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Rhodium Nanoparticle Shape Dependence in the Reduction of NO by CO

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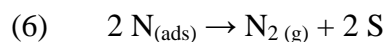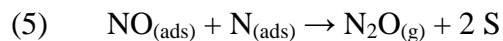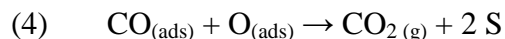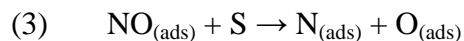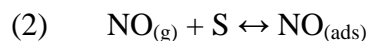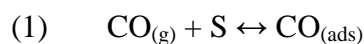
Abstract

The shape dependence of the catalytic reduction of NO by CO on Rhodium nanopolyhedra and nanocubes was studied from 230 – 270°C. The nanocubes are found to exhibit higher turnover frequency and lower activation energy than the nanopolyhedra. These trends are compared to previous studies on Rh single crystals.

Introduction

In recent years, intense efforts have been directed towards the development of a molecular understanding of the role of nanoparticle properties such as size, structure, and composition on catalytic activity and selectivity[1, 2]. Nanoparticle shape, in particular, has been demonstrated to play an important role in catalysis[3-8]. The role of shape is thought to be closely related to the role of structure-sensitivity in catalysis. As an example, a study of benzene hydrogenation on ~12-13 nm Pt nanoparticles found that both cyclohexene and cyclohexane were formed on cuboctahedral nanoparticles, which are dominated by 111-faces, whereas only cyclohexane was formed on 100-dominated cubic nanoparticles[5]. These selectivities were consistent with previous results on (111) and (100) Pt single crystals[9, 10]. Nanoparticle shape was also shown to play an important role in selectivity in pyrrole hydrogenation on Pt nanopolyhedra and nanocubes[4]. This study found that although *n*-butylamine was the dominant product for both 5 and 9 nm Pt nanocubes regardless of temperature, both pyrrolidine and *n*-butylamine were formed on 5 nm Pt nanopolyhedra. These studies demonstrate the importance of the role of nanoparticle shape in catalysis and, in particular, the importance of characterizing this role in relation to single crystal studies on structure-sensitive reactions.

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The reaction studied here, the catalytic reduction of Nitric Oxide (NO) by Carbon Monoxide (CO) on Rhodium metal, is extremely important because of its role in the three-way catalytic converter used in automobile exhaust systems[11]. The reaction proceeds much faster on Rh than on Pd or Pt[12] and is known to be structure sensitive on Rh single crystals[13]. The products of the reaction are CO_2 at all temperatures, N_2O primarily (~75%) at the lower (< 320°C) temperatures investigated in this study, and N_2 primarily at higher temperatures (> 320 °C)[12]. Although many mechanisms have been proposed for this reaction[14-20], it remains an open area of investigation[21, 22] due to its enormous complexity. One relatively simple model, proposed by Permana et al.[23], is as follows, where S refers to an available surface site:

(1) $CO_{(g)} + S \leftrightarrow CO_{(ads)}$

(2) $NO_{(g)} + S \leftrightarrow NO_{(ads)}$

(3) $NO_{(ads)} + S \rightarrow N_{(ads)} + O_{(ads)}$

(4) $CO_{(ads)} + O_{(ads)} \rightarrow CO_{2\ (g)} + 2\ S$

(5) $NO_{(ads)} + N_{(ads)} \rightarrow N_2O_{(g)} + 2\ S$

(6) $2\ N_{(ads)} \rightarrow N_{2\ (g)} + 2\ S$

More detailed models, such as that proposed by Chuang and Tan[24], account for the role of Rh oxidation in the reaction, which is very important in strongly oxidizing conditions and for smaller, more easily oxidized catalysts. Other models, such as that proposed by Avalos et al., account for experimental evidence of N-island formation[25] and concerns that Step (6), above, may be too slow to adequately account for N_2 production during reaction. In light of this, these authors suggest that the decomposition of an intermediate surface species, N-NO, is responsible for N_2 formation during the reaction. Much work has also been done to elucidate the role of

