Precursor Aluminum Effect in the Synthesis of Sol−Gel Si−Al Catalysts: FTIR and NMR Characterization

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Aluminosilicates were prepared by the sol−gel method using tetraethoxysilane as silica source and aluminum ethoxide, aluminum iso-propoxide, or aluminum *sec*-butoxide as alumina sources. An important effect of the alkylaluminum substitutes is observed in the BET specific area, ethoxide > isopropoxide > *sec*-butoxide. The ^{27}Al NMR spectra of the solids showed that the relative concentrations of tetrahedral, octahedral, or pentacoordinated aluminum strongly depend on the aluminum alkoxide source. It is shown by ^{29}Si NMR spectra that the formation of pentacoordinated aluminum is related to the odd silicon substitution, Si(1Al, 3Si) and Si(3Al, 1Si). The odd Si substitution was confirmed by FTIR spectroscopy following the Si−O−Si vibration band. The shift of the 1092 cm^{-1} band to 1029 cm^{-1} agrees well with the ^{29}Si NMR odd substitution. In general the aluminum coordination as well as the odd Si substitution is largely affected when the hydrolysis water concentration is varied. High activity is shown by the aluminosilicates during the 2-propanol dehydration reaction.

Introduction

Aluminosilicates have important application in the development of FCC catalysts. Active zeolites lose activity during cracking since large amounts of coke are formed at the high temperatures at which this process occurs. For the passivation of the catalyst are used FCC catalysts in which the active zeolite is supported on an amorphous silicoaluminate. The silicoaluminate by itself produces more coke than the zeolites.[1−3] However, the coke formed is mainly deposited on the surface of the matrix and then after passivation the deactivation of the FCC catalyst is diminished. The role of the silicoaluminate as support is then correlated to its complementary catalytic properties. The activity of an aluminosilicate strongly depends of the substitution of an aluminum atom in the network of silica. When the substitution of a tetracoordinated silicon atom is done by an aluminum, in the Si−O−Al bonds formed, the aluminum is tetrahedrally coordinated. A net negative charge is formed and is compensated by the presence of a proton. At a higher amount of tetrahedral aluminum, a higher amount of Bronstend acidity and then higher cracking activity is observed.[4−6]

The formation of silicoaluminates with a high content of tetracoordinated aluminum, strongly depends of the preparation conditions. A great variety of precursors sources are used for silicon and aluminum, including mineral and organic salts. The use of alkoxides as precursors is also described in various papers recently published.[6−9] In them, the major attention is given to the difficulty of avoiding surface segregation of alumina in a high silica content silicoaluminate. The main problem of the synthesis of silicoaluminates from silicon and aluminum alkoxides is aimed at promotion of a fast hydrolysis and a simultaneous copolymerization. Obviously the pH of the reaction, the amount of water, the gelation temperature and the appropriate addition of the precursors (simultaneously or by steps) are the main parameters to be controlled and studied.[10−13] Additionally, the nature of the alkoxides is of great importance. In the present paper, we report the preparation of silicoaluminates using tetraethoxysilane (TEOS) as silicon precursor and three aluminum alkoxides: ethoxide, isopropoxide, and *sec*-butoxide. The dried and calcined gels were characterized by FTIR and NMR. Their activities were determined in the reaction of 2-propanol dehydration.

Experimental Section

All the silicoaluminates were prepared at 13 wt % Al_2O_3. Appropriated amounts of tetraethoxysilane and aluminum alkoxide were mixed in an alcoholic solution containing (a) TEOS and aluminum ethoxide in ethanol, (b) TEOS and aluminum isopropoxide in 2-propanol, and (c) TEOS and aluminum *sec*-butoxide in *sec*-butanol. A value of 10 was chosen for the alcohol/alkoxides ratio. The alcoholic solution was put in a vessel and constantly stirred under reflux at 70 °C. Afterward, the hydrolysis water in a mole ratio H_2O/alkoxides of 2, 4, and 8 was slowly added during 30 min to the gelling solution. After formation, the gel, was dried at 70 °C (fresh samples) and subsequently thermally treated at various temperatures in air.

