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Influence of the Nature of the Carrier on the Catalytic Activity of the Catalyst in the Gas-Phase Synthesis of Vinyl Acetate

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Abstract: The article examines the steam phase activity of the synthesis of ethylene vinyl acetate catalyst consisting of palladium, copper and potassium acetates of high silicon zeolite (HSZ), expanded clay and bentonite separated from bentonite and γ-Al2O3, the porosity of the structure, methods and techniques of preparation. Vinilacet synthesis is carried out in a pilot device using a catalyst containing 0,4%Pd+4%Cu+7%CH3COOK/HSZ a temperature of 165 ˚C (438,15 K), a pressure of 0.1 MPa(14,5 Psig), volumetric velocity of the vapor-gas mixture is 200 and the amount of oxygen in the mixture with ethylene is 7 volume/%. Also the duration is 2000 hours. During this time, the activity of the catalyst is 95-97% selectivity 370-350 grams of vinyl acetate / liter. catalysis. hours.

Keywords: ethylene, acetic acid, acetoxylat, vinilacetate, carrier, selectivity.

INTRODUCTION

Vinilacetate (VA) is one of the most important monomers in the plastics industry and serves as the main raw material for the synthesis of polymers of complex vinyl esters of carbonic acids. Polyvinyl acetate is a complex of polyvinyl alcohol, as well as derivatives of polyvinyl alcohol and polyvinyl alcohol – polyvinylacetals, in particular polyvinylbutyral, polyvinylformal, etc. [1-4].

Acetylene, ethylene, acetaldehyde, methanol and ethylidendiacetate are used as the main raw materials in the production of vinyl acetate. Until 1967, in industry, vinyl acetate was produced only from acetylene and acetic acid by the vapor-phase method. By the mid-1980s, two-thirds of the vinyl acetate produced was derived from ethylene, acetic acid, and oxygen. In recent years, there has been great interest in the processes of obtaining vinyl acetate using methyl acetate and ethylidendiacetate on the basis of methanol, a much cheaper and more common cheap raw material [2-8].

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The synthesis of vinyl acetate is carried out in the gas phase in a stationary layer of a heterogeneous catalyst, the spherical particles of aluminosilicate containing finely dispersed palladium, copper and potassium acetate act as a catalyst. The activity of the catalyst is 270-300 g of vinyl acetate / l cat.h, the selectivity for the formation of vinyl acetate on ethylene is 89-91%. The service life of the catalyst is at least 1 year.

Synthesis of vinyl acetate from ethylene is carried out at a pressure of 0.8 Mpa and a slow rise in temperature from 145 to 200 ° C to maintain the specified activity of the catalyst throughout the year; the volumetric velocity of the gas mixture is 2000 h-1, the proportion of oxygen in relation to ethylene to dry gas is 7.0% by volume, which is limited by the explosive limit of the mixture of ethylene with oxygen. It should be noted that the synthesis of vinyl acetate is carried out by incomplete conversion of the primary reagents — ethylene, acetic acid, and oxygen (~ 8; 18 and 45%, respectively). After appropriate purification, the initial components that did not react are returned to the vinyl acetate synthesis reactor node. Therefore, the problems remain relevant on the basis of research, including palladium and its compounds, aimed at accelerating the process of synthesis of vinyl acetate from ethylene and finding new catalytic systems [6-15].

In addition to the search for more active catalysts based on the optimization of the chemical composition of the catalyst and the methods of its preparation, the study of the nature and effectiveness of the inorganic carrier as an important component of the catalyst is of great interest.

Relatively inexpensive and widely used inorganic materials are activated carbon, pumice, alumina, asbestos, silicon carbide, zeolites, aluminosilicate gel, silica gel [7-21] and other materials resistant to acetic acid as catalyst holders in the synthesis of vinyl acetate. Despite the large selection of materials available, most of the published work, based on experimental data, states that alumina and silica gel-based carriers are preferred [6-13].

This paper examines the effect of g-Al2O3, high-silicon zeolite (HSZ) derived from bentonite, keramzite, the nature of bentonites, their porous structure, methods of preparation and regimes on the activity of the catalyst consisting of palladium, copper and potassium acetate for the vapor phase synthesis of ethylene vinyl acetate.

