Isotopic tracing study of K promotion of NH₃ synthesis on Ru

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There has been much discussion based on indirect evidence about the site heterogeneity of catalysts for ammonia as well as the effect of alkali promotion. This paper presents the results from direct measurements using steady-state isotopic transient kinetic analysis (SSITKA) of surface site heterogeneity on Ru/SiO_2 induced by K promotion. This heterogeneity is caused by the creation of a set of super active sites. It is the high activity of these sites, more than just the increase in number of surface intermediates, which produces the high activity of K-promoted Ru for ammonia synthesis.

Keywords: ammonia synthesis; ruthenium; promotion; alkali; potassium; isotopic tracing; surface heterogeneity

1. Introduction

The high activity of Ru-based catalysts at low temperatures coupled with their ease of reduction and good tolerance toward common reaction poisons make them potentially excellent catalysts for use in ammonia synthesis at thermodynamically favored low temperatures. This explains, in part, the amount of research done in recent years on Ru-catalyzed ammonia synthesis [1–11]. There has also been significant interest in fundamental questions regarding the nature of the interactions between Ru and various adspecies [12–15]. The promotion effect of potassium on the ammonia synthesis activity of Ru is much more substantial than that observed on the Fe-catalyzed reaction.

The interaction of metal catalyst surfaces with alkali promoters has been the subject of a number of theoretical treatments [16–18], surface science analyses using well-defined single crystal surfaces [19–22], and IR spectroscopic studies of supported metals [23–28]. Results from these studies have expanded our understanding of alkali promotion; however, direct measurements of the effect of alkali

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promotion under actual reaction conditions, especially for ammonia synthesis, have been severely lacking.

It would be expected that information about surface coverage of reactive intermediates and the degree of kinetic heterogeneity of Ru-catalysts under steady-state reaction conditions would greatly expand our knowledge about the role of alkali species in promoting Ru-catalyzed ammonia synthesis. Work in our laboratories using steady-state isotopic transient kinetic analysis (SSITKA) has yielded some interesting results pertinent to such questions for a commercial Fe ammonia synthesis catalyst, KMIR [29]. In particular, this method with proper mathematical analysis is able to produce conclusions about the heterogeneity of a reaction surface.

During an isotopic switch under steady-state reaction, transients of isotopically labeled products / reactants as well as an inert gas tracer (such as Ar) are obtained which are normalized. The transient of the inert gas tracer is used to correct for gas phase holdup. This results in the transient functions represented by $F_i(t)$. Fig. 1 shows a schematic of typical isotopic transients. The area between the inert gas and the labeled product curves gives the surface residence time of the labeled atoms in the molecule being traced. The amount of surface species giving rise to product i can then be determined from

$$N_i = \tau_i R_i ,$$

where R_i equals the rate of i leaving the reactor. To be absolutely precise, τ_i and N_i really apply only for the element whose isotopes are being switched in species i.

This paper reports the results of a study utilizing SSITKA to explore the effect of K promotion on ammonia synthesis on Ru under reaction conditions.
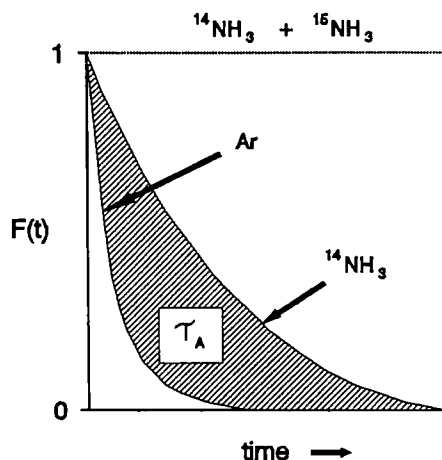

Fig. 1. Schematic of typical isotopic transients.

2. Experimental

2.1. CATALYST PREPARATION AND CHARACTERIZATION

The Ru catalysts were prepared from $Ru(NO)(NO_3)_3$ (Alfa) and SiO_2 (Cabot Cab-O-Sil L90, surface area 90 $m^2 g^{-1}$) by the incipient wetness method. After drying in air at 383 K for 24 h, the catalyst was reduced under H_2 for 16 h at 823 K. The catalyst was then dechlorinated by hot water washing in the manner earlier described by Miura et al. [30]. This step reduced the chlorine content of the original catalyst from 0.07 to 0.011 wt%. The K-promoted catalyst was prepared by impregnating a portion of the reduced and dechlorinated catalyst to incipient wetness using a solution of KNO_3, corresponding to a nominal K/Ru atom ratio of 0.3. The promoted catalyst was then dried at 313 K for 24 h and re-reduced at 673 K for 16 h. A second portion of the dechlorinated catalyst was treated in the same manner as above but was wetted, prior to reduction, by pure distilled water. This catalyst was then used as the unpromoted one. This permits one to factor out, as much as possible, effects of K promotion due simply to water impregnation and drying. While the form of K in the promoted catalyst was actually K^+, K will be used throughout when referring to the promoter for simplicity sake.

