

Short communication

## Identification of step-edge sites on Rh nanoparticles for facile CO dissociation



D.A.J. Michel Ligthart, Ivo A.W. Filot, Abdulkarim A.H. Almutairi, Emiel J.M. Hensen\*

Schuit Institute of Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

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## ABSTRACT

Understanding the dependence of the rate of catalytic reactions on metal nanoparticle size remains one of the great challenges in heterogeneous catalysis. Especially, methods to probe step-edge sites on technical supported nanoparticle catalysts are needed to put structure–activity relations on a surer footing. Herein, we demonstrate that N<sub>2</sub> is a useful IR probe for the semi-quantitative identification of step-edge sites on zirconia-supported metallic Rh nanoparticles. The intensity of the strongly perturbed band at 2205 cm<sup>-1</sup> correlates with the CO bond dissociation rate under conditions relevant to the Fischer–Tropsch reaction. Due to the intermediate reactivity of Rh, step-edge sites are required to dissociate the strong CO bond. DFT calculations show that N<sub>2</sub> prefers to adsorb on top of low-coordinated surface atoms such as steps, corners and edges. The occurrence of the intensity maximum at intermediate particle size is explained by the presence of surface overlayers on terraces that give rise to step-edges. These step-edge sites are important in the dissociation of di-atomic molecules such as CO, NO and N<sub>2</sub>.

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### 1. Introduction

Supported metal nanoparticles are among the most used heterogeneous catalysts for important reactions such as steam methane reforming, ammonia synthesis, automotive exhaust gas clean-up and Fischer–Tropsch synthesis. Understanding the dependence of the rate of catalytic reactions on metal nanoparticle size remains one of the great challenges in heterogeneous catalysis [1–5]. Nanoparticles expose terraces, edges, corners, kinks and atomic steps. The different degree of coordinative unsaturation of these surface atoms leads to variations in chemical reactivity. Quantum-chemical calculations provide insight into the dependence of particular elementary reaction steps on surface topology. For the cleavage of  $\sigma$ -bonds (e.g. C–H bonds in CH<sub>4</sub>), low-coordinated corner and edge atoms are necessary [4–7]. Dissociation of molecules with strong  $\pi$ -bonds (CO, NO and N<sub>2</sub>) is favored on step-edge sites because of the favorable geometry that relates to the strong overlap of the transition metal *d*-orbitals with the molecular  $\pi$ -bonds and the absence of surface metal atom sharing with the dissociating fragments in the transition state [4,5,8]. Below a critical size, nanoparticles do not contain step-edges and they will only expose terrace, edge and corner atoms [9,10]. The highest density of step-edge sites will therefore occur on particles of intermediate size and the surface of large particles is dominated by terraces. A case in point of structure sensitivity of considerable commercial interest is the Fischer–Tropsch

reaction, which employs metal nanoparticles to convert synthesis gas into transportation fuels and chemicals [11–13]. Step-edge sites are presumed to be the reaction centers for the dissociation of the carbon–oxygen bond in CO, which is one of the important steps in the overall Fischer–Tropsch reaction [14–16]. The strong dependence of CO conversion rate on metal nanoparticle size has been argued to relate to variation in the density of step-edge sites at the nanoparticle surface [9,14,17,18], yet convincing evidence for this assertion is lacking.

Important contributions to the structure sensitivity issue in heterogeneous catalysis mainly derive from single crystal surface science studies. Ertl and co-workers convincingly demonstrated that step-edge sites on single-crystal surfaces are the reaction centers for NO dissociation [1]. Nørskov and co-workers proved that N<sub>2</sub> dissociation also occurs on step-edge Ru sites [2]. While enumeration of step-edge sites on single-crystal models is straightforward, identification of step-edge sites on nanoparticles in technical catalysts is not possible yet. The earliest suggestion that steps at the nanoparticle surface are important for the activation of small molecules was made by Van Hardeveld and Van Montfoort [19,20]. Based on the strong perturbation of the N–N bond in of adsorbed N<sub>2</sub> on Ni, Pd and Pt nanoparticles observed in IR spectra, the authors claimed that the nanoparticle surface contains ensembles of surface atoms arranged in the form of a step. This unique B<sub>5</sub> step-edge site comprises five surface metal atoms. Based on geometric considerations, Van Hardeveld concluded that B<sub>5</sub> sites occur most frequently on the surface of ~2 nm particles [19,21,22]. This interpretation is supported by work of others [23,24].

In this work, we demonstrate that N<sub>2</sub> can be used as a semi-quantitative IR probe for coordinatively unsaturated sites that are a

\* Corresponding author at: Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands.

