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Supported vanadium oxide-based catalysts for the oxidehydrogenation of propane under cyclic conditions

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Abstract

Heterogeneous catalysts were prepared by deposition of vanadium oxide on different supports, namely alumina, titania, titania–alumina cogel and silica. Catalysts were tested in the reaction of propane oxidehydrogenation to propylene under co-feed and under redox-decoupling conditions (i.e., by alternating the reducing and the re-oxidation steps). Under cyclic conditions, the selectivity to propylene was higher than under co-feed conditions when the catalyst was treated for longer reduction times, but this was due to the fact that in the former case the mechanism was dehydrogenative rather than oxidative. On the contrary, on oxidized catalysts the mechanism was an oxidative one even in the absence of molecular oxygen, and conversions were higher than 20%; however, in this case the improvement in selectivity to propylene with respect to the co-feed operation was low. Catalysts made of vanadium oxide either dispersed inside a high-surface-area silica gel, or supported over silica, allowed higher instantaneous propane conversions than catalysts in which vanadium oxide was deposited over alumina or titania, and also gave the greater improvement of selectivity to propylene with respect to the co-feed conditions. These differences were attributed to the nature of the vanadium species which develop when silica is the support.

Keywords: Propane oxidehydrogenation; Supported vanadium oxide; Propylene synthesis; Redox-decoupling operation; Cyclic conditions

1. Introduction

The oxidative dehydrogenation (ODH) of light paraffins represents one possible alternative to the current industrial productions of olefins via highly energy-intensive, endothermal catalytic dehydrogenation (DH) or steam cracking [1–4]. Of particular interest for possible industrial application is the ODH of propane and of ethane to the corresponding olefins. Several papers have been published in recent years, which examine a variety of catalytic systems for this reaction [1–3]. Many include vanadium oxide, either supported or in combination with other ions to form mixed oxides [5]. In the case of propane ODH, however, the selectivity to propylene, sometimes very high for low hydrocarbon conversion, falls when propane conversion increases [1–3], due to the increased contribution of consecutive combustion reactions. It has been proposed that in selective oxidation one way to limit combustion is to carry out the reaction under cyclic conditions (redox-decoupling operation), in which the two steps of the redox mechanism are carried out separately: (i) during the “reducing step”, the hydrocarbon is put in contact with the oxidized catalyst; the hydrocarbon is transformed to the product and to by-products, and the catalyst progressively reduces along with the half-cycle reduction time; (ii) during the “oxidizing” step, the reduced catalyst is put in contact with air, to restore the original oxidation state [6–8]. Some papers have appeared in literature, in which the performance of V/Mg/O in propane ODH under cyclic operation is investigated [9,10]. In these works, an improvement in selectivity to propylene was reached with respect to the co-feed ODH. In previous papers [11,12], we compared the performance of V/Nb mixed oxides and of V-silica cogels

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Table 1
Main characteristics of samples prepared

Sample, *n*	Support, surface area (m^2/g)	Method of sample preparation	V_2O_5 loading (wt.%)	Surface area (m^2/g)	Temperature (°C), time (h) of calcination
1	SiO_2 gel, amorphous	Co-gelation	6.8	490	500, 5
2	γ-Al_2O_3	Aq. ion-exchange	6.3[a,b]	180	400, 6
3	TiO_2 (anatase)	Aq. ion-exchange	5.1[b]	110	400, 6
4	TiO_2 (anatase) + γ-Al_2O_3	Aq. ion-exchange	5.0[b]	170	400, 6
5	SiO_2 gel, amorphous	Wet impregnation	6.8	270	550, 3

[a] Determined by atomic absorption.
[b] Determined by SEM-EDX.

in propane ODH under cyclic and under co-feed operations. It was found that the mechanism was indeed a combination of propane ODH (the prevailing reaction on the fully oxidized catalyst for short reduction times) and of propane DH (the operating mechanism on the reduced catalyst, for longer reduction times). An improvement of the selectivity to propylene could be achieved under redox-decoupling conditions with respect to co-feed operation, for the same level of propane conversion, by using a V-silica cogel in which vanadia was well dispersed, so to provide isolation of the active sites [11]. In the present work we compare the performance of several vanadium oxide-based catalysts, in which the active phase has been supported over different high-surface-area supports, in order to elucidate the role of the support in determining the catalytic properties.

