# Liquid Phase Disproportionation of Propylene over $MoO_3$-$Al_2O_3$ Catalyst in the Presence of Solvents

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Liquid phase disproportionation of propylene using hydrocarbon solvents over $MoO_3$–$Al_2O_3$ (atomic ratio: Mo/Al = 1/25) catalyst was investigated at 80 °C at a pressure of 50 kg/cm$^2$. The catalytic activity in heptane solution was preserved for a long time, because the small amount of polyolefins produced by polymerization reactions was entirely dissolved in the heptane and carried away from the catalyst surface. Selectivity for ethylene and butenes increased slightly in the heptane solvent. Benzene was not a suitable solvent because of poor solubility of the polymers and the formation of alkylbenzenes. A small amount of dissolved hydrogen also was found to be somewhat effective in lengthening the catalyst life. The polymers were found to be composed of larger amounts of ethylene than propylene and to have two molecular weight distribution maxima.

Disproportionation of olefins has been studied by numerous investigators in heterogeneous gas and homogeneous liquid phases. From an industrial point of view, it is important that the catalytic activity be preserved for a long time. In gas-phase disproportionation over $MoO_3$–$Al_2O_3$ catalyst, the catalytic activity decreases rapidly with reaction time on stream.[1,2] The catalyst life and selectivity have been improved by the addition of third materials to the catalysts, but this is not yet fully successful.[1–5] Previously,[6] the present authors have shown that the activity of $MoO_3$–$Al_2O_3$ in liquid-phase propylene disproportionation is preserved much longer than in the gas phase, and decreases very slowly after a long time at low temperatures. It was assumed that the main effect of deactivation of the catalyst was due to the covering of the active site with the polymers produced. If this is true, a longer life of the catalyst can be expected using a solvent which dissolves the polymers and maintains a clean active site for disproportionation.

In this paper, the catalytic activity, selectivity, and catalyst life in propylene disproportionation over $MoO_3$–$Al_2O_3$ catalyst in the presence of solvents were investigated. In addition, the formation of polymers was studied by measuring the molecular weight and constituents of the polymers produced.

## Experimental

The disproportionation reaction was carried out in an ordinary up-flow system of a fixed-bed catalyst in the liquid phase at a total reaction pressure of 50 kg/cm$^2$. About 0.025 to 1.000 g of the catalyst and twice that amount of $\gamma$-alumina were used as a catalyst bed and packed in the middle of a tube reactor with an 8 mm inside diameter and a 400 mm length. The upper and lower spaces of the catalyst bed were filled with $\gamma$-alumina. Propylene and the solvent were introduced into the catalyst bed from two cylindrical pumps after mixing in the lower part of the catalyst bed. The reaction products were analyzed by gas chromatography as reported in a previous paper.[7]

The preparation method and composition of the $MoO_3$–$Al_2O_3$ (atomic ratio: Mo/Al = 1/25) catalyst, pretreatment of the catalyst for activation, and propylene used were the same as indicated in a previous paper.[6] Heptane and benzene were of purities above 99.7% and added after drying with a 13X molecular sieve and the removal of the small amount of air in the solution by the bubbling of helium, nitrogen or hydrogen gases.

The polyolefins produced by a side reaction of the disproportionation were analyzed by the following method in order to determine their molecular weights. Polymers soluble in heptane and benzene were dried at 95 °C at 1 mmHg for 1 h. Polymers adhering to the catalyst surface were extracted by tetrahydrofuran using a Soxhlet extractor at 65 °C for 15 h, and the extracts were dried at 95 °C under 1 mmHg for 1 h. The number average molecular weight $\overline{M}_n$ for the polymers was measured in a tetrahydrofuran solution using a Mechrolab Inc. vapor pressure osmometer (Model 301A). The molecular weight distributions of the polymers were measured in a tetrahydrofuran soluble at 20 °C and 40 °C using a Toyo Soda Manufacturing Co., Ltd. high-speed liquid chromatograph of the gel-permeation type (Model HLC-801A). The column used was 4 feet in length and packed with a TSK GEL MIX. of the polystyrene type prepared by the Toyo Soda Co. Samples for liquid chromatography were prepared as about 1 wt% polymer solutions in tetrahydrofuran. Six kinds of paraffinic hydrocarbons ($C_{12}$–$C_{32}$) and eight kinds of mono-disperse polystyrene standards (with molecular weights of 2100—2000000) prepared by the Pressure Chemical Co. were used as standard molecular weight samples. The estimate of the molecular weight distribution was corrected for the mono-disperse polystyrene standard by multiplying by a factor of 0.6 and for paraffinic hydrocarbon by multiplying by a factor of 1.2. Infrared spectra of the polymers were measured using the KBr pellet method, as well as the film method using a Hitachi Co., Ltd. Model IRA-2.

