variable pH showed the maximal catalytic activity to oxidation of 4-*tert*-butylphenol (TBF) with aqueous hydrogen peroxide solutions (the conversion of 4-*tert*-butylphenol was 45 wt.%, selectivity for 4-*tert*-butylpyrocatechol 66 wt.%; conditions: 10 wt.% titanosilicate, $TBF/H_2O_2 = 1/2$, 75 °C, 1 h).

**Keywords:** sol-gel synthesis, titanosilicates, ethylsilicate-40, oxidation, hydrogen peroxide, 4-*tert*-butylphenol, 4-*tert*-butylpyrocatechol.



Analytic consideration was focused on the efficiency of methods for the introduction of multilayer carbon nanotubes (MCNT) to polymer composites based on polyethylene (PE) and ultrahigh molecular weight polyethylene (UHMWPE). The methods under consideration were: (1) mechanical mixing of MCNT and a polymer melt; (2) ethylene polymerization over a disperse titanium-magnesium catalyst (TMC) in the presence of MCNT; (3) ethylene polymerization over a $TiCl_4$ catalyst which was pre-anchored on the MCNT surface. MCNT/PE and MCNT/UHMWPE composites with different MCNT contents (3,5 to 19 wt.%) were prepared at varying the polymerization conditions, and their properties (uniformity of MCNT distribution through the polymer, molecular-mass characteristics, viscosity, fluidity, electrical conductivity) were characterized. The most uniform distribution was shown to achieve when ethylene is polymerized over the catalyst anchored directly to the nanotube surface (method 3). Method 1 is only of limited use in preparation of MCNT/UHMWPE because of the high viscosity of UHMWPE. Practically identical molecular weights are characteristic of polymers are obtained upon ethylene polymerization over the TMC catalysts and over catalysts anchored on MCNT. The proper choice of the catalytic system and polymerization conditions makes it possible to synthesize MCNT/PE composites with the required polymer properties.

**Keywords:** carbon nanotubes, polyethylene, UHMWPE, composites, concentrates.

## CATALYSIS IN CHEMICAL AND PETROCHEMICAL INDUSTRY



Methanation of carbon supports in a hydrogen-containing medium results in degradation of the support and sintering of the active component of ruthenium catalysts for ammonia synthesis. In the review, key publications on approaches to inhibiting methanation are analyzed. It is demonstrated that the solution algorithm is, in general, determined. This is graphitization of the carbon supports at high temperatures (up to 2000 °C) and addition of promoter such as alkali (Cs, K) and alkali-earth (Ba) oxides to modify the ruthenium electron state and to prevent the carbon surface from interaction with active hydrogen. The most effective catalyst that does not suffer from methanation at temperature up to 700 °C and hydrogen pressure of 100 atm is identified. The analysis can be useful to choose and prepare Me/C catalysts, where Me is a 8 group metal.

**Keywords:** carbon supports, ruthenium catalysts, ammonia synthesis, methanation.

## CATALYSIS IN PETROLEUM REFINING INDUSTRY



The technologies of heterogeneous oligomerization of light alkenes $C_2$–$C_4$, both currently used in industry and potentially applicable for production of motor fuel components are considered. Main types of systems used as heterogeneous catalysts for the said processes are discussed, among which are «solid phosphoric acid», amorphous aluminosilicates, zeolites, ion exchange resins, anion modified metal oxides, as well as nickel-containing catalysts. Particular attention is paid to dimerization of isobutylene to produce isooctene to be hydrogenated to isooctane.

**Keywords:** oligomerization, ethylene, propylene, butenes, isobutene, acid catalysts, motor fuels.



The process of steam cracking of heavy oil (HO) was studied under static conditions at 425 °C in the presence of a nanodisperse Ni-containing catalyst (0,3–2,0 wt.% of Ni). This catalyst was established to promote upgrading of the semi synthetic oil produced from HO: the H : O ratio increases (against noncatalytic steam cracking) but the sulfur content and viscosity decreases. An increase in the catalyst loading results only in a minor increase in the H : O ration, while the yield of the liquid products decreases from 81 to 76 % at an increase in the yield of coke and gas products (from 8 to 13 and from 2 to 4 wt.%, respectively). X-ray phase analysis and transmission electron spectroscopic techniques were used for characterization of the catalyst-containing coke residue. The formation of $Ni_9S_8$ nanoparticles (15–40 nm in size) from the catalyst precursor ($Ni(NO_3)_2 \cdot 6H_2O$) under the process conditions was shown. To improve efficiency of the upgrading process needs further choice and studies of catalytic systems for cracking of heavy oil feedstock in the presence of overheated steam and optimization of the process conditions.

