in activity observed after about 20 wt% is merely a consequence of surface area decrease by dilution of the support.

As a result of some amount of copper forming part of the bulk aluminate, and hence not being available at the surface, it should be expected that the optimum r_w value in the supported catalyst is not the same as in the unsupported catalyst, i.e., not corresponding to the stoichiometry of $CuCr_2O_4$ ($r_w = 0.62$), but corresponding to a smaller r_w value, probably tending to the stoichiometry of $Cu_2Cr_2O_4$ ($r_w = 0.45$). This has been reported in the patent literature (Farrauto et al., 1975), the optimum catalyst concentration corresponding to r_w between the two above.

Finally, the difference in resistance to water inhibition between supported CuO and $CuCr_2O_4$ (Table III) suggests that the latter should be preferred in a situation where water is present, as happens in auto-emission control of CO. The nature of the inhibition of the CO oxidation by water is a matter for further research.

Acknowledgment

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Synthesis of Faujasite Type Zeolites from Calcined Kaolins

Pedro Bosch, Lourdes Ortiz, and Isaac Schifter*

Instituto Mexicano del Petróleo, Subdirección de Investigación Básica de Procesos, Eje Central Lázaro Cárdenas #152, C.P. 07730, Mexico, D.F.

The A, X, and Y zeolites are synthesized from kaolins whose calcination temperature is related to the type of zeolite; the effect of the alkalinity as well as the induction time is considered. It is concluded that the kaolin is used as the supply of the silica and the alumina units necessary to synthesize the zeolites; however, not all the Al and Si atoms that compose the kaolin are useful, so the correlations established between the initial composition of the kaolin and the Si/Al ratio of the zeolite can be misleading. The results are compared with those obtained in the synthesis of zeolites from soluble salts.

Introduction

Synthetic zeolites can be used in several processes as diverse as ionic exchange, adsorption, and selective separation of hydrocarbons or many catalytic reactions (Breck, 1963; Griesmer et al., 1960; Schwochow and Puppe, 1975). In the wide variety of zeolites, the A, X, and Y zeolites (related to faujasites) are the most requested. It has been shown (Barrer, 1968) that these materials can be synthesized from aluminosilicate gels heated between 50 and 150 °C. Generally an aqueous solution of a silicon salt or colloidal silica reacts with an aluminum salt. In a strongly alkaline medium they form a gel that generates zeolite after an "induction time"; the mechanism of this reaction seems to be autocatalytic (Kerr, 1968; Ciric, 1968). Almost all these works have been done with gels obtained from soluble salts (Zhdanov, 1971) but the zeolites can also be synthesized from natural clays, particularly kaolins. Although studies of the formation of A and X zeolites have been reported (Breck, 1974), the way to generate high SiO_2/Al_2O_3 faujasites is only found in the patents bibliography.

In this work, the A, X, and Y zeolites are synthesized from kaolins whose calcination temperature is related to the type of zeolite; the effect of the alkalinity and the induction time are considered.

Theory

Not all the clays can be regarded as kaolins. From a strictly clay-mineral standpoint, the most important

Table I. Composition of the Kaolins Calcinated at 750 °C

kaolin	% SiO_2 (wt)	% Al_2O_3 (wt)	% TiO_2 (wt)	% Fe_2O_3 (wt)	% Na_2O (wt)	% K_2O (wt)
E.P.K.	54.06	45.94	1.00	0.228	-	-
AH	20.00	73.80	0.35	0.951	0.74	0.74

minerals to be considered are the hydrated aluminosilicates; kaolinite, halloysite, dickite, and nacrite, whose chemical analysis conform rather closely with the ideal oxide ratios Al_2O_3:SiO_2:H_2O, 1:2:2. Kaolinite is a very common mineral; it is present in almost all clay fractions. Its crystalline structure is formed by tetrahedral silica and octahedral alumina layers that share some of their oxygen atoms (Brindley, 1961; Grim, 1953). From the bibliography it can be pointed out that the kaolinite must be "activated" by a thermal treatment previous to the zeolite synthesis process (Haden and Dzierzanowski, 1968, 1972). Then it seems interesting to discuss the structural changes of the kaolins due to the temperature.

