The influence of the size of metal particles on the catalytic activity of Ni and Cu-supported catalysts in methanol reforming reaction

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Abstract

The aim of the work was to investigate how the size of Ni and Cu-supported nanoparticles influence their activity in an oxidative steam reforming of methanol. The size of metal particles was controlled by the initial introduction or elimination of oxygen-containing groups on the surface of carbon nanotubes. The results of the activity tests showed that catalysts with the smallest metal nanoparticles were the least active since they easily underwent oxidation during the process.

Keywords Carbon nanotubes · Hydrogen · Particle size · Functionalization

Introduction

Hydrogen has been recognized as a promising alternative energy carrier as it is a powerful source of clean energy that can be used to directly feed either combustion engines or different types of fuel cells and could avoid the emission of greenhouse gases. Most of the hydrogen is currently derived from nonrenewable natural gas and petroleum [1]. Alternatively, hydrogen can be potentially generated from biomass-derived hydrocarbons through catalytic reforming. The reaction mixture of reforming process often consists of both oxidizing (oxygen, water vapor) and reducing (hydrogen, carbon monoxide) agents. Therefore, the metal catalyst can undergo either oxidation or reduction depending upon the reaction temperature. Moreover,

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the ease or either reduction or oxidation of metal particles is likely to be depended on their size.

Therefore, the aim of the work is to investigate how the size of metal particles influences the activity of catalysts in the reforming process. The oxidative steam reforming of methanol was chosen as a probe reaction. This process consists in the coupling of the endothermic methanol steam reforming (SRM, Eq. 1) with the exothermic partial oxidation (POM, Eq. 2) allowing the production of hydrogen with an autothermal process (Eq. 3).

The overall heat of reaction depends upon the value of p , which directly influences the thermal properties of the OSRM system as well as hydrogen concentration [2].

The catalytic systems used in reforming reactions are closely related to those that have been applied for the synthesis of methanol [3, 4]. They are mostly based on copper dispersed in a matrix formed by pure or mixed oxides like ZnO [5, 6], Al₂O₃ [7], ZnO/Al₂O₃ [8], Cr₂O₃/Al₂O₃ [9, 10], and ZrO₂/Al₂O₃ [9]. A good catalytic activity was reported to be at the following conditions: oxygen/methanol molar ratio=0.15–0.3 and steam/methanol molar ratio=1.3–1.6 depending on the catalyst used [11].

Carbon nanotubes have proven to possess ability as support for the fabrication of efficient heterogeneous catalysts in hydrogen production processes. Savva et al. developed a new Ni catalyst supported on CNTs for the direct decomposition of ethylene at 400 °C to produce CO-free hydrogen [12]. This catalytic system showed the highest hydrogen yield and carbon capacity ever reported in the literature for both the ethylene and methane decomposition reactions. In particular, the 0.5 wt% Ni/CNT catalyst exhibited 50 times higher hydrogen yield compared to a 0.3 wt% Ni/SiO₂ catalyst which has been examined under the same experimental conditions [12]. Moreover, the adsorption and hydrophilic properties of carbon nanotubes can be modified by the introduction of surface functionalities which could have a direct impact on the deposition process of metal particle and, as a result, on their size [13].

Therefore, the work is devoted to the investigation of how the initial pretreatment of carbon nanotubes (presence of surface oxygen-containing groups) affects the catalyst preparation process and ultimate the size of supported metal particles. And, then, how the size of catalytic particles influence their catalytic performance in the oxidative steam reforming of methanol.

Experimental part

Functionalization of carbon nanotubes

Multi-walled carbon nanotubes (outer diameter: 10 ± 1 nm, internal diameter: 4.5 ± 0.5 nm, length: 3–6 μm , purity > 96 wt%) were purchased from Sigma-Aldrich. The surface of nanotubes was oxidized in the acidified solution of KMnO_4 . The solid KMnO_4 and CNTs (in ratio 3:1) were suspended in 8 M H_2SO_4 water solution, put in a flask and stirred for 100 min at 95 °C. Then the suspension was cooled down and filtered. The obtained solid mixture was washed on the filter with water, with concentrated HCl solution to dissolve MnO_2 byproduct and then was re-filtered. Following this step, the obtained CNTs were washed with water until the filtrate became neutral and then dried in air at 110 °C for 16 h.