nanoparticle size on this reaction[26-28]. Oh and Eickel, for example, found that increased Rh particle size leads to a significant increase in turnover frequency, a decrease in calculated activation energy, and no significant effect on selectivity[26]. The role of nanoparticle shape in the NO-CO reaction, however, has not yet been addressed. This paper reports results of a study on the role of nanoparticle shape in this reaction. Rh nanopolyhedra and nanocubes were synthesized, characterized, and studied in reaction conditions similar to those used in previous studies on Rh single crystals[14, 17, 23]. Our results show a clear shape-dependence for the NO-CO reaction at low temperatures (230-270°C) based on observed differences in turnover frequency and activation energy on the Rh nanopolyhedra and Rh nanocube catalysts.

Experimental Details

Rh NPs of (111)-oriented nanopolyhedra[29] and (100)-oriented nanocubes[30] were synthesized using two similar techniques, both of which have been published previously. In brief, to make the nanopolyhedra, 0.00625 mmol $[Rh(Ac)_2]_2$ and 0.25 mmol poly(vinylpyrrolidone) (Mw = 55,000, in terms of the repeating unit) were added to 20 ml ethylene glycol in a 50 ml three-necked flask at room temperature. The solution was then heated to 100 °C and degassed for 20 min under vacuum while stirring, resulting in a green solution. The flask was then heated to 185 °C at 10 °C min-1, and maintained at this temperature for 2 h under Ar. When the reaction was complete, an excess of acetone was added at room temperature and the resulting Rh nanopolyhedra were separated by centrifugation and washed twice by precipitation/dispersion[29].

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The procedure used to synthesize Rh nanocubes was similar to that used to synthesize Rh nanopolyhedra, except that 0.2 mmol $RhCl_3$, 1 mmol tetramethylammonium bromide, and 4 mmol poly(vinylpyrrolidone) (Mw = 24,000, in terms of the repeating unit) were added to 20 ml ethylene glycol in a 50 ml three-necked flask at room temperature, which was evacuated at 80 °C for 20 min, and heated at 185 °C for 1.5 h[30]. Both the nanopolyhedra and nanocube samples were subsequently deposited onto 1 x 1 cm^2 pieces of Si wafer using the Langmuir-Blodgett technique, which has been described previously[29].

The shape, size, and lattice structure of the Rh nanocrystals were analyzed using a Philips FEI Tecnai 12 Transmission electron microscope (TEM) and Philips CM200/FEG high-resolution TEM (HRTEM), operated at 100 and 200 kV, respectively. Analysis of at least 50 particles from each synthesis determined that the sizes of the two types of nanoparticle catalysts are comparable, with the nanopolyhedra measuring approximately 6.5 ± 0.6 nm in diameter and the nanocubes measuring approximately 6.2 ± 0.6 nm in diameter, as shown in Figure 1. Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 GADDS diffractometer using Co-Kα radiation (λ = 1.79 Å). Both TEM and XRD indicated that the nanopolyhedra have predominantly (111) surface sites, whereas the nanocubes have predominantly (100) surface sites. The presence of some (111) and (220)-oriented sites in the XRD is likely due to a combination of defects in the nanoparticles and, especially for the (111) peak, the sensitivity of XRD to bulk crystallinity in addition to surface orientation. Sample coverage, uniformity, and aggregation were checked before and after reaction using a Zeiss Ultra 55 Field Emission Scanning Electron Microscope. No significant surface melting or particle aggregation was observed within the limits of detection of SEM for nanoparticles subjected to a reaction

temperature of 270°C. Nanoparticles subjected to higher reaction temperatures typically showed evidence of melting and aggregation. Prior to reaction, particles were difficult to image, presumably due to the PVP capping layer, which may have been partially removed during reaction[31].

