MICROPOROUS AND MESOPOROUS MATERIALS

Materials derived from synthetic organo-clay complexes as novel hydrodesulfurization catalyst supports[1]

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MICROPOROUS AND MESOPOROUS MATERIALS

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Abstract

A series of mesoporous synthetic organo-clay complexes has been prepared by hydrothermal crystallization of gels containing silica, magnesium hydroxide, lithium fluoride, and an organic of choice, followed by calcination to remove the organics. The organic serves to impart structural order to the inorganic network that does not disappear upon its removal. The choice of organic modifier can be used to control the pore structure of the resulting mesoporous materials. Pore size distributions appear in some cases to be related to the type of polymer packing upon clay formation in situ. These materials are being explored as Co–Mo hydrodesulfurization (HDS) catalyst supports. Preliminary HDS results show performance commensurate with commercial catalysts for the mesoporous materials when a model heavy oil feed is used (1 wt% S as dibenzothiophene in hexadecane). Temperature programmed reduction experiments of used catalysts suggest a relationship between HDS activity and ease of reduction of the CoMo/clay catalysts. Reactivity of the CoMo/clay also correlates with the percentage of mesopore volume remaining after reaction. Losses in mesopore volume are largely recouped by recalcination, suggesting that reversible coke is formed inside the pore structure of clays faster than inside conventional alumina. © 1998 Elsevier Science B.V.

Keywords: Hectorite clay; Clay–organic complex; Hydrodesulfurization; Polymer-clays; HDS supports; Mesopores

1. Introduction

Hydroprocessing represents a crucial component of current petroleum refining operations in terms of both environmental and economic considerations. The literature in this area is extensive and many reviews are available for an in-depth look at the field [1–3]. A focus of intensive effort has been the development of adequate catalysts particularly for hydrodesulfurization (HDS) [4–8].

Regulations concerning maximum sulfur contents of oil and subsequent SO_x emissions upon combustion are becoming increasingly more stringent. At the same time, crude oils are becoming heavier and contain increasing amounts of sulfur. HDS catalysts with higher performance are therefore being sought in order to meet tighter environmental restrictions. Typical industrial HDS catalysts are comprised of Co(Ni)–Mo sulfides on an alumina support. As refiners have begun to process heavier crude oil feedstocks, modification of the pore structure of the alumina support has attracted increasing attention [9–16]. Specifically, several groups have investigated the effects of incorporat-

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ing varying percentages of macroporosity into the alumina pore structure [13,15,16]. In its resid upgrading plant, Texaco has recently successfully implemented Co–Mo catalysts with some macroporosity [17]. We describe here the development of a new class of support materials with pore sizes primarily in the mesoporous range, in addition to some macroporosity.

Our approach is to create synthetic organo-clay complexes called SOCCs. This entails a clay mineral synthesis from a silicate sol–gel that contains an organic species. The pore size arises when the SOCCs are calcined to remove the organics occluded in the pore network. Clay minerals are layered aluminum or magnesium silicates of significant cation exchange capacity and both external and internal surface area [18]. Because natural clays are abundant and inexpensive, they have a rich history of use in the hydroprocessing industry [19,20]. The SOCCs are unique for several reasons, including: (1) the pore size and distribution can be controlled via synthetic methods, and (2) the purity is high compared to natural minerals which contain many dopants and impurity phases. The mineral of choice for this work is hectorite, a magnesium silicate smectite clay, because of its ease of crystallization at relatively low temperatures and because of its lower surface acidity (and therefore low cracking activity) compared to aluminosilicate clays such as montmorillonite.

Systematic investigations of the synthesis–structure relationships for the SOCC materials have been performed [21–24]. The pore size distributions and information concerning the extended microstructure of some calcined SOCCs have also been reported [25]. This work represents the first application of these materials to catalysis, in particular HDS. Fig. 1 provides a schematic representation of what the SOCCs are postulated to look like before and after calcination. The evidence indicates that small clay crystallites with polymer-intercalated layers are themselves somewhat imbedded in a matrix whose pores and voids are also filled with polymer. After removal of the polymer upon calcination, the open network remains behind to accommodate the Co–Mo–S catalytic phase and subsequent catalytic reaction.

2. Experimental

The details for the hydrothermal crystallization of these hectorites are provided elsewhere [25], although a general description follows. Hydroxypropylmethyl cellulose (HPMC) was from Dow Chemical Co., Midland, MI (Methocel 240S), hydroxyethyl cellulose (HEC) was from Aqualon Co., Wilmington, DE (Natrosol 250 HHXR), and poly(dimethyl diallyl ammonium chloride) (PDDA, Agefloc WT40) was obtained from CPS Chemical Co., Inc., Old Bridge, NJ. Tetraethyl ammonium chloride (TEA, Aldrich) was also used in some clay preparations.

