



# Designed Pt Promoted 3D Mesoporous Co<sub>3</sub>O<sub>4</sub> Catalyst in CO<sub>2</sub> Hydrogenation

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Controlled size Pt nanoparticles were anchored onto the surface of 3D mesoporous cobalt-oxide support and was tested in  $CO_2$  hydrogenation reactions compared to commercial cobalt-oxide supported Pt nanoparticles prepared by the wet impregnation method as well as SBA-15 silica supported nanoparticles. Designed Pt/mesoporous cobalt-oxide catalysts showed the highest activity as well as the highest methane selectivity. Such catalyst was active at 573 K, while other catalysts showed activity >673 K.

Keywords: CO<sub>2</sub> Hydrogenation, Mesoporous Co<sub>3</sub>O<sub>4</sub>, Controlled Size Pt Nanoparticles.

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## **1. INTRODUCTION**

The catalytic conversion of carbon dioxide to more valuable compounds has again become of great interest since  $CO_2$  is one of the most dangerous greenhouse gases. As an economical safe and renewable carbon source,  $CO_2$  turns out to be an attractive  $C_1$  building block for making other chemicals, or to reduce and store the energy as hydrocarbons. The hydrogenation of  $CO_2$  is a promising possibility for realization these processes. Number of excellent reviews have summarized the results and discussed them in detail.<sup>1,2</sup> The Sabatier reaction ( $CO_2 + 4H_2 = CH_4 + 2H_2O$ ) for synthesizing methane from  $CO_2$  is also in the main focus of research and of industry.<sup>3-6</sup>

The chemical activation of  $CO_2$  is a quite popular term nowadays in catalysis and surface science when discussing  $CO_2$  chemistry, which involves the activation and cleavage of the strong carbon-oxygen bonds and subsequently an establishment of new chemistry with higher enthalpy.<sup>7,8</sup>  $CO_2$  in the gas-phase is non-reactive. One possible way to reduce  $CO_2$  is to generate  $CO_2^{*-}$ , the electron attached state of  $CO_2$ , which is controlled by the reduction potential of the  $CO_2^-/CO_2$  redox couple, although the probability of this mechanism under mild conditions is very low because of the high redox potential.<sup>9,10</sup> The activation of  $CO_2$  in

favorable.<sup>11</sup>

It was an important finding that the catalytic performance of Pt metals in the hydrogenation of  $CO_2$  is strongly affected by the nature of the supports. TiO<sub>2</sub> was found to be the most effective one, which was attributed to the electronic interaction between the metals and TiO<sub>2</sub>.<sup>12</sup> Using both SiO<sub>2</sub> and defected TiO<sub>2</sub> with oxygen vacancy as support, Pt nanoparticles (NP) is able to enhance the overall  $CO_2$  conversion via increased  $CO_2$  binding. The enhancement is more significant for Pt/TiO<sub>2</sub> than Pt/SiO<sub>2</sub> and therefore higher activity is expected for TiO<sub>2</sub>.<sup>13</sup>

Recently enhanced CO oxidation rates at interface of mesoporous oxide and Pt nanoparticles were observed.<sup>14</sup> Nanoporous  $Co_3O_4$ , NiO,  $MnO_2$ ,  $Fe_2O_3$  and  $CeO_2$  with loading Pt nanoparticles were synthesized and utilized in CO oxidation reaction. Much higher reaction rate was observed when  $Co_3O_4$  was the support.<sup>15</sup> Using this analogy, we investigated the CO<sub>2</sub> hydrogenation in the presence of Pt/Co<sub>3</sub>O<sub>4</sub> and Pt/SBA-15 catalysts. In this project, size controlled Pt nanoparticles with 3.6 nm diameter were anchored onto the surface of designed 3D mesoporous cobalt oxide support. Pt/Co<sub>3</sub>O<sub>4</sub> (commercial), as well as Pt supported on SBA-15 catalysts were also tested. The catalytic results pointed out the importance of nature of metal-interface.

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## 2. EXPERIMENTAL DETAILS

## 2.1. Synthesis of 3.6 nm Pt Nanoparticles

20 mg of  $H_2PtCl_6 \cdot 6H_2O$  and 110 mg of PVP was dissolved in 5 ml ethylene-glycol, separately. The solutions were mixed in a 25 ml round bottom flask and refluxed at 160 °C for 60 min under Ar purging. The Pt nanoparticles were collected by precipitation with 40 ml of acetone, followed by several washing cycles based on ethanol dispersion and hexane precipitation. The product was finally redispersed in 10 ml ethanol.