The Ru content of these catalysts was determined by atomic absorption to be 2.71 wt%.

The catalysts were characterized by static hydrogen chemisorption at room temperature following the methods of Dalla Betta [31] and Goodwin [32]. The reversibly chemisorbed H_2 was determined after a ten minute evacuation, at room temperature, of the samples immediately following the total adsorption measurements. The results are given in table 1. The % dispersion of the Ru on the unpromoted catalyst was ca. 27%.

2.2. REACTION ANALYSIS

A gradientless reactor [33] was employed for all the kinetic analyses. The activation of the catalyst samples was conducted in situ under a flow of pure hydrogen

Table 1
Hydrogen chemisorption results

K/Ru	Hydrogen chemisorption		Avg. Ru particle size (nm)
	total (H_2 μmol/g)	irreversible (H_2 μmol/g)	
0.0	57.8	35.8	3.2
0.3	34.7	16.8	3.2 [a]

[a] Based on the unpromoted catalyst since sequential promotion has little effect on the metal particle size distribution.

according to the temperature program, 300–673 K (2 h). The gases used in the reaction system were hydrogen, helium, and nitrogen. Hydrogen (99.999%) was further purified by passage through an activated carbon trap (Matheson) and a deoxo unit (Engelhard) followed by a type 13X molecular sieve trap immersed in liquid nitrogen. He (99.999%) was also purified in a similar manner. Normal nitrogen ($^{14}N_2$) containing a trace amount of Ar (Linde Custom Grade) and $^{15}N_2$ (98+%, Monsanto) were purified by Supelco high capacity carrier gas purifiers. The argon trace in the nitrogen-14 acted as an internal time base for the isotopic switches and was used to define the hold-up in the gas phase. The reaction conditions used for this study were: total pressure of 204 kPa, temperature of 673 K, H_2/N_2 ratio of 3, and GHSV based on the inlet gas of ca. 5 000–23 000. Care was taken to keep conversion well below thermodynamic limitations. For SSITKA, the isotope switches used were from ($^{14}N_2$ + Ar(trace) + H_2) to ($^{15}N_2$ + H_2). By carefully balancing the pressures for the two flows, perturbation of the steady-state reaction during the switch was eliminated.

3. Results

3.1. CHARACTERISTICS OF THE RUTHENIUM CATALYSTS

K promotion resulted in a decrease in the amount of irreversibly chemisorbed H_2 from 35.8 to 16.8 μmol/g_{cat} (table 1). Such a decrease is usually seen due to the blockage of H-chemisorbing Ru surface sites by the promoter. It should be noted that the chemisorption data on the alkali-promoted catalyst represent limiting values of the parameters since unproportionate suppression of hydrogen chemisorption can occur with such adspecies. Since the amount of K^+ on the catalyst was ca. 80 μmol, one can surmise that perhaps as much as half of the K species was resident on the surfaces of the Ru particles while the rest was distributed over the SiO_2 surface. This method of preparing the promoted catalyst from a reduced metal base catalyst is not necessarily the best way to get maximum promoter–metal contact. However, it holds the advantage in that the resulting unpromoted and promoted catalysts have very similar distributions of metal particle sizes – a critical issue when investigating a structure sensitive reaction such as ammonia synthesis.

3.2. NH₃ SYNTHESIS

Table 2 summarizes the ammonia synthesis results at steady-state. K promotion resulted in almost two orders of magnitude increase in the reaction rate. It also brought about modifications in the partial pressure dependencies of the rate. The significant increase in rate upon K promotion of Ru is well known, and these results are in line with what one would expect.