## Results and Discussion

*Effects of Reaction Temperature.* The results of propylene disproportionation over $MoO_3$–$Al_2O_3$ catalyst in the liquid phase are shown in Table 1 and Fig. 1. In a run at 0 °C, the propylene conversion was very low in the initial period and gradually increased with reaction time. The conversion showed a broad maximum after 100 to 200 h and was still at about 80% of the maximum even after 460 h. The reaction time when the conversion fell to one-half its maximum value ($\tau_{1/2}$) was more than 1000 h.

On the other hand, the activity of the $MoO_3$–$Al_2O_3$ catalyst at 80 °C increased rapidly and showed maximum conversion for as short as 25 h (Run No. 2). Thereafter, the catalytic activity decreased rapidly with in a $\tau_{1/2}$ of about 25 h.

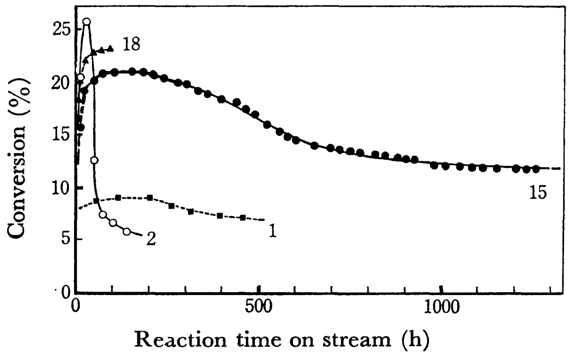

Fig. 1. Effects of reaction temperature and solvent on preservation of activity of $MoO_3$–$Al_2O_3$ catalyst in liquid phase disproportionation of propylene under 50 kg/cm$^2$.
Numbers correspond to the Run No. in Table 1.

*Effect of Hydrogen.* The effect of hydrogen in the liquid phase disproportionation of propylene was studied because it is known that hydrogen gas in the reaction system increases the catalytic activity and prolonges the catalyst life in the gas-phase disproportionation of propylene and 1-butene over a Co–Mo/$Al_2O_3$ catalyst.[8] As shown in Fig. 2, it was found that the catalyst retained its activity slightly longer in the presence of 0.1—3.5 mol% of dissolved hydrogen (Run No. 3—7). The hydrogen effect was much less marked than in the gas-phase reaction.[8] The product distribution shows that most dissolved hydrogen in the feed was consumed by the hydrogenation of propylene to propane, and the optimum amount of hydrogen in the reaction system was estimated to be about 0.1—0.3 mol% for ethylene and butenes production and for the prolongation of the catalyst life.

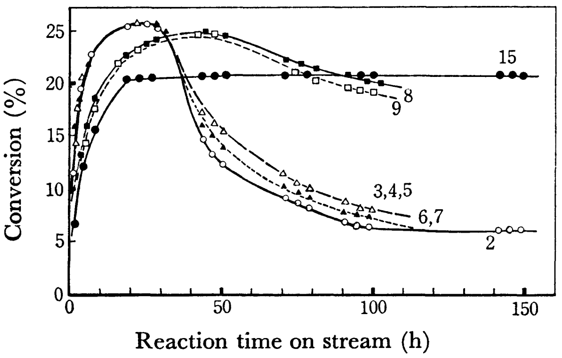

Fig. 2. Solvent and hydrogen effects on preservation of activity of $MoO_3$–$Al_2O_3$ catalyst in liquid phase disproportionation of propylene at 80 °C under 50 kg/cm$^2$.
Numbers correspond to the Run No. in Table 1.

