

Synthesis, characterization and HDS activity of Co catalysts supported on natural, acid, Al- and Fe-pillared smectite clays

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Abstract

Two montmorillonites, SWy-2 (Wyoming, USA) and STx-1 (Texas, USA) (henceforth referenced as SW and ST) were acid activated, pillared with aluminum or iron and then impregnated with Co. Catalysts using the raw clays were also prepared. The synthesized catalysts were characterized by X-ray diffraction, thermal analysis, surface area, acidity determinations and temperature programmed reduction. The catalytic activity was measured using the hydrodesulfurization of thiophene at 350°C. Acid and pillaring treatments increased the surface area, porosity and acidity. In all catalysts, microporosity and mesoporosity were observed. The surface area and porosity of the catalysts were not affected by Co incorporation, however the acidity decreased. The reduction profiles showed the formation of several surface species of cobalt with aluminum and iron in both Al- and Fe-pillared clays. The activity for the hydrodesulfurization of thiophene depended on the chemical properties and textural characteristics of the support. The most active Co catalysts were those supported on acid activated clays (11 and 45% for Co/HSW and Co/HST), followed by those supported on Al-pillared clays (7 and 15% for Co/AlSW and Co/AlST) and Fe-pillared clays (2 and 17% for Co/FeSW and Co/FeST) and on the raw clays, which showed the lowest conversions (2 and 6% for Co/SW and Co/ST).

Key words: Clays; co catalysts; hydrodesulfurization; pillared clays.

Síntesis, caracterización y actividad en HDS de catalizadores de Co soportados sobre arcillas esmectitas naturales, acidificadas y pillareadas con aluminio o hierro

Resumen

Dos arcillas montmorillonitas, SWy-2 (Wyoming, USA) y STx-1 (Texas, USA) (referidas como SW y ST), fueron tratadas con ácido, pillareadas con aluminio o hierro y luego impregnadas con Co. También se prepararon catalizadores utilizando las arcillas en su forma natural. Los catalizadores sintetizados fueron caracterizados por difracción de rayos X, análisis térmi-

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co, área superficial, determinaciones de acidez y reducción a temperatura programada. Se evaluó la actividad catalítica usando la hidrodesulfuración de tiofeno a 350°C. El tratamiento ácido y la pilarización incrementaron el área superficial, la porosidad y la acidez. En todos los casos, se observó microporosidad y mesoporosidad. El área superficial y la porosidad no fueron afectadas por la incorporación de Co, sin embargo la acidez disminuyó. Los perfiles de reducción mostraron la formación de varias especies superficiales de cobalto con aluminio o hierro en las arcillas pilareadas. La actividad para la hidrodesulfuración de tiofeno dependió de las propiedades químicas y de las características texturales del soporte. Los catalizadores de cobalto más activos fueron los soportados sobre las arcillas activadas con ácido (11 y 45% para Co/HSW y Co/HST), seguido por los soportados sobre las arcillas pilareadas con aluminio (7 y 15% para Co/AlSW y Co/AlST), las arcillas pilareadas con hierro (2 y 17% para Co/FeSW y Co/FeST) y sobre los soportados sobre las arcillas naturales, las cuales mostraron las conversiones más bajas (2 y 6% para Co/SW y Co/ST).

Palabras clave: Arcillas; arcillas pilareadas; catalizadores de Co; hidrodesulfuración.

Introduction

Hydrodesulfurization process has received considerable attention in the last decades, because one of the main goals of the Clean Air Act (CAA) is to improve fuels quality. In this regard, the sulfur content must be less than 0.05 wt.-% in diesel fuels and aromatic less than 10 vol.-% (1, 2).

HDS catalysts used in the industry are mainly derived from oxides of a metal of group VIB (Mo or W) and/or a metal of group VIII (Co or Ni) supported on γ -alumina (3, 4). Better hydrotreating catalysts performance may be obtained by the use of new supports of outstanding properties such as higher dispersability of the metal phase, improved thermal stability, high mechanical resistance and good pore distribution. Additionally, low reactivity of the support with the active phase is very desirable to avoid the formation of mixed phases which could deactivate the catalyst.