Table 2
Ammonia synthesis results

K/Ru	Rate (μmol NH_3/g h)	P_{NH_3} (Pa)	x [a]	y [a]	z [a]	TOF_H [b] $\times 10^4$ (s^{-1})
0.0	15.5	63.2	1.1 ± 0.1	-0.48 ± 0.05	-0.56 ± 0.02	0.6
0.3	748	191	0.70 ± 0.04	-1.0 ± 0.2	-0.13 ± 0.01	61.8

[a] $r = k P_{N_2}^x P_{H_2}^y P_{NH_3}^z$
[b] Rate per H-atom irreversibly adsorbed.

3.3. MEASUREMENTS USING SSITKA

The surface concentrations, N_A, of the most abundant reaction intermediates (MARI) containing N on the working catalysts are tabulated in table 3. These surface concentrations have also been used to calculate the fractional coverages of the H-adsorbing sites by these N-containing reaction intermediates. The mean lifetimes of these intermediates on the working surfaces (τ_A) are also listed. These lifetimes which were determined from the areas under the isotopic NH_3 response curves, corrected for hold-up in the gas phase, are inversely proportional to what Biloen et al. [34] have termed "the intrinsic turn-over frequency" (TOF_{intr}) for surfaces containing no more than one main pool of N-intermediates in series [33]. The calculated TOF_{intr}'s for the catalysts are given in table 3. The rate can be expressed as

$$\text{rate} = k N_A,$$

where k is the pseudo-first-order rate constant and may contain also the hydrogen coverage dependence. The hydrogen-based TOF_H can be related to actual surface coverage by

$$TOF_H = k\theta_A.$$

Since k can be estimated using

$$k = 1/\tau_A$$

and

Table 3
Effect of K-promotion on SSITKA measurements

K/Ru	N_A, conc. of N-MARI (μmol/g_{cat})	θ_A [a]	τ_A (s)	TOF_{intr} [b] $\times 10^4$ (s^{-1})
0.0	7.8	0.09	1797	5.6
0.3	23.7	0.71	114	87.7

[a] Fractional N-coverage based on irreversible H_2 chemisorption.
[b] Calculated from τ_A^{-1}.

$$\text{TOF}_{\text{intr}} = 1/\tau_A$$

then

$$\text{TOF}_H = \text{TOF}_{\text{intr}}\theta_A \, .$$

4. Discussion

As can be seen in table 2, if one were to draw conclusions based on TOF calculated from the rate divided by hydrogen chemisorption, TOF_H, one would conclude that the addition of K increased site activities by two orders of magnitude. However, the SSITKA results in table 3 clearly show that the increase in activity with K promotion was actually due to two causes: a significant increase by a factor of 3 in absolute N-MARI coverage and at the same time an increase by a factor of 16 in the average intrinsic intermediate activity, approximated by τ_A^{-1} and labeled TOF_{intr}. This parameter gives the upper limit for the true TOF of the average site. The difference in surface-intermediates coverage is in part due to the three-fold difference in the partial pressure of ammonia for the two catalysts. It has been found that the surface coverage in N-species increases somewhat in this pressure range with increasing partial pressure of ammonia [33]. It can be estimated that, at a partial pressure of ammonia equal to that seen by the unpromoted catalyst, the surface coverage of the K-promoted catalyst would have been 21 μmol/g, equivalent to $\theta_A = 0.63$ – still significantly different from that for the unpromoted catalyst. However, the ammonia partial pressure has an added effect. With an increase in partial pressure, the average surface residence time also increases. Thus, the residence time, τ_A, for the promoted catalyst would have been even less if the ammonia partial pressure had been at 63 Pa. Consequently, the TOF_{intr} would have been even larger. Thus, even taking into account the difference in partial pressure of ammonia, both N_A and TOF_{intr} would still have increased by a similar amount upon K promotion.

