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PROXIMITY REQUIREMENT FOR Pd ENHANCED REDUCIBILITY OF Co^{2+} IN NaY

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The temperature which is required to reduce Co^{2+} ions in NaY can be markedly lowered by the presence of Pd in the same zeolite. Temperature programmed reduction (TPR) in combination with diffuse reflectance spectroscopy shows, however, that the reducibility of Co is enhanced only if Pd^{2+} and Co^{2+} ions share the same zeolite cages. No hydrogen spillover effect is detected, if this proximity requirement is not fulfilled.

1. Introduction

Hydrogen reduction of transition metal ions in zeolite cages differs significantly from reduction of the corresponding transition metal oxides. In the former case, protons are formed along with very small metal clusters, while in the latter case the reaction products are water and larger metal particles. Therefore, both the kinetics and the thermodynamics are different; some ion exchanged transition metals are virtually irreducible in zeolites, while for others the reduction process is reversible, i.e., metal atoms are readily reoxidized to ions by zeolite protons [1,2]. In view of the high potential of zeolite supported transition metals as active and stereo-selective catalysts, there is incentive for improving their reducibility.

Strategies which have been reported in recent years for this purpose include: hydrolysis of transition metal ions in supercages to (hydr-)oxides [3,4], blocking of small cages by other ions [1,5], or use of organometallic precursors [6,7]. Recently, it has been reported that the reduction of Ni^{2+} in X or Y type zeolites can also be enhanced by the presence of Pt or Pd [2,8]. This strategy has also been applied to metals on amorphous supports [9,10]. However, reduction of the less reducible metal is not always enhanced by the presence of a readily reduced metal on the same support; additional conditions have to be satisfied; for instance the reduction of Re on Al_2O_3 is enhanced by Pt only if the Re precursor is highly mobile on the support surface [9]. If pretreatment conditions are used such that Re precursors are immobilized on the surface, no enhancement of the Re reduction is observed. For zeolite supported systems there is evidence [10,11] that the reduction of Cu is strongly catalyzed by Pt; it is assumed that Cu ions migrate to reduced Pt clusters.

These results show that proximity between the easily reduced metal and the less easily reduced second element is a prerequisite for the catalyzed reduction of the latter. This conclusion is at variance with an alternative model, which assumes that hydrogen spillover over the support surface provides a means, for Pt particles to catalyze the reduction of other elements on the same support over considerable distances. This spillover model has been proposed for chlorine containing supports [12]. Although hydrogen spillover was also proposed for catalytic reactions, Baumgarten et al. [13] and Del Angel et al. [14] were unable to detect it in some real catalytic reaction systems.

The objective of the present study is to decide, under which conditions the reduction of ions inside zeolite cages can be enhanced by the presence of a second element which is reducible at low temperature. The system Co + Pd/NaY is used as an example.

Faujasite zeolites such as NaY have supercages of about 12 Å diameter and sodalite cages of about 6.6 Å, as well as hexagonal prisms with a dimension only capable of accommodating one small cation in each of them [15]. The initial location of the ions can be detected by a number of techniques [1,16]. We selected $Pd(NH_3)_4^{2+}$ and $Co(H_2O)_6^{2+}$ ions as precursors. Recent results of this lab show that the location and coordination of the Pd ions in NaY can be controlled by the calcination conditions [22,24].

2. Experimental

SAMPLE PREPARATION

A slurry (1 gram/200 ml) of commercial NaY (LZY-52) was adjusted to $pH = 6.0$ with HCl before dropwise addition of a dilute 0.01 M $CoCl_2$ solution. The slurry was then stirred for 24 hours and maintained at $pH = 6.0$. The suspension was filtered and washed repeatedly with deionized water. After drying in air, the sample was stored in a desiccator containing an aqueous NH_4Cl solution. The cobalt loading of the samples was determined by atomic absorption.