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Table 1. Catalysts Identification and Specific BET Areas of TEOS and Aluminum Alkoxides Sol−Gel Si−Al Preparation

sample	H_2O/alkoxide (mol ratio)	aluminum alkoxide precursor	BET area (m^2/g)
SiAle2	2	ethoxide	350
SiAli2	2	isopropoxide	251
SiAls2	2	*sec*-butoxide	228
SiAls4	4	*sec*-butoxide	366
SiAls8	8	*sec*-butoxide	339

The specific BET area of the samples treated at 500 °C was determined in an automated ASAP 2000 Micromeritics apparatus using nitrogen as adsorbent. The pore size distribution of the samples was calculated from the desorption isotherm and the BJH method was used for calculations.

FTIR studies were carried out in a Paragon-1000 Perkin-Elmer apparatus using transparent pellets of unmixed samples.

^{29}Si and ^{27}Al NMR spectra of the solids were recorded in a 300 MHz Bruker spectrometer. A 4.5-μs pulse (90°) was used with a repetition time of 5 s between pulses in order to avoid saturation effects. Zirconia cylindrical sample spinners with 5 mm inner diameter were used, and the spinning frequency was in the range 4−4.5 kHz. The number of accumulations was 500. All measurements were carried out at room temperature with $Al(H_2O)_6^{3+}$ and tetramethylsilane as standard reference for aluminum and silicon, respectively.

The catalytic activity of the silicoaluminates was determined in samples calcined at 500 °C in a fixed bed reactor at low conversions and atmospheric pressure. The 2-propanol was passed through the reactor by means of a saturator using nitrogen as carrier. The partial pressure of the alcohol in the feed was 22.4 Torr and the reaction temperature was 150 °C. The products of the reaction were analyzed in a gas chromatograph apparatus coupled to the reactant system. The only products detected were propene and acetone.

Results and Discussion

The specific BET areas of the catalysts are reported in Table 1. It can be seen that the catalysts prepared with aluminum ethoxide show a great area when compared with the other preparations. On the other hand, in Table 1, is shown the effect of water on the specific area. With aluminum *sec*-butoxide as aluminum precursor, the BET areas show a small maximum at a water/alkoxides molar ratio equal to 4. It is evident that two factors affect the specific area of sol−gel silicoaluminates, the size of the alkyl group and the amount of hydrolysis water. Large amounts of water produce a larger hydrolysis of the alkoxides, and hence copolymerization is better accomplished. However, the effect of the aluminum precursor and hydrolysis water amount obviously should also be observed in the pore size distribution. In Figure 1 the pore size distribution of the various silicoaluminates is shown. It can be seen that large pore size diameter corresponds to a large alkylaluminum group. The effect of water amount can be seen as an effect that constrains the pore size diameter. In supports or catalysts the pore size distribution is of great importance. Figure 1 shows that in the synthesis of silicoaluminates, it is possible to control the pore size by varying the aluminum precursor as well as the amount of hydrolysis water. Large pores can be obtained using large alkylaluminum precursors; the opposite case is observed when small alkyl groups were used.

The hydrolysis rate is faster for the aluminum alkoxide having the smaller alkyl group or under water excess. Then a great number of terminal Al−OH groups will be formed, and expansion of the network is favored during aging. Compacted Si−Al structures with small pore size diameter will then formed.

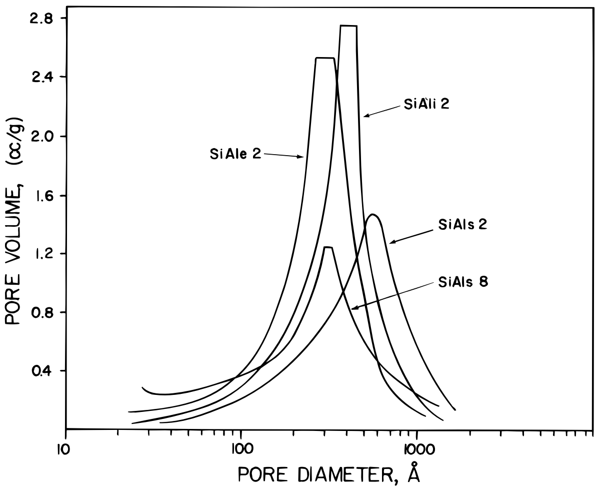

Figure 1. Pore size distributions of the various Si−Al sol−gel catalysts.