EXPERIMENTAL PART

The content of Pd and Cu in catalytic compositions is determined by X-ray spectral fluorescent method on the analyzer VR A-30 c Cr-anode X-ray tube. ASAP 2400 Micrometrics at 77 K. Morphological features covered by the method of scanning electron microscopy (SEM) with the help of a microscope JSM 6460LV (JEOL, Japan) and transmission electron microscopy (TEM) on a microscope JEM-2010 (JEOL, Japan). The local elemental composition of the surface of the catalysts is studied by the method of energy-dispersion X-ray analysis with the help of energy-dispersion X-ray spectrometer EDA X (EDA X Co). The activity of catalysts in the reaction of acetoxylation of ethylene was measured in the flow type reactor at a volumetric speed of 1000 h^{-1}.

Weighed portions of polyvinylpyrrolidone and sodium hydroxide were dissolved in ethylene glycol with constant vigorous stirring and heating under reflux. The resulting reaction mixture was heated to 120°C, and aqueous solutions of PdCl2 and CuCl2 were slowly added dropwise. The resulting solution was kept at 120°C for 60 min and cooled to room temperature. The resulting colloid containing palladium nanoparticles stabilized with polyvinylpyrrolidone was precipitated with acetone with stirring, followed by redispersion of the precipitate formed in ethanol. Catalysts supported with palladium nanoparticles on a high silica (HSC) carrier were prepared as follows.

The required volume of a colloidal solution was added to the high-silica supports preliminarily dried at 200°C, based on the content of 0.4% Pd and 4% Cu in the finished catalyst, and dried, stirring occasionally, at 75–80°C, preventing the solution from boiling, s further drying at 160°C for 4 h. The deposition of palladium and copper nanoparticles on HZS was carried out as follows. The support was preliminarily crushed, a fraction of 0.25–0.5 mm was taken, and calcined at 650°C in a muffle furnace. Cooled VCC was mixed with an appropriate amount of palladium colloid to obtain 0.4% Pd + 4% Cu + 7% CH3COOK / HZS and evaporated at 85°C with occasional stirring until the catalyst was completely dry. The resulting mass was dried at 130°C for 4 h. Samples for TEM imaging were prepared by applying a drop of a colloidal solution of nanoparticles in ethanol onto a copper grid coated with a thin carbon film. A sample of 600–800 particles was used to construct particle size distribution diagrams.

Samples of 0.4%Pd+4%Cu+7%CH3COOK/HZS were ground in an agate mortar to a powder and dispersed in ethanol, after which TEM images were obtained in a similar manner. The content and concentration of acid sites were determined by the Boehm method. A weighed sample was kept in a 0.05 N NaOH solution for a day, after which the sample was filtered, and a given volume of hydrochloric acid was added to the filtrate. The resulting sample was titrated potentiometrically with 0.05N sodium hydroxide solution.

According to the TEM data (Figure 1), the original sample (calcined at 630 °C) contains palladium in the form of PdCl2 chloride nanoparticles with a size of 2-4 nm. Thermal aging of the sample at 1000°C leads to significant particle agglomeration. The size of the resulting agglomerates, according to TEM data, is 150–200 nm.

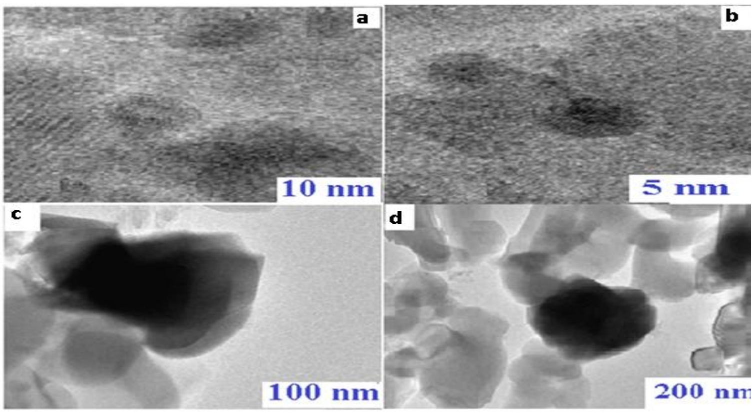
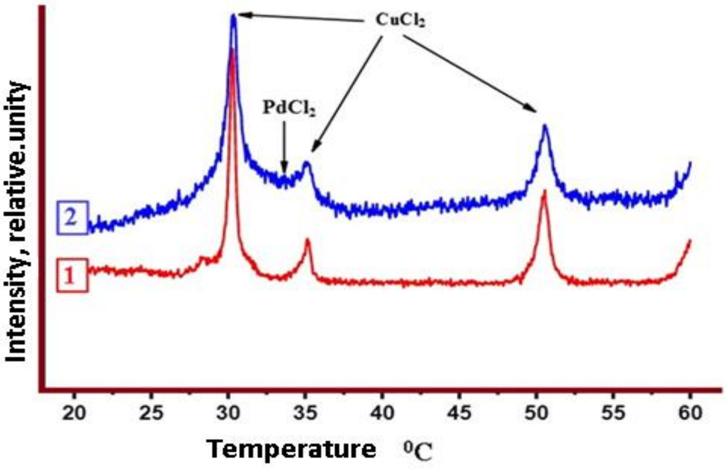


