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Potassium Dispersion on Silica-Supported Ruthenium Catalysts

T. EDDY HOOST[1] AND JAMES G. GOODWIN, JR.[2]

Chemical and Petroleum Engineering Department, University of Pittsburgh, Pittsburgh, Pennsylvania 15261

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Alkali modifiers are known to be quite effective at improving catalyst activity or selectivity for several metal-catalyzed reactions of industrial importance. Yet it is still difficult to address the location and distribution of alkali species in most catalysts. This paper reports on an investigation of the potassium dispersion in a series of 3 wt% Ru/SiO_2 catalysts sequentially doped with potassium nitrate up to $(K/Ru)_{atom} = 0.2$ followed by rereduction. This series was evaluated extensively using gas volumetric hydrogen chemisorption and the structure-sensitive ethane hydrogenolysis reaction. Hydrogen chemisorption results indicate that the alkali was apparently atomically dispersed on the ruthenium surface. The added potassium species interfered with hydrogen chemisorption on a one-to-one atomic basis. Potassium addition resulted in a decrease in the apparent activation energy and an increase in the apparent hydrogen reaction order for ethane hydrogenolysis. Using the statistical poisoning model of Martin (*Catal. Rev.-Sci. Eng.* **30,** 519 (1988)) which assumes that the metal surface is uniform for adatom adsorption, the apparent ensemble required for the reaction was estimated to be made up of 12 ± 3 adjacent exposed surface ruthenium atoms. Using an extension of Martin's model, this structure-sensitive reaction also revealed that at the higher potassium levels the alkali dispersion became nonuniform. This nonuniform dispersion is suggested to be due to a preference of the dopant for certain metal sites. Because of this nonuniform dispersion, the "true" reaction ensemble size is suggested to be less than 12.

1. INTRODUCTION

Many studies of alkali modification of metal catalysts have been reported (*1, 2*); however, numerous fundamental issues remain unresolved, such as the mechanism of promotion and the location of the alkali species in a working catalyst. This makes it difficult to distinguish completely the various roles that the alkali promoter can play in modifying catalytic phenomena.

Most often alkali dopants do not populate real catalysts in their atomic state. Rather, depending on their precursor and the reaction atmosphere it has been suggested that they may be present in the form of compounds such as Cs_2O, KOH, K_2CO_3, or as surface-complexed compounds (*3–6*). In many instances the modifier's location is not obvious. In a study on alkali-promoted Pd/SiO_2, Rieck and Bell (*7*) noted that only a fraction of the dopant was associated with the Pd particles. Depending on the method of preparation of Rh/SiO_2, Kesraoui *et al.* (*8*) suggested that the alkali species can associate with the silica support or reside at the silica–Rh interface; the latter possibility implying that in potassium-promoted Rh/SiO_2, K^+ might not be atomically dispersed on the metal surface.

Certain reactions have been found useful in determining how adspecies or supports may modify catalyst surface morphology (*9–12*). These reactions for which the turnover frequency changes with the particle size and/or the fraction exposed of the catalyzing metal have been called structure-sensitive (*13–15*). When the ensemble of sites required for reaction is sufficiently large, it is possible to use such reactions to detect disruptions in the metal surface structures due to poisoning or other forms of catalyst

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[1] Present address: Research Staff, Ford Motor Company, P.O. Box 2053, Dearborn, MI 48121.

[2] To whom correspondence should be addressed.

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modification (16). There are several factors that can affect the observed rates of structure-sensitive reactions. Several hydrogenolysis and isomerization reactions have been found to proceed at different rates over different planes of metal single crystals (17–20); that is, these reactions appear to be sensitive to the coordination of the catalyzing metal atoms. The availability of enough contiguous metal atoms to make up ensembles required for the reaction also rules the observed rates of structure-sensitive reactions. Moreover, the larger the size of these reaction ensembles, the more structure-sensitive the reaction will be because any change in the catalyst's surface structure by surface decoration or in particle size will influence the rate more severely. The probe reaction used in the investigation reported here is the hydrogenolysis of ethane which is one of the more structure-sensitive reactions, requiring a large reaction ensemble (21, 22). Previous studies have reported potassium to be a poison for this reaction (23–25).