Clay minerals are interesting materials as catalyst supports due to their great abundance, low cost and particular properties. Despite that natural untreated clays have a very low ability to catalyze reactions in either polar or non-polar media, the structural properties of these materials can be modified by different activation methods to

produce catalysts of improved surface characteristics and thermal stability (5, 6).

Acid activation of clay minerals is one of the most effective methods that have been used to produce active materials for adsorption and catalysis purposes. The surface properties of natural clays can be also modified by incorporating large inorganic cations onto the clay's gallery leading to the formation of metal oxide pillars after calcination, which prop apart the clay structure and improve the available surface area (from ca. 50 to 350 m²/g) and pore volume (from 0.08 to 0.2-0.3 cm³/g). These materials have the additional advantage that the pillars themselves may be catalytically active and stable up to 500-700°C (7, 8). Furthermore, in addition to expanding the layer structure, the metal oxide pillars also possess themselves a certain amount of acidity (9, 10). Nowadays, research on pillared clays is taking new directions, one of them being the impregnation of PILCs with catalytically active metal solutions to introduce new acidic or redox properties into the clay (11, 12).

In particular, montmorillonites and its pillared derivatives have been used as catalyst supports in many reactions. Particularly in HDS, Gil et al. (13) reported the use of Al- or Ti-pillared clays as supports in the synthesis of nickel and molybdenum catalysts, ob-

taining good activity for the hydrodesulfurization of various crude fractions. Kloprogge et al. (14) observed high activity for the hydrodesulfurization of thiophene over sulfured Ni-catalysts supported on Al-pillared montmorillonites and found a strong influence over the catalytic activity by changes in the preparation conditions. Hayashi et al. (15) studied the activity for the same reaction over a series of cobalt catalysts supported on montmorillonites, hectorites and saponites, finding that Co/saponite catalyst was the most active for sulfur removal.

Synthetic smectite-like materials have also been evaluated as catalysts in these processes; however the literature only reports the use of natural and synthetic clays as well as Al-PILCs (13-15). Therefore, the aim of this work is to study other materials such as acid treated and Fe-pillared clays as supports for Co-catalysts and to compare their catalytic performance with that of conventional Al-pillared clay cobalt catalysts.

Experimental

Starting materials

Two source clays were selected: Caumontmorillonite (STx-1, dioctahedral bentonite of low iron content) Texas-USA and Naumontmorillonite (SWy-2, dioctahedral aluminum rich bentonite) Wyoming-USA, both obtained from The Clay Mineral Repository of the Clay Mineral Society, and used without further purification. Both clays are henceforth referenced as ST and SW; the CEC of these clays are 80 and 87 meq per 100g of clay.

Supports and catalysts preparation

ST and SW clays were pillared by ion-exchange of aluminum or iron complexes as follows: 1 wt.% of a clay suspension (ST or SW) was subjected to constant stirring at room temperature for 2 h. Afterwards, a solution containing the aluminum or iron complex was added drop-wise. The stirring was maintained for 3 h and then stopped

for 1 h to allow sedimentation. The solid obtained was centrifuged, washed with de-ionized water, dried at 120°C for 1 h and calcined at 450°C for 3 h. The aluminum complex $[Al_3O_4(OH)_{24}(H_2O)]^{7+}$ was synthesized by basic hydrolysis of $AlCl_3$ using the procedure described by Bradley et al. (16), while the iron complex $[Fe_3O(OCOCH_3)_6 \cdot 3H_2O]^{7+}$ was obtained using the procedure reported by Stake (17). The aluminum and iron pillared clays were referred to as AlST, FeST, AlSW and FeSW, respectively.