Figure 1. TEM micrographs of the 0.4%Pd+4%Cu+7%CH3COOK/HZS catalyst calcined at 630°C (a, b) and 1000°C (c, d).

Sample containing 0.4% Rd + 4% Cu + 7% CH3COOK /HZS was examined by X-ray phase analysis. Figure 1 shows the diffractograms for this sample as well as for the carrier. It can be seen that the diffractogram for the catalyst also clearly shows the enlarged region in the 33 ° region belonging to the dispersed phase of C l2. It should be noted that no similar changes were observed in the relatively pure carrier diffractograms for other samples with lower metal content.



(1) VKTs (after rolling at 1100 ℃);

(2) 0.4% Rd + 4% Cu + 7% CH3COOK /HZS (after rolling at 110 ℃)

Figure 2. RFA diffractograms of HZS (not processed and rolled at 1100 ° C) and catalyst 0.4% Rd + 4% Cu + 7% CH3COOK / HZS.

The IR spectra of the synthesized samples were recorded using a Nexus Nicolet Fourier transform IR spectrometer (Thermo Scientific) in a reflection mode in the range of 400–4000 sm^{-1}. Thermal studies (TG / DTG-DTA) were performed on a STA-1500 H thermobalance.The specific surface area was determined by low-temperature nitrogen adsorption using a Quantachrome Autosorb -6B instrument. X-ray diffraction analysis (XRD) was studied on a DRON 3 M diffractometer in the 5–80 ° 2th range using a CuKa radiation source (l = 1.54178 ̊A). X-ray photoelectron spectra were recorded on a Kratos SERIES 800XPS photoelectron spectrometer.

Industrial and experimental carriers g-Al2O3, expanded clay, bentonite and HZS were used to prepare catalyst samples. In studying the effect of the nature of carriers on catalytic activity, their initial samples were pre-treated.

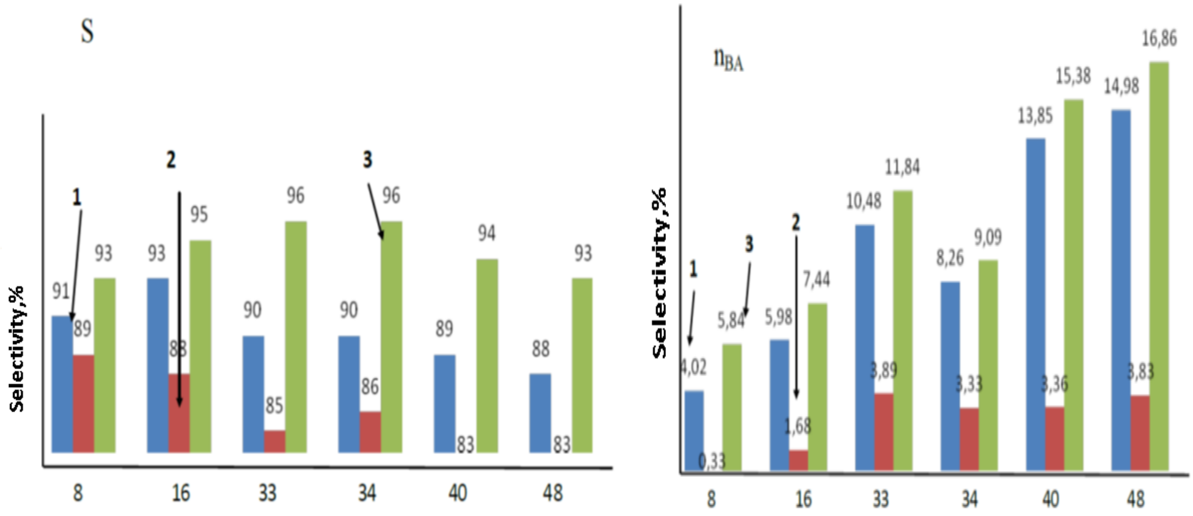
Thus, carriers based on g-Al2O3 (cylindrical particles of height 4–25 mm and diameter 4–6 mm) are heated in air at 1000 ° C, while expanded clay (diameter 5 ± 0.2 mm) is processed at 1050 ° C. ° C. HZS is processed in an autoclave at a temperature of 200 to 300 ° C for a certain period of time at a hydrothermal and equilibrium vapor pressure into carrier samples (spherical, medium porous, 5-6 mm in diameter).