Reaction studies were performed in batch mode with 8 torr NO, 8 torr CO, and 744 torr He in a 1 L ultrahigh vacuum chamber with a base pressure of $1.0 \times 10-8$ Torr. These reactant pressures were chosen in order to be consistent with conditions used for high-pressure single crystal studies [14, 17, 23]. Sample temperature was measured with a Type-K thermocouple mounted on a 8 mm^2 piece of blank Si wafer on the same ceramic button heater (Momentive) used to heat the sample. Products were measured with an HP Series II gas chromatograph equipped with a thermal conductivity detector and separated with two columns in parallel – a 1 m x 1/8" 60/80 Argon sieve (Supelco) to separate N_2, NO, and CO, and a 3 m x 1/8" 100/120 Hayesep D (Supelco) to separate N_2O and CO_2. The reaction was carried out multiple times over fresh samples of each catalyst. The reaction temperature was kept between 230 and 270°C to ensure that product formation was fast enough for accurate measurement and that the nanoparticles did not aggregate or sinter significantly. Data gathered above the 270°C threshold was not reliable and is not reported here. Turnover frequency at each temperature was determined over the course of 3 hours. No significant deactivation was detected. The measured reaction rates are reported as turnover frequencies (TOF) and are measured in units of product molecules per metal surface site per second. The number of surface sites was determined from SEM images taken from randomly-selected areas of the sample, analyzed with conventional image processing software to determine nanoparticle coverage, and converted into surface sites

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based purely on geometrical considerations. This method is intended to calculate the total

number of surface sites and cannot account for site blocking by the PVP capping agent or other

means. Consequently, the results presented here are overestimates of the number of active

reaction sites and thus underestimate the true turnover frequency. It is also possible that some

PVP capping agent is removed during reaction[31], which could result in an increased number of

active reaction sites at high temperature. Previous studies have established the difficulty of

determining truly exact turnover numbers and the importance of qualitative analysis of turnover

frequencies even on comparatively stable samples in the same reaction system[32-34].

Results and Discussion

The turnover frequencies (TOF) for CO_2, N_2O, and N_2 formation for the Rh

nanopolyhedra and Rh nanocube catalysts are reported in Figure 3. The activation energies as

calculated from the accumulation of each product from 230 - 270°C are presented in Table 1 for

both the nanopolyhedra and nanocube catalysts, as compared to single crystal data taken at

similar temperatures and pressures[13, 17]. The measured turnover frequencies were higher for

the nanocube catalysts than for the nanopolyhedra catalysts at all temperatures. The measured

activation energies of the products from the reaction on the Rh nanopolyhedra catalysts were

37.0 ± 3.3, 39.3 ± 4.3, and 26.6 ± 3.7 kcal/mol for CO_2, N_2O, and N_2 formation, respectively.

The activation energies of the products from the reaction on the Rh nanocube catalysts were 28.4

± 1.6, 30.6 ± 4.5, and 22.0 ± 3.1 kcal/mol, for CO_2, N_2O, and N_2 formation. The selectivity for

N_2O versus N_2 was similar for both catalysts and increased with temperature, from ~70% N_2O at

230°C to ~84% N_2O at 270°C. Both catalysts produced primarily N_2O in this temperature range.