For most studies dealing with alkali modification, the modifier precursor has been coimpregnated with the active metal precursor into the support. Although generally a more effective way to closely associate the active metal and the modifier, this method of adding the alkali also tends to bring about changes in the particle size of the metal (26). Such secondary effects of the alkali species complicate the development of an understanding of how the promoter affects catalytic behavior. Sequential impregnation of a prereduced supported metal catalyst with the alkali has been used in the past to avoid changing the particle size distribution so that any shifts in adsorptive and catalytic phenomena could be directly related to an alkali effect. Thus, on sequential addition of potassium to silica-supported Pd and Rh catalysts, Angevaare *et al.* (27, 28) found no appreciable changes in d_p as observed by electron microscopy and X-ray diffraction.

This paper reports the results of an investigation using ethane hydrogenolysis, a structure-sensitive reaction, and hydrogen chemisorption to assess the dispersion of potassium in a series of K^+-promoted Ru/SiO_2 catalysts prepared by sequential impregnation.

2. EXPERIMENTAL

Fumed silica (200 m^2/g, nonporous Cabosil M5, Cabot Corp.) was impregnated to incipient wetness with an aqueous solution containing ruthenium nitrosylnitrate (Alfa) in order to produce a 3 wt% Ru catalyst. After drying in air at 80°C for 12 h, the catalyst was reduced in flowing hydrogen at 400°C for 8 h. This procedure resulted in the prereduced 3 wt% Ru/SiO_2 base catalyst which was washed with hot water to remove chlorine following the method of Miura *et al.* (29). After drying and rereduction, portions of the washed catalyst were impregnated with aqueous KNO_3 solutions of different concentrations in order to prepare a series of K^+-promoted catalysts. For the K^+-free catalyst this impregnation was carried out with distilled water instead. The catalysts prepared in this batch were designated K*xx* in order to indicate that nominally $(K/Ru)_{atom} = xx/100$. Relevant characteristics of these catalysts are listed in Table 1. In order to test for consistency in preparation a second series of catalysts was also prepared. These are designated sK*xx* where the s indicates the second series. Properties of these catalysts are also listed in Table 1.

The procedure for gas volumetric hydrogen chemisorption used was similar to that of Sayari *et al.* (30). Briefly, after static hydrogen reduction and desorption of the catalyst at 400°C, the total hydrogen desorption isotherm at 25°C was obtained by allowing equilibrium to be reached at each H_2 pressure. Then, after a 2-min evacuation of the catalyst the corresponding reversible hydrogen desorption isotherm was measured. To determine the number of free Ru atoms at the surface, the amount of irreversibly chemisorbed hydrogen was used with the assumption that $H_{irrev}/Ru_S = 1$ (31).

For ethane hydrogenolysis reaction, hy-

TABLE 1

Properties of K^+-Doped 3 wt% Ru/SiO_2 Catalysts

Catalyst	K/Ru (atomic)	K^+_{added} (μmol/g)	H_{irrev}[a] (μmol/g)	Ru_S[b] (μmol/g)	θ_K
K00	0.00	0.0	110	110	0.0
sK00	0.00	0.0	—	—	—
K01	0.01	3.0	112	112	0.03
K05	0.05	14.8	98	98	0.13
sK10	0.10	29.7	76	76	0.28
K20	0.20	59.4	49	49	0.55

[a] From static hydrogen chemisorption at room temperature.