E-mail address: [e.j.m.hensen@tue.nl](mailto:e.j.m.hensen@tue.nl) (E.J.M. Hensen).

part of these step-edge sites. The choice for Rh in this study derives from the large activation barrier difference for CO dissociation on step-edge ( $\sim 167$  kJ/mol) and planar surfaces (300 kJ/mol) [5,8,25]. Accordingly, we expect the rate of CO dissociation on Rh nanoparticles to be proportional to the step-edge site density. As compared with Co and Fe that mainly produce long-chain hydrocarbons in the Fischer–Tropsch reaction, the use of Rh is interesting because in this way also oxygenates can be obtained [26]. Herein, we seek to correlate the IR intensity of  $N_2$  molecules perturbed by step-edge sites to the CO dissociation rate. We use a set of zirconia-supported Rh catalysts, which have been used before in studying the structure sensitivity in steam methane reforming [7]. The interpretation of the IR spectra is supported by DFT calculations of  $N_2$  adsorption on various Rh model surfaces.

## 2. Results and discussion

ZrO<sub>2</sub>-supported Rh nanoparticles were prepared by incipient wetness impregnation of Rh-nitrate on zirconia [7]. The Rh particle size was varied by changing the calcination temperature of the support, the Rh loading and the calcination/aging procedure of the final catalyst (see Table S1 in Supplementary material). In this way, a set of Rh nanoparticle catalysts was obtained comprising nanoparticles in the 1–8 nm range stabilized by a monoclinic zirconia support. Some of these catalysts were taken from earlier work, where it was shown that the conversion rate during steam methane reforming correlates linearly with Rh dispersion [7]. This is because C–H bond activation in CH<sub>4</sub> occurs on reactive single surface metal atoms.

Fig. 1 shows very different particle dependence of the CO dissociation rate during syngas conversion. Catalytic performance data including the product distribution for representative catalysts are given in Table 1. Methane is the main hydrocarbon product with only small amounts of higher hydrocarbons (C<sub>2+</sub>). In line with literature [27–31], Rh also catalyzes the formation of methanol and higher oxygenates. The alcohols selectivity can be improved by the use of promoters. The turnover frequency (TOF) for CO dissociation was determined on the

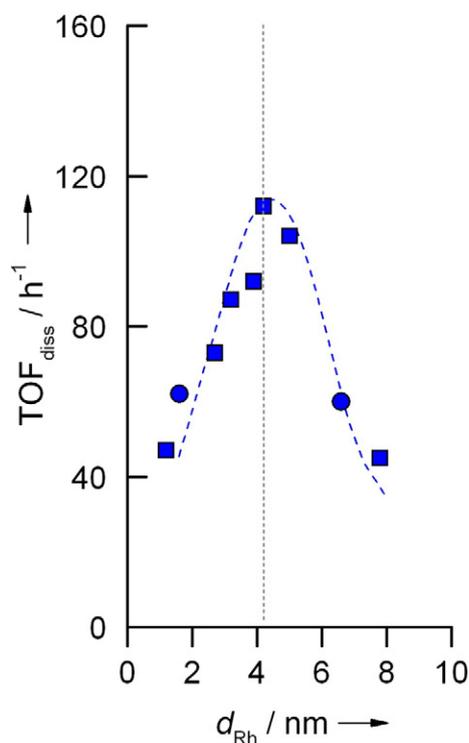


Fig. 1. Turnover frequency for CO dissociation during syngas conversion ( $T = 275$  °C,  $P = 20$  bar,  $H_2/CO = 2$ ) on Rh/ZrO<sub>2</sub> (cubes: newly prepared catalysts; circles: catalysts from Ref. [18]) as function of particle size ( $d_{Rh}$ ).

Table 1

Catalytic performance data on Rh/ZrO<sub>2</sub> ( $T = 275$  °C,  $P = 20$  bar,  $H_2/CO = 2$ ).

$d_{Rh}^a$ [nm]	$d_{Rh}^b$ [nm]	TOF <sub>diss</sub> [h <sup>-1</sup> ]	S <sub>CH4</sub> [%]	S <sub>C2+</sub> [%]	S <sub>MeOH</sub> [%]	S <sub>C2-O</sub> <sup>c</sup> [%]
1.5	n.d.	63	63	6	6	23
3.9	3.3	92	58	9	5	26
4.7	4.2	112	58	4	5	31
n.d.	6.6	60	57	8	4	30
n.d.	7.8	45	66	7	5	22

<sup>a</sup> H<sub>2</sub> chemisorption.