2. Experimental

Catalysts prepared and characterized are listed in Table 1. The preparation of sample 1 (V-silica cogel), has been described in a previous work [11]. The preparation of supports for samples 2–4: (i) alumina, (ii) titania, and (iii) alumina–titania cogel, was carried out using the sol–gel procedure: the sols were prepared by hydrolysis and condensation of the metallorganic precursors, $[Ti(OC_3H_7)_4]$ and $[Al(OC_4H_9)_3]$; support for sample 4 was obtained by mixing the individually prepared sols of alumina and titania. This procedure made it possible to obtain high-surface supports. Commercial silica spheres (Sud Chemie T4359E1) were used for the preparation of sample 5. Samples 2–4 were prepared by ion-exchange, by submerging the supports in an aqueous solution of $(NH)_4VO_3$ (0.5 g/l) for 24 h at room temperature. The suspension was filtered, and the solid was first washed with water, then dried at 100 °C overnight and finally calcined at 400 °C. Sample 5 was prepared by wet impregnation of silica with an aqueous solution of $(NH)_4VO_3$, followed by calcination at 550 °C. It is worth mentioning that before catalytic tests all samples were treated in flowing air, inside the reactor, at 550 °C for 0.5 h.

Catalytic tests were carried out in a quartz, fixed-bed reactor loading 1.5–2.0 cm^3 of catalyst (0.7–1.0 g, 30–40 mesh particles). Tests under co-feed conditions (feed composition: 20% propane, 20% oxygen, remainder He; residence time: 2 s) were carried out at 400–550 °C, while cyclic tests (reducing step: feed 20% propane in helium, gas residence time: 4 s; oxidizing step: feed air, gas residence time: 2 s) were carried out at 550 °C. The time for the oxidation half-cycle was always 0.5 h. The reducing step was run for different reaction times. In addition to propylene, the reaction products were carbon monoxide, carbon dioxide, light hydrocarbons (ethane, ethylene, methane), water (not analysed) and molecular hydrogen. No oxygenated compounds were found.

Catalysts were characterized before and after reaction by Raman spectroscopy (Renishaw 1000 instrument, equipped with a Leika microscope, Ar laser at 514 nm, power 25 mW). Scanning electron microscope (SEM, Leo Stereoscan 440), equipped with an EDX probe (Ge Probe, Link Oxford, UK) was used to quantitatively analyse the vanadium, titanium and aluminium amount in samples 2–4.

3. Results and discussion

3.1. Characterization of samples

Raman spectra of samples after calcination are shown in Fig. 1; spectra of corresponding samples after reaction under redox-decoupling conditions (final step before downloading: oxidation at 550 °C for 0.5 h) are shown in Fig. 2. Spectra of calcined samples 1 and 5 were very similar, and correspond to those reported by Wang et al [13]; bands have been attributed to isolated mono-oxo tetrahedral vanadate species. Sample 1 however was rather heterogeneous, and focussing the laser beam over darker particles evidenced the presence of V_2O_5. Samples 5 was homogeneous, and exclusively highlighted the presence of dispersed vanadium species. In the case of sample 2, a single, broad band was evident, with maximum positioned at Raman shift 910–930 cm^{-1}, which according to literature may be assigned to V–O–V linkages or dioxo groups in polymeric vanadate [14]. Analogous attribution can be given to the band at Raman shift 930–970 cm^{-1} observed in sample 3, while in sample 4 a broader band suggests the contemporaneous presence of both vanadium species observed in samples 2 and 3, as a consequence of the interaction with titania and alumina. Therefore, vanadium oxide in samples 2–5 was quite homogeneously dispersed over the corresponding supports.