Also, the pristine CNTs were annealed at 800 °C in an Ar atmosphere for 2 h to eliminate possible surface functionalities.

Catalyst preparation

The CNT-supported copper catalysts were prepared by traditional wet impregnation method. The corresponding amounts of the aqueous solution of nickel nitrate were dropwise added to nanotubes and left under magnetic stirring for 12 h. Next, the excess of solvent was evaporated under vacuum. Finally, the impregnated samples were dried at 110 °C for 4 h and then calcined at 500 °C for 4 h in an argon flow. The Cu/CNT catalysts were prepared with the similar procedure using copper nitrate as catalyst precursor. In this case, the catalysts were calcined at 350 °C for 4 h in the inert atmosphere.

Physicochemical characterization

Nitrogen adsorption isotherms of catalyst and supports were obtained at -196 °C using a Sorptomatic 1900 (Carlo Erba Instruments). The samples were previously outgassed at 300 °C and equilibrated under vacuum for at least 4 h before measuring the adsorption–desorption isotherm. Specific surface areas were evaluated from the measured monolayer capacity (Brunauer–Emmett–Teller method) using the range of relative pressure from -0.05 to 0.33 and the value for nitrogen cross-section 0.162 nm².

Room temperature X-ray powder diffraction patterns were collected using a PANalytical X'Pert Pro MPD diffractometer in Bragg–Brentano reflection geometry. The diffractometer was equipped with Cu K_α radiation source ($\lambda = 1.5418$ Å). Data was collected in the 2θ range of 5° – 90° with a step size of 0.0167° and exposure per step of 27 s. Because the raw diffraction data contain some noise, the background during the analysis was subtracted using the Sonneveld, E. J. and Visser algorithm. The data were then smoothed using a cubic polynomial function. The average of size crystallites of the metallic active phase was calculated using the Scherrer equation:

$$L = \frac{K\lambda}{\beta \cos \theta}, \quad (4)$$

Here L is the crystallite size, K is a constant, λ is the X-ray wavelength, β is the peak width, θ is the Bragg angle.

The relative concentration of phases was calculated using reference intensive ratio (RIR) method. RIR refers to the ratio between the integrated intensities of the peak of interest and that of the strongest reflection of an internal standard ($\alpha\text{-Al}_2\text{O}_3$) in a one-to-one mixture. The weight percent of component X in a given mixture was calculated according to the following equation:

$$X_i = \frac{X_c I_i}{k_i I_c}, \quad (5)$$

Here X_c is the internal standard percent, k_i is the RIR of the considered reflection, I_i is the integrated area of the same reflection, I_c is the integrated area of $\alpha\text{-Al}_2\text{O}_3$.

Thermogravimetric measurements were performed using Derivatograph (Type 34-27T, MOM BUDAPEST). The TG and DTA curves were obtained in an air atmosphere and linear heating rate of $10^\circ\text{C min}^{-1}$ from 25 to 1000°C with a sample mass of 50.0 mg in a ceramic pan.

The SEM measurements were performed using S-4700 scanning electron microscope HITACHI, equipped with an energy dispersive spectrometer EDS. Images were recorded at several magnifications using secondary electron or BSE detector. The surface elemental composition of the catalysts was determined by energy distribution spectrum using X-ray microanalysis. The accelerating voltage was 25 kV. Supports and catalysts were investigated without any preliminary treatment.

The amount of oxygen-containing surface groups was determined by Boehm method. A 0.25 g of each CNT sample was placed in a 250 cm^3 flask. After adding 50 cm^3 of 0.1 M solution of NaOH, NaHCO_3 and 0.05 M solution of Na_2CO_3 (for determination of acidic groups) or 0.1 M HCl (for determination of basic groups), the mixtures were shaken for 24 h. After filtering the mixtures, 10 cm^3 of each filtrate was pipetted and the excess of base and acid was titrated by 0.1 M solution of HCl or NaOH. All experiments were twice repeated. Blank samples, with no nanotubes, were carried through the same procedure. The amount of specific functional group was then calculated from the difference in HCl (or NaOH) consumed by the CNT sample and blank sample.