[b] Based on an assumption of $H_{irrev}/Ru_S = 1$.

drogen (Linde, UHP with further purification using a deoxo unit and an activated charcoal filter), helium (Linde, UHP with a molecular sieve trap), and a 10% ethane in hydrogen gas mixture (Linde, CP grade without further purification) were used. The catalyst rested on a fritted disk fixed in a Pyrex glass tubular, differential reactor which could be bypassed using a six-way valve. Composition of the reactor effluent was determined by on-line gas chromatography using a Porapak Q packed column and an FID detector. Before reaction the catalysts were rereduced *in situ* in hydrogen at 400°C for 2 h. The reaction rates reported—except for those in the time-on-stream studies—were those obtained from product analysis after 5 min on stream rather than the steady-state values in order to avoid complications that may arise due to catalyst deactivation by deposited carbon. Hydrogen bracketing for 30 min at temperature between reaction conditions effectively restored the catalysts' activities. The standard reaction conditions used were 160°C, 101 kPa, and $H_2/C_2H_6/He = 15/0.3/84.7$ ml/min but the hydrogen partial pressure and temperature were also varied to determine the apparent hydrogen reaction order and activation energy, respectively. The operating domain was also tested to ensure that there were no mass transfer limitations on the measured rates of reaction and that conversion did not affect these rates. Time-on-stream studies of the catalysts were carried out at the standard reaction conditions.

3. RESULTS

From the available surface Ru of the K^+-free catalyst (Table 1) the average metal particle size (d_p) was estimated to be 23 Å. It can be assumed that d_p was the same throughout the catalyst series since it has been shown that, for sequentially doping of prereduced catalysts, the modifier typically does not bring about any significant changes in the d_p of the reduced metal (*27, 28, 32*). Hydrogen chemisorption results were used to determine the amount of exposed surface Ru, Ru_S, for the K^+-promoted catalysts by assuming $Ru_S = H_{irrev}$. The K^+-blocked surface atoms of Ru, Ru_K, were taken to be the difference in Ru_S of the catalysts with respect to that of the K^+-free catalyst. In Table 1, the nominal potassium content, K^+_{added}, is also given in μmol/g. Comparison of Ru_K to K^+_{added} in Fig. 1 shows a linear trend with slope = 1.02 ± 0.05. This correlation also supports the assumption that d_p did not significantly change with sequential K^+ addition.

Reaction rate results for the structure-sensitive ethane hydrogenolysis reaction on the two K^+-free catalysts (Table 2) indicate that the preparation method of the base catalysts was consistent. The time-on-stream

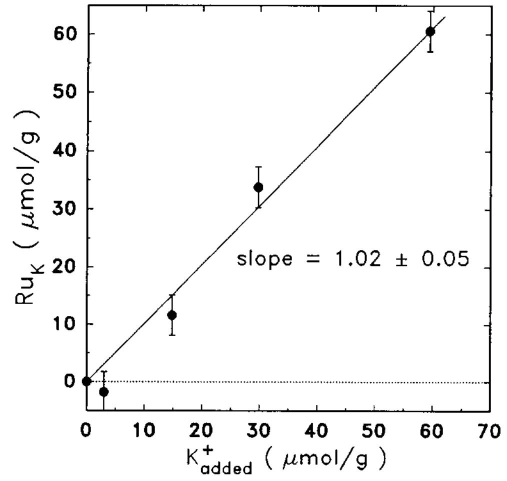

FIG. 1. Correlation between surface Ru blocked for hydrogen chemisorption and sequentially added K$^+$.