Reactants in molar ratios of $LiF:MgO:SiO_2$ 0.266:1.00:1.52 are refluxed for 2 days as a 2 wt% aqueous slurry. This yields the ideal hectorite composition $Ex_{0.66}[Li_{0.66}Mg_{5.34}Si_8O_{20}(OH)_4]$, where Ex = exchangeable monocation. The amount of polymer added is chosen such that, if all of the polymer is incorporated into the clay and assuming complete reaction, 20 wt% of the SOCC would be organic. Lithium(I) ions occur in the lattice as isomorphous substitutions for Mg(II), leaving a negative charge that is carried by the basal oxygen
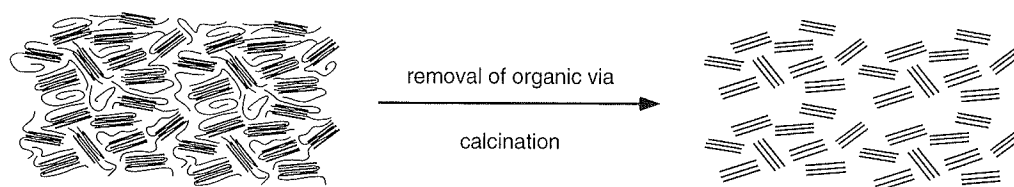

Fig. 1. Schematic of what synthetic organo-clay complexes, SOCCs, could look like at the molecular level of polymer chains and individual silicate clay layers. After calcination, although the layers themselves are collapsed upon each other, the large voids previously filled by organic are now open and available for catalytic reaction.

surface and compensated for by the presence of exchangeable cations and water molecules within the interlayer or gallery. In the inorganic synthetic hectorite, Li(I) is also the exchangeable cation. A certain amount of this Li(I) can be replaced by organic or organometallic cations directly from a precursor organic-containing gel. When the neutral polymers are used, Li(I) ions are also present in the interlayer in the cation exchange sites. The source of MgO was a freshly synthesized $Mg(OH)_2$ slurry. The source of silica was Ludox HS-30. To isolate the clay, the slurry was centrifuged and washed three times or until the decant was clear, allowed to air dry, then ground to a powder. Calcination of the SOCCs was carried out in a tube furnace using quartz boats at 400°C under air or oxygen flow for at least 4 h and often longer. For brevity, the synthetic organo-hectorites are referred to as synHPMC, synHEC, synPDDA, and synTEA. The purely inorganic hectorite is synLi.

2.1. Catalyst preparation

After drying the clay supports at 400°C in N_2 (<3 ppm H_2O) overnight, the clays were calcined at 400°C for 5 h in air which had been passed through a moisture trap consisting of Drierite and molecular sieves. Aqueous ammonium heptamolybdate (Alfa, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, 99.999%) solutions were prepared so that a metal loading of 6 wt% Mo would fill 80% of the available pore volume of the clays. Following Mo impregnation and recalcination using the aforementioned conditions, the pore volumes were measured again using an established LN_2 physisorption protocol. Aqueous cobalt nitrate (Alfa, $Co(NO_3)_2 \cdot 6H_2O$, 99.999%) was impregnated onto the calcined Mo/clay materials so as to provide a 2 wt% Co loading spread out over 80–85% of the remaining pore volume. For comparison purposes, commercially available oxidized Co–Mo (Crosfield 465) and Ni–Mo (Crosfield 504) were also tested. The Crosfield 465 and Crosfield 504 reference catalysts were first calcined at 600°C for 1 h in 1% O_2/He, cooled to room temperature under N_2, and stored in a N_2-purged glovebox for later use.

2.2. Catalytic HDS testing

The catalyst pretreatment process for both the clay-supported and the reference catalysts consisted of loading into the HDS reactor under N_2, purging in N_2 at 20°C for 30 min at 1000 cm³/min, drying in N_2 at 150°C for 60 min and at 400°C for 60 min, and finally sulfiding in a 5% H_2S/H_2 mixture at 400°C for 2 h prior to use as catalysts. The laboratory scale liquid-phase continuous-flow HDS unit is shown schematically in Fig. 2. The reactor consists of a thick-walled 0.375 in ID 316 SS tube, with 1 g catalyst diluted with 5 g tabular alumina (LaRoche T-1061, 10 m²/g) sitting between plugs of quartz wool. Beneath the lower plug was a 0.125 in ID, 0.375 in OD deadman used to minimize volume between the reactor and the liquid receiver. The liquid test feed consists of 1.0 wt% sulfur as dibenzothiophene (DBT), dissolved in hexadecane and is representative of a middle distillate oil. All liquid-filled lines were heated to 50°C. Typical conditions for catalytic testing are also provided in Fig. 2.