Catalytic activity tests

Catalytic tests were conducted at the atmospheric pressure in a quartz fixed-bed reactor loaded with 0.1 g catalyst. The reaction conditions were as follows: temperature range of $175\text{--}300^\circ\text{C}$, the ratio of $\text{Ar}:\text{CH}_3\text{OH}:\text{H}_2\text{O}:\text{O}_2 = 25:1:1:0.4$, and the total flow rate equal 27.5 ml/min .

Before each run, the Ni and Cu catalysts were reduced “in situ” in a flow of $5\%\text{H}_2\text{--}95\%\text{Ar}$ mixture for 1 h at 500 and 300°C . The steady-state activity

measurements at each temperature were taken after at least 1.5 h on stream. The analysis of the reaction organic products was carried out by using an on-line gas chromatograph equipped with an FID and a 10% Carbowax 1500 on a Graphpac column. The CO, CH₄, and CO₂ concentrations were monitored by a GC chromatograph equipped with a TCD (150 °C, 60 mA) and a Carbosphere 60/80 (50 °C) column. The hydrogen concentration was measured by a GC chromatograph equipped with a TCD (120 °C, 60 mA) and a Molecular Sieve 5a (120 °C) column. The conversion of methanol and concentration of products were calculated according to the following equations:

$$Con_{CH_3OH}(\%) = \frac{f_{CH_3OH}^{in} - f_{CH_3OH}^{out}}{f_{CH_3OH}^{in}} \times 100, \quad (6)$$

Here $f_{CH_3OH}^{in}$ and $f_{CH_3OH}^{out}$ are the inlet and outlet molar flow of methanol.

$$C_{product}(\%) = \frac{n_X^{out}}{\sum n_X^{out}} \times 100, \quad (7)$$

Here n_X^{out} is the molar flow rate of the products at the outlet of the reactor.

Results and discussion

Physicochemical properties of supports and catalyst

The physicochemical properties of pristine and modified CNTs investigated using BET, TGA/DTA, and Boehm titration were summarized in Table 1. The results of acid–base titration showed that, before functionalization, the concentration of oxygen-containing groups on the surface of CNTs was quite low; carboxylic groups were the most often encountered followed by phenolic and lactonic groups. These

Table 1 The physicochemical properties of the carbon nanotubes

Sample	Functional groups, mmol/g					Oxidation onset temp., °C	Specific surface area, m ² /g
	Acidic			Acidic (total)	Basic (total)		
	Carboxyl	Lactonic	Phenolic				
CNT-Ar	—	—	0.02	0.02	1.34	580	324
CNT-pristine	0.23	0.10	0.05	0.38	1.29	560	272
CNT-KMnO ₄	1.34	0.14	0.17	1.65	0.50	460	301

Fig. 1 SEM image of the pristine (a) and oxidized (b) CNTs

Table 2 The physicochemical properties of Ni and Cu catalysts

Sample	Actual metal loading (wt%)	Particle size (nm)	Sample	Actual metal loading (wt%)	Particle size (nm)
Ni/CNTs-pristine	20,8	11	Cu/CNTs-pristine	20,1	23
Ni/CNTs-Ar	20,8	14	Cu/CNTs-Ar	20,2	25
Ni/CNTs-KMnO ₄	19,6	7	Cu/CNTs-KMnO ₄	19,4	17

groups were probably introduced during the purification [14] and/or storage of carbon nanotubes [15].

After wet oxidation treatment, the concentration of surface functional groups increased pronouncedly. Particularly, the oxidation of CNTs in the acidic KMnO₄ yielded primarily carboxyl groups along with small concentrations of phenolic and then lactonic groups. On the contrary, the nanotubes heated in Ar atmosphere were characterized by the lowest surface acidity as most of the previously mentioned groups decomposed at this temperature.

The results obtained from TG–DTA imply the good agreement with those of acid–base titrations. The presence of surface oxygen-containing groups altered the thermal stability of carbon nanotubes as they are more reactive towards oxygen, which makes the sample combusted at a lower temperature. The increase of specific surface area of carbon nanotubes upon oxidation treatment can be attributed to the exposing the internal pore volumes due to (i) opening up the tube ends (if they are closed), (ii) generation of defects on the sidewall of nanotubes and/or cutting up the tubes [16, 17]. Nevertheless, the increase in SSA was not so considerable probably due to simultaneous agglomeration of CNTs [18] (Fig. 1) as well as partial blocking of pore entrances by introduced oxygen-containing groups preventing the entry of the adsorbing gas into inner cavity [19]. These groups were also present on the surface of pristine CNTs; therefore, their elimination could also be the reason for a slight increase in SSA in the case of CNTs annealed at 800 °C.