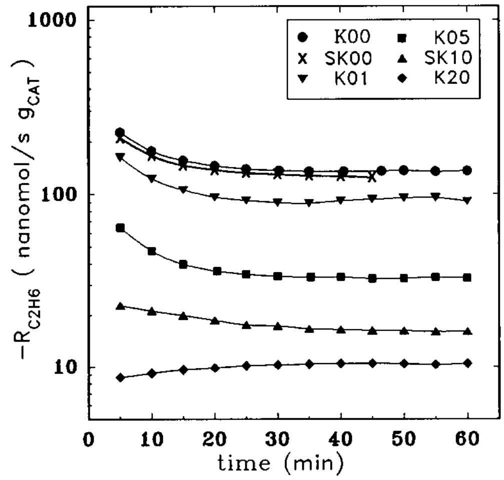

FIG. 2. Time-on-stream ethane hydrogenolysis activity.

performances of the catalysts at the standard reaction conditions (Fig. 2) show that the catalysts generally deactivated considerably with time to some steady-state rate, except for the highest K$^+$ loading, in spite of the large excess of hydrogen (H_2/C_2H_6 = 50) in the reactor feed.

The apparent activation energy (E_{app}) of the reaction shifted downward by ca. 7 kcal/mol due to the addition of potassium (Fig. 3). At the same time the absolute value of the apparent hydrogen reaction order assuming a power-law rate expression, $-n_{H2}$, decreased by 25% (Fig. 4). Table 2 also shows that for this structure-sensitive reaction both the reaction rate and the turnover frequency decreased dramatically with K$^+$ addition.

It has been proposed by Martin (*16*) that, for structure-sensitive reactions such as eth-

TABLE 2

Ethane Hydrogenolysis Reaction[a] Characteristics of K$^+$-Doped Ru/SiO$_2$ Catalysts

Catalyst	$-R_{C2H6}$ (nmol/s g)	TOF[b] (mHz)
K00	223	2.02
sK00	215	1.96[c]
K01	157	1.43
K05	64.0	0.65
sK10	22.3	0.29
K20	8.6	0.18

[a] 160°C, 101 kPa, $H_2/C_2H_6/He$ = 15/0.3/84.7 ml/min.
[b] Based on static hydrogen chemisorption.
[c] Based on static hydrogen chemisorption of K00.

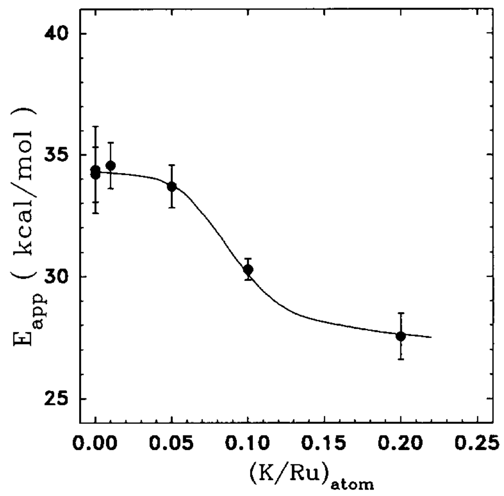

FIG. 3. K$^+$-induced changes in the apparent activation energy of ethane hydrogenolysis. Reaction conditions were 140–170°C, 101 kPa, and $H_2/C_2H_6/He$ = 15/0.3/84.7 ml/min.

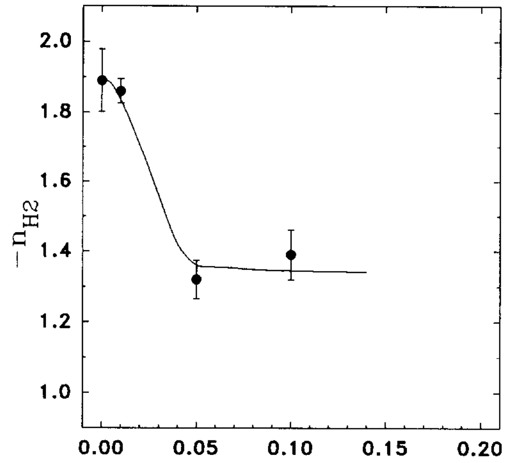

FIG. 4. Potassium-induced variations in the apparent hydrogen reaction order for ethane hydrogenolysis. Reaction conditions were 160°C, 101 kPa, total flow/C_2H_6/H_2 = 100/0.3/2.7–15 ml/min using He as a diluent.