**Keywords:** heavy oil, catalytic steam cracking, nanodisperse catalyst, nickel, heavy oil upgrading.

## ENGINEERING PROBLEMS



The studies were focused on the influence of various factors on the stability of catalysts for oxidative chlorination of methane due to evolution of the active catalyst components (copper chlorides). The volatility of copper chlorides was shown to depend mainly on the catalyst composition and temperature. When the average temperature in the reactor was 350 °C, 0,45 % and 0,72 % of copper chlorides escaped, respectively, the catalyst containing copper and nickel oxides and the catalyst containing lanthanum chloride as the activating impurity after 5 hours. Another way to improve the catalyst stability, apart from diminishing the copper chloride volatility, is to feed hydrogen chloride bearing copper chloride solutes isolated from the outlet reaction gas in order to abstract the reaction heat and to feed back the unreacted hydrogen chloride.

**Keywords:** oxidative chlorination, methane, catalyst deactivation, copper chloride, catalysis.

## DOMESTIC CATALYSTS



The influence of the promotion of Fischer – Tropsch Co-Al catalysts with ruthenium on the temperature of the reductive catalyst activation and on the catalytic behavior in the Fischer – Tropsch synthesis was studied. The ruthenium addition in proportion of 0,2 % to 1 wt.% was shown

to reduce the temperature of the reductive activation from 500 down to 330–350 °C at the preserved high catalytic activity and selectivity to $C_{5+}$ products of the Fisher – Tropsch synthesis. The ruthenium promoted Co-Al catalysts were more selective to high-molecular hydrocarbons, their experimental parameter $\alpha_{ASF}$ of the paraffin series distribution was 0,93–0,94; hence the estimated selectivity to synthetic waxes $C_{20+}$ was 48 wt.% including 23 wt.% selectivity to ceresins $C_{35+}$. The ruthenium promoted catalysts also were more selective to olefins.

**Keywords:** cobalt-containing catalysts, promoting, ruthenium, reductive activation, Fischer – Tropsch synthesis.



The influence of an aqueous solution of activated methyldiethanol amine (MDEA, an absorbent of carbon dioxide) on the physicochemical and physicomechanical characteristics of catalysts for hydrogenation of carbon oxides (methanation) – nickel-aluminium catalyst NIAP-07-01 (NKM-1) and cement-containing catalyst NIAP-07-07 (NMK-7). It was shown that phase compositions of the catalysts do not change under the action of MDEA. The NIAP-07-07 (NMK-7) catalyst but not NIAP-07-01 (NKM-1) preserves its mechanical strength. The both catalysts were established to restore their catalytic properties after washing with hot condensate or after blowing through with moist saturated steam. The cement-containing nickel catalyst NIAP-07-07 (NMK-7) in the form of pellets, rings or extrudates is recommended for lengthening the service cycle of the methanator.

**Keywords:** nickel catalyst, calcium aluminate, methanation, solution, methyldiethanol amine, hydrogenation, carbon oxides, catalytic activity, mechanical strength.

## CATALYTIC ACTIVE CENTERS IN RUSSIA



The experience on commercial production of low pressure polyethylene to produce polymer pipes and connecting elements for gas distribution network and cold water supply in PJSC «Kazanorgsintez» is provided. Depending on pipes material requirements increase development and expansion of catalyst base for production and technology is demonstrated.

**Keywords:** low pressure polyethylene, pipes, catalyst, minimum required strength criteria (MRS), bi-centered catalyst, molecular-mass distribution.

## CHRONICLE