Acid activated clays were prepared by adding 1 g of ST or SW to a solution containing 1.5 M hydrochloric acid (Fisher, 38%) equivalent to 48 mmol of H^+ . The mixture was vigorously stirred overnight at room temperature and then centrifuged, washed with de-ionized water, dried at 120°C overnight and ground. Samples from this treatment were designated as HSW and HST.

Cobalt catalysts supported over the natural, acid and Al- or Fe-pillared ST or SW clays were prepared by the incipient wetness impregnation method using a cobalt nitrate solution. The clay support was added into the cobalt solution and heated under constant stirring to evaporate water, dried at 120°C for 1 h and finally calcined at 450°C in air atmosphere for 3 h. The cobalt content in the catalysts was 4 wt.%. The nomenclature used for these catalysts was Co/ST, Co/HST, Co/AlST and Co/FeST and Co/SW, Co/HSW, Co/AlSW and Co/FeSW, respectively.

Catalysts characterization

BET surface areas of the supports and catalysts were measured by N_2 adsorption at -196°C, using a Micromeritics Gemini 2375 porosimeter. Samples were outgassed at 150°C for 4 h before the adsorption measurements.

The bulk chemical composition was determined by X-ray fluorescence analysis (XRF, Shimadzu EDX-700HS). X-ray powder diffraction patterns of the clay catalysts

were recorded on a Philips PW 1720 diffractometer, operating at 30 kV and 30 mA and at a scan speed of $2^\circ/\text{min}$ from 2° to $60^\circ 2\theta$, using Co $K\alpha$ radiation.

The thermal desorption of cyclohexylamine was used to estimate the surface acidity of the prepared catalysts. The experimental procedure is identical to that reported elsewhere (18).

Temperature programmed reduction experiments were carried out in a U-shape quartz reactor using 50 mg of catalyst. Before reduction, the catalyst was dried at 120°C for 1 h in a flow of air of 30 mL/min and then cooled down to room temperature using Ar at a flow rate of 30 mL/min. The reduction mixture used was 5% H_2/Ar with a flow rate of 30 mL/min. The temperature of the reactor was increased using a heating rate of $10^\circ\text{C}/\text{min}$ from 25 to 800°C . The water formed during the reduction was collected on a molecular sieve trap and the hydrogen concentration was determined with a thermal conductivity detector.

Catalytic activity

The catalytic activity was determined using the hydrodesulfurization of thiophene at low pressure, sending from 7 to 10 pulses, in a loop of 0.25 mL, of a mixture of approximately 7% of thiophene in hydrogen at 350°C . The mixture of the reactants was obtained by passing pure hydrogen into two saturators which contained thiophene, one at room temperature and the other at 0°C . One hundred milligrams of catalyst was placed in a U-shape Pyrex reactor, supported on ground Pyrex glass in both ends (40-60 mesh). The catalyst was previously activated with $\text{H}_2\text{S}/\text{H}_2$ (20:80) at a flow rate of 30 mL/min. The temperature of the reactor was programmed to increase linearly from room temperature to 350°C by a heating rate of $10^\circ\text{C}/\text{min}$ and then maintained at 350°C for 30 min, then the thiophene pulses were sent to the reactor. The reaction products were analyzed on a Perkin-Elmer Auto-System XL FID gas chromatograph

equipped with a 2 m SS column containing 20% Carbowax 400 and 80% Chromosorb 102. The column was kept at 150°C .

Results and Discussion

The chemical composition of supports and catalysts determined by XRF is given in Table 1. The starting clays are mainly composed by SiO_2 , Al_2O_3 , MgO and traces of Fe_2O_3 , CaO, Na_2O , K_2O and TiO_2 . However, SW has a higher Fe_2O_3 content than that in ST. The pillaring process with aluminum or iron increases the percentage of Al_2O_3 and Fe_2O_3 of the raw clays, indicating the formation of pillars, as it will be discussed later with XRD data. The cobalt content in all catalysts varied between 4.2 and 8.5%. The iron content is higher for SW in comparison to ST, when both clays were impregnated with the iron polycation. This behavior is attributed to the CEC difference and that the main exchangeable cation in SW is sodium while in ST is calcium. The sodium cation is more susceptible to displacement than calcium during the exchange process; therefore higher iron content should be expected in SW clay (19). Additionally, the relative high iron content incorporated in both clays is due perhaps to the deposition of Fe_2O_3 on the clay surface as well as that located on exchange sites that form the pillars.