The actual metal content and the size of metal nanoparticles were determined using TGA and XRD. The obtained results are summarized in Table 2. It can be seen that all samples had quite the same metal loading of about 20 wt%. The oxidation of carbon nanotubes resulted in decreasing the Ni particle size from 11 to 7 nm. Such result was most likely caused by the ability of acidic KMnO_4 to generate new defects and shorten the nanotubes [20] since the major amount of formed oxygen-containing groups decompose during calcination and/or reduction steps. As expected, the largest size of nickel particles among the catalyst with the same metal loading was observed on the surface of preheated nanotubes due to the low amount of anchoring sites. The results of XRD calculations also revealed that the size of supported Cu particles was approximately two times greater than that of nickel particles. Similarly, as in the case of Ni catalysts, the size of the active phase was affected by the method of pretreatment of carbon nanotubes. The size of Cu nanoparticles slightly increased after heat treatment from 23 to 25 nm and significantly decreased up to 17 nm after oxidation of nanotubes in acidic KMnO_4 .

Catalytic activity measurements

Blank tests

Prior to the catalytic activity measurements, blank runs using an empty reactor and reactor filled with carbon nanotubes only were carried out in order to have a better understanding of the impact of CNT-supported catalyst on the course of reforming reaction. A blank test with the empty reactor showed that only negligible amounts of methanol (<6%) were converted at 350 °C (Table 3). This result indicates that no reaction takes place before the catalyst bed during a typical test run in the investigated range of temperatures. As the temperature is further raised, the reaction proceeds more readily. The efficiencies of methanol conversion were about 27 and 32% at 400 and 450 °C, respectively. The carbon nanotubes alone were found to catalyze insignificantly the methanol reforming. When the reactor was filled with CNTs, the methanol conversion increased from 6 to 25% and from 32 to 38% at 350 and 450 °C, respectively. Although the observed trends of methanol conversion in both cases (with and without CNTs) were quite similar, the product distributions were

Table 3 Selectivities toward reaction products during OSRM in the empty reactor and in the reactor filled with CNTs

Experimental condition	Temperature, °C	$\text{Con}_{\text{CH}_3\text{OH}}$, %	C_{H_2} , %	C_{CO} , %	C_{CO_2} , %	C_{DME} , %
Blank test without CNTs	350	6	–	–	–	–
Blank test with CNTs		25	58	10	27	5
Blank test without CNTs	400	27	68	13	19	–
Blank test with CNTs		32	53	11	29	7
Blank test without CNTs	450	32	69	14	17	–
Blank test with CNTs		38	56	14	25	4

different. The main identified products were H_2 , CO_2 , CO and, in the case when reaction performed over CNTs, dimethyl ether (DME). The same results but under different reaction conditions were obtained by Mierczynski et al. [21]. It indicates that during the reaction CNTs alone catalyze mainly the formation of DME through methanol dehydration (Eq. 8).

This reaction involves the coupling of methoxide ions along with the formation of water and therefore can be considered as undesirable one as it significantly lowers the hydrogen yield. The highest selectivity towards DME formation was observed at a temperature of 400 °C and its value decreased with an increase in temperature because of the exothermic nature of the reaction [22].

The following undesired product obtained during the reaction was carbon monoxide. The increase in CO content decreases the hydrogen yield and acts as a poison to the downstream fuel cell catalysts [23, 24]. When the reaction was carried out in the empty reactor, no detectable amounts of CO were observed at 350 °C (methanol conversion of about 6%). With increasing temperature, more CO is formed by simultaneous methanol decomposition (MD) and the reverse water–gas shift (WGS) reaction [25–27]. Hence, the CO formation could be almost entirely suppressed or severely reduced by decreasing reaction temperature, where the MD and RWGS reactions are less likely to occur.

The enhanced formation of DME over CNTs can be due to the presence of iron compounds [21], such as metallic iron, cementite, and iron oxides within the structure of CNTs. In our case, XRD analysis revealed the presence of metallic iron and iron carbide (data not shown). These species originate from the catalyst precursor used in the CNT synthesis and their amount is depended on the reaction conditions [28].