*Effect of Heptane Solvent.* The effect of solvents was investigated at 80 °C where remarkable deactivation was observed. Since the catalyst activated in nitrogen was more active than that activated in air as reported previously,[6] oxygen must be poisonous to the active site of olefin disproportionation.[2] The decrease in activity of disproportionation in the heptane solvent purged by helium (Run No. 8) or nitrogen (Run No. 9) was less extensive than that in the absence of the solvent (Run No. 2) as shown in Fig. 2. Heptane containing about 0.3 mol% hydrogen was more effective for prolonging the catalytic activity. As shown in Fig. 3, $\tau_{1/2}$ was increased by a factor of about three by using a half-liquid volume of heptane to feed (Run No. 10) as compared with neat propylene. The duration of catalytic activity and the pressure drop in the reactor were improved by increasing the heptane/propylene ratio (Run No. 12—16).

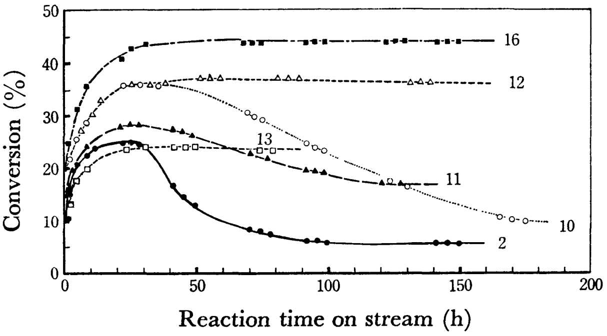

Fig. 3. Solvent effects on preservation of activity of $MoO_3$–$Al_2O_3$ catalyst in liquid phase disproportionation of propylene at 80 °C under 50 kg/cm$^2$.
Numbers correspond to the Run No. in Table 1.

According to the catalytic activity duration test at a heptane/propylene volume ratio of two and a large liquid hourly space velocity of 120 (Run No. 15), the propylene conversion after 1250 h decreased to 58% of the maximum, and $\tau_{1/2}$ was estimated by extrapolation to be about 2000 h. As shown in Table 1, propylene conversion is mostly dependent on the space velocity of the propylene and is affected only slightly by the total space velocity. These results indicate that the adsorption of propylene on the active site is hardly affected by the use of heptane as the solvent.

The selectivity to ethylene and butenes always increases with reaction time on stream. The selectivity was 95—97% within the initial period of 20 h, and it increased to about 99% after 50 h. When heptane was used as the solvent, the selectivity of disproportionation was improved about 0.3% as compared with the case of neat propylene. As shown in Table 2, comparatively more polymers were produced doing the initial period and most oligomers and polymers produced were carried away from the catalyst surface by the heptane solution, because the amount of polymers (Polymer C) extracted from the catalyst bed was much less than that (Polymer B) soluble in heptane (Run No. 14). On the average, 0.028 wt% of solid products (Polymer E) based on the converted propylene was recovered by concentrating to one-fiftieth of the heptane solution obtained from Run No. 15. Further evacuation of the heptane solution gave viscous hydrocarbons (Polymer D, 0.32 wt% on the average). Small amounts of white solid polymers were observed in the space down stream of the reaction system after a reaction time of 1250 h.

These results show that various kinds of polymers, that is, very soluble, slightly soluble, and insoluble polymers, in heptane were produced by the accompanied

Table 1. Effects of reaction temperature, hydrogen, and solvent on the preservation of activity of the $MoO_3$–$Al_2O_3$ catalyst in the liquid-phase disproportionation of propylene at 50 kg/cm²