ane hydrogenolysis, the statistical dependence of the rate on simple site blockage by a poison P may be expressed as

$$R/R_{P=0} = \binom{Q-N_E}{q} \Big/ \binom{Q}{q}, \qquad (1)$$

where R is the reaction rate of the given poisoned catalyst, $R_{P=0}$ is the rate of the nonpoisoned catalyst, N_E is the ensemble size required for reaction, Q is the number of metal atoms at the particle's surface, and q is the number of adatoms on the particle. If the number of available surface atoms on a particle is larger than the ensemble size, Eq. (1) can be simplified to an exponential expression

$$R/R_{P=0} = (1 - \theta_P)^{N_E}, \qquad (2)$$

where θ_P is the fraction of the surface metal atoms blocked by the poison and $(1 - \theta_K) = \theta_{Ru}$. If the reaction rate complies with this model, a logarithmic plot of the normalized rate versus θ_{Ru} will yield a straight line with slope N_E. However, Fig. 5 shows that such a plot of the rate data for the K$^+$-promoted Ru/SiO$_2$ catalyst series does not yield the straight line predicted by Martin's model but, rather, a curve with an initial slope = 12 ± 3. Based on calculations using the Ru_S data of catalyst K00 (Table 1), it can be estimated that on average each metal particle potentially has about 316 surface Ru atoms (Q) while a doping level of $(K/Ru)_{atom} = 0.2$ would correspond to 171 potassium adatoms/particle (q). These model calculations indicate—as is also shown in Fig. 5 by the fit of the initial slope of the data and the 12-atom ensemble model—that the metal particles are indeed large enough for a 12-atom ensemble model to be plausible at low potassium loadings assuming that at low adspecies coverages poisoning is approximately uniform.

Martin's model has been extended by us to be able to consider the effects of site preference of the poison. A new, preferential-poisoning model was developed that allowed the partitioning of the available metal surface into two kinds of sites, one of which—type A—is preferred for modifier adatom adsorption. This simple model also allows for dissimilar intrinsic rates of reactions for the two types of sites. For such a model the overall surface-exposed coverage of the metal can be expressed as

$$\theta_M = X_A\theta_A + X_B\theta_B, \qquad (3)$$

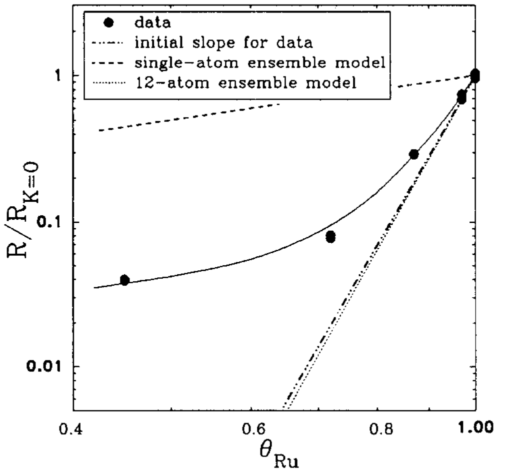

FIG. 5. K$^+$-induced effects on the ethane hydrogenolysis reaction rate vs. fraction of Ru surface exposed.

where X_A and X_B are the fractions of the favored and the unfavored metal surface atoms while θ_A and θ_B are the fractions of each surface site type not covered by modifier adatoms. Using the simplification afforded by Eq. (2) the normalized global rate of reaction of the metal surface can be expressed as

$$R/R_{P=0} = \frac{X_A \mathrm{TOF}_A \theta_A^{N_E} + X_B \mathrm{TOF}_B \theta_B^{N_E}}{X_A \mathrm{TOF}_A + X_B \mathrm{TOF}_B}, \tag{4}$$

where TOF_A and TOF_B are the relative kinetic strengths of the favored and the unfavored metal sites, respectively. For any given partitioning of the adatoms over the two types of sites, the observed initial slope of the logarithmic plot of $R/R_{P=0}$ vs. θ_M would be equivalent to the *apparent* ensemble size, $N_{E,app}$, given an ensemble size N_E. This treatment permits some understanding of how preferential poisoning may affect how the observed rate of reaction varies with θ_M.