#### 2.2. Synthesis of Mesoporous Cobalt-Oxide

For the preparation of mesoporous cobalt-oxide support  $(Co_3O_4)$ , KIT-6 silica was used as template. The synthesis of KIT-6 was described before.<sup>16</sup>  $Co_3O_4$  was prepared through the hard template method using the as-prepared KIT-6. In a typical synthesis, 4.65 g  $Co(NO_3)_2 \cdot 6H_2O$  was dissolved in 8 ml water and mixed with a suspension of 4 g KIT-6 in 50 ml toluene. Vigorous stirring was applied to the mixture at 65 °C until the total evaporation of toluene. After the evaporation, the precipitated product was collected and dried at 60 °C overnight, followed by calcination at 300 °C for 6 h. The silica template was completely removed by several washing steps using 2 M aqueous NaOH solution. The filtered product was dried at 60 °C overnight.

#### 2.3. Synthesis of SBA-15 Mesoporous Silica Support

SBA-15 mesoporous silica support was synthesized from tetraethyl orthosilicate (TEOS) by a soft template method. Here, 8 g of pre-melted Pluronic-123, 60 ml distilled water and 240 ml of 2 M HCl solution were mixed at 40 °C for 2 hours. After the dissolution of P-123, 17 g of TEOS was added dropwise to the mixture at 40 °C and continuous stirring was applied for 20 hours. Stirring was continued for 36 hours at 60 °C. After the synthesis, the product was filtered and washed with distilled water. Then, the product was heated to 100 °C with a heating rate of 2 °C · min<sup>-1</sup> and aged for 5 hours; then the temperature was elevated to 550 °C with a heating rate of 1 °C · min<sup>-1</sup>. After 4 hours of calcination, the product was ready for further use.

### 2.4. Synthesis of Mesoporous Cobalt-Oxide and SBA-15 Supported Pt Catalysts

To fabricate supported catalysts, the ethanol suspension of Pt nanoparticles and  $Co_3O_4$  or SBA-15 were mixed in ethanol and sonicated in an ultrasonic bath (40 kHz, 80 W) for 3 hrs. The supported nanoparticles were collected by centrifugation. The products were washed with ethanol three times before they were dried at 80 °C overnight.

## 2.5. Synthesis of Bulk Co<sub>3</sub>O<sub>4</sub> Supported Pt Catalyst by Wet Impregnation Method

Cobalt-oxide support (product of Merck) was impregnated at room temperature in aqueous solution of

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 $H_2PtCl_6 \times 6H_2O$  (Reanal) to yield the desired amount of Pt content (1%). The suspension was stirred for 3 h at ~353 K, after that it was dried at 373 K for 2 h under infrared lamp. The prepared catalyst pellets (~200 mg) were loaded into the catalytic reactor and was pretreated *in situ* before the catalytic experiments.

# 2.6. Hydrogenation of Carbon-Dioxide in a Continuous Flow Reactor

The catalytic reactions were carried out at 1 atm pressure in a fixed-bed, continuous-flow reactor (8 mm i.d.), made from quartz. The dead volume of the reactor was filled with quartz beads. The operating temperature was controlled by a thermocouple placed inside the oven close to the reactor wall. For catalytic studies small fragments (about 1 mm) of slightly compressed pellets were used. Typically, the reactor filling contained 200 mg of catalyst. In the reacting gas mixture, the CO<sub>2</sub>:H<sub>2</sub> molar ratio was 1:4. The CO<sub>2</sub>:H<sub>2</sub> mixture was introduced to the reactor with mass flow controllers (Aalborg), the flow rate was, in general, 40 mLmin<sup>-1</sup>. The reacting gas mixture flow entered and left the reactor through an externally heated tube to avoid condensation. Analysis of the gases was performed with an Agilent 4890 gas chromatograph using Equity-1 capillary and Porapak QS packed columns to allow the complete separation of the reactants and products. The gases were detected simultaneously by thermal conductivity (TCD) and flame ionization (FID) detectors. Before the catalytic experiments either in a continuousflow reactor the as received catalysts were oxidized in O<sub>2</sub> atmosphere at 573 K for 30 min to remove the surface contaminants as well as the PVP capping agent<sup>2,3</sup> and thereafter were reduced in H<sub>2</sub> at 573 K for 60 min to reduce the Pt on the surface.