Catalytic performance of CNT-supported Ni and Cu catalysts

The results of catalytic activity measurement (Table 4) showed that the nickel catalysts were significantly more active than the Cu catalysts. The Ni/CNT-pristine exhibited about 50% methanol conversion at 200 °C and above 80% at temperatures

Table 4 Selectivities toward reaction products during OSRM over Ni and Cu catalysts supported on pristine nanotubes

Catalyst	Temperature, °C	Con_{CH_3OH} , %	C_{H_2} , %	C_{CO} , %	C_{CO_2} , %	C_{DME} , %
20%Ni/CNT-pristine	200	50	68	30	0	2
	225	80	67	31	0	2
	250	90	68	30	0	2
20%Cu/CNT-pristine	200	23	63	5	27	5
	250	68	70	10	14	6
	300	91	71	16	9	4

higher than 225 °C. The supported Cu catalyst, on the other hand, showed conversion efficiencies of only 23% at 200 °C and 68% at 250 °C. At 300 °C, both catalysts demonstrated almost complete conversion of methanol while at 175 °C they were completely inactive.

The analysis of the outlet gases showed that their composition varied widely depending on the catalysts used. In the case of Ni catalyst, the produced gas consisted mainly of hydrogen (near ~67%) and carbon monoxide (about 30%) irrespectively of the reaction temperature. When the copper catalyst was used, the gas mixture contained primarily hydrogen (63–71%), carbon dioxide (9–27%), and carbon monoxide (5–16%). With increasing temperature from 200 to 250 °C, the catalyst selectivity towards CO increased and CO₂ decreased. As discussed earlier, this is related to high active reverse water gas shift reaction.

The obtained results suggest that Ni and Cu nanoparticles catalyze the reactions by different routes. The Ni-based catalyst increases the rate of methanol decomposition while Cu catalyzes methanol reforming and water–gas shift reaction. Similar conclusions were drawn by N. Takezawa and N. Iwasa [29]. They proposed that the difference in the catalytic behavior between copper and group VIIIB metals originates from the difference in the reactivity of HCHO intermediates formed on these metals in the course of methanol steam reforming.

The influence of the functionalization method of carbon nanotubes on the catalytic activity of nickel catalyst is depicted in Fig. 2. It can be seen that catalyst with the largest catalyst particles (Ni/CNT-Ar) was the most active whereas the sample with the smallest metal particles (Ni/CNT-KMnO₄) was one of the least active in the studied reaction. The selectivities towards different products of the reaction were quite the same as it was reported previously irrespectively of the functionalization method used.

Similar results were obtained for Cu-supported catalysts. According to the catalytic activity measurements (Fig. 3), the Cu/CNT-Ar exhibited the highest

Fig. 2 Influence of functionalization of CNTs on conversion of methanol over Ni/CNT catalysts

Fig. 3 Influence of functionalization of CNTs on conversion of methanol over Cu/CNT catalysts

methanol conversion (about 78 and 100% at 250 and 300 °C, respectively). The least active catalyst was copper supported on the nanotubes oxidized in acidic KMnO_4 . In this case, the conversion of methanol did not exceed 60%. The analysis of outlet gas showed that with decreasing the size of Cu particles the selectivity towards CO decreased. This is related to the surface-structural sensitivity of the water–gas shift reaction. It was reported that catalysts with the highest dispersion of the metal particles are the intrinsically active terms of CO conversion [30–32].

The oxidation state of the active catalytic phase during the oxidative steam reforming of methanol

Even though the investigated catalysts were reduced before activity measurements, the metal nanoparticles can be readily oxidized by oxygen and/or water vapor during the reaction. At the same, they can undergo re-reduction by produced hydrogen at a specific temperature. Therefore, the active component can be either in the metallic state, oxide form or both states simultaneously.

The XRD measurements of the used catalysts revealed that only 18% of nickel was oxidized at temperatures of 175–200 °C. At higher temperatures, the concentration of nickel(II) oxide decreased to 13% at 250 °C and to less than 4% at 300 °C due to the reduction process (Fig. 4).