The products were diluted with hexane (1 mg product/200 ml hexane), separated using a DB5-MS column, and analyzed using a HP 5890 GC-MS Series II Plus. Random errors associated with GC-MS concentration measurements were less than 5%, and the reproducibility of conversion measurements was ±15% of the reported values. Selectivity has been defined as the percentage of biphenyl (the selective HDS product from dibenzothiophene) divided by the percentage of dibenzothiophene converted times 100.

2.3. Characterization

The hydrodesulfurization activities of a wide range of transition metal sulfides correlate with the ease of reduction of surface-bound sulfur [26]. One way to determine the reducibility of a material is to heat the material at a fixed heating rate in the presence of H_2 and monitor the off-gases using either a thermal conductivity detector (used here) or a mass spectrometer. Such an experiment is hereafter referred to as temperature-programmed reduction (TPR). Approximately 0.10 g of spent catalyst was placed into a 0.25 in ID stainless steel
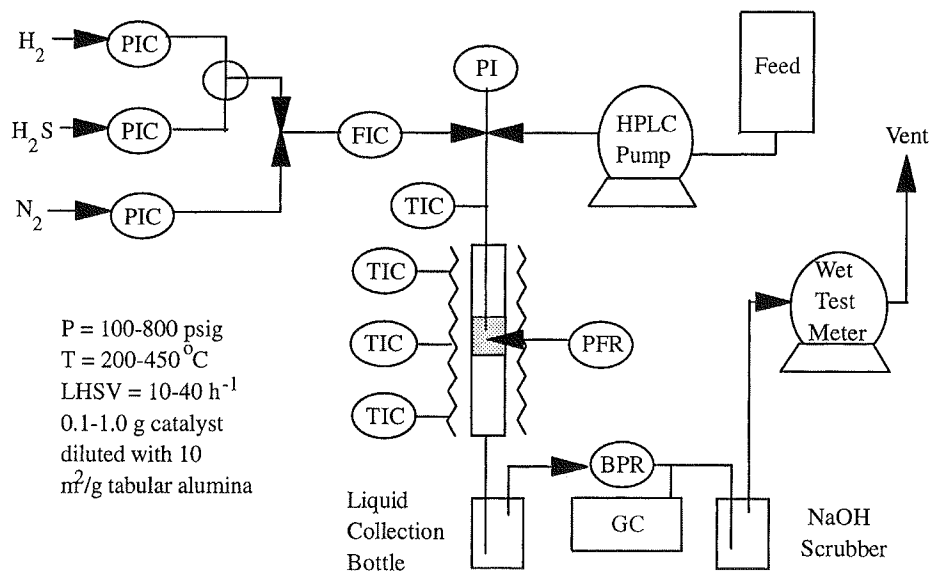
Fig. 2. HDS catalytic reactor schematic. PIC = pressure indication controller, FIC = flow indicating controller (mass flow controller), PFR = plug flow reactor, BPR = back pressure regulator, and PI = pressure indicator (transducer).

U-tube in between plugs of quartz wool and attached to an Altamira AMI-1 dynamic chemisorption apparatus. The pretreatment protocol consisted of purging in Ar at 35°C for 1 h, drying in Ar at 150°C for 1 h, heating in Ar to 500°C for 1 h, cooling in Ar to 450°C, reducing in H_2 at 450°C for 1 h, purging in Ar at 500°C, and cooling to 35°C in Ar. The TPR experiments for each catalyst consisted of H_2 chemisorption at 35°C and 60 sccm for 1 h, followed by TPR at 5°C/min.

N_2 adsorption and desorption isotherms were collected on an Autosorb-6. Approximately 0.10 g of material was weighed into a Pyrex sample tube and evacuated to 80 mTorr overnight at room temperature, then backfilled with He. The static physisorption experiments measured the amount of nitrogen adsorbed or desorbed as a function of pressure ($P/P_0 = 0.025–0.999$, increments of 0.025). Pore size distributions were calculated using the Barett–Joyner–Halenda (BJH) method. Normally, the desorption isotherm is used as a basis for the calculation of pore size distributions. However, an artifact at 19.5 Å radius occurs for all layered materials [27,28], and indeed was observed for all of our clay samples (see Fig. 3). Hence, the adsorption pore volumes and pore size distributions are reported in all tables.