| Run No. | Temp (°C) | Solvent | Purging gas[a] | Solv./$C_3H_6$ (vol/vol) | LHSV($h^{-1}$) $C_3H_6$ | LHSV($h^{-1}$) Solv. | LHSV($h^{-1}$) Total | Max. conv. (%) | $\tau_{1/2}$[b] |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0 | none | none | 0.0 | 3 | 0 | 3 | 9.3 | ~1000 |
| 2 | 80 | none | none | 0.0 | 30 | 0 | 30 | 25 | ~25 |
| 3 | 80 | none | $H_2$ (0.1) | 0.0 | 30 | 0 | 30 | 25 | ~35 |
| 4 | 80 | none | $H_2$ (0.2) | 0.0 | 30 | 0 | 30 | 25 | ~35 |
| 5 | 80 | none | $H_2$ (0.5) | 0.0 | 30 | 0 | 30 | 25 | ~35 |
| 6 | 80 | none | $H_2$ (3.0) | 0.0 | 30 | 0 | 30 | 25 | ~30 |
| 7 | 80 | none | $H_2$ (3.5) | 0.0 | 30 | 0 | 30 | 25 | ~30 |
| 8 | 80 | $n$-$C_7H_{16}$ | He (0.3) | 2.0 | 30 | 60 | 90 | 24 | — |
| 9 | 80 | $n$-$C_7H_{16}$ | $N_2$ (0.3) | 2.0 | 30 | 60 | 90 | 24 | — |
| 10 | 80 | $n$-$C_7H_{16}$ | $H_2$ (0.3) | 0.5 | 20 | 10 | 30 | 35 | ~90 |
| 11 | 80 | $n$-$C_7H_{16}$ | $H_2$ (0.3) | 0.8 | 25 | 20 | 45 | 29 | — |
| 12 | 80 | $n$-$C_7H_{16}$ | $H_2$ (0.3) | 2.0 | 20 | 40 | 60 | 37 | — |
| 13 | 80 | $n$-$C_7H_{16}$ | $H_2$ (0.3) | 2.0 | 30 | 60 | 90 | 24 | — |
| 14 | 80 | $n$-$C_7H_{16}$ | $H_2$ (0.3) | 2.0 | 30 | 60 | 90 | — | — |
| 15 | 80 | $n$-$C_7H_{16}$ | $H_2$ (0.3) | 2.0 | 40 | 80 | 120 | 21 | ~2000 |
| 16 | 80 | $n$-$C_7H_{16}$ | $H_2$ (0.3) | 4.0 | 10 | 40 | 50 | 44 | — |
| 17 | 80 | $C_6H_6$ | $H_2$ (0.3) | 2.0 | 30 | 60 | 90 | — | — |
| 18 | 80 | $C_6H_6$ | $H_2$ (0.3) | 2.0 | 30 | 60 | 90 | 23 | — |

a) The gas used to remove oxygen from the solvent. The numbers in parentheses are the contents (in mol %) of the gas in propylene (Run No. 3—7) or in the solvent (Run No. 8—18).

b) The reaction time when the conversion falls to one-half of its maximum value.

Table 2. Product distributions in liquid-phase propylene disproportionation at 80 °C, 50 kg/cm², a volume ratio of solvents/propylene of 2, and an LHSV of 90

| Solvent | | Heptane[a] | | Benzene[a] | | | |
|---|---|---|---|---|---|---|---|
| Run No. | | 14 | 15 | 17 | | | 18 |
| Reaction time (h) | | 0—10 | 0—1250 | 0—1 | 9—10 | 0—10 | 0—100 |
| Total propylene conversion (%) | | 23.45 | 16.05 | — | — | 20.64 | 23.81 |
| Disproportionation (%) | | 23.00 (98.07) | 16.00 (99.65) | 14.3 | 16.2 | 15.00 (72.66) | 23.00 (97.5) |
| Alkylation (%) | | — (—) | — (—) | 8.3 | 4.0 | 5.00 (24.22) | 0.81 ( 3.5) |
| Soluble polymers in solv. (%) | | 0.41 ( 1.76)[b] | 0.05 ( 0.35)[d] | — | — | 0.39 ( 1.90)[e] | — (—) |
| Insoluble polymers on cat. (%) | | 0.04 ( 0.17)[c] | — (—) | — | — | 0.25 ( 1.22)[f] | — (—) |
| Components of diisopropylbenzene produced (mol %) | $o$- | — | — | 25.2 | 12.8 | 20.0 | — |
| | $m$- | — | — | 33.6 | 31.8 | 32.6 | — |
| | $p$- | — | — | 41.3 | 55.4 | 47.4 | — |
| Components of isopropylbutylbenzene produced (mol %) | $o$- | — | — | — | — | 13.2 | — |
| | $m$- | — | — | — | — | 29.5 | — |
| | $p$- | — | — | — | — | 57.3 | — |

a) The numbers in parentheses are the selectivity of converted propylene. b) Polymer B. c) Polymer C. d) Polymer D+Polymer E. e) Polymer F. f) Polymer G.

polymerization.