## 2.7. High Resolution Transmission Electron Microscopy (HR-TEM)

Imaging of the different supports, Pt nanoparticles and derived catalysts, as well as the size distribution of the nanoparticles before and after the catalytic reaction, was performed by an FEI TECNAI G2 20 X-Twin high-resolution transmission electron microscope (equipped with electron diffraction) operating at an accelerating voltage of 200 kV. The samples were drop-cast onto carbon film coated copper grids from ethanol suspension.

#### 2.8. Powder X-ray Diffraction (XRD)

XRD studies of the silica supports were performed on a Rigaku MiniFlex II instrument with a Ni-filtered  $CuK_{\alpha}$  source in the range of  $2\theta = 10-80^{\circ}$ .

#### 2.9. Gas Sorption Measurements

The specific surface area (BET method), the pore size distribution and the total pore volume were determined by the BJH method using a Quantachrome NOVA 2200

gas sorption analyzer by  $N_2$  gas adsorption/desorption at -196 °C. Before the measurements, the samples were pretreated in vacuum (< $\sim$ 0.1 mbar) at 473 K for 2 hours.

## 2.10. Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

The loading of the Pt on the supported catalysts was determined by ICP-MS technique. The measurements were performed using an Agilent 7700× type ICP-MS spectrometer. Typically, 10 mg of Pt/silica catalysts were dispersed in 10 ml of cc. HCl solution and the mixture were heated at elevated temperatures for 30 min before the tests. The as-prepared samples were washed into a 100 ml flask than it was connected to the sample introduction system consisted of an I-AS type autosampler, a MicroMist pneumatic micronebulizer and a Peltier-cooled (2 °C) Scott type double-pass spray chamber. The sample uptake rate was 200  $\mu$ L · min<sup>-1</sup>. The ICP plasma and interface parameters were set according to the standard hot plasma configuration (e.g., RF forward power: 1550 W, argon carrier gas flow rate: 1.05 L/min, sampling depth: 8.0 mm). Fine tuning was performed before the analytical measurements using tuning solutions supplied by the manufacturer (G1820-60410, 5185-5959 Agilent Technologies). All measurements were carried out using the He mode of the ORS<sup>3</sup> collision cell, by monitoring the signal of <sup>195</sup>Pt isotope. For calibration purposes, six standard samples were prepared from a certified, multielement ICP-MS standard stock solution (8500-6948 Agilent Technologies) via dilution with trace quality deionized water (Synergy + Elix 3, Millipore). QC samples were also used to ensure the accuracy of determinations. All labware (PE autosampler vials, PMP certified volumetric flasks, etc.) were thoroughly cleaned before use with dilute ultratrace quality nitric and hydrochloric acid (Ultrapure Normatom, VWR).

## 3. RESULTS AND DISCUSSION

## 3.1. Characterization of the Catalysts

Controlled size Pt nanoparticles were synthesized by a polyol method using ethylene glycol as a media and PVP as a capping agent from Pt-salts.  $3.6 \pm 1.25$  nm Pt nanoparticles were obtained where the particles have narrow size distributions as well as spherical shape (Fig. 1(A)). Commercial cobalt-oxide support has no controlled structure. TEM image show particles of 5–100 nm size with no controlled shape (Fig. 1(B)). The crystal structure was determined as Co<sub>3</sub>O<sub>4</sub> by powder XRD technique (not shown here). Wet impregnation of cobalt-oxide with Pt-salt resulted in tiny Pt nanoparticles hardly observable with TEM (white arrows at Fig. 1(B)).

However, ICP-MS results (Table I) proof the presence of platinum in the catalysts. Electron Diffraction patterns (not shown here) confirmed the presence of Pt (111), Pt (200), and Pt (220) crystallite planes characteristic for metallic face-centered cubic (fcc) platinum.

Replica method using KIT-6 as a hard template resulted in mesoporous cobalt-oxide with ordered pore structure (Fig. 1(C)). The N<sub>2</sub> adsorption/desorption studies of the Co<sub>3</sub>O<sub>4</sub> support show isotherms with hysteresis loop characteristic for mesoporous materials (Fig. 2(A)). The shapes of the isotherm grouped into the mesoporous materials with type V isotherms. The specific surface areas of the mesoporous cobalt-oxide, the commercial cobalt-oxide and the SBA-15 silica support are 51 m<sup>2</sup> · g<sup>-1</sup>, 16 m<sup>2</sup> · g<sup>-1</sup> and 799 m<sup>2</sup> · g<sup>-1</sup>, respectively (Table I). The crystal structure of mesoporous cobalt-oxide was Co<sub>3</sub>O<sub>4</sub> similar to the commercial cobalt-oxide catalyst support (Fig. 2(B)).