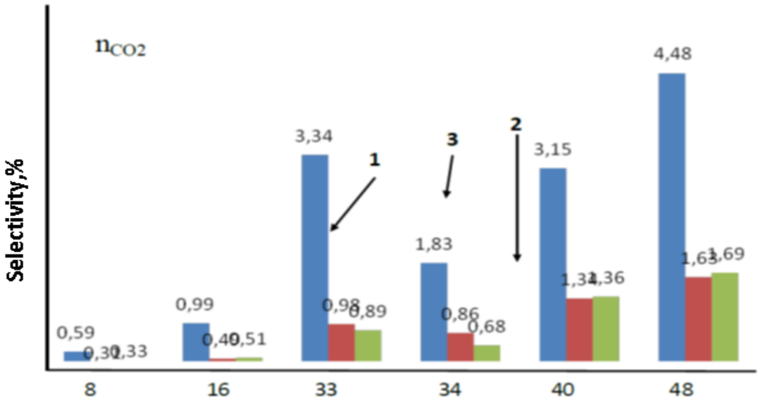
The specific surface area of these carriers was determined by low-temperature argon adsorption on a Crystallux-4000M gas chromatograph. The size and radius of the pores were determined using mercury porometry directly on the amount of mercury compressed in them in a mercury porometric device that allows to measure the size of the pores. The cell density of the holder was determined as the ratio of the total mass of the particles measured in the measuring cylinder to the total mass of the sample.

RESULTS DISCUSSION

In the first stage, a comparison of the efficiency of alumina carriers (g-Al2O3 and expanded clay) and catalysts prepared on the basis of spherical large-porous and medium-porous silica gels (bentonite and expanded clay, respectively) was carried out.

For this purpose, catalysts used in carrier samples 1-6 were prepared: mass content: 0.4% Rd + 4% Cu + 7% CH3COOK / HZSs. Catalysts were tested in the equipment at a temperature of 165 ° C, pressure 0.1 MPa, ethylene: acetic acid ratio 4: 1, the total duration of the process with an 18-hour periodicity of 48 hours analysis. Test results showing changes in the amount of vinyl acetate and CO2 in samples with different carriers over time are shown in Figure 3.





Mass composition of the catalyst: 0.4% Rd + 4% Cu + 7% CH3COOK / HZS

Figure 3. Variation in the selectivity of the product (n) formed over time and the formation of vinyl acetate on ethylene, depending on the type of carrier.

It follows from these data that catalysts in g-Al2O3 carriers are more active than primary and processed silica gels. However, samples in primary g-Al2O3 carriers (g-Al2O3, expanded clay) are significantly less selective than bentonite and HZS. Significant increase in the rate of formation of vinyl acetate and the formation of a by-product-CO2, resulting in a sharp increase in the selectivity of catalysts for vinyl acetate. However, thermal treatment did not improve the stability of the catalysts: in almost all cases, changes in activity over time are nonlinear and indicate a decrease in activity.