Table 2 shows the BET surface area, pore volume and surface acidity values of supports and catalysts. As can be seen from this table, acid treatment increases the surface area and the pore volume as a consequence of the leaching of the clay layer structure, giving microporosity and increasing the laminar disorder. Similarly, the pillaring process of the starting clays also causes an increase in the surface area and the pore volume.

The surface area of the starting clays slightly increased after Co impregnation and this is attributed to the ion exchange process with cobalt cations which generates cobalt oxide, after calcination, on the clay sur-

Table 1
Chemical composition of supports and catalysts

Sample	SiO ₂	Al ₂ O ₃	MgO	Fe ₂ O ₃	TiO ₂	CaO	Na ₂ O	K ₂ O	Co ₂ O ₃
ST	76.7	16.8	3.6	0.7	0.05	1.8	0.4	0.02	—
HST	79.2	16.5	3.2	0.6	0.04	0.3	0.09	0.01	—
AlST	67.7	27.6	3.4	0.7	0.04	0.4	0.2	0.01	—
FeST	60.5	15.5	3.4	20.0	0.04	0.4	0.2	0.01	—
Co/ST	71.1	15.2	3.3	0.6	0.04	1.6	0.3	0.02	7.9 (5.6)*
Co/HST	73.8	15.4	3.0	0.5	0.03	0.2	0.08	0.01	7.0 (4.9)
Co/AlST	63.1	25.8	3.2	0.6	0.03	0.3	0.2	0.01	6.7 (4.8)
Co/FeST	56.9	14.4	3.2	18.8	0.03	0.3	0.2	0.01	6.2 (4.4)
SW	68.0	20.6	2.8	4.6	0.09	1.8	1.7	0.4	—
HSW	72.0	20.3	2.3	4.3	0.08	0.2	0.5	0.3	—
AlSW	60.4	31.5	2.5	4.4	0.08	0.3	0.6	0.3	—
FeSW	42.9	15.1	2.1	39.0	0.07	0.2	0.4	0.2	—
Co/SW	62.3	18.9	2.6	4.2	0.08	1.6	1.5	0.3	8.5 (6.0)
Co/HSW	66.9	18.7	2.1	3.9	0.07	0.2	0.5	0.2	7.5 (5.3)
Co/AlSW	56.4	29.4	2.3	4.1	0.07	0.2	0.5	0.2	6.9 (4.9)
Co/FeSW	40.5	14.2	2.0	36.6	0.06	0.2	0.4	0.2	5.9 (4.2)

*Values in parentheses represent the cobalt content in the catalysts.

Table 2
Surface area, specific pore volume and acidity of the prepared supports and catalysts

Sample	S _{BET} (m ² /g)	V _p (cm ³ /g)	Acidity (mmolH ⁺ /g)
ST	68	0.107	0.40
HST	96	0.131	0.48
AlST	114	0.118	0.27
FeST	121	0.151	0.22
Co/ST	75	0.108	0.15
Co/HST	93	0.119	0.14
Co/AlST	114	0.113	0.19
Co/FeST	108	0.143	0.20
SW	23	0.032	0.19
HSW	76	0.086	0.35
AlSW	52	0.048	0.23
FeSW	107	0.139	0.28
Co/SW	33	0.033	0.11
Co/HSW	83	0.087	0.16
Co/AlSW	56	0.051	0.12
Co/FeSW	88	0.119	0.24

face in a similar manner to aluminum and iron oxides but in lower proportion due to the small amount of Co incorporated. The nitrogen adsorption-desorption isotherms (not shown) for all catalysts were typical of micropore solids (type IV isotherm using Brunauer's classification) with a clear hysteresis loop (of type B) at higher P/P^0 . The hysteresis loop for FeST support was larger, indicating the formation of pores of lower diameter compared to the acid treated and aluminum pillared ST clay. Huerta et al. (20) in line with this observation, reported a significant increase in the microporosity for materials similar to FeST and FeSW.