This preferential-poisoning model was applied to the situation of "extreme adspecies partitioning" in which the distribution of the poison over the two types of metal surface atoms is assumed to be as follows: the metal surface atoms not favored for adatom adsorption (type B) did not begin to be poisoned until the entire segment of favored metal surface atoms had been poisoned, and each metal surface atom could accommodate exactly one modifying molecule. The effects of the fraction of the favored metal surface atoms (X_A) and the relative kinetic strengths of the two types of metal surface atoms, $\mathrm{TOF}_A/\mathrm{TOF}_B$), on the apparent ensemble size ($N_{E,app}$) are illustrated in Figs. 6 and 7 and are discussed in the following section.

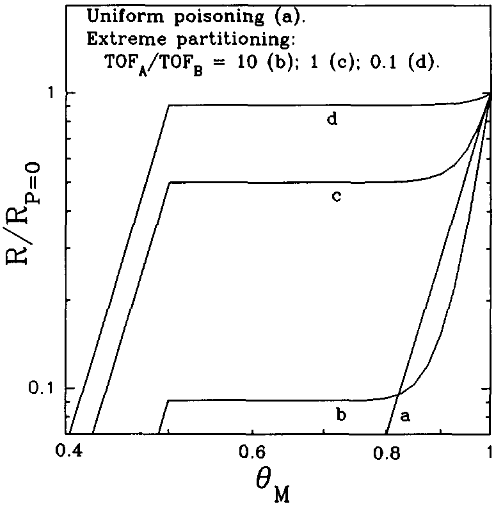

FIG. 6. Predicted reaction rates for $N_E = 12$, $X_A = 0.5$, and varying degrees of kinetic site heterogeneity.

4. DISCUSSION

The adsorption results in Table 1 show that sequentially added K^+ affected hydrogen chemisorption on a one-to-one basis. This indicates simple site blocking by the potassium compound, although it is possible that K^+ modified the strength of chemisorption but not enough to affect the surface hydrogen population. It should be noted there is evidence from XPS (*33, 34*) measurements that indicates that after hydrogen reduction the potassium exists in compounded form with a neutralizing anion on nonuniform metal surfaces. The adsorption results furthermore imply that all of the compounded potassium cations were located on the Ru surface where they were distributed in an atomically dispersed state. It would seem highly unlikely that, if one K^+ blocked more than one surface Ru atom, the partitioning of the dopant between Ru and the SiO_2 support would exactly compensate to result in $K^+_{added}/Ru_K = 1$ at all K^+ doping levels (Fig. 1). Similarly, it is very doubtful that a situation was prevailing in which the K/Ru_S stoichiometry exceeded 1 but where K^+ partitioned and formed clusters on the metal surface in such a way to result in this one-to-one correlation between Ru_K and K^+_{added}.

Many studies of the alkali promotion of metal catalysts have reported the possibility of electronic effects due to the alkali compound (e.g., (*35, 36*)) while in many others such effects could not be discerned (e.g.,

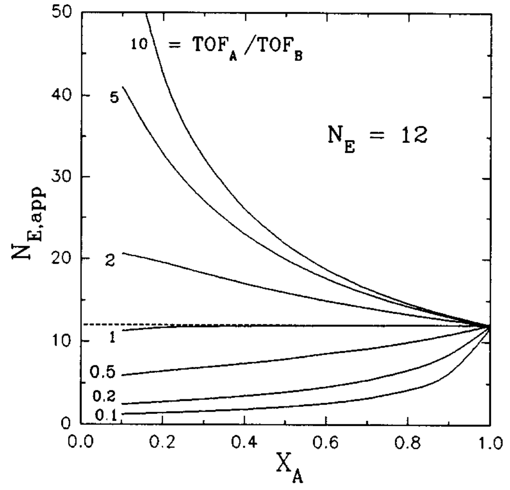

FIG. 7. Apparent reaction ensemble size vs fraction of preferred poison-adsorption metal sites for varying TOF_A/TOF_B turnover ratios.