The DTA and TGA studies of pure kaolinites show an endothermic hydroxilation in the range of 400–600 °C. Several factors as the crystallinity, particle size, impurities, etc., determine the initial temperature of this reaction as well as the maximum of the endothermic peak (Grim, 1953). The resulting compound, metakaolin, does not have the same chemical properties; indeed even if it is composed of silica and alumina, it is not crystalline (Levedev, 1956). For some kaolins an exothermic reaction without change of mass occurs in the range of 900–1000 °C. The interpretation of this transition has been frequently discussed, the X-ray diffraction and transmission electron microscopy results tend, in some cases, to demonstrate the presence of compounds such as γ-alumina, amorphous silica, mullite, or their mixtures (Grim, 1953). Brindley and Nakahira (1958) have shown that the exothermic peak occurring at 925 °C is due to the crystallization of the metakaolin into a spinel compound that, afterwards at 1100 °C, evolutes to mullite whose oxide ratios are SiO_2:Al_2O_3 = 1:1 and cristobalite. At 1400 °C the product becomes mullite (oxide ratio = 2:3).

Experimental Section

Materials. Two commercial kaolins were used, known as E.P.K. (The Feldspar Co., U.S.A.) and AH (Ventas Técnicas, México City). The other materials were sodium silicate solution containing 29.5 wt. % SiO_2 and 9.16 wt. % Na_2O as supplied by Silicatos y Derivados, S.A., México City; hydrated alumina C-30, 64.5 wt % Al_2O_3 (Kaiser Chemicals, U.S.A.) aqueous colloidal silica sol (Ludox HS, 30% SiO_2, Du Pont) and sodium hydroxide pellets (Baker Analysed, México).

Methods. The kaolins were analyzed by X-ray diffraction and chemical analysis. Also DTA and TGA were performed.

The silica and alumina contents after dissolution of the sample were estimated following classical methods. The other elements were evaluated by flame spectrophotometry performed on a Perkin-Elmer 303 Unit. The results corresponding to samples calcined at 750 °C for 3 h are summarized in Table I. The noncalcined samples diffractograms were registered with a horizontal Philips goniometer mounted on a copper radiation tube. The κ_β wavelength was eliminated with a diffracted beam monochromator. It was, then, found that the main component of the E.P.K. kaolin was ordered kaolinite. In fact, kaolin structures are complex because generally they are not pure; however, the kaolinite can be recognized by its laminar structure and, in the "ordered" case by the peaks (0,0.2)

in d = 3.57 Å and (2,0,1) in d = 2.56 Å. The kaolinite found in the AH kaolin was a disordered one; then it seems that the AH kaolin is a mineral clay less crystalline than kaolinite but more ordered than halloysite; it was also seen that it contained alunite, clearly recognized by the X-ray diffraction peaks in d = 4.29 Å and d = 2.96 Å. In both cases the 900 °C and 1000 °C calcined samples did not reveal any crystalline compound with the exception of quartz.

In the DTA–TGA studies, the samples were calcined from ambient temperature to 1100 °C in air atmosphere (80 mL/min) at a rate of 10 °C/min. The apparatus were Du Pont 950 (TGA) and 951 (DTA). The study of the E.P.K. revealed that the beginning of the endothermic peak was located at 395 °C and the exothermic peak at 960 °C. In the same range of temperatures, the TGA measurements showed a 12.5 wt % loss corresponding to the two water molecules.

In the case of the AH kaolin the beginning of the endothermic peak was located at 400 °C and the exothermic peak at 1005 °C; the weight loss was equal to 14.6%. Using soluble salts and depending of the initial ratios required, the sources of silica were sodium silicate solution or aqueous colloidal silica. The parent gels were prepared dissolving the aluminum hydroxide in the NaOH solution in appropriate quantity and then mixing the resultant solution with silica. The products were stocked at ambient temperature without agitation for 24 h and then heated also without agitation at 85 °C for 24 h in polypropylene containers. The solids were filtered off, washed, and dried at 120 °C. The samples were then calcined 3 h at 350 °C and rapidly transferred into a glass chamber maintained at 75% humidity content. The same procedure was used in the synthesis with clays, previously ground to less than 200 mesh (Tyler) and mixed to an NaOH solution. In several cases, when AH kaolin was used, the required alumina content was adjusted adding a sodium aluminate solution.