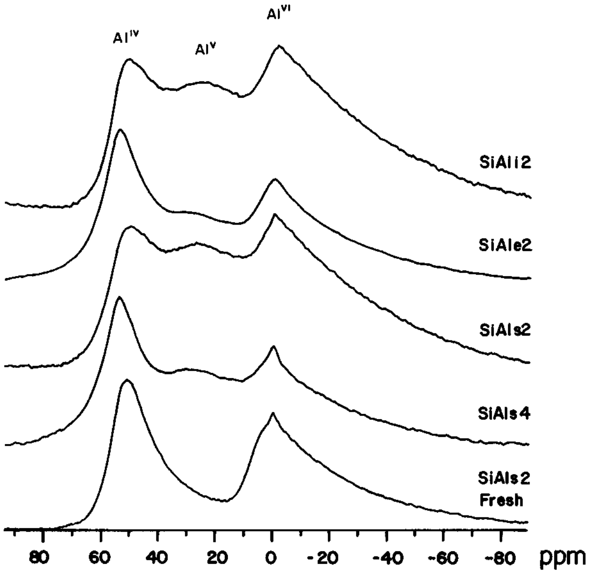

Figure 2. ^{27}Al−NMR spectra for the various Si−Al sol−gel catalysts.

^{27}Al NMR spectra of the samples were obtained with samples either fresh or calcined at 500 °C. The resonance position is reported between 55 and 70 ppm for tetrahedral aluminum Al^{IV}, around 25−30 ppm for the pentacoordinated aluminum Al^{V}, and at 0−11 ppm for the octahedrally coordinated Al^{VI}.[1,7−10,14−17] In Figure 2 it can be seen that tetrahedral, octahedral, and small amounts of pentacoordinated aluminum are formed in the sol−gel silicoaluminates. In the SiAls2 fresh sample only tetrahedral and octahedral aluminum was found. However, when the sample was treated at 500 °C in air, the SiAls2 develops the formation of pentacoordinated aluminum, and a relative increase of the octahedral

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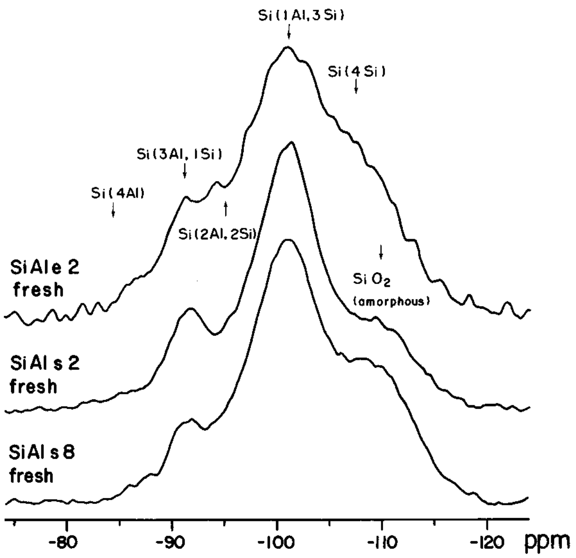

Figure 3. ^{29}Si NMR spectra for the various fresh Si−Al sol−gel catalysts.

aluminum is observed. The effect of water on the formation of Al^{IV} and Al^{VI} can be seen in Figure 2, where a large amount of Al^{IV} is observed. High hydrolysis of the aluminum *sec*-butoxide forms preferentially Al^{IV} and notably diminishes the formation of Al^{V}. The ^{27}Al NMR spectra of the silicoaluminates show an important effect of the alkyl groups in the formation of the different coordinations of aluminum. When the alkyl group is small (ethoxide), the quantity of Al^{IV} is higher if compared to the formation of Al^{VI}. Additionally no formation of Al^{V} could be suggested. On the other hand, when isopropoxide or *sec*-butoxide aluminum precursors were used for the preparation, a large alkyl group corresponds to the higher formation of Al^{VI} and Al^{V}. These results show that when the formation of octahedral aluminum is higher than the tetrahedral aluminum, such an effect is accompanied by the formation of Al^{V}.