The sonication method for catalyst prepration were succesful showing the presence of controlled size Pt nanoparticles dispersed on the surface of mesoporous cobalt-oxide and SBA-15 silica (Figs. 1(C–D)). The concentration of Pt on the surface of the catalysts were 0.82 wt%, 0.57 wt% and 0.55 wt% for Pt/Co<sub>3</sub>O<sub>4</sub> (impregnated), Pt/Co<sub>3</sub>O<sub>4</sub> (mesoporous) and Pt/SBA-15, respectively (Table I).

#### **3.2.** Reaction of CO<sub>2</sub> and H<sub>2</sub>

The catalytic measurements between  $CO_2$  and  $H_2$  were carried out with stoichiometric ratio of 1:4 in all cases. The nominal Pt content was 1 w%, the actual metal concentration was determined by inductively coupled plasma mass spectrometry (ICP-MS), the obtained Pt contents are presented on Table I. The catalytic conversions and the product distributions were determined on three different catalysts. The conversion of  $CO_2$  was calculated taking into account the amount of carbon-dioxide consumed. It was also determined basis of the sum carbon balance. Selectivity values were defined as

$$S_i = \frac{x_i n_i}{\sum x_i n_i}$$

where  $x_i$  is the mol fractions of product (*i*) and  $n_i$  is the number of carbon atoms in each molecule of product (*i*). Experiments were executed in the temperature range of 573–973 K.

On Figure 3(A) the conversions of the  $CO_2$  hydrogenation are plotted obtained on Pt supported by mesoporous  $Co_3O_4$ , on commercial (Merck)  $Co_3O_4$  and on SBA-15 as a function of temperature. Significant differences can be concluded based on the results.

Very low activities were observed at 570–600 K on both Pt/Co<sub>3</sub>O<sub>4</sub> (where the Pt was loaded by impregnation method) and Pt/SBA-15. An increasing with temperature was found on both catalysts. Outstanding activity (~60%) was observed when mesoporous oxide was used even at 573 K (Fig. 3(A)). Catalytic stability experiments were also performed at 973 K, and the high activity remained stable at all time under the reaction (5 hours). The conversion values were between 69–70% in the case of Pt/Co<sub>3</sub>O<sub>4</sub> (imp.), and 68–64% range in the matter of mesoporous sample.

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Figure 1. Typical TEM images of 3.6 nm Pt nanoparticles (A), Pt/cobalt-oxide support made by impregnation (B), mesoporous cobalt-oxide supported Pt nanoparticles (C), SBA-15 supported Pt nanoparticle catalyst (D).

The product distributions were also different as can be seen on Figures 3(B), (C). The CO production monotonically increased with temperature and approximately the same values were measured in every temperature on the three samples (Fig. 3(C)). Exclusively almost CO was formed on Pt/SBA-15 during CO<sub>2</sub> dehydrogenation. In contrast, on Pt supported on mesoporous  $Co_3O_4$ large amount of methane was formed at low temperature (570–600 K). When the temperature was raised, the methane formation decreased and CO production increased (Fig. 3(B)).

The differences in selectivity are well demonstrated on the three samples at 673 K in Figure 4. When mesoporous  $Co_3O_4$  was used as support for uniform size of platinum, only methane was detected with traces of CO.

 Table I.
 Specific surface area and Pt content of the supports and catalysts.

Support	$S_{\rm BET} \ ({\rm m}^2 * {\rm g}^{-1})$	Catalyst	Pt content (wt%)
Co <sub>3</sub> O <sub>4</sub> (bulk)	16	Pt/Co <sub>3</sub> O <sub>4</sub> (bulk)	0.82
Co <sub>3</sub> O <sub>4</sub>	51	Pt/Co <sub>3</sub> O <sub>4</sub>	0.57
(mesoporous)		(mesoporous)	
SBA-15	799	Pt/SBA-15	0.55

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When the Pt was loaded by impregnation on commercial Co<sub>3</sub>O<sub>4</sub>, 80% methane and only 20% CO was the product ratio at 673 K. In the case of Pt/SBA-15 CO was the main product, only the trace amount of methane was observed. This large difference in the activity and selectivity can be explained by significant support effects. It is well known that the electronic interaction is very weak between noble metal and silica-based oxide.<sup>13</sup> The interaction is significant on Pt/Co<sub>3</sub>O<sub>4</sub>. X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure spectroscopy (NEXAFS) showed that cobalt oxide reduction occurs in presence of Pt.14 Powder XRD analysis of the mesoporous cobalt-oxide supported Pt sample after CO<sub>2</sub> hydrogenation reaction (not shown here) showed the presence of pure fcc phase metallic cobalt as well as CoO. In addition, it is interesting to acknowledge the presence of cubic  $CoC_{x}$ which can also contribute to the high activity of the mesoporous cobalt supported catalysts. We may assume that a special interface is more effective in the case of mesoporous  $Co_3O_4$  during the interaction with Pt. The different product distributions on Pt/SBA-15 and Pt/Co<sub>3</sub>O<sub>4</sub> suppose different reaction mechanisms.