X-ray diffraction analysis of the synthesized samples were carried out comparing the diffraction patterns with those reported by the Powder Diffraction File Search Manual (1975). The quantity of zeolite present in samples, defined as crystallinity, was carried out comparing the peak intensities with those of a pure standard (Zénith et al., 1981). In addition of zeolite A, several samples included minor proportions of hydroxysodalite zeolite, HS, whose typical oxide formula is $Na_2O\cdot Al_2O_3\cdot 2SiO_2\cdot 2.5H_2O$ as described by Breck (1974). For pure faujasite samples, crystallinity was determined by a cyclohexane sorption curve obtained in a McBain type balance (Zénith et al., 1981).

With X-ray diffraction the SiO_2/Al_2O_3 ratio in the final product was estimated from the measurements of the cell constants according to Dempsey et al. (1969), determining the peak position of the (6,4,2) reflection with a graphite internal standard. In the case of some faujasite samples, cubic P zeolite also referred as B zeolite, was also identified (Breck, 1974). For faujasites obtained from kaolins, crystallinity was also estimated by the method of peak summation from X-ray diffraction patterns using standard reference samples.

Results

Synthesis from Soluble Salts. Table II summarizes the results obtained using soluble salts and heating the samples during 24 h. In Figure 1 the initial molar ratios Na_2O/SiO_2 and SiO_2/Al_2O_3 are plotted. It is clear that five zones exist where crystallization of the A, X, and Y zeolites is observed.

Table II. Characterization of the Zeolites Synthesized from Soluble Salts

	initial molar ratios			zeolite properties		
sample	Na_2O/SiO_2	SiO_2/Al_2O_3	H_2O/Na_2O	X-ray ident	SiO_2/Al_2O_3	crystallinity, %
161	1.48	1.00	60	A	2.00	95
311	1.79	1.00	50	A	2.00	95
378	1.20	1.50	40	A	2.00	95
377	1.80	1.50	40	A	2.00	93
204	1.20	2.00	40	A	2.00	87
185	1.48	2.00	60	A + X	2.47	
385	1.56	2.19	40	A + X	2.45	
205	1.50	2.25	40	A + X	2.45	
386	1.80	2.94	40	X > A	2.45	
142	1.43	2.93	40	X	2.45	92
199	1.03	2.94	30	X	2.42	
203	0.80	2.94	60	Y	2.92	
170	0.75	3.25	30	Y	3.40	
191	1.00	4.00	30	Y	2.80	90
431	1.00	6.00	30	Y	3.30	
186	1.44	10.0	40	Y	3.40	
18	1.44	10.0	20	Y	3.40	
209	0.751	11.2	20	Y	3.11	15
207	0.83	21.0	30	Y	3.29	
083	0.37	9.35	40	Y	4.91	92
084	0.49	28.2	40	Y	4.93	92
201	3.00	2.93	30	amorphous	-	-

Table III. SiO_2/Al_2O_3 Ratio of the Zeolite Compared with the Kaolin Calcination Temperature (E.P.K./NaOH = 4.42)

	calcination		kaolin E.P.K.					zeolite properties		
sample	temp, °C	time, h	kaolin/ NaOH (wt)	kaolin/ H_2O (wt)	Na_2O^a/ SiO_2 (mol)	SiO_2 ^{a}/ Al_2O_3 (mol)	H_2O/ Na_2O (mol)	X-ray ident	SiO_2/ Al_2O_3	crystallinity, %
480	750	1	4.42	0.74	0.36	2.00	28.57	A	2.00	82
158	900	1	4.42	0.74	0.36	2.00	28.57	A	2.00	70
160	950	1	4.42	0.74	0.36	2.00	28.57	Y	4.31	43
481	1000	1	4.42	0.74	0.36	2.00	28.57	Y	4.30	15
241	1000	2	4.42	0.74	0.36	2.00	28.57	Y	4.30	11
459	1100	1	4.42	0.74	0.36	2.00	28.57	amorphous	-	-

^{a} Calculated theoretically.