A different situation was observed in the case of copper catalysts (Fig. 5). Before the reaction, the fresh catalyst contained mainly copper (I and II) oxides, which were completely reduced to metallic copper in the hydrogen stream before the reaction began. Even though the copper nanoparticles reduced at a relatively low temperature, they almost entirely underwent oxidation to copper(I) oxide (87%) during the reaction at 200 °C. Then, with the increase in temperature up to 250 °C, the copper oxides were partially reduced to metallic copper (74%) as it can be observed from

Fig. 4 XRD profiles of nickel catalyst after reaction at 175 °C (a), 200 °C (b), and 225 °C (c)

Fig. 5 XRD profiles of copper catalyst: a—as-received; b—reduced; c, d—after reaction at 200, 250, and 300 °C

the appearance of characteristic diffraction bands. At 300 °C, the copper species were again re-oxidized mainly to copper(II) oxide. The total relative concentration of oxide phase was about 79%. Thus, during the reaction, the copper nanoparticles were mainly in the oxidized state (except the temperature of 250 °C).

In order to explore the role of oxide metallic phase in the catalytic activity of investigated samples, they were fully oxidized (instead of reduction) and then tested

Table 5 The activity of oxidized Cu and Ni catalysts in the OSRM

Catalyst	Temperature, °C	Con_{CH_3OH} , %	C_{H_2} , %	C_{CO} , %	C_{CO_2} , %	C_{DME} , %
20%Ni/CNT-oxidized	225	0	—	—	—	—
	300	100	70	20	8	2
20%Cu/CNT-oxidized	250	44	64	4	32	—
	300	63	66	12	21	1

in the OSRM at different temperatures (Table 5). The obtained results showed that oxidized samples were less active in comparison to the reduced catalysts. The biggest difference was observed in the case of oxidized nickel catalysts which was completely inactive at low temperature. At 300 °C, however, the catalyst demonstrated the same activity as the reduced sample due to gradual reduction of oxide phase by hydrogen formed as a result of methanol decomposition.

There are several scientific publications regarding the influence of catalyst particle size on the course of reforming of methanol [33–35]. For example, Lakshmanan prepared Au/CeO₂–ZrO₂ catalysts with different Au particle sizes (from 2 to 12 nm) for steam reforming of methanol. The catalytic activity of obtained samples was found to decrease significantly with increasing particle size of the gold [33]. However, the opposite situation was observed in the case of application of Ni and Cu catalysts. The highest conversion efficiencies of methanol were obtained over catalysts with the largest particle sizes. In order to understand such observation, the XRD measurements of the most/least active catalysts were performed, and the concentration of metallic phase in each catalyst was calculated using RIR method (Table 6). According to the obtained data, the catalysts with the largest particle sizes (most active) had the highest concentration of metallic phase during the reaction while the samples with small particle size were mostly oxidized. It is likely that the activity of investigated catalysts to be governed by the dispersion of the active phase and the ease of the oxidation of metal particles. The influence of these two factors on the catalytic activity seems to be mutually opposite. The high dispersion leads to a high number of catalytic sites available to the reactants (high activity) and,

Table 6 The dependence of the catalytic activities of the investigated samples on the concentration of metallic phase

Sample	Reaction temperature, °C	Relative concentration of metallic phase, %	Relative concentration of oxide phase, %	Methanol conversion, %
20%Cu/CNT-Ar	300	56	44	100
20%Cu/CNT-pristine		21	79	91
20%Cu/CNT-KMnO ₄		10	90	60
20%Ni/CNT-Ar	225	87	13	98
20%Ni/CNT-pristine		79	21	80
20%Ni/CNT-KMnO ₄		67	33	60

at the same time, to a low concentration of metallic Cu or Ni (low activity) due to more easily oxidation of small nanoparticles.

Conclusions

The presence of oxygen-containing group on the surface carbon nanotubes and structural defects were proven to be responsible for decreasing the size of catalyst nanoparticles. The result of catalytic tests showed that nickel and copper nanoparticles catalyzed the OSRM by different routes; the Ni catalysts increased the rate of methanol decomposition reaction, while Cu nanoparticles catalyzed the methanol reforming and water–gas shift reactions. Moreover, both metals were found to undergo oxidation or reduction depending upon the reaction temperature. The most active catalysts were those in which the metal particles remained largely reduced during the reaction. Therefore, the catalysts with the smallest nanoparticles were least active due to their ease of oxidation.

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