After reaction, major modifications with respect to corresponding calcined samples were observed in samples 1

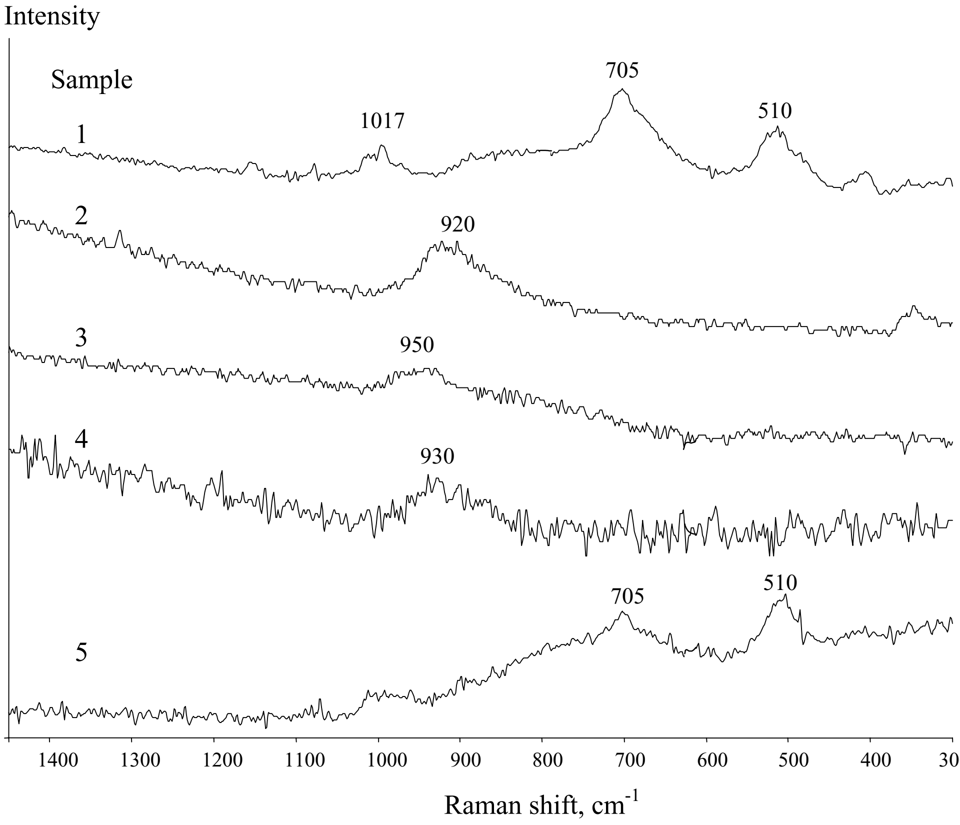

Fig. 1. Raman spectra of calcined samples. Spectra have been recorded by subtracting the spectrum of the corresponding support.