Table IV. SiO_2/Al_2O_3 Ratio of the Zeolite Compared with the Kaolin Calcination Temperature (E.P.K./NaOH = 9)

	calcination		kaolin E.P.K.					zeolite properties		
sample	temp, °C	time, h	kaolin/ NaOH (wt)	kaolin/ H_2O (wt)	Na_2O^a/ SiO_2 (mol)	SiO_2 ^{a}/ Al_2O_3 (mol)	H_2O/ Na_2O (mol)	X-ray ident	SiO_2/ Al_2O_3	crystallinity, %
380	750	1	9.0	0.74	0.17	2.00	28.57	A	2.00	78
482	900	1	9.0	0.74	0.17	2.00	28.57	A	2.00	49
463	950	1	9.0	0.74	0.17	2.00	28.57	Y	4.82	29
483	1000	1	9.0	0.74	0.17	2.00	28.57	Y	4.30	8
384	1100	1	9.0	0.74	0.17	2.00	28.57	amorphous	-	-

^{a} Calculated theoretically.

Zone number 1 corresponds to the A zeolite and zone number 2 to the mixtures of A and X. In zone number 3 the X faujasite is obtained; in zone number 4 the faujasites have an SiO_2/Al_2O_3 ratio lower than 4. The high ratio faujasites of zone number 5 can only be synthesized using colloidal silica. Qualitatively these results agree with those recently reported by Kostinko (1982).

Synthesis from E.P.K. Kaolin. Two concentrations of alkaline solution were used to study the effect of time and temperature of calcination of the kaolin. The calcination temperatures include those where the DTA analysis reports the formation of the metakaolin and the maximum of the exothermic peak. Table III shows the results obtained for a kaolin/NAOH weight ratio of 4.42 and Table IV corresponds to a relation equal to 9 (lower alkalinity). These weight ratios were calculated theoretically from the initial composition of the kaolin. As is seen in both tables, in the 750–900 °C calcination range, zeolite A is obtained, but between 950 and 1000 °C, the faujasite is Y and the SiO_2/Al_2O_3 ratio is greater than 4. If the 950 °C samples

of the tables are compared, it seems that the lower the alkalinity the greater the silica content of the zeolite. For both series, at 1100 °C no zeolite is obtained even if the period of heating of the aluminosilicate gel is prolonged for 96 h. As a general rule the degree of crystallinity of these materials is lower than the one of the samples obtained by the soluble salts methods. Table V shows the consequences of the alkalinity changes from a sample calcined at 950 °C for 1 h. The Si/Al ratio increases as the alkalinity decreases. This fact was previously reported for samples prepared using other minerals (Aiello and Colella, 1970) as well as for soluble salts (Zhdanov, 1971). It can also be pointed out that if the initial oxide ratios (assuming that all the Si and Al are used in the transformation) are calculated theoretically, and if the results are referred to those of Figure 1, it is observed that the faujasite of high SiO_2/Al_2O_3 ratios should not be formed in those zones. This remark was verified using soluble salts with the same oxide ratios; it was then confirmed that faujasite did not crystallize even for long periods of heating.

Table V. SiO₂/Al₂O₃ Ratio of the Zeolite Compared with the Alkalinity for E.P.K. Kaolin

| | calcination | | kaolin E.P.K. | | | | | zeolite properties | | |
| | temp, °C | time, h | kaolin/ NaOH (wt) | kaolin/ H₂O (wt) | Na₂O/ SiO₂ (mol) | SiO₂/ Al₂O₃ (mol) | H₂O/ Na₂O (mol) | X-ray identi- fication | SiO₂/ Al₂O₃ | crystallinity, % |
sample										
456	950	1	2.94	0.74	0.54	2.00	28.57	Y	2.47	8
160	950	1	4.42	0.74	0.36	2.00	28.57	Y	4.31	44
455	950	1	6.99	0.74	0.23	2.00	28.57	Y	4.93	26
463	950	1	9.00	0.74	0.17	2.00	28.57	Y	4.82	29

[a] Calculated theoretically.