*Effect of Benzene Solvent.* When benzene was used as the solvent (Run No. 17 and 18), the conversion during the initial period was nearly equal to that for the heptane solution. However, after a comparatively short time on stream, the introduction of propylene and benzene mixtures became difficult due to the increased flow resistance, caused by the produced polymers adhering on the down stream side of the reaction system. As shown in Table 2, about 24% of the converted propylene was comsumed in the alkylation of benzene within the first 10 h (Run No. 17), but the alkylation decreased rapidly to 3.5% after 100 h (Run No. 18). The composition of alkylbenzenes decreased in the following order: cumene, butylbenzenes, diisopropylbenzenes, styrene and isopropylbutylbenzenes. From the results in Table 2, it is clear that large amounts of polymers (Polymer G) insoluble in benzene were produced, and the solubility of the polymers in benzene is lower than in heptane. Therefore, benzene was not a suitable solvent for the propylene disproportionation.

*Molecular Weight Determination of Polymers Produced.* When the reaction was carried out without any solvent at an LHSV below two (80 °C), large amounts of oligomers and polymers (Polymer A) were produced in the reaction system and propylene could no longer be introduced after 10 hr.

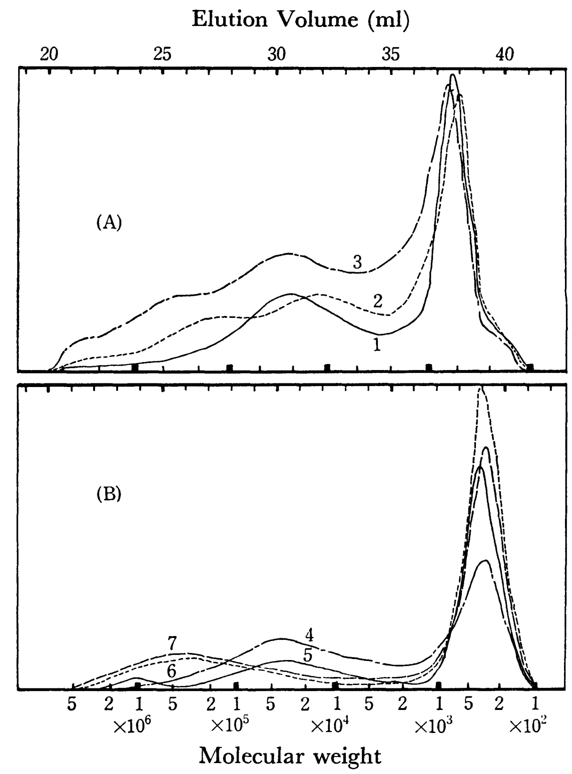

Fig. 4. Molecular weight distribution of polymers produced in liquid phase disproportionation of propylene at 80 °C under 50 kg/cm$^2$.
Condition of high speed liquid chromatograph (Toyo Soda, HLC-801A);
Column; TSK GEL MIX. (G3000H-G7000H), 4 ft., Solvent; tetrahydrofuran, Flow rate; 1.4 ml/min, Temperature; 20 °C (Fig. 4, A) and 40 °C (Fig. 4, B), Sample: 1 wt% solution in tetrahydrofuran, Detector; refractive index.
1: Polymer A, 2: Polymer D, 3: Polymer E, 4: Polymer B, 5: Polymer C, 6: Polymer F$^{a)}$; 7: Polymer G.
a): Polymers soluble in benzene obtained from Run No. 17.

Although the number average molecular weight $\overline{M}_n$ of all polymers determined was between 900 and 1800 (Table 3), very small amounts of lower molecular weight materials were observed in both gas and liquid chromatographic analyses of the products.

The molecular weight distribution of these polymers is shown in Fig. 4. Each polymer has two maxima at molecular weights of 300 to 500 and 20000 to 200000. Each sample includes a small amcunt of higher polymers with molecular weights of several millions. Polymers produced in the benzene solvent contained larger amounts of high molecular-weight fractions and of sligptly soluble polymers than the polymers produced in the heptane solvent. About 1 wt% of Polymers A, E, and G homogeneously dissolved in tetrahydrofuran at temperatures above 60 °C, while at 20 °C some of them precipitated. Therefore, still higher fractions than observed in Fig. 4 may be included in the original polymer solution.