3. Results and discussion

3.1. Effect of calcination on SOCCs

Table 1 shows the physical properties of the weight per cent organic incorporated (determined by CHN microanalysis) and the subsequent basal spacing (d_{001}) from the X-ray diffraction (XRD) pattern. It also shows the effect that calcination has upon the surface area and pore volume. The behavior can be divided between two groups of organics: cationic vs. neutral. For the cationic organics (Li, TEA, PDDA), the weight per cent organic uptake is <10%, the *d*-spacing is low (14–16 Å), and neither the surface areas nor pore volumes change appreciably after calcination. All of these properties can be explained by the cation exchange behavior of the clay, which sets a limit on the amount of organic that can be sorbed (up to the cation exchange capacity of the clay). Therefore, the amount is a low but typical value
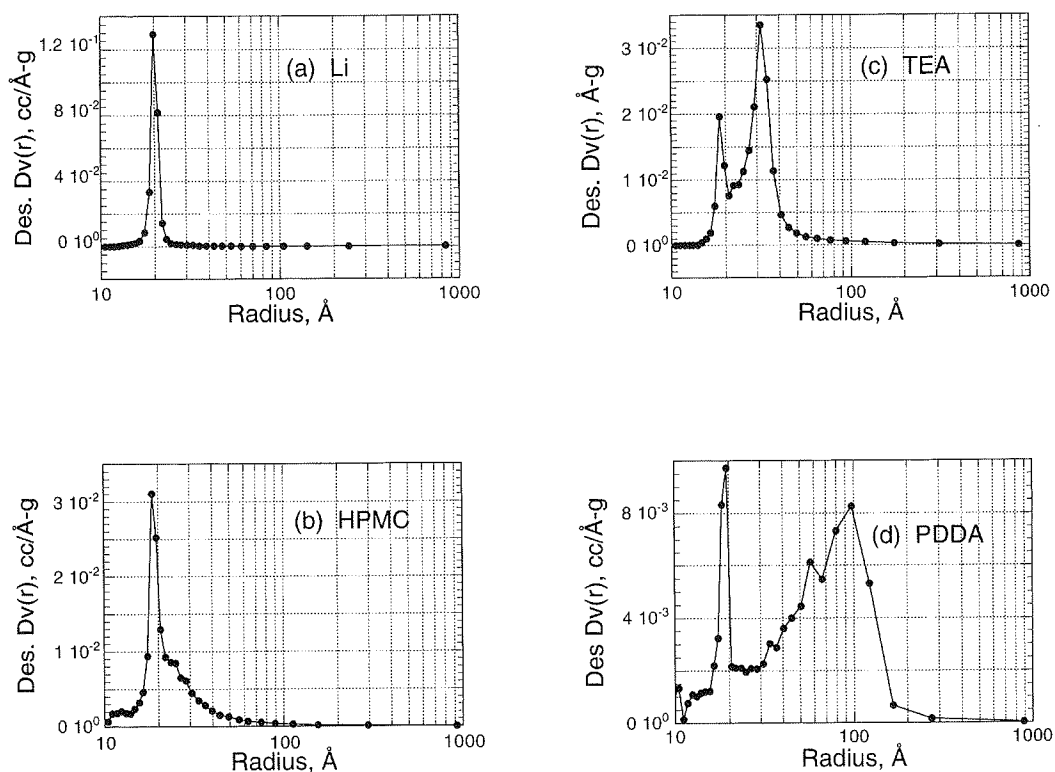
Fig. 3. Pore size distributions of various calcined SOCCs based on nitrogen desorption isotherms: (a) synLi-, (b) synHPMC-, (c) synTEA-, and (d) synPDDA-derived SOCC materials.

Table 1
Physical properties of various SOCCs and the effect of calcination

Organic species in SOCC	wt% Organic	XRD $d(001)$ (Å)	Surface area (m²/g)		Pore volume (cc/g)	
			Before[a]	After[a]	Before[a]	After[a]
Li$^+$, TEA$^+$, PDDA$^+$	<10	14–16	~200	~200	~0.5	~0.5
HEC, HPMC	~20	18–21	<100	~200	~0.1	~0.3

[a] Before and after calcination to remove the organic species from the SOCC (=synthetic organo-clay complex).

of <10%. Because this value is low the d-spacing is not appreciably swollen—both Li and TEA are fairly small cations, and the PDDA polymer chains are apparently uncoiled. Because not much organic is present in these SOCCs, their removal by calcination is not significantly affecting either the surface area or the pore volume. The situation is much different for the neutral cellulose and poly (vinyl alcohol) [21] polymers, however. The percentage of organic uptake is much higher (~20%),

resulting in a much higher d-spacing in the XRD of 18–21 Å. The basal spacing swells to incorporate this large amount of organic. In addition, both the surface area and pore volume values increase appreciably when pores and voids previously occluded by organic are opened up after calcination.