The copolymerization of multicomponent systems from alkoxides often presents problems due to the differences in the rates of hydrolysis of the metal alkoxides: terminal hydroxides as well as terminal alkyl groups will be present and the relative concentrations will depend of the conditions of hydrolysis. As the alkyl group of the aluminum alkoxide is large, the number of terminal O−R groups present in the silicoaluminate increases. Elimination of alkyl groups requires thermal degradation, creating a high number of broken bonds. Nonstoichiometry structures reducing the network connectivity and large number of structural defects will be formed. Aluminum VI coordination will be higher in little hydrolyzed aluminum alkoxides (large alkyl groups), and strong structural defects such as formation of Al^{V} will occur. The ^{27}Al NMR results confirm such an assumption: the qualitative amounts of Al^{VI} and Al^{V} are higher in the thermally treated silicoaluminates prepared with aluminum isopropoxide and with aluminum *sec*-butoxide (Figure 2).

^{29}Si NMR spectra of the various samples of fresh and calcined catalysts are shown in Figures 3 and 4, respectively. The silicon substitution by aluminum in Si−O−Si bonds can be studied in relation with the corresponding signals as follows: ^{29}Si signals around −84 ppm are related to Si(4Al) substitution, those at −90 ppm to Si(3Al,1Si), at −95 ppm to Si(2Al,2Si), at −101 ppm to Si(1Al,3Si), and at −106 ppm to Si(4Si) not substituted silicon by aluminum.[1,15−18] A broad signal can also be observed at −109 ppm, assigned to amorphous SiO$_2$. In fresh samples the ^{29}Si signal substitution is shown as a function of water amount (SiAls2 and SiAls8) as well as a function of the aluminum precursor (SiAle2). In samples prepared with aluminum *sec*-butoxide we can see that the water amount does not have a noticeable effect on the number and substitution of Si atoms. The signals corresponding to Si(3A1,Si), Si(1Al,3Si), and amorphous SiO$_2$ are of the same order. However, it can be seen that the most important modification of the ^{29}Si spectra are observed when the alkyl group of the aluminum alkoxides is varied. In such a way, the spectrum corresponding to the preparation using aluminum ethoxide shows additionally the peak corresponding to Si(2Al,2Si) substitution. Upon thermal treatment of the samples, the NMR lines of ^{29}Si became less resolved. In Figure 4 are shown the spectra: the peaks corresponding to Si(3Al,1Si) and Si(1Al,3Si) substitution are defined only in the spectrum corresponding to high hydrolysis water amount, and a small progressive substitution of groups Si(4Si) to Si(3Al,1Si) and Si(1Al,3Si) with the increase of the water content is observed. It is difficult to put in evidence a correlation between the aluminum coordination and the Si substitution. However, in calcined samples we can experimentally observe that the higher formation of Al^{V} corresponds to the spectra of ^{29}Si which show the larger odd substitution Si(1Al,3Si) and Si(3Al,1Si).

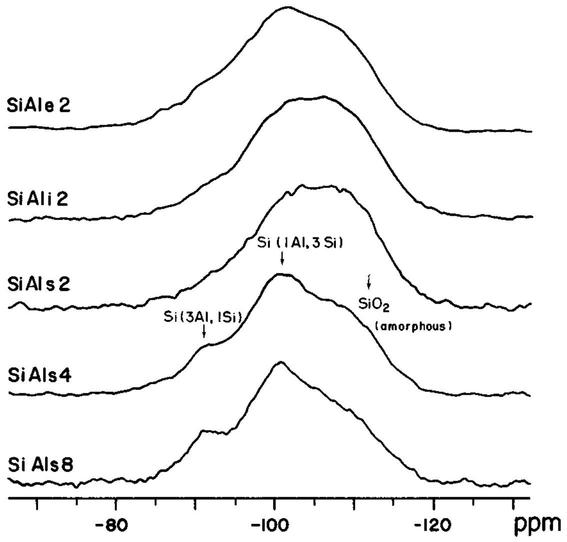

Figure 4. ^{29}Si NMR spectra for the various calcined Si−Al sol−gel catalysts.