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The Rh nanopolyhedra and Rh nanocubes compare well to trends in Rh single crystals studied at similar pressures. Previous reports in this temperature range have found higher turnover frequencies for Rh (100) single crystals than for Rh (111) single crystals[13, 17]. Both Rh (100) and Rh (111) single crystals are strongly selective towards N_2O in this temperature range[13, 17]. The similarities in the trends between these single crystal results and the shape-dependent results presented here for (111)-dominated nanopolyhedra and (100)-dominated nanocubes indicate that the effect of surface structure on turnover frequency and selectivity is similar in both nanoparticle and single crystal regimes. Evidence from measured activation energies, however, implies more complexity, as shown in Table 1. Although the activation energies for CO_2 and N_2O formation on the nanopolyhedra catalysts are similar to those previously reported for this reaction on Rh (111) single crystals[17], the measured activation energies for CO_2 and N_2O formation on the nanocube catalysts are intermediate to the two separate temperature regimes reported previously on Rh (100) single crystals[13]. Rh (100) single crystals have been reported to feature both a low temperature regime with higher activation energies for all products and a high temperature regime with lower activation energies for all products starting at about 315°C[13, 15]. Herman et al. attributed this breakpoint to a higher coverage of adsorbed N and adsorbed NO species on the (100) surface at lower temperatures and a consequent shortage of available sites for NO dissociation, a shortage which is alleviated at high temperatures to the extent that the rate of NO dissociation begins to limit the reaction rather than the availability of sites[13] The activation energy measured for N_2 formation on both the nanopolyhedra and nanocube catalysts was lower than that reported on single crystals[13], as reported in Table 1. This may be due to the increased selectivity towards N_2O

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observed in the nanoparticle catalysts. In addition to the effect of NO adsorption and dissociation site availability, another possible explanation for the intermediate activation energies found for the nanocubes is that the small size of the nanoparticles leads to different kinetics than for (100) single crystals. In this case, the observed differences could be attributed to the role of Rh oxide in catalytic reactivity[24, 35, 36], because relatively small transition metal nanoparticles develop stable oxides at lower temperatures than single crystals[37], which may amplify the effect of differences in the oxidation of Rh (111) and Rh (100)[38] on the catalytic reactivity of the 6.2 nm nanocubes and 6.5 nm nanopolyhedra.

Surface reconstruction and rearrangement is also a possible cause of the intermediate activation energies measured on the cubic nanoparticles, as single crystals are well-known to reconstruct at elevated temperatures and pressures[39] and nanoparticle surface melting is a growing part of present day inquiry[40]. Surface reconstruction is also known to be effected by surface oxidation in some cases[36], a phenomenon which may be important in the system investigated in this work. Although not presented in detail here, some experimental evidence during reaction above 270°C and subsequent re-reaction at lower temperatures on the same Rh nanocube sample suggested surface reconstruction and a shift towards (111)-like kinetics in the nanocubes which did not occur for the nanopolyhedra, which were already in the low surface energy (111) surface atom arrangement. In this case it is possible that the intermediate activation energies reported for the cubic nanocatalysts may have been a result of temperature-dependent surface reconstruction and the measurement of a temperature regime either intermediate to or inclusive of two separate crystal-face regimes – a (100)-dominated low temperature regime and a (111)-dominated post-melting high temperature regime. Further work is required to fully

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understand the role of surface reconstruction in structure sensitive catalytic reactions on shape-controlled nanoparticles.

The differences in the overall catalytic activity between the nanopolyhedra and nanocubes are likely due to several mechanistic differences in the reaction between NO and CO on Rh (100) and Rh (111) [13-15, 17, 19, 21-23, 25, 41-46]. In summary, the reaction between CO and O is faster and the products of NO dissociation have a higher heat of adsorption on the (100) surface than on the (111) surface[41]. These differences mean that CO_2 formation and NO dissociation are faster on (100) surfaces at low temperatures, which leads to higher turnover frequencies for all products on (100) surfaces at relatively low temperatures. As temperature increases, however, the accumulation of strongly bound N leads to a lower rate of N_2 formation and desorption, which eventually leads to site blocking and a greater degree of lateral interactions with coadsorbed species[46]. When the temperature is high enough (~320°C on the (100) single crystal), N_2 is formed more easily and there is an abrupt change in selectivity towards N_2 which also affects the formation of the other products[13].