Based on the reaction products (CO and water) on Pt/SBA-15 we propose a direct C–O bond cleavage



Figure 2. Adsorption-desorption isotherm (A) as well as powder XRD pattern (B) of mesoporous cobalt-oxide.

pathway and a reverse water-gas shift reaction mechanism in first approximation. It is generally accepted in  $CO_2$ transformation reactions the formation of activated  $CO_2$ (vibrationally or electronically;  $CO_2^{*-}$ ).<sup>7</sup> The activated carbon dioxide dissociates to CO and O on the surface of the Pt nanoparticle (Eq. (1)).

$$\mathrm{CO}_{2(\mathrm{g})} \to \mathrm{CO}_{2(\mathrm{Pt})}^{*-} \to \mathrm{CO}_{(\mathrm{Pt})} + \mathrm{O}_{(\mathrm{Pt})} \tag{1}$$

$$CO_{(Pt)} \rightarrow CO_{(g)}$$
 (2)

The presence of adsorbed hydrogen, which is formed on Pt sites during dissociation of molecular hydrogen, makes this process more easily.<sup>4, 10</sup> The adsorbed hydrogen may react with oxygen forming water: 91.243.93.135 On: Web

extent. Although detail DRIFTS measurements are planned in the future, we propose a formate pathway which was established in the case of Pt/TiO<sub>2</sub><sup>13</sup> and for Pd/Al<sub>2</sub>O<sub>3</sub>.<sup>18, 19</sup> In this case the carbon dioxide can be activated on oxygen vacancies of oxide support nearby the platinum with the mediation of hydrogen atoms. The formed CO<sub>2</sub> radical anion (CO<sub>2</sub><sup>\*-</sup>) captures a nearby hydrogen atoms forming formate via carboxylate:

$$\mathrm{CO}_{2(\mathrm{CoO})}^{*-} + \mathrm{H}_{(\mathrm{Pt})} \to \mathrm{HCOO}_{(\mathrm{Pt}/\mathrm{CoO})}^{-} \tag{4}$$

This reaction step was supposed on supported noble metals, probably it occurs at metal/oxide interface.<sup>17,18</sup> This formate species may reacts and decomposes further forming methane<sup>12</sup> or CO.<sup>18,20</sup>

$$2H_{(g)} + O_{(Pt)} \rightarrow H_2O_{(g)} \qquad \text{Deliv}(3) \text{d by Ingent} HCOO^-_{(Pt/CO)} + H_{(Pt)} \rightarrow CH_{4(g)} + H_2O_{(CoO)} \qquad (5)$$

When the reducible oxide is the catalysts support, the reaction mechanism could be different, although the above-mentioned mechanism could be also valid in certain  $HCOO_{(Pt/CO)}^{-} + H_{(Pt)} \rightarrow CO_{(Pt)} + H_2O_{(CoO)}$ (6)

$$\mathrm{HCOO}^{-}_{(\mathrm{Pt/CO})} \to \mathrm{CO}_{(\mathrm{Pt})} + \mathrm{OH}^{-}_{(\mathrm{CoO})} \tag{7}$$



Figure 3. Effect of support in the hydrogenation of  $CO_2$  on Pt anchored Merck  $Co_3O_4$ , mesoporous  $Co_3O_4$  and SBA-15 catalysts. Conversion (A), formation rate of methane (B) and carbon-monoxide (C).

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Figure 4. Selectivity values of the products in the  $CO_2 + H_2$  reaction on different Pt promoted catalysts at 673 K.

The product distribution obtained on  $Pt/Co_3O_4$  suggests that Step 5 is dominant at low temperatures while the CO formation mechanism (Steps 6 and 7) are favorable at higher temperatures. The CH<sub>4</sub> formation via formate hydrogenation may involve the hydrogenation of adsorbed carbonyl.