Regarding the acidity, acid treated clays have the highest acidity followed by those of Al- and Fe-pillared clays. Cyclohexylamine has a direct interaction with protons provided by the acid activation and those arisen from polarization of water molecules by Al and Fe. After Co impregnation, a dramatic reduction is observed in the acidity values, especially in acid treated clays. The decrease in the acidity is moderate in Co impregnated Al-pillared clays and negligible in Co impregnated Fe-pillared clays. This trend is attributed to the blockage of proton by cobalt oxide. The insignificant decrease in the acidity for Co impregnated Fe-pillared clay is believed to be due to the relatively high Fe content that generates protons that interact strongly with cyclohexylamine, despite the presence of cobalt.

Figure 1 shows the X-ray diffraction patterns of SW, HSW, FeSW, AISW and Co/AISW; samples derived from ST clay showed similar patterns. The starting SW clay presents a d-spacing of 15.1 Å and other well-defined reflection peaks. The acid treatment shifts the d_{001} reflection to a higher angle and a spacing of 14.6 Å is obtained. No d_{001} is detected in FeSW due to a loss of its crystallinity as a consequence of the incorporation of iron and delamination of the mineral structure. This observation is consistent with that found by Nguyen-Thanh and Badosz (21) in an iron doped Al-

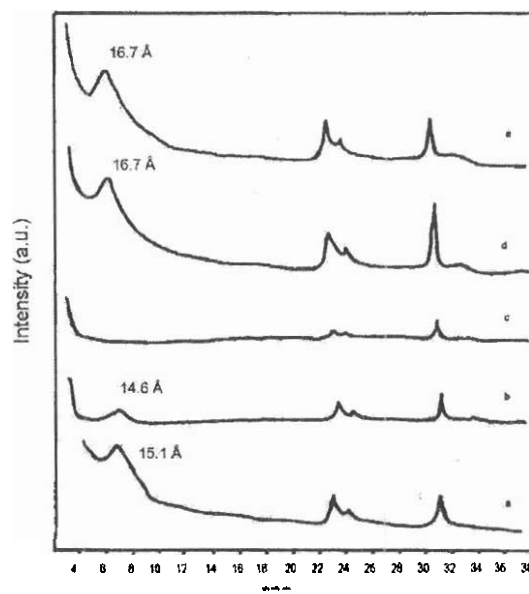


Figure 1. X-ray diffraction patterns for (a) SW, (b) HSW, (c) FeSW, (d) AISW and (e) Co/AISW.

pillared montmorillonite (SW). The Al-pillaring increased the d-spacing of the starting clay to 16.7 Å; on the other hand, the Co incorporation did not modify this value (compare Figures 1d and 1e).

The reduction programmed temperature profiles for supports and Co catalysts derived from SW clay are given in Figures 2 and 3. Similar TPR patterns were obtained for supports and Co catalysts derived from ST clay. Taking into consideration the reduction profiles for cobalt oxide supported on alumina (22, 23), it is possible to infer that the first maximum in Figure 2, at 300-500°C is due to the reduction of Co_3O_4 , while the peaks at 400 and 550°C are attributed to the reduction of Co^{3+} and Co^{2+} in an amorphous phase. The maximum observed at 700-750°C in pillared samples is ascribed to Co^{3+} and Co^{2+} species that interact strongly with the support.