The isotopic transients in the time domain, while useful for determining surface concentrations of reactive intermediates and residence times, do not readily allow us to determine the degree of surface heterogeneity. However, by using a deconvolution technique based either on Laplace transform inversion [35] or a constrained Tikhonov regularization of Fredholm integral equations of the first kind [36], it is possible to deconvolute the isotopic transients after correction for gas phase holdup and produce the distribution function for τ_A^{-1}. Fig. 2 shows the distribution of site/intermediate activities for the unpromoted and promoted Ru catalysts determined by the Laplace transform inversion method [35]. The unpromoted catalyst had essentially only one kind of sites (β). The addition of K resulted in an increase in average activity of these sites from 5.6×10^{-4} to 22×10^{-4} s⁻¹. However, the most important result was the creation of a class of "super" active sites
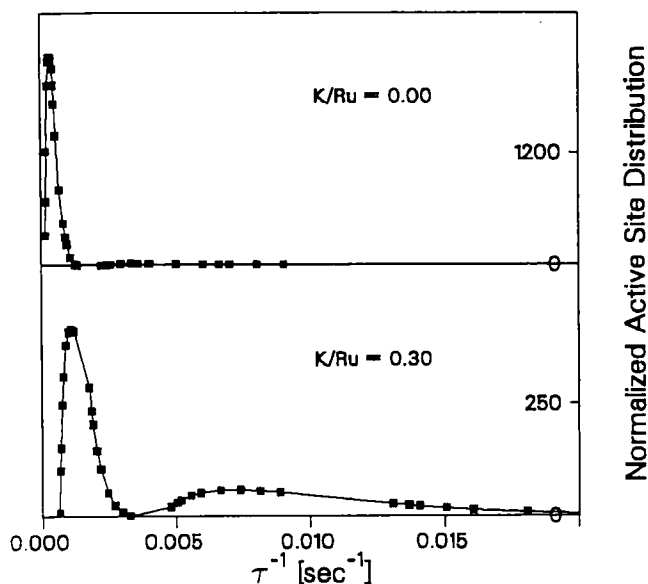
Fig. 2. Effect of alkali promotion on active site distribution of Ru/SiO$_2$ for ammonia synthesis.

having an average activity of 250×10^{-4} s^{-1}. While these "super" active α-sites constituted only 20% of the total in the promoted catalyst, they accounted for 78% of the reaction rate.

The creation of high-activity α-sites suggests a very strong interaction involving the alkali-promoter. This interaction may be an electrostatic through-space inter-action of the N-intermediates with the promoter as has been postulated previously on the basis of theoretical calculations [37,38] as well as experimental findings [39–41]. The alternate explanation is that the α-sites result from a short-range inductive (through-metal) effect of K – the interpretation favored by Praliaud et al. [26,27] based on their XPS data suggesting K$^+$ electron enrichment of their Ni surface and a K–Ni interaction, but no interaction between K and co-adsorbed CO. According to this view, islands of K form on some fraction of the metal surface while the remainder remains free of K. Considerable screening of the charge around the K-rich islands limit the range of the strong K-interaction. While the promoter may indeed not be uniformly distributed on the catalyst surface, it is diffi-cult to reconcile the rest of the latter hypothesis with the duality of the K-interac-tion as observed in the present study and the strong influence on the relative contributions to the active surface from the different groups of sites.

It is therefore suggested that under the ammonia synthesis conditions of this study, two types of K–Ru interactions occur on the working promoted catalyst sur-face, viz:

– a short-range interaction involving K and perhaps the N-intermediates which lead to a very strong promotion of the reaction and result in the emergence of the α-sites;

– a long-range Ru–K interaction which moderately modifies the original surface (β-sites), thus giving rise to a shift toward higher activity and a broadening of the β-peak.

This suggestion is in line with the UHV and infrared spectroscopic observations by Uram et al. [39] of a "kernel-effect" during CO adsorption on K-promoted Ni single crystal surfaces. The present observations, however, were made at more practical reaction conditions and pertain to the ammonia synthesis reaction. However, the similarity in the results is significant.

5. Conclusions

New and important information on the nature of Ru-catalyzed ammonia synthesis has resulted from SSITKA measurements. The N-intermediates coverage of the working catalyst surface was directly measured for the first time. Contrary to previous beliefs, alkali-promoted Ru sustains a substantial inventory of N-intermediates, in spite of having a relatively low ammonia-inhibition coefficient. The unpromoted catalyst was found to be much less populated by N-intermediates. It may be concluded that a key role of the alkali-promoter is in the stabilization of the reactive intermediates on the working surface without adversely affecting intrinsic activity. The presence of K on the surface led to a bimodal distribution of site activities. It was concluded that a short-range K-interaction was probably responsible for creating "super" active sites while a weaker long-range interaction produced a shift in the mean activity of the more distant sites to higher values while broadening this latter distribution. Addition of K to Ru resulted in a kinetically more heterogeneous reaction system in contrast to what has been found for Fe [33].

The results suggest that rate of reaction results can be well approximated by Langmuirian assumptions in many cases because of the dominance of the rate by the most active sites. In this case, while the surface was distinctly heterogeneous, most of the measured reaction (78%) derived from a single type of sites (the α-sites).

Acknowledgement

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