Table VI. Importance of Aging Time

| | calcination | | | | |
sample	temp, °C	time, h	aging time, h	X-ray ident	crystalln time, h
239	950	1	6	Pc	64
243	950	1	12	Pc	64
241	950	1	24	Y	24

Table VI shows the effect of aging time at ambient temperature upon the type of zeolite obtained. Agings lower than 12 h produce cubic P zeolite only if the samples are heated for a long time.

Synthesis from AH Kaolin. Table VII summarizes the results obtained for the variation of calcination temperature with a constant volume of alkaline solution. In this case, the faujasite X obtained is always impurified with hydroxysodalite zeolite. It is also remarked that, as in the case of the E.P.K. samples, no zeolite is observed for calcination temperatures greater than 1000 °C. Also if the calcination temperature is kept constant (950 °C, 1 h) and

the alkalinity is increased, Table VIII, the Si/Al ratio decreases, as in the case of E.P.K. kaolin.

Finally, several A zeolites were prepared adding the required Al in order to evaluate the reactivity degree of the AH kaolin. The results are compared with those obtained with E.P.K. (sample no. 140) in Table IX. The calculated value indicated in the table is based on the assumption that all the aluminum is consumed in the transformation.

Discussion

The crystallization of the zeolites can be explained as a new ordering of the aluminum octahedra (Al^{3+}) and silicon tetrahedra (Si^{4+}) that constitute the initial compounds. The electrical charge deficiency is neutralized with an additional positive ion located in the interstices of the framework. So the formation of zeolite nuclei is due to the interaction of the silicate anions with those of the aluminate, and the type of zeolite that results depends on the initial composition of the mixture. If the zeolite is crystallized from soluble salts and the relative concen-

Table VII. SiO₂/Al₂O₃ Ratio of the Zeolite Compared with the Kaolin Calcination Temperature (AH/NaOH = 4.42)

| | calcination | | kaolin AH | | | | | zeolite properties | |
| | temp, °C | time, h | kaolin/ NaOH (wt) | kaolin/ H₂O (wt) | Na₂O[a]/ SiO₂ (mol) | SiO₂[a]/ Al₂O₃ (mol) | H₂O/ Na₂O (mol) | X-ray ident | SiO₂/Al₂O₃ |
sample									
499	750	1	4.42	0.74	0.22	6.27	28.36	X + HS	2.38
457	950	1	4.42	0.74	0.22	6.27	28.36	Y + HS	3.55
448	1000	1	4.42	0.74	0.22	6.27	28.36	X + HS	2.42
458	1100	1	4.42	0.74	0.22	6.27	28.36	amorphous	-

[a] Calculated theoretically.

Table VIII. SiO₂/Al₂O₃ Ratio of the Zeolite Compared with the Alkalinity for AH Kaolin

| | calcination | | kaolin AH | | | | | zeolite properties | |
| | temp, °C | time, h | kaolin/ NaOH (wt) | kaolin/ H₂O (wt) | Na₂O[a]/ SiO₂ (mol) | SiO₂[a]/ Al₂O₃ (mol) | H₂O/ Na₂O (mol) | X-ray ident | SiO₂/Al₂O₃ |
sample									
466	950	1	1.14	0.74	0.88	6.27	28.36	X + HS	2.38
454	950	1	2.94	0.74	0.34	6.27	28.36	X + HS	2.38
457	950	1	4.41	0.74	0.23	6.27	28.36	Y + HS	3.55
465	950	1	5.50	0.74	0.18	6.27	28.36	amorphous	-
464	950	1	6.99	0.74	0.14	6.27	28.36	amorphous	-

[a] Calculated theoretically.