Sirijaruphan et al. (24) reported that the maxima of hydrogen consumption between 200 and 400°C, for $\text{Co}/\text{Al}_2\text{O}_3$ system, is due to the reduction of Co_3O_4 to Co^0 , and

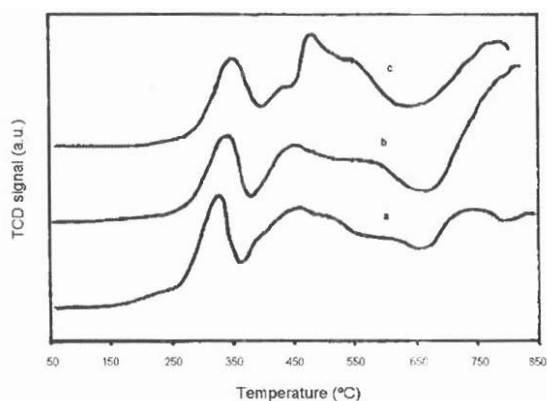


Figure 2. H₂ consumption for (a) Co/SW, (b) Co/HSW and (c) Co/AlSW catalysts.

CoO to Co⁰, while the peaks at temperatures higher than 400°C are due to the reduction of Co²⁺ and Co³⁺ interacting strongly with the support. Hayashi et al. (15) working with Co- supported clay systems observed that the Co₃O₄ phase is easily reducible. They also reported that when the Co content is higher than 2%, the superficial phase constituted by Co²⁺ is not reducible, but partially sulphurized.

Figure 3 shows the reduction profiles for iron oxide pillared SW support and its cobalt catalyst. In the pillared support, three reduction peaks are observed at 260-460°C, 470-580°C and 660-700°C, respectively. Based on Kustrowsky et al. (23) findings, the first two peaks are attributed to the reduction of massive Fe₂O₃ to Fe₃O₄ and Fe₂O₃ particles of small size that interact with the support. The third peak corresponds to Fe₃O₄ species that are reduced to Fe⁰. The increase in the baseline in the TPR profiles, after the third peak, seems to indicate the reduction of FeO to Fe⁰. The reduction of FeO was observed at a temperature > 850°C for FeSW support. In Co/Fe-PILCs, there is a significant increase of the peaks intensity, especially in those at 470-580 and 660-700°C, giving evidence of the simultaneous reduction of both oxides. The first two maxima are shifted to lower temperatures, indicating

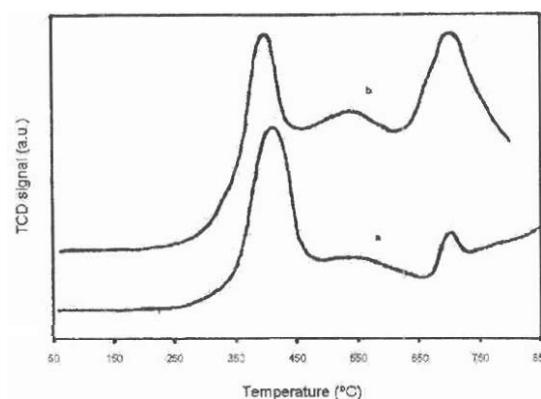


Figure 3. H₂ consumption for (a) FeSW and (b) Co/FeSW.

possible interactions between Fe and Co species.

The catalytic activity results for the hydrodesulfurization of thiophene over the synthesized catalysts, previously activated with H₂S/H₂, as a function of the surface area and the Co reduction temperature are shown in Figures 4 and 5. No activity was detected over the prepared supports. It can be noticed that the most active Co catalysts were those supported over acid treated clays. Catalysts supported over aluminum and iron pillared clays presented higher HDS conversions than those supported over natural clays. This trend is attributed to the high surface area of these supports which favors the dispersion of the active phase in comparison with those derived from the natural clays. However, despite that Co/PILCs catalysts have relative high surface areas, they present a lower activity than those of Co/acid clay catalysts. It is possible that this behavior could be due to the decrease of active surface by sintering and/or formation of Co-Fe alloys.