(*37, 38*)). Furthermore, catalyst preparation by sequential impregnation of the alkali dopant is generally expected to lead to a poorer association of the alkali with the active metal, so that electronic effects in such systems would be expected to be less pronounced than in coimpregnated ones. Even though there were changes in the apparent activation energy and hydrogen reaction order (Figs. 3 and 4) these results do not necessarily signify electronic effects since they were at least in part indirectly brought about by changes in the coverage of adsorbed reaction intermediates due to the added K^+ species. On the other hand, it could still be possible that there were electronic effects but that their range of influence did not extend beyond the reaction ensemble in which case the alkali would not be able to affect the hydrogenolysis rate except as a result of blockage. Thus, for the sequentially K^+-promoted catalyst series under consideration, there is no conclusive evidence of any electronic effects on ethane hydrogenolysis due to the potassium compound. Potassium, however, can have pronounced effects on other reactions, such as CO hydrogenation (*35, 36, 39*) and ammonia synthesis (*40–42*), which cannot be explained in terms of blockage alone. It is possible that the catalytic activity varies due to the abundance of a particular type of chemisorbed hydrogen. However, the ability of the proton to move about the surface as is known from the hydrogen-spillover phenomena in the well-studied Ru–Cu system (*43, 44*), the fact that the rate-determining step of the ethane hydrogenolysis is the C–C bond scission (*45, 46*), and the fact that hydrogen chemisorption was carried out at room temperature in the absence of ethane caution against conclusions about changes in catalytic activity based on detailed analysis of the hydrogen adsorption results.

It has been reported that metal surface atoms of lower coordination generally have higher hydrogenolysis activities (*17–20, 47*). Thus, highly dispersed catalysts which have significant numbers of differently coordinated metal surface atoms might be expected to show deviations from the statistical ensemble model which assumes surface uniformity. Although Martin (*16*) provided arguments to discount possible deviations from this model due to such surface kinetic heterogeneity, this issue has remained a concern to us. We emphasize that there can actually be two types of heterogeneity. Using the preferential-poisoning model, the effects of both surface kinetic heterogeneity and adspecies-adsorption heterogeneity (or adspecies partitioning) on overall rates of reactions can be addressed. Calculations using the model presented earlier have shown that, in the case of uniform poisoning of two metal surface segments with different average turnover frequencies, the predicted reaction rates are the same as those of the kinetically uniform case. Consequently, when the surface is kinetically heterogeneous the apparent reaction ensemble size is also the true one provided that poisoning occurs uniformly.

As can be seen in Fig. 7, in the case of extreme adspecies partitioning over a kinetically uniform surface (i.e., $TOF_A/TOF_B = 1$) the model predicts that the deviation of the apparent ensemble size from the true one would be small. On the other hand, if there is kinetic heterogeneity, the preferential-poisoning model predicts large deviations in the apparent ensemble size at small X_A. In fact, if a small, highly active segment of the surface is poisoned preferentially, the actual ensemble size is predicted to be greatly over/underestimated by $N_{E,app}$ in the case of extreme partitioning.