Preparation of Pd containing zeolite samples was carried out by a similar procedure using a dilute $Pd(NH_3)_4(NO_3)_2$ solution. Metals were introduced into NaY by successive ion exchange, introducing Co first. Its ion exchange was followed by an "ion migration" step, to enable the Co ions to migrate to small zeolite cages. In this phase the sample was heated in vacuo from 25 to 50 ° C with a ramp of 10 ° C/h, then maintained at 500 ° C for 6 h. After cooling and storing the sample in a desiccator over a saturated NH_4Cl solution, $Pd(NH_3)_4^{2+}$ ions were exchanged into the Co/NaY zeolite from an aqueous solution of $Pd(NH_3)_4(NO_3)_2$ at pH = 6. The samples are identified by a code such as $Pd_{8.7}Co_{8.9}Na_{20.8}Y$, where the subscripts state the number of metal ions per unit cell.

TEMPERATURE PROGRAMMED REDUCTION (TPR)

Samples for TPR were calcined under a flow of oxygen (180 ml/min) at a heating rate of 0.5 ° C/min. The calcination temperature (T_c) was varied in order to control the degree of deammination of $Pd(NH_3)_4^{2+}$ ions and the locations of Pd ions with respect to the Co^{2+} ions. At the end of calcination the final temperature was maintained for 2 h. Samples were then flushed with a stream of Ar gas to remove oxygen. After cooling to -78 ° C, a reducing gas mixture of H_2/Ar (5% H_2) was led through the reactor with a flow rate of 25 ml/min. TPR was then carried out at a heating rate of 8 ° C/min. Hydrogen consumption was calculated from the integrated TPR spectra after calibration with CuO. All experiments were repeated and the data were found reproducible within $\leqslant 10\%$.

3. Results and discussion

Diffuse reflectance spectroscopy has been used by Hutta and Lunsford [17] to identify the location of Co^{2+} ions in NaY. These authors report migration of a significant fraction of the Co^{2+} ions into hexagonal prisms at 600 ° C in vacuo. Gallezot and Imelik [18] used X-ray diffraction to determine the location of Co^{2+} ions for a sample with 14 Co^{2+} ions per unit cell in NaY zeolite. They report that Co^{2+} occupies SI′ and SII′ sites in sodalite cages at 200 ° C in vacuo, but at 600 ° C about 78% of Co^{2+} ions are located in hexagonal prisms. We, therefore, assume that under the conditions of our ion migration procedure, the majority of the Co^{2+} ions will migrate into hexagonal prisms, while a minority may be located in sodalite cages. Rehydration after ion migration will cause Co ions to migrate out of the hexagonal prisms, and they will distribute themselves over supercages and sodalite cages.

As the secondary ion exchange of $Pd(NH_3)_4^{2+}$ ions requires immersion of the sample in an aqueous solution, we also rehydrated our CoNaY samples after ion migration. The TPR results in fig. 1 (A) show that this rehydration has no effect on the reduction profile of Co. Absence of hydrolysis is also clear from the data in fig. 1 (A), which show that no Co^{2+} ions are reduced below 750 ° C. It is known that hydrolysed cobalt would be reduced at significantly lower temperature [4].

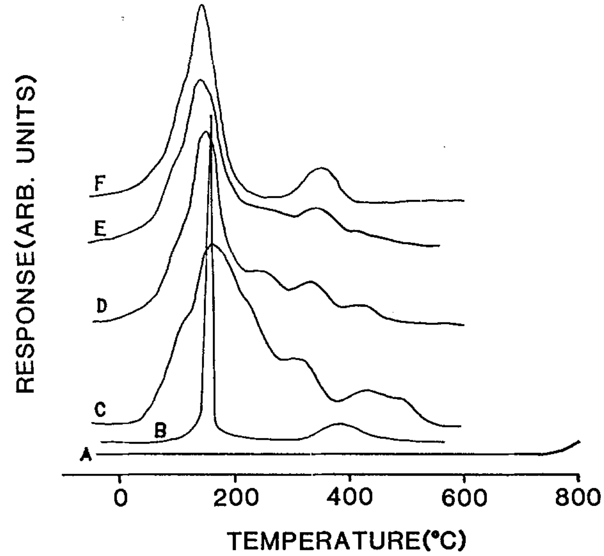

Fig. 1. A. TPR spectrum of CoNaY calcined at various temperatures, B. TPR spectrum of $Pd_{8.7}Co_{8.9}NaY$ calcined at 250 ° C, C. same as B except calcined at 300 ° C, D. same as B except calcined at 400 ° C, E. same as B except calcined at 500 ° C, F. same as B except calcined at 600 ° C.