Co/AlST catalyst showed similar conversion to that of Co/FeST, but Co/FeSW catalyst was less active than that of Co/AlSW. The latter observation could be caused by a higher cobalt-iron interaction, as evidenced by the shift to higher tempera-

tures in the reduction maxima for Co/FeSW catalyst compared to Co/AlSW counterpart.

The surface area of the support plays a key role over the HDS conversion. In Figure 4, it can be appreciated that the activity rises as the surface area increases. Only Co/FeSW does not seem to show the same tendency; as mentioned before, the low performance of this catalyst is due to loss of active sites by strong Co-Fe interactions.

Figure 5 illustrates the thiophene conversion as a function of the reduction temperature for the Co_3O_4 phase, obtained from the TPR profiles. The highest conversions were reached when Co_3O_4 is reduced at a low temperature, excepting Co/SW and Co/AlSW catalysts. The former finding is because of Co_3O_4 phase that is easily sulphurized, and thus, generating active sites. Co/SW catalyst has a low reduction temperature but a depressed conversion in comparison with other catalysts. This behavior can be explained in terms of its small surface area. Despite that Co/AlST catalyst has a surface area higher than that of Co/HST, showed lower HDS conversion possibly caused by loss of active sites induced by the formation of cobalt-aluminates type species. Hayashi et al. (15) observed that the HDS activity decreased as the metallic loading increased, reflecting that the activity depend not only on the support characteristics, but also on the cobalt dispersion.

Conclusions

Support treatments strongly affected the catalytic properties of Co catalysts on acid treated and aluminum or iron pillared clays. The TPR profiles evidenced the formation of different Co and Fe species and interactions of Co-Fe and Co-Al in the pillared systems. The HDS performance depended on the reduction temperature. Co over acid treated clays were the most active catalysts for HDS of thiophene, whereas Co over pil-

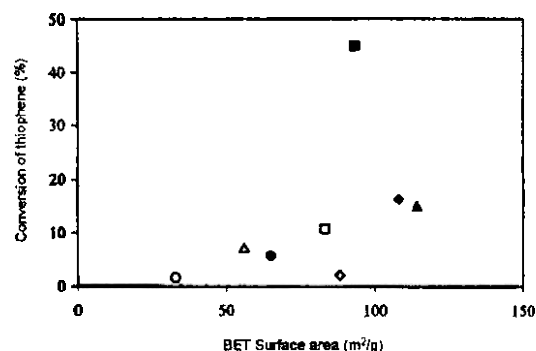


Figure 4. Relation between the conversion of thiophene at 350 °C and surface area of Co catalysts. (●) Co/ST, (■) Co/HST, (▲) Co/AlST, (◆) Co/FeST, (○) Co/SW, (□) Co/HSW, (△) Co/AlSW and (◇) Co/FeSW.

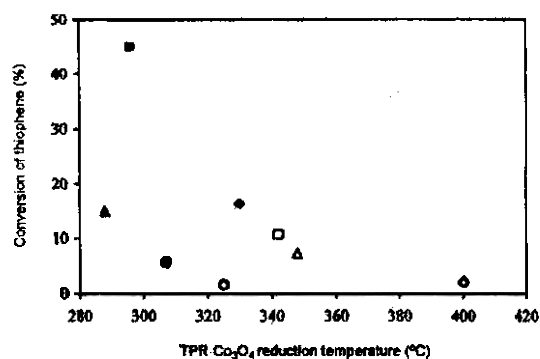


Figure 5. Relation between the conversion of thiophene at 350 °C and reduction temperature of Co catalysts obtained by TPR. (●) Co/ST, (■) Co/HST, (▲) Co/AlST, (◆) Co/FeST, (○) Co/SW, (□) Co/HSW, (△) Co/AlSW and (◇) Co/FeSW.

lared clays showed less activity, but higher than that of Co over natural clays.

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