Table IX. "Reactivity" of the AH Kaolin

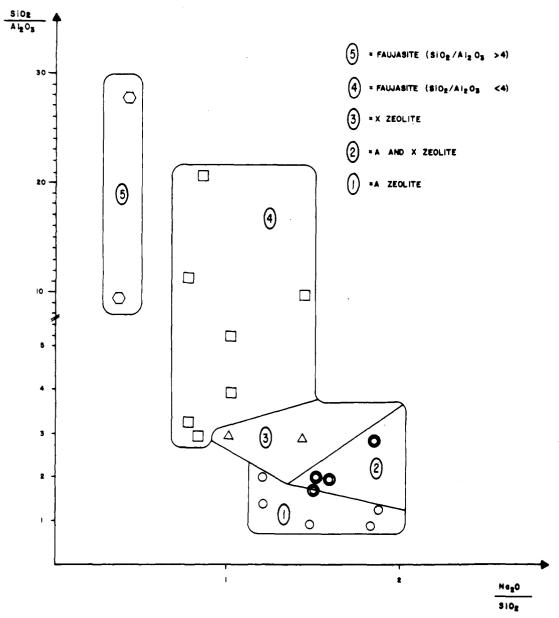| | calcination | | kaolin AH | | | zeolite properties | | |
| | | | Na₂O/ SiO₂ (mol) | SiO₂/ Al₂O₃ (mol) | H₂O/ Na₂O (mol) | | crystallinity % | |
sample	temp, °C	time, h				X-ray ident	exptl	calcd
374	750	2	1.80	1.50	40	A	58	67
375	750	1	1.20	1.50	40	A	55	69
317	750	1	0.60	2.00	40	A	64	45
200	750	1	0.95	2.00	40	A	66	54
338	750	1	1.20	2.00	40	A	59	70
140 (EPK)	750	2	1.20	2.00	40	A	85	93

Figure 1. Plot of Na_2O/SiO_2 against SiO_2/Al_2O_3 for soluble salts.

trations of the reactants are known, the map that predicts the type of zeolite can be established, Figure 1, in the same way as other workers have done it (Bajpal et al., 1978; Zhdanov, 1971). However, if the zeolites are crystallized from kaolins this prediction is no longer maintained. The synthesized solids show a Si/Al ratio that disagrees from the expected one assuming that all the Si and Al atoms are used to build the structure. As suggested by Table III, the Si/Al ratio depends on the temperature of calcination of the kaolin; it remains constant from 750 °C to 900 °C giving a certain kind of zeolite and from 950 °C to 1000 °C giving X and Y zeolites. Between 900 and 950 °C there is a drastic change in the Si/Al ratio of the faujasite that is coincident with the crystallographic change that appears in the kaolinite (main compound of the kaolins used in this work). Around 950 °C for E.P.K. a compound is formed that solubilizes into a highly reactive Si and Al species that can produce faujasites of high Si/Al ratio which using soluble salts are only obtainable with colloidal silica. The values of crystallinity, as a measure of the Al and Si available, suggest that a certain fraction of the clay remains unreactive; otherwise, only a fraction of the kaolin is solubilized in highly reactive form.

When the crystallinity changes, it means that the

Table X. Kaolin Amount and Soluble Salts Amount Needed To Obtain the Same Zeolite

source	initial molar ratios			zeolite
	Na_2O/ SiO_2	SiO_2/ Al_2O_3	H_2O/ Na_2O	SiO_2/ Al_2O_3
soluble salts	1.48	2.00	60	2.47
kaolin E.P.K.	0.54	2.00	28	2.47

amount of aluminate or silicate ions solubilized also varies, inducing a shift in the composition of the liquid phase. Then the zeolite obtained from this solution has a Si/Al ratio different from the expected one. Logically this effect is observed when the alkalinity varies; i.e. when the Na_2O/SiO_2 ratio is modified, Table V.

In order to evaluate what percentage of kaolin is not reacting, one has to compare the amount of kaolin with the amount of soluble salt necessary to obtain a zeolite with the same Si/Al ratio. This is done in Table X, which clearly shows that the Na_2O/SiO_2 ratio is three times lower for the kaolin sample, suggesting that only a third of the clay is available. The same comparison can be done for some other synthesis that confirm that the amount of non-used silica and alumina is not constant and that it

depends on the amount of Na$_2$O, Table VI.