FTIR spectra of the fresh samples were obtained and they are reported in Figures 5 and 6. The bands assigned to sol−gel Si−O−Si symmetric and asymmetric vibrations are reported to appear around 1092[18] and 780 cm^{-1}, respectively, and the Si−O stretching vibration band at 450 cm^{-1}.[1,18−20] Bending vibrations of Si−O^{-} and Si−OH groups are also observed at 900

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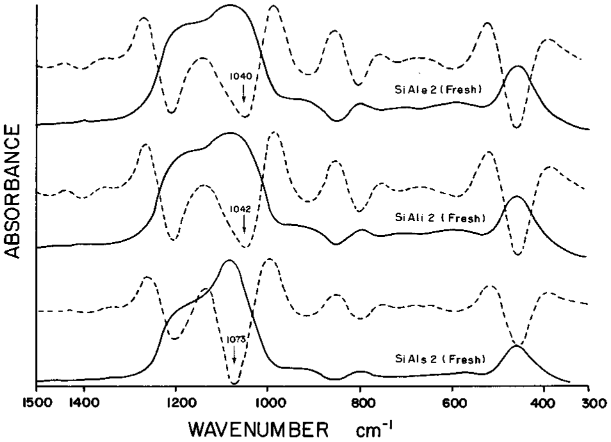

Figure 5. FTIR absorption spectra and second derivative of the various fresh Si−Al catalysts: aluminum precursor effect.

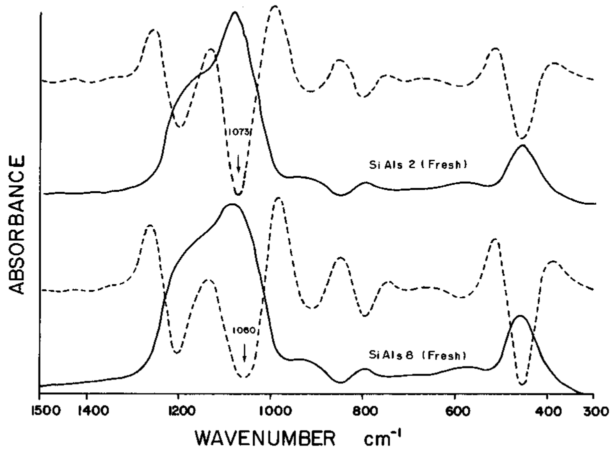

Figure 6. FTIR absorption spectra and second derivative of the various fresh catalysts: water effect.

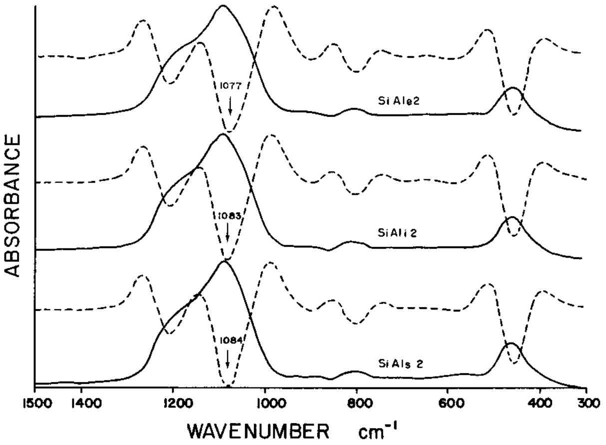

Figure 7. FTIR absorption spectra and second derivative of the calcined Si−Al catalysts: aluminum precursor effect.