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supported noble metals, probably it occurs at metal/oxide interface, at Pt-CoO in present case. Finally, it was proved that the controlled size Pt nanoparticles on a mesoporous material as a designed catalyst, was more efficient in the same catalytic reaction, than the prepared by the classic method. The authors assume that the catalyst design is an essential step in the future of the heterogeneous catalysis.

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#### **References and Notes**

1. W. Wang, S. Wang, X. Ma, and J. Gong, *Chem. Soc. Rev.* 40, 3703 (2011). 2018 01:46:37

## 4. CONCLUSION

Controlled size Pt nanoparticles were synthesized by a polyol method using ethylene glycol as a media and PVP as a capping agent from Pt-salts.  $3.6 \pm 1.25$  nm Pt nanoparticles were obtained where the particles have narrow size distributions as well as spherical shape. Pt nanoparticles were supported on SBA-15, on mesoporous cobalt-oxide and on commercial Co<sub>3</sub>O<sub>4</sub> with impregnation method. Exclusively almost CO was formed on Pt/SBA-15 during CO<sub>2</sub> dehydrogenation. In contrast, on Pt supported on mesoporous Co<sub>3</sub>O<sub>4</sub> large amount of methane was formed at low temperature (570-600 K). When the temperature was raised the methane formation decreased and CO production increased. The different product distributions on Pt/SBA-15 and Pt/Co<sub>3</sub>O<sub>4</sub> suppose different reaction mechanisms in carbon-dioxide hydrogenation. Based on the reaction products (CO and water) on Pt/SBA-15 we propose the reverse water-gas shift reaction mechanism in first approximation. When the reducible oxide  $(Co_3O_4)$  is the catalysts support, the reaction mechanism could be different, although the above-mentioned mechanism could be also valid in certain extent. We suppose that formate species is an important reaction intermediate. This formate species may reacts and decomposes further forming methane or CO. This reaction step is supposed on

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- 3. C. Schild, A. Wokaun, and A. Baiker, J. Mol. Catal. 63, 243 (1990).
- 4. I. A. Fisher and A. T. Bell, J. Catal. 162, 54 (1996).
- 5. X. Wang, H. Shi, J. H. Kwak, and J. Szanyi, ACS Catal. 5, 6337
- (2015). 6. S. Rönsch, J. Schneider, S. Matthischke, M. Schlüter, M. Götz,
- J. Lefebvre, P. Prabhakaran, and S. Bajohr, *Fuel* 166, 276 (2016).
- 7. F. Solymosi, J. Mol. Catal. 65, 337 (1991).
- 8. H. J. Freund and M. W. Roberts, Surf. Sci. Rep. 25, 225 (1996).
- N. M. Dimitrijevic, B. K. Vijayan, O. G. Pouektov, T. Rajh, K. A. Gray, H. He, and P. Zapol, J. Am. Chem. Soc. 133, 3964 (2011).
- H. Narayanan, B. Viswanathan, and S. Yesodharan, *Curr. Catal.* 5, 79 (2016).
- Gy. Halasi, A. Gazsi, T. Bánsági, and F. Solymosi, *Appl. Catal. A Gen.* 506, 85 (2015).
- 12. F. Solymosi, A. Erdőhelyi, and T. Bánsági, J. Catal. 68, 371 (1981).
- 13. S. Kattel, B. Yan, J. G. Chen, and P. Liu, J. Catal. 343, 115 (2016).
- K. An, S. Alayoglu, N. Musselwhite, S. Plamthottam, G. Melaet, E. Lindeman, and G. Somorjai, J. Am. Chem. Soc. 135, 16689 (2013).
- B. Ouyang, S. Xiong, Y. Zhang, B. Liu, and J. Li, *Applied Catal. A Gen.* 543, 189 (2017).
- A. Sápi, D. G. Dobó, D. Sebők, Gy. Halasi, K. L. Juhász, A. Szamosvölgyi, P. Pusztai, E. Varga, I. Kálomista, G. Galbács, A. Kukovecz, and Z. Kónya, J. Phys. Chem. C 121, 5130 (2017).
- F. Solymosi, A. Erdőhelyi, and T. Bánsági, J. Chem. Soc. Faraday Trans. 77, 2645 (1981).
- 18. X. Wang, Y. Hong, H. Shi, and J. Szanyi, J. Catal. 343, 185 (2016).
- 19. X. Wang, H. Shi, and J. Szanvi, Nature Comm. 8, 513 (2017).
- 20. J. Raskó, T. Kecskés, and J. Kiss, J. Catal. 226, 183 (2004).

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