Catalysts based on heat-treated bentonite and HZS showed high selectivity at very low activity compared to similar catalysts in heat-treated carriers. The nature of the changes in activity is that the catalysts also have a gradual decrease in activity over time, but are more stable in the catalyst-based HZS carrier.

Therefore, it is important to take into account the time factor when selecting a carrier, i.e. how the catalytic characteristics change over time. The selectivity (S) for the formation of vinyl acetate on ethylene was selected as the solvent characteristic, and its variation during continuous operation of the device was considered for 48 and 300 h.

The numerical values of the time-independent constants and the instability coefficients of the catalyst with respect to the formation of vinyl acetate and SO2 are given in Figure 4.

By varying the temperature and processing time, modified samples of HZS with different porous structures were produced. At the same time, with increasing the duration of hydrothermal treatment at 300 ° C, the specific surface area decreases and the radius of the pores increases.

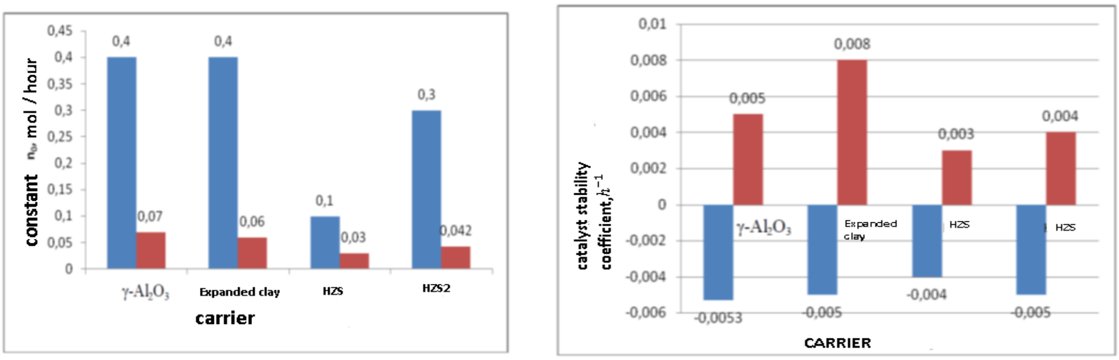


Figure 4. The instability coefficients of the time-independent constant n0 and the catalyst for the formation of vinyl acetate and SO2, depending on the nature of the carrier

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Increasing the duration of hydrothermal treatment allows a uniform distribution of the pores along the radius. From the results obtained, carrier samples for subsequent experiments for the preparation of mixed palladium catalysts were selected on the basis of porous structure and mechanical strength.

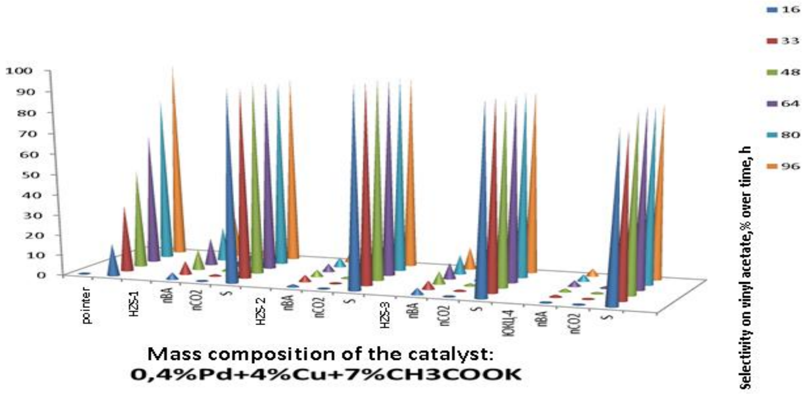

Figure 5. Changes in the selectivity (S,%) of the formation of vinyl acetate on ethylene over time, depending on the appearance of modified HZS and the amount of products formed.

It follows that hydrothermal treatment of carriers has a significant effect on the rate of formation of reaction products. The activity of the catalyst HZS-1 and HZS-2 in hydrothermally treated silica gel samples can be compared with analogs for catalysts in thermally treated carriers. However, the selectivity of the process decreases over time as before, indicating instability in catalyst performance.

The results of a comparative prediction of the performance stability of catalysts in time-modified silica gel carriers are shown in Figure 6.The test results are shown in Figure 5.