While the ethane hydrogenolysis reaction results given in Fig. 5 show that sequentially added K^+ seemed to have interfered with the catalyst's activity according to a 12-atom ensemble model at low K^+ doses, at higher K^+ levels there was a significant deviation from this model. For the data in Fig. 5, the initial slope reflects N_E if it can be assumed that the surface is for the most part either kinetically homogeneous or else uniform for adspecies adsorption. However, as demonstrated by the simulations (in particular, curves a and c) in Fig. 6, the fact that there is a significant deviation from the apparent 12-atom ensemble model at high potassium loadings indicates that in terms of surface heterogeneity, adspecies partitioning must have been a factor. There are several possible reasons why such a deviation may be observed. One could propose that this deviation might not be linked to the potassium's metal site preference due to the heterogeneity in surface topography but that, instead, during preparation the adsorption of the K^+ dopant on metal particles was so strong that it associated preferentially with the Ru particles located on the external surface of the SiO_2 but not with others that may have been in places inaccessible to the K^+precursor. However, in that case one would expect aggregation of the alkali dopant to occur at very low K^+ doses. In contrast, the hydrogen chemisorption results indicate that the compounded potassium was atomically dispersed on the metal. Moreover, it is expected that all the ruthenium particles were accessible to the alkali dopant since the aqueous ruthenium nitrosylnitrate anionic complexes that carried the metal onto the silica support before catalyst reduction were much larger than the potassium cations so that the ruthenium would not have been deposited in places inaccessible to the alkali precursor.

The most likely cause for the deviation of the catalyst's activity from the apparent 12-atom ensemble model in Fig. 5, based on our modeling, appears to be a tendency of the potassium dopant to favor interaction with certain ruthenium surface atoms due to heterogeneity in the surface topography of the metal. The surface of small supported metal particles are made up of edges, corners, and flat planes of different coordination numbers. It appears that the alkali has different preferences for adsorption/interaction on the various sites of such a heterogeneous surface, most likely favoring the generally more active low-coordination surface metal atoms. At low potassium loadings there would be enough favored metal surface atoms so that the potassium could spread out enough to follow approximately a statistical 12-atom ensemble model. However, for larger amounts of K^+, reaction ensembles containing favored metal surface atoms would be poisoned repeatedly before other ensembles made up of less favored sites for alkali adsorption. Thus, as can be seen in Fig. 6, the catalysts would maintain higher activities than predicted by statistical poisoning since the overall rate would be constant over a range of alkali loadings reflecting the total reaction activity of the less active but unpoisoned facets. Eventually, one would expect the overall rate to again decline significantly with additional alkali after the preferred sites for alkali adsorption were filled and the less favored sites began to be poisoned, and this is what is shown by the model plotted in Fig. 6.

In light of a recent ethane hydrogenolysis study on a stepped Ru(1,1,10) surface (*47*), preferential site location of an adspecies seems especially credible. Using CO TDS, Egawa and Iwasawa (*47*) showed that H_2S preferentially poisons the step sites of this surface, and they suggested that the hydrogenolysis rate is higher at the low-coordination sites of the steps. In another study, Smale and King (*10*) did Monte Carlo calculations for a model ruthenium–copper catalyst system which suggest that, in an equilibrium situation, Cu associates preferentially with the low-coordination surface sites of a Ru particle. There have also been reports of similar adatom tendencies on other metals such as Pt (*17, 48, 49*).

5. CONCLUSIONS

The results of hydrogen chemisorption suggest that all the potassium species were atomically dispersed on the surface of the ruthenium particles. From a statistical treatment of the poisoning phenomenon the required reaction ensemble for ethane hydrogenolysis over these ruthenium catalysts was estimated to be made up of about 12 contiguous metal atoms ($N_{E,app}$). Analysis of the results suggested that the distribution of the potassium over the metal was nonuniform. It appears very likely that a small fraction of highly reactive low-coordination metal atoms are poisoned preferentially by K^+ in which case, according to the preferential-poisoning model calculations, it is likely that $N_{E,app}$ may be a considerable overestimation of the actual reaction ensemble size depending on the extent of modifier location specificity. Application of an extension of Martin's poisoning model such as presented here seems to offer interesting possibilities for exploring the dispersion of modifier species on metal surfaces.

6. ACKNOWLEDGMENTS

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