For short aging times, the formation of cubic P zeolite is favorable, so more time is necessary to destroy the kaolin structure providing the amounts of silica and alumina units necessary to build in this case the Y zeolite. The results of kaolin AH confirm the previous remarks; taking into account that this kaolin is not pure kaolinite, their initial crystallinity determines the solubility of the Si and Al and, then, the composition of the resulting zeolite, Tables VII and VIII.

Table VIII shows that the Si/Al dissolved fraction of kaolin varies with the kaolin/NaOH ratio; indeed the X zeolite is obtained first, then the low Si/Al ratio Y, and finally no zeolite can be crystallized. Hydroxysodalite zeolite, whose generation is favored by high silica content of the gel (Breck, 1974), is always detected.

Conclusion

In this work it has been shown that kaolin is used as a supply of the silica and the alumina units necessary to synthesize the zeolites.

The thermal treatment of the kaolin is needed to destroy the initial crystallinity and to favor the dissolution of highly reactive species, but it has to be such that the sample does not recrystallize in a more stable phase. However, it is impossible to use all the Al and Si atoms that compose the kaolin; only a fraction of the original material is useful. This remark can be related to the suggestion of Brindley and Nakahira (1958) that around 925 °C new phases are formed. Finally, it has then to be kept in mind that the correlations established between the initial composition of the kaolin and the Si/Al ratio of the zeolite can be misleading.

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Activity and Durability of Iron Oxide–Titanium Oxide Catalysts for NO Reduction with NH$_3$

Akira Kato,* Shimpei Matsuda, and Tomoichi Kamo

Hitachi Research Laboratory, Hitachi Ltd., Kuji-cho, Hitachi-shi, Ibaraki-ken, 319-12 Japan

The reduction of NO with NH$_3$ on iron oxide–titanium oxide catalysts was studied with a flow reactor between 300 and 450 °C. Preparation of the catalysts has much influence on the activity. The activity was found to be enhanced with increase in the content of SO$_4{}^{2-}$ in the catalyst. The content of SO$_4{}^{2-}$ affected the amount of adsorbed NH$_3$. The iron oxide–titanium oxide catalyst whose major component was TiO$_2$ showed high durability to the SO$_x$ poisoning. On the other hand, the iron oxide catalyst lost its activity in the presence of SO$_3$ due to the physical property change caused by the formation of iron sulfate from reaction of Fe$_2$O$_3$ with SO$_3$.

Introduction

Nitrogen oxides (NO$_x$) from stationary combustion facilities such as power plant boilers comprise a considerable part of total NO$_x$ emitted to the atmosphere. The emission standards have been set forth for boilers and other stationary emission sources in Japan, and they will be stricter in the future. Several methods for the control of NO$_x$ have been proposed and tested using pilot plants (Bartok et al., 1969). It has been found that the selective catalytic reduction (SCR) process is most feasible for industrial application. By the end of 1981 several tens of commercial plants based on the SCR process were constructed in Japan, the largest one treating 2 million normal cubic meter per hour (Nm^3/h) of flue gas at a power station (700 MW) (Kuroda and Nakajima, 1978).

It has been known that NO$_x$ are selectively reduced by NH$_3$ in the presence of a large excess of oxygen (Bartok et al., 1969). Several catalysts, for example, V, Mo, W oxides (Nonnenmacher and Kartte, 1966), platinum metals (Anderson et al., 1962), CuO (Griffing et al., 1969), V$_2$O$_5$–Al$_2$O$_3$ and Fe–Cr (Bauerle et al., 1975; Wu and Nobe, 1977), Cr$_2$O$_3$–Al$_2$O$_3$ (Niiyama et al., 1977), and zeolite (Seiyama et al., 1977) have been known to enhance the NO$_x$–NH$_3$ reaction.

A catalyst used in a commerical plant must possess high activity and selectivity, since the volume of flue gas to be treated is extraordinarily large. In addition, the catalyst must be resistant to the SO$_x$ poisoning, since sulfur dioxide and sulfur trioxide are usually contained in an oil or coal-fired boiler flue gas.