<sup>b</sup> TEM.

<sup>c</sup> S<sub>C2-O</sub>: selectivity ethanol, acetaldehyde and ethylacetate.

basis of the number of dissociated CO molecules. Fig. 1 shows that the catalyst containing on average  $\sim 4$  nm Rh particles displayed maximum CO conversion rate. The C<sub>2</sub>-oxygenates selectivity correlates with the CO dissociation rate, which is likely due to the importance of surface coupling reaction between CH<sub>x</sub>, obtained by CO dissociation, and CO for C<sub>2</sub>-oxygenates formation.

Representative IR spectra of adsorbed N<sub>2</sub> at 90 K for the ZrO<sub>2</sub> support, calcined Rh/ZrO<sub>2</sub> and reduced Rh/ZrO<sub>2</sub> are given in Fig. 2a. N<sub>2</sub> adsorption on ZrO<sub>2</sub> results in a very weakly perturbed band at 2341 cm<sup>-1</sup> (fundamental stretching frequency of gas-phase N<sub>2</sub> = 2359 cm<sup>-1</sup>). The IR spectrum of calcined Rh/ZrO<sub>2</sub> contains an additional band at 2293 cm<sup>-1</sup> due to perturbation of N<sub>2</sub> by Rh cations in the calcined Rh-oxide precursor [31–33]. In reduced Rh/ZrO<sub>2</sub>, this band is absent and, instead, an intense strongly perturbed band at 2205 cm<sup>-1</sup> is observed. Based on its location, we conclude that this band is similar in nature to the bands observed for N<sub>2</sub> adsorbed on Ni, Pt and Pd nanoparticles by Van Hardeveld and Van Montfoort [19,20]. A recent study of Dillinger et al. reveals IR frequencies in the 2180 to 2290 cm<sup>-1</sup> range for N<sub>2</sub> adsorbed on size-selected Co clusters [34]. Fig. 2b shows the intensity of the perturbed adsorbed N<sub>2</sub> IR band at 2205 cm<sup>-1</sup> as a function of Rh nanoparticle size in reduced Rh/ZrO<sub>2</sub> catalysts. The reasonable correlation between CO dissociation rate and the adsorbed N<sub>2</sub> IR intensity indicates that IR spectroscopy of adsorbed N<sub>2</sub> may be used to probe sites for CO dissociation.

To verify whether the 2205 cm<sup>-1</sup> band can be directly linked to step-edge sites, we investigated by DFT the adsorption of N<sub>2</sub> on three different Rh model systems: tetrahedral Rh<sub>10</sub> and Rh<sub>20</sub> clusters and a stepped Rh(211) surface. These three systems were chosen, because they contain a variety of low-coordinated corner and edge sites (Rh<sub>10</sub> and Rh<sub>20</sub> clusters) as well as step, step-edge and terrace sites on the Rh(211) surface. N<sub>2</sub> was adsorbed on different adsorption sites. For the stable geometries, the N–N stretching frequencies and intensities were calculated. Table 2 lists adsorption energies, stretching frequencies and intensities. All structures are shown in Fig. 3.

Except for the more reactive Rh<sub>10</sub> cluster, N<sub>2</sub> adsorption in three-fold sites on the terrace surfaces was not stable and N<sub>2</sub> was found to migrate to top positions during geometry optimization. For the stepped surface, N<sub>2</sub> was initially adsorbed in the three-fold position on the terrace site behind the step-edge site. This configuration was not stable and, in this case, N<sub>2</sub> preferred location on top of the Rh step atom, presumably because it has a lower coordination number than the terrace atoms. The stretching frequency of top adsorbed N<sub>2</sub> was in the 2195–2216 cm<sup>-1</sup> range for all considered models.

The strong top adsorption of N<sub>2</sub> results in high computed IR intensities. For the Rh<sub>20</sub> model, we compared top adsorption of N<sub>2</sub> on surface metal atoms with coordination numbers of 3 and 9. The adsorption and the intensity were higher when N<sub>2</sub> was top-adsorbed to a Rh atom with a coordination number of 3. The N–N stretching frequencies were 2195 cm<sup>-1</sup> and 2212 cm<sup>-1</sup>, respectively.

Bridge adsorption resulted in a stronger IR shift due to increased back-donation of metal *d*-electrons into antibonding 2π\* orbitals of N<sub>2</sub>. Decreased surface metal atom reactivity for increasing size of the surface model explains the lower N<sub>2</sub> adsorption energies. The lower reactivity of the surface metal atoms, which results in increased electron

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