The virtual irreducibility of Co^{2+} ions in zeolites had been reported before [19]. The causes of this phenomenon include the low electrochemical reduction potential of Co^{2+} ions and the strong bond of Co^{2+} to the zeolite framework oxygens [18].

X-ray diffraction and chemical techniques such as TPO and TPR have been used to study the system of NaY zeolite with exchanged $Pd(NH_3)_4^{2+}$ ionic precursors [20–22]. The location of complexed palladium ions is determined by their size. $Pd(NH_3)_4^{2+}$ are initially in supercages. After losing two ammines at $T_c \leqslant 250\,°C$, they are still unable to pass through the ~ 2.6 Å windows separating supercages and sodalite cages. However, after losing one more NH_3 or both, the Pd^{2+} ions rapidly migrate into sodalite cages where they are stabilized due to the higher density of negative charge. The temperature where the complete oxidation of NH_3 ligands takes place depends on the pH the original ion exchange had been carried out. For the present samples (pH = 6), diffuse reflectance spectroscopy shows the presence of $Pd(NH_3)_2^{2+}$ after $T_c = 250\,°C$, whereas no NH_3 ligands are detectable after $T_c = 300\,°C$ [23]. Diffuse reflectance was also used in the present research to monitor the locations of Co^{2+} and Pd^{2+} ions in NaY.

In view of the proximity requirement described in the Introduction, we have attempted to approach one of the two extreme situations: either most Co and Pd ions share the same sodalite cage, or most Pd ions are in supercages and most Co ions in sodalite cages. These situations can be achieved by choosing appropriate metal loadings and controlling the calcination temperature after ion exchange of the second metal. When both ions are driven into the small cages, the change for

Table 1
Extent of reduction of Co^{2+} ions

# of Pd per u.c.	# of Co per u.c.	Calcination temp. (° C)	% of Co reduced
–	8.9	250	– +
–	8.9	300	– +
–	8.9	400	– +
–	8.9	500	– +
8.7	8.9	250	12.0
8.7	8.9	300	75.0
8.7	8.9	400	70.0
8.7	8.9	500	44.8
8.7	8.9	600	34.8
3.0	8.9	500	12.2
0.8	3.0	500	6.64

+ Co^{2+} reduction not detectable below 750 ° C.

cage sharing is high e.g. in $Pd_{8.7}Co_{8.9}Na_{20.8}Y$, since the faujasite lattice has eight supercages and eight sodalite cages per unit cell. The TPR spectra of this sample are shown in fig. 1 (B), (C), (D), (E) and (F) after calcination at 250 ° C, 300 ° C, 400 ° C, 500 ° C, and 600 ° C, respectively.

In evaluating these results, it is essential that at $T_c = 250$ ° C, most of the Pd ions are located in supercages with two ammine ligands, but at $T_c = 300$ ° C, they are in sodalite cages. As is the case for Pd/NaY, the TPR peak of Pd is narrow in the former case, but broader and shifted to higher temperature with $T_c = 300$ ° C. The remarkable new result is, however, that reduction of Co^{2+} takes place at a much lower temperature when the Pd ions have been deamminated and moved into the sodalite cages, as will be evident from fig. 1 and table 1. Although Co reduction is not complete, most Co^{2+} ions are reduced for the sample with $T_c = 300$ ° C. These results show that reduction of Co can be dramatically enhanced by the presence of Pd, but the extent of this effect strongly depends on the relative locations of Co and Pd ions, which is controlled by the calcination temperature. Only about 12.0% of the Co^{2+} ions are reduced for $T_c = 250$ ° C, but 75% for $T_c = 300$ ° C. Further increase of T_c lowers the fraction of the Co^{2+} ions reducible at low temperature.