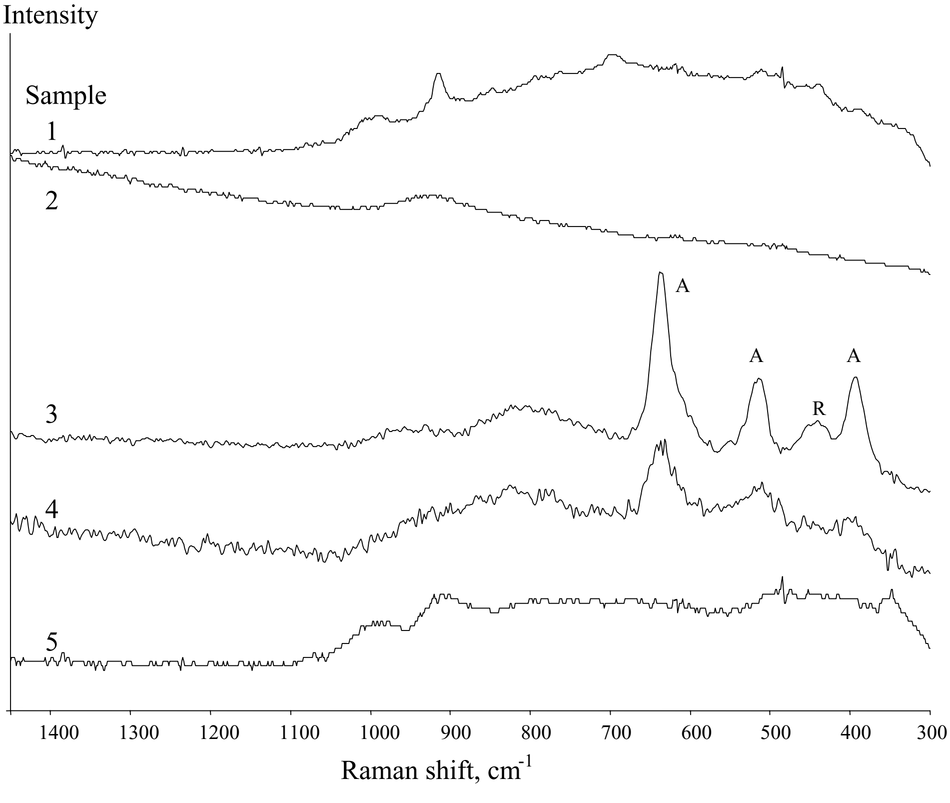

Fig. 2. Raman spectra of samples after reaction under redox-decoupling conditions (last step before downloading: re-oxidation): A = anatase; R = rutile. Spectra have been recorded by subtracting the spectrum of the corresponding support.

and 5. In fact, vanadia aggregates disappeared in sample 1, which after reaction was quite homogeneous; the spectrum was similar to that of sample 5 after reaction. The appearance of a broad band at around 980–1000 cm^{-1} indicates the development of isolated monomeric vanadyl species, possibly as a consequence of breaking of V–O–V bonds and re-dispersion of polyvanadate species. Analogous band, but less intense, was observed with samples 3 and 4. In sample 3, a weak band at 450 cm^{-1} can be attributed to rutile, indicating that under reaction conditions a partial transformation of anatase into the most stable titania form had occurred; moreover, the appearance of bands relative to anatase suggests an increase of crystallinity of titania in the reaction environment. The spectrum of sample 2 did not exhibit any remarkable change with respect to the catalyst before reaction.

3.2. Reactivity under redox-decoupling conditions

Fig. 3 plots the effect of the half-cycle reduction time on propane instantaneous conversion, at 550 °C and 4 s residence time, for samples 1–5. In all cases, the conversion progressively declined for increasing reduction times, finally reaching a stable value. This means that even after consumption of all the ionic oxygen available for the reaction, the catalyst was still active in propane transformation. This is in favour of a shift from an ODH, which was the prevailing mechanism on the oxidized catalysts, to a DH, occurring on the reduced catalysts [11].

The most active catalysts were samples 1 and 5, while the least active one was sample 4; samples 2 and 3 had comparable, intermediate activity. The high activity of samples 1 and 5 can be attributed to their high surface area, which possibly provided a better dispersion and availability of vanadium sites accessible to reactants. In a previous work, it was found that the large surface area of samples synthesized with the cogel procedure (sample 1) made most of vanadium available for the reaction, even if a fraction of it should be in principle occluded in the silica gel, as a consequence of the preparation adopted [11].

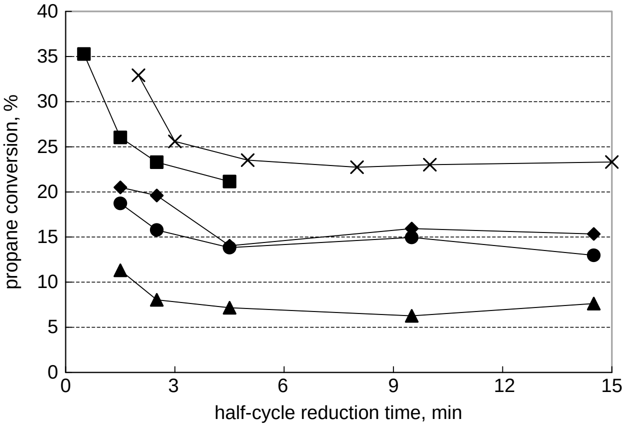

Fig. 3. Instantaneous conversion of propane as a function of the half-cycle reduction time. Samples: 1 (■), 2 (◆), 3 (●), 4 (▲), 5 (×).

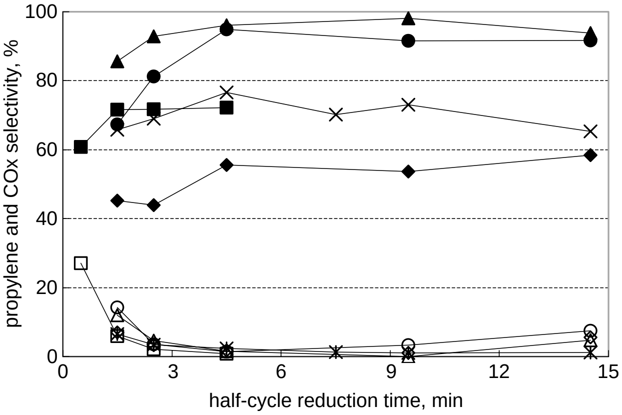

Fig. 4. Instantaneous selectivity to propylene [samples: 1 (■), 2 (◆), 3 (●), 4 (▲), 5 (×)] and to carbon oxides [samples: 1 (□), 2 (◇), 3 (○), 4 (△), 5 (✳)] as functions of the half-cycle reduction time.