Conclusions

The study of the role of shape is important to the understanding and development of new nanocatalysts for future applications. In this study, we showed a relationship between nanoparticle shape and catalytic properties for the reduction of NO by CO. We synthesized PVP-capped 6.5 nm nanopolyhedra and 6.2 nm rhodium nanocubes and deposited them evenly across silicon wafers using the Langmuir-Blodgett technique. We then characterized the nanoparticles with TEM, XRD, and SEM, and studied their behavior in the NO + CO reaction. Our study

found that nanocubes show higher turnover frequency and lower activation energies for all products and similar selectivity toward N_2O between 230 and 270°C as compared to nanopolyhedra due to the differences in surface structure. The activation energies for product formation on the Rh nanopolyhedra was found to be comparable to previous reports on Rh (111) single crystals, whereas the activation energies measured on the Rh nanocubes were found to be intermediate to those previously reported for two temperature regimes studied on Rh (100) single crystals. This study clearly shows that nanoparticle shape has an important effect on the reduction of NO by CO at low temperatures and implies that nanoparticle shape is an important criterion in the development of nanocatalysts for a wide range of structure-sensitive heterogeneous catalytic reactions.

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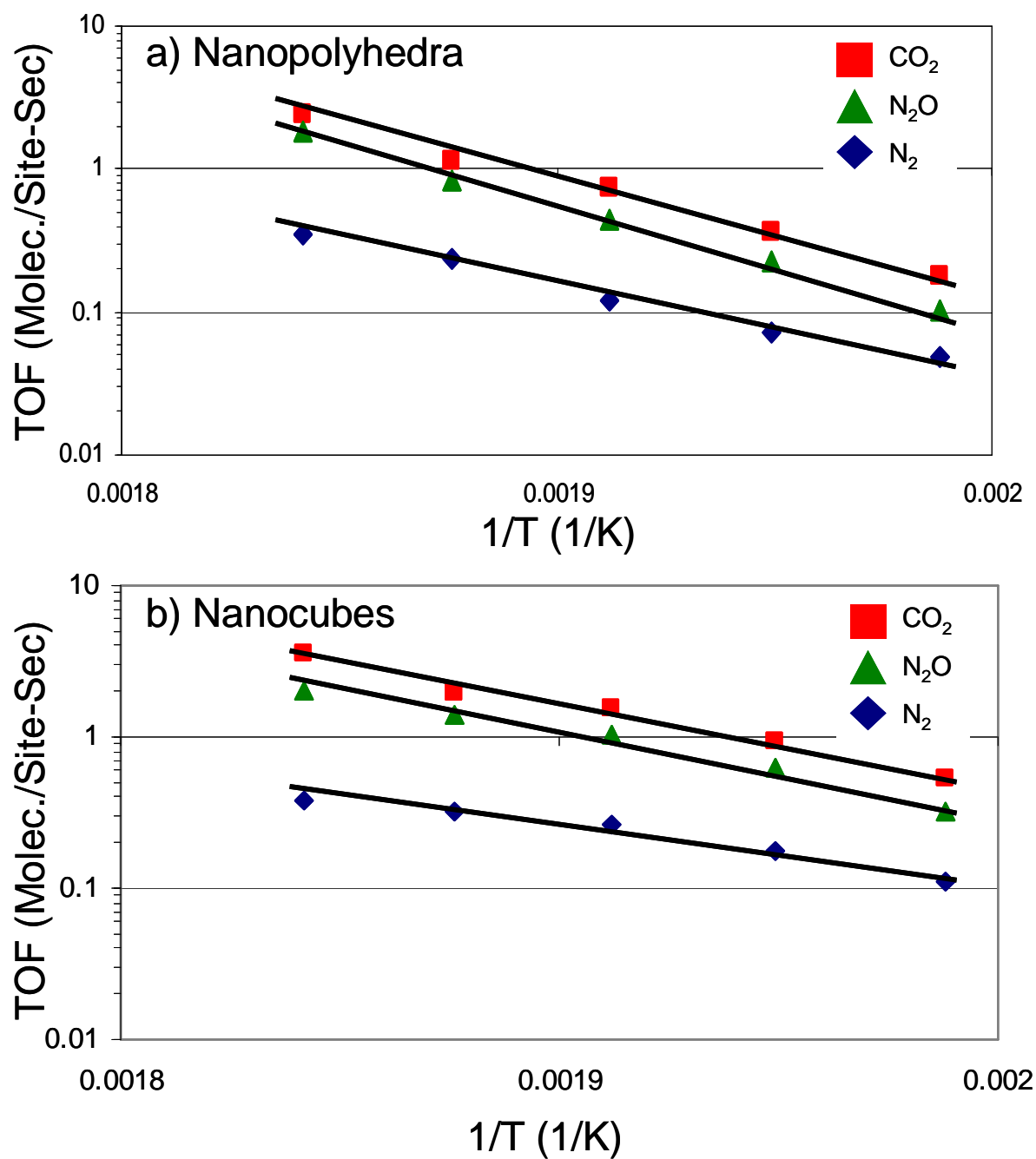
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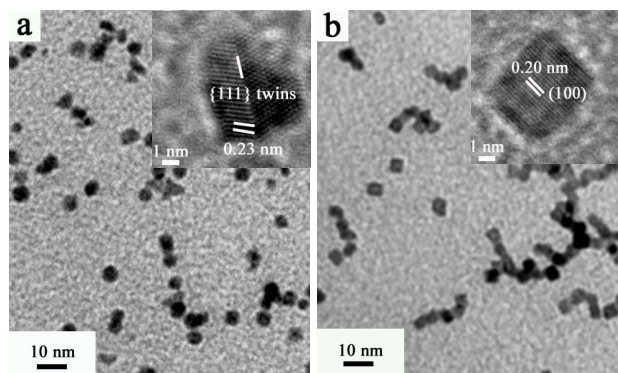
Figure 1. TEM images of (a) 6.5 nm Rh nanopolyhedra, and (b) 6.2 nm Rh nanocube catalysts.