These results clearly show that the location of the ions is of decisive importance for the Pd enhanced reduction of Co^{2+} ions in NaY. The majority of the Co^{2+} ions occupies SI′ and SII′ sites in sodalite cages [17,18], but a small fraction might occupy sites in supercages at $T_c = 250$ ° C. Only these Co ions thus share a cage with Pd^{2+}; they might be reduced after calcination at 250 ° C. After calcination at $\geqslant 300$ ° C, Pd^{2+} and some Co^{2+} ions share the same sodalite cages. This is evidently a prerequisite for efficient reduction enhancement by Pd. The decrease in Co reducibility by further increasing the calcination temperature may be due to escape of Co^{2+} ion from sodalite cages into hexagonal prisms which is known to occur at higher calcination temperature [17,18]. Our data suggest that Co^{2+} ions in hexagonal prisms are not affected by Pd in sodalite cages. Due to its size, the Pd^{2+} ion is unable to migrate into hexagonal prisms [21].

For the metal loads used in the above experiments, at least one Pd^{2+} ion should be present in each sodalite cage, if the Pd^{2+} ions are equally distributed. Since every sodalite cage is surrounded by four hexagonal prism and every hexagonal prism is shared by two sodalite cages, the reduction of Co^{2+} ions would be complete after high temperature calcination, if Pd ions in sodalite cages could catalyze the reduction of Co^{2+} ions in an adjacent hexagonal prism. The decrease in the fraction of reduced Co^{2+} ions with increasing calcination temperature, therefore, indicates that the positive effect of Pd on the reduction of Co^{2+} is limited to ions in the same sodalite cage.

A rough estimate of the fraction of Co^{2+} ions in hexagonal prisms can be obtained by assuming that one Pd ion is present in each sodalite cage and that the unreduced Co^{2+} ions are located in hexagonal prisms, while the fraction of Co ions in supercages is negligible. It then follows that at $T_c = 600\,^\circ C$, some 65% of the Co^{2+} ions are in hexagonal prisms. This is reasonably close to the value of 78% found by Bergeret et al. [21] from XRD for a sample containing 14 Co atoms per unit cell. These authors also mention that the fraction of Co^{2+} ions in hexagonal prisms decreases with decreasing metal loading [21]. As the metal loading of the present sample (8.9 Co^{2+} ions per unit cell) is significantly lower than in the samples of Bergeret et al., the agreement of their numbers and ours appears quite satisfactory.

The strong proximity requirement indicated by the present results does not agree with the model, assuming spillover of hydrogen over large distances. If that model were valid, the majority of Co^{2+} ions in sodalite cages would have been reduced when Pd particles are formed in the supercages, which is obviously not the case.

The coreduction of Pd and Co ions pairing up in same sodalite cages, suggests some cation-cation interaction. Since the diameter of the sodalite cages in NaY is about 6.6 Å, the distance between two cations, each attached to a cage wall, can be roughly estimated by subtracting the Co-O and Pd-O bond distances from the cage diameter. The resulting value of ≈ 3 Å is in agreement with the assumption of some cation-cation bond and, hence, consistent with the model that reduction of this ion pair is a coherent chemical process. It has been suggested by Homeyer and Sachtler [24], that Pd ion pairs in the same sodalite cages are reduced at a lower temperature than isolated Pd ions. This is consistent with results obtained for other systems [9]. For Pt-Fe^{3+} and Pd-Fe^{3+} in NaY it has been found that the reduction of Fe^{3+} to Fe^{2+} is strongly enhanced by the Pt or Pd [25,26]; in the case of Pt-Fe the direct interaction of both elements on an atomic scale has been demonstrated by Mössbauer data of Balse et al. [16].