Fig. 4 reports the instantaneous selectivity to propylene and to carbon oxides as functions of the half-cycle reduction time. The selectivity to propylene increased along with time, and correspondingly the selectivity to carbon oxides ($CO_2 +$ CO) decreased, until it was very low for longer reduction times. Fig. 5 plots the instantaneous C balance (thus, the % ratio between the sum of yields and the conversion of propane), and the molar percentage of hydrogen in the exit stream, as functions of the reduction time. Catalysts most selective to propylene were samples 3 and 4; this was not due to the lower selectivity to carbon oxides (which was comparable for all samples), but rather to the lower extent of coke formation. The latter was estimated by considering the complement of the C balance to 100, that is by assuming that all missing C was due to coke accumulated on the catalyst under non-steady conditions. The formation of coke was

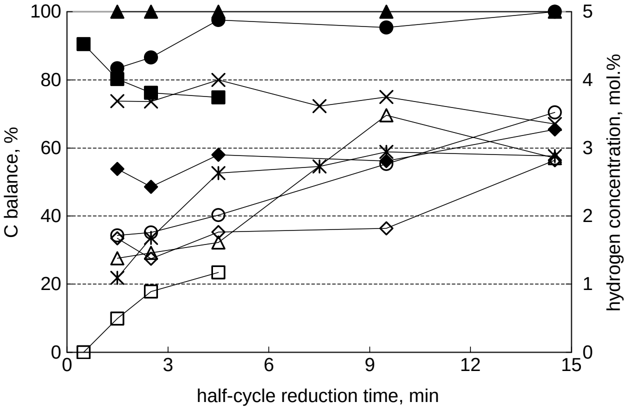

Fig. 5. Instantaneous C balance [samples: 1 (■), 2 (◆), 3 (●), 4 (▲), 5 (×)] and molar percentage of hydrogen in the exit stream [samples: 1 (□), 2 (◇), 3 (○), 4 (△), 5 (✳)] as functions of the half-cycle reduction time.

very low in samples 3 and 4, while it was very high in sample 2, as inferred from the low C balance.

The formation of molecular hydrogen increased along with the reduction time; it was almost negligible over the oxidized catalyst (i.e., for short reduction times), while it became remarkable for longer reduction times. This confirms that samples act as ODH catalysts when they are oxidized, while they act as DH catalysts when they are reduced. It is worth mentioning that an instantaneous conversion of 15%, with an almost total selectivity to propylene, over a feed containing 20% propane, corresponds to an hydrogen concentration of 3%, which indeed is the value experimentally obtained. However, other reactions may contribute to hydrogen formation (e.g., the formation of coke). The data do not allow to exclude the possibility that propylene is formed by propane DH even on the oxidized catalyst, and that ionic oxygen is only involved in hydrogen combustion and in propane combustion to CO_x.

For what concerns the distribution of products, a contribution to the differences observed can be attributed to the role of the support. In fact, the least selective catalyst is sample 2, in which the higher surface acidity of alumina is likely responsible for the higher formation of coke.

3.3. The comparison between co-feed and redox-decoupling operations

Fig. 6 compares the selectivity to propylene as a function of propane conversion under redox-decoupling and co-feed operations. With co-feed of reactants, conversion of oxygen was complete at 550 °C, and corresponding propane conversion was for all samples around 40–50% (oxygen being the limiting reactant). Under these conditions, all catalysts had comparable selectivity to propylene, close to 20–25%. The conversion of the two reactants decreased when the reaction temperature was lowered (in the range 400–550 °C), but even at relatively low conversion selectivity to the olefin was not better than 35% (sample 2) and 50% (sample 5). Therefore, the selectivity under redox-decoupling conditions was clearly better than that obtained by co-feeding of reactants; however, in the former case the lower conversions (and higher selectivities) were achieved with the reduced catalyst, thus under conditions at which the prevailing operating mechanism was a DH, rather than an ODH.