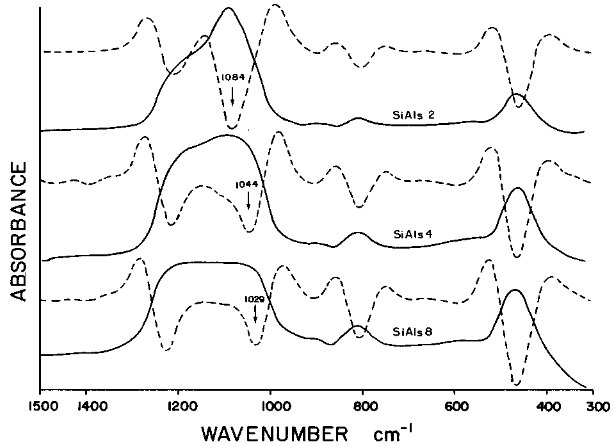

Figure 8. FTIR absorption spectra and second derivative of the calcined Si−Al catalysts: water effect.

and 570 cm^{-1} respectively.[1,18−20] In Figure 5 can be observed the effect of the aluminum precursor by the shift of the 1092 cm^{-1} band.[18] As the alkyl substitutes of the aluminum alkoxide become smaller, the shift becomes higher. The sample SiAle2 (ethoxide) shows the Si−O−Si band at 1040 cm^{-1}, whereas for the samples Si−O−Si prepared from isopropoxide and *sec*-butoxide the bands are at 1042 and 1073 cm^{-1}, respectively. The higher the shift of the band, the higher the Si−O−Si substitution. Comparing the ^{29}Si NMR spectra with the FTIR, we can observe that the higher Si substitution by Al corresponds to the SiAle2 sample. Such result is in agreement with the shift of the FTIR band at 1092 cm^{-1}. On the other hand, a small water effect (Figure 6) is observed. A small shift from 1073 cm^{-1} for the SiAls2 sample to 1060 cm^{-1} in the SiAls8 sample is shown. As mentioned previously in the ^{29}Si NMR spectra of such samples, only a small different substitution can be also observed.

In calcined samples the FTIR spectra of solids prepared with different alkylaluminum precursor are shown in Figure 7. The higher shift of the 1092 cm^{-1} band corresponds to the sample prepared using the small alkoxide group (ethoxide). The water effect in the shift of the 1092 cm^{-1} band is observed in Figure 8 (from 1084 to 1029 cm^{-1}).

The band shift to 1029 cm^{-1} corresponds to the sample prepared with higher water content (SiAls8). This sample shows the ^{29}Si NMR spectrum in which the Si(3Al,1Si) and Si(1Al,3Si) peaks are better resolved (Figure 4).

Table 2. Catalytic Activity in the 2-Propanol Decomposition of the Various Si−Al Sol−Gel Catalysts

sample	10^5 rate (mol/g s)	propene selectivity (% mol)
SiAle2	3.1	89
SiAli2	2.3	88
SiAls2	2.9	89
SiAls4	2.1	86
SiAls8	2.3	88

The catalytic activity of the various samples in the 2-propanol decomposition at 150 °C are reported in Table 2. Comparable activities are found for all the catalysts, and the high selectivity to propene formation shows that in such solids an important acidity is developed. NMR is a bulk characterization technique while activity is a surface characterization, and no correlation between both studies was found. Therefore additional characterizations of surface acidity will be made, and the studies are in progress.

Conclusions

It is shown in the present paper that different aluminum coordinations in silicoaluminates prepared by the sol−gel method can be obtained. The most important effect in silicon substitution stems from the aluminum alkoxide precursor. Only slight effects were observed in aluminum coordination and silicon substitution by varying the hydrolysis water amount. However, the water effects are very important in increasing the BET areas of the solids. On the other hand, a narrow pore size distribution is reached using small aluminum alkyl substitutes such as ethoxides. The solids prepared by the cogelation of silicon tetraethoxide and aluminum alkoxides are very active in the 2-propanol decomposition, showing that an important acidity is developed using this method.

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