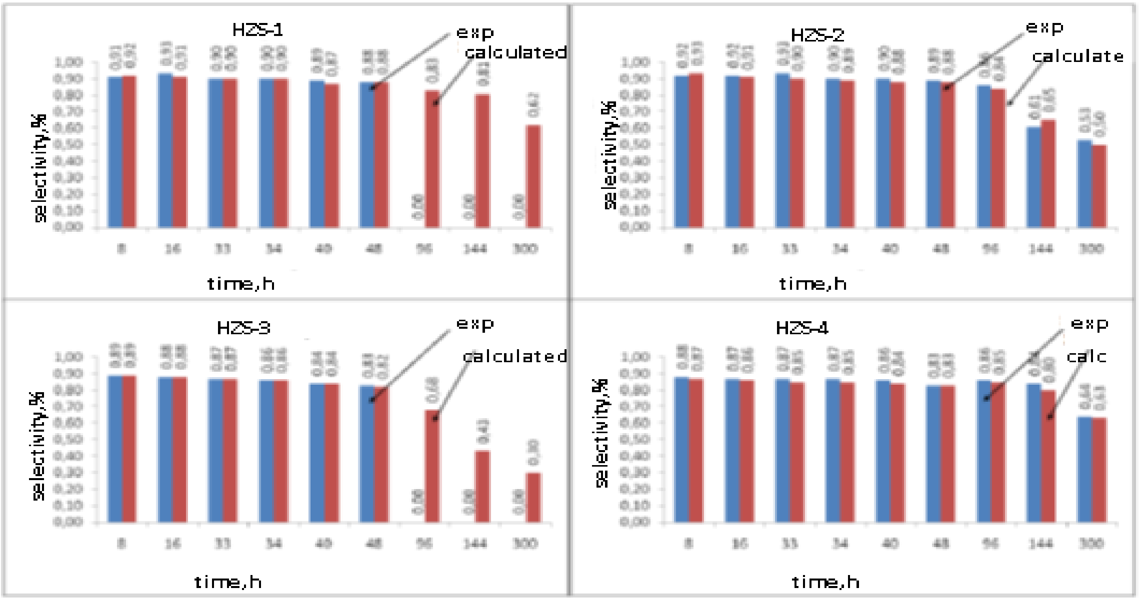

Figure 6. Variation of experimental and calculated values of selectivity for the formation of vinyl acetate on ethylene over time, depending on the nature of the carrier

It follows from the above data that the calculated values of ΔS selectivity changes over time are consistent with the experimental values. From this it can be concluded that the proposed description allows to predict the performance of catalysts of long-term operation of the device even in this case

CONCLUSION

The study of catalysts for the gas-phase synthesis of vinylacetate by oxidative acetylation of ethylene showed that the nature of the carrier and the porous structure have a significant effect on the parameters of the catalytic process of vinylacetate synthesis.

The nature of the change in the amount of vinyl acetate (n0) formed over time indicates a decrease in the activity of the catalysts over time, but the time dependence of n for the catalyst in the HZS-1 carrier is almost linear, indicating stable catalyst performance.

To confirm this conclusion, an experimental test of the stability of 1 dm3 of catalyst performance in the reactor on a HZS-1 carrier containing 0.4% Rd + 4% Cu + 7% CH3COOK / HZS was carried out in a vinyl acetate synthesis pilot plant. The test was carried out by ingestion of potassium acetate with a vapor-gas mixture at a temperature of 165 ℃ for 2000 h, a pressure of 0.1 MPa, a volumetric velocity of 2000 $h^{-1}$and a volume of oxygen with ethylene in the mixture of 7 h.%. During 2000 hours of operation, the catalyst activity is 370-350 g of vinylacetate / l.kat at 95-97% selectivity. hours.

A batch of catalysts with a similar composition of 100 l was then produced under industrial conditions and loaded into 20 (5 l each) tubes of the industrial reactor. The catalyst was operated at a temperature of 145–165 ℃ for about 6 months and, after removal, was tested in a pilot device: its activity was 97–95% selectivity at 380–360 g of vinyl acetate / l. hours, which is 22-27% higher than the values obtained in the industrial catalyst (270-300 g of vinyl acetate / l.kat.hours at 89-91% selectivity of vinyl acetate formation on ethylene).

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