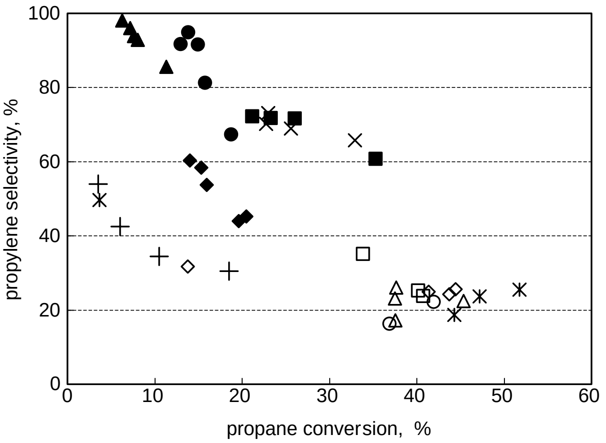

Fig. 6. Selectivity to propylene as a function of propane conversion under redox-decoupling conditions [samples: 1 (■), 2 (◆), 3 (●), 4 (▲), 5 (×)] and under co-feed conditions [samples: 1 (□), 2 (◇), 3 (○), 4 (△), 5 (✳, ✚)]. Tests under co-feed conditions for sample 5 were done with both the fresh calcined catalyst (✳), and the catalyst after the redox-decoupling tests (last cycle: re-oxidation) (✚).

Different is the case for samples 1 and 5, the most active ones, which during the reductive half-cycle could maintain high selectivity to the olefin (higher than that achieved with co-feed operation) even at the highest propane conversion, thus under conditions at which the catalyst was still, at least in part, oxidized. In this case the operating mechanism was an ODH (or a DH followed by hydrogen combustion). In a previous work [11], this was attributed to the higher dispersion of vanadium oxide in these catalysts. This provided an efficient “site-isolation” effect [15], which prevented the olefin from being transformed on neighbouring oxidized sites, limiting the consecutive combustion of propylene to carbon oxides.

Data reported in the present work indicate that also the nature of the active species may play a role on activity and selectivity. Raman spectra of samples after reaction evidenced that the nature of the active species depends on the support type; similar species developed in samples 1 and 5 (support silica), different from those which formed with samples 2–4. The species characterized by Raman shift at around 980–1000 cm^{-1}, well evident in samples 1 and 5, is attributable to isolated monomeric vanadyl species; this species may provide a better isolation of the active species than oligomeric or polymeric vanadia species in samples deposited over supports other than silica.

It is worth mentioning that even under co-feed conditions, the amount of hydrogen formed was non-negligible; this represents an important point, often neglected in papers which report about the performance of catalysts in paraffin ODH. For instance, sample 5 at 500 °C yielded a concentration of hydrogen under steady conditions which corresponded to approximately half of the propylene produced.

4. Conclusions

Catalysts based on vanadium oxide dispersed over different high-surface-area supports, namely alumina, titania, alumina–titania cogel, and silica, or dispersed inside silica gel, were prepared and tested in the reaction of propane transformation to propylene under co-feed and under cyclic, redox-decoupling conditions. In the latter case, the reaction mechanism was a function of the half-cycle reducing time. With short times, on still oxidized catalysts, the mechanism was an ODH (or a DH followed by hydrogen combustion), and instantaneous conversions obtained were higher than for longer reduction times, due to the progressive reduction of vanadium oxide under the stream of diluted propane. In the latter case the mechanism was undoubtedly a DH one, and catalysts were more selective than under co-feed conditions. Differences between the samples were mainly due to the different extent of coke formation, and could be attributed to the different acidity of the support.

Under redox-decoupling conditions, catalysts made of vanadium oxide either dispersed inside a high-surface-area silica gel or impregnated over silica, gave instantaneous propane conversions and propylene selectivity higher than for the other supported catalysts. In this case, the performance reached was remarkably better than that obtained under co-feed conditions. This was attributed to the higher dispersion of vanadium oxide, and to the nature of the V species which develop when silica is used as the support or the dispersing agent.

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