Figs. 3 and 4 show the desorption and adsorption pore size distributions, respectively, of the calcined SOCCs. In Fig. 3, the control mineral
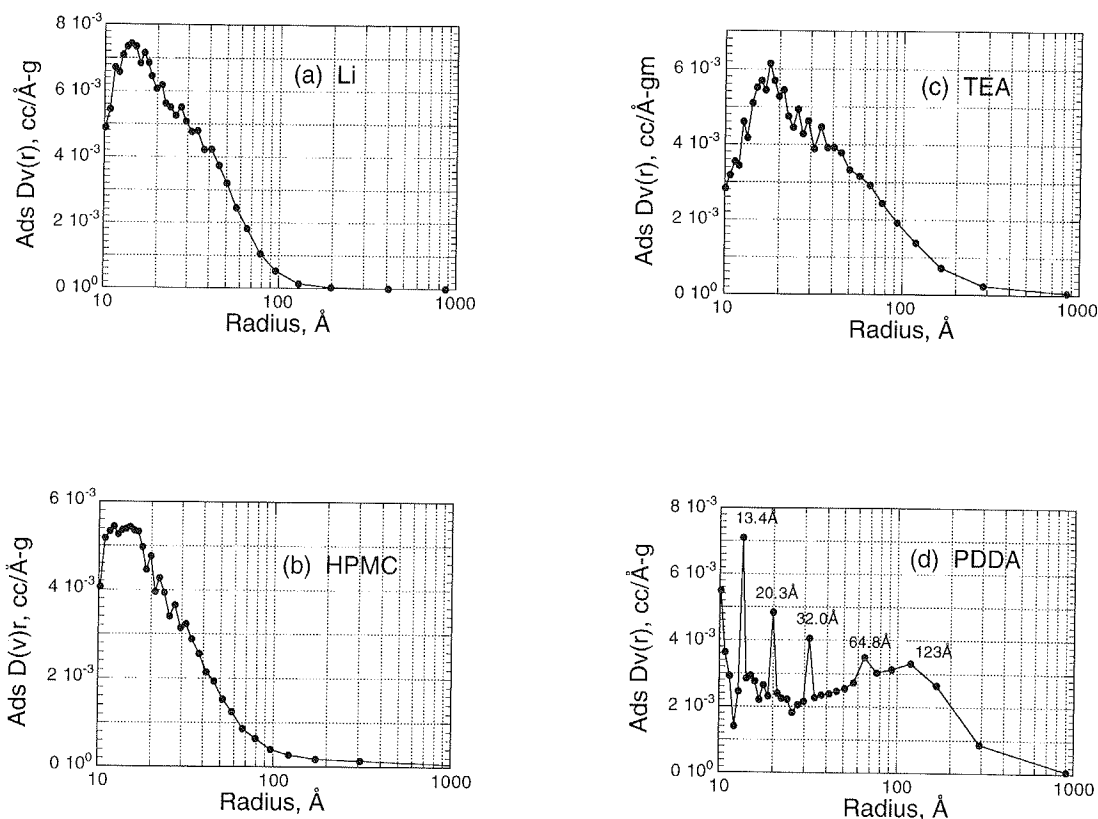
Fig. 4. Pore size distrubutions of various calcined SOCCs based on nitrogen adsorption isotherms: (a) synLi-, (b) synHPMC-, (c) synTEA-, and (d) synPDDA-derived SOCC materials.

with no organic (synLi) displays only the sharp peak at about 19 Å that is always observed as an artifact for lamellar materials [27,28]. The other three samples also display this artifact but there are also real contributions to porosity, especially when cationic organics are used. For example, peaks at 31 Å and 120 Å radii occur for synTEA and synPDDA, respectively. An additional, quite interesting feature occurs for synPDDA in the adsorption-based data [Fig. 4(d)]. This sample displays a reproducible and distinguishable series of sharp spikes upon the overall background. These spikes correspond to certain pore radii that are well-defined within the overall matrix, at 13 Å, 20 Å, 32 Å, 65 Å, and 123 Å. It is proposed that these arise from individual polymer strands or threads arranging themselves in concentric circles ('onion skins') as fibrils of differing radii in the initial clay sol–gel. The result is a somewhat peri-

odic distribution of pores resulting from clay layers arranging themselves around such fibrils. A visual representation of such a scheme is given in Fig. 5. It is well-known that the best solvents for a particular polymer will greatly lessen the degree of coiling and enhance the tendency to form linear chains [29], which may be the factor of importance here. Previous