As the sodalite cage can accommodate only two divalent cations for the Si/Al ratio of the NaY zeolite used in this work, the chances for obtaining Pd-Co ion pairs should depend on their overall abundances. If the Pd load is lower than one Pd atom per sodalite cage, less Pd-Co pairs an be formed. This aspect of the model is also consistent with the data in table 1. Assuming that the percentage of Co^{2+} ions in hexagonal prisms is equal for the samples with 8 Co ions per unit cell, this leaves 4 Co^{2+} ions in sodalite cages per unit cell at $T_c = 500\,^\circ C$, as calculated above for $Pd_{8.7}Co_{8.9}NaY$. In the $Pd_{3.0}Co_{8.9}NaY$ the three Pd ions should then be able to catalyze the reduction of 16% of the Co^{2+} ions. The number found and shown in table 1 for $Pd_{3.0}Co_{8.9}NaY$ is 12.2%. Similarly, the estimate for $Pd_{0.8}Co_{3.0}NaY$ is 5% Co^{2+} reduction at low temperature, which compares favorably with the experimental value of 6.6%. The validity of these estimates is, of course limited by the unproven assumption that the distribution of Co^{2+} ions is independent of the metal loading, which is presumably not correct. [18].

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References

[1] M.S. Tzou, B.K. Teo and W.M.H. Sachtler, J. Catal. 113 (1988) 220.
[2] H.J. Jiang, M.S. Tzou and W.M.H. Sachtler, Catal. Lett. 1 (1988) 99.
[3] M. Suzuki, K. Tsutsumi, H. Takahashi and Y. Saito, Zeolites 8 (1988) 284.
[4] M. Suzuki, K. Tsutsumi, H. Takahashi and Y. Saito, Zeolites 8 (1988) 381.
[5] M.S. Tzou, H.J. Jiang and W.M.H. Sachtler, Reaction Kinet. Catal. Lett. 35 (1987) 207.
[6] T. Bein and P.A. Jacobs, J. Chem. Soc., Faraday Trans. 1 180 (1984) 1391.
[7] K.E. Lewis, D.M. Golden and G.P. Smith, J. Am. Chem. Soc. 106 (1984) 3905.
[8] M. Guilleux, M. Kermarec and D. Delafosse, J. Chem. Soc. Chem. Comm. (1977) 102.
[9] S.M. Augustine and W.M.H. Sachtler, J. Catal. 116 (1989) 184.
[10] G. Moretti and W.M.H. Sachtler, J. Catal. 115 (1989) 205.
[11] W.M.H. Sachtler, M.S. Tzou and H.J. Jiang, Solid State Ionics 26 (1988) 71.
[12] P. Malet, G. Munuera and A. Caballero, J. Catal. 115 (1989) 567.
[13] E. Baumgartner, R. Wagner and C. Lentes-Wagner, J. Catal. 104 (1987) 307.
[14] G. Del Angel, B. Coq, R. Dutartre, F. Fajula, C. Figueras and C. Leclercq, in: *Spillover of Adsorbed Species*, eds. G.M. Pajonk, S.J. Teichner and J.E. Germain (Elsevier, Amsterdam, 1983) p. 301.
[15] B.C. Gates, J.R. Katzer and G.C.A. Schuit, *Chemistry of Catalytic Processes*, (McGraw-Hill, 1979) p. 51–57.
[16] V.R. Balse, W.M.H. Sachtler and J.A. Dumesic, Catal. Lett. 1 (1988) 275.
[17] P.J. Hutta and J.H. Lunsford, J. Chem. Phys. 66 (1977) 4716.
[18] P. Gallezot and B. Imelik, J. Chim. Phys. 71 (1974) 155.
[19] *Molecular Sieve-II*, ACS Symposium, No. 40, ed. J.R. Katzer (ACS, 1977).
[20] P. Gallezot and B. Imelik, Adv. Chem. Ser. 121 (1973) 66.

[21] G. Bergeret, P. Gallezot and B. Imelik, J. Phys. Chem. 45 (1981) 411.
[22] S.T. Homeyer and W.M.H. Sachtler, J. Catal. 116 (1989) (in press).
[23] Z. Zhang and W.M.H. Sachtler, unpublished results.
[24] S.T. Homeyer and W.M.H. Sachtler, J. Catal. (1989) (in press).
[25] S.T. Homeyer and W.M.H. Sachtler, unpublished results.
[26] M.S. Tzou, H.J. Jiang and W.M.H. Sachtler, Applied Catalysis 20 (1986) 231.