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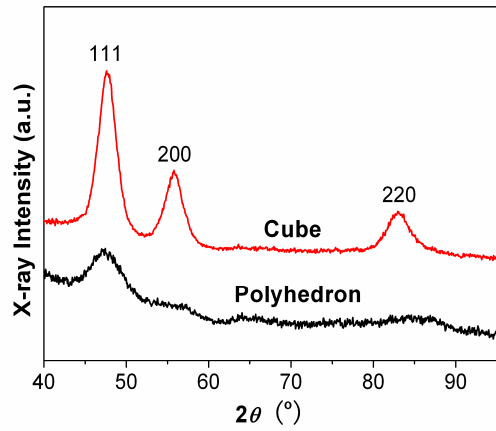
Figure 2. XRD of Rh nanopolyhedra and nanocube catalysts.

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Figure 3. CO_2, N_2O, and N_2 turnover frequencies of a) Rh nanopolyhedra and b) Rh nanocube catalysts as a function of inverse temperature.

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	CO_2 E_a	N_2O E_a	N_2 E_a	Selectivity
Nanopolyhedra[a]	37.0 ± 3.3	39.3 ± 4.3	26.6 ± 3.7	84%
Nanocubes[a,]	28.4 ± 1.6	30.6 ± 4.5	22.0 ± 3.1	84%
Rh (111)[17]	34.2	35.7	32.1	~72%[b]
Rh (100) LT[13]	35.0	35.8	33.8	~64%[b]
Rh (100) HT[13]	22.2	15.3	26.2	

[a] E_a (kcal/mol) measured from 230 - 270°C

b Estimated from published results

Table 1. Apparent activation energies (E_a, kcal/mol) for CO_2, N_2O, and N_2 and selectivity toward N_2O (where Selectivity = $N_2O/(N_2O + N_2)$ * 100%) at 270°C for the NO-CO reaction at 8 torr NO and 8 torr CO over Rh nanopolyhedra, Rh nanocube, Rh (111) single crystal, and Rh (100) single crystal catalysts. Single crystal values are as reported previously[13, 17]. LT refers to a temperature range of ~255 - 320°C and HT refers to a range of ~320 - 400°C.

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