*Component of Polymers by Infrared Spectroscopic Analysis*, Infrared spectra of the polymers produced in the propylene disproportionation are shown in Fig. 5. The absorption bands at 1380 and 1460 cm$^{-1}$ are assigned respectively to the methyl symmetrical C–H bending vibration and the methylene C–H scissoring vibration. On the assumption that the polymers are produced only by the polymerization of ethylene and propylene, the propylene contents of the polymers were measured using the method of Corish[9] with the results shown in Table 3. The propylene contents varied with the polymer samples, but they were always less than that for ethylene. Methyl groups in polymers should also be produced to some extent by the polymerization of ethylene as the terminal and branched methyl groups. Therefore, the real propylene contents in each polymer may be lower than those measured by the method of

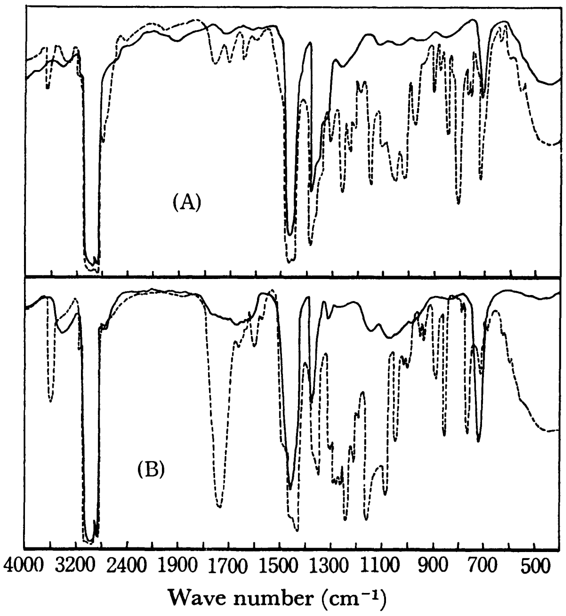

Fig. 5. Infrared spectra of polymers produced in the disproportionation of propylene over $MoO_3$-$Al_2O_3$ catalyst in the presence of heptane and benzene.
[A]: ······; Polymer B, film method on NaCl,
——; Polymer E, film method on KBr,
[B]: ······; Fraction of Polymer G soluble in heptane, film method on NaCl,
——; Fraction of Polymer G slightly soluble in heptane, film method.

TABLE 3. NUMBER AVERAGE MOLECULAR WEIGHTS AND COMPONENTS OF POLYMERS PRODUCED IN PROPYLENE DISPROPORTIONATION AT 80 °C AND 50 kg/cm$^2$

| Polymers | States | $\overline{M}_n$$^{a)}$ | Propylene content$^{b)}$ (%) |
|---|---|---|---|
| Polymer A | Gummy materials | 900 | 34 |
| Polymer B | Viscous liquid | — | 45 |
| Polymer D | Viscous liquid | 1300 | 23 |
| Polymer E | Solid | 1800 | 40 |
| Polymer G$^{c)}$ | Solid | — | 20 |

a) Number average molecular weights determined using a vapor pressure osmometer. b) Propylene contents of polymers determined by infrared spectroscopic analysis on the assumption that the polymers were produced only by the polymerization of ethylene and propylene. c) Fraction of Polymer G slightly soluble in heptane.

Corish.[9] Since the absorption band at 722 $cm^{-1}$ was stronger than those at 733, 752, and 815 $cm^{-1}$, it is clear that the *n*-values in $\leftarrow CH_2 \rightarrow_n$ are higher than four according to the reports of Bucci.[10] Hashimoto *et al.* reported that the polymerization rate of ethylene over $MoO_3$–$Al_2O_3$ catalyst reduced at 400 °C at a hydrogen pressure of 150 mmHg was larger by a factor of seven to ten than that for propylene.[11] In a previous paper[6] it was shown that the polymerization rate decreases in the following order: ethylene, propylene, and butenes. The tendencies of the polymerization and oligomerization rates of the various olefins over $MoO_3$–$Al_2O_3$ catalysts activated in nitrogen must be similar to those over reduced catalysts. As shown in Fig. 5 (A and B), polymers produced in the initial period have some absorption bands in the regions of 1700—1750 and 3400—3700 $cm^{-1}$, which may be related to oxygen compounds. These results imply that the oxygen compounds are produced by the oxidation of olefins with oxygen of the catalyst, reducing the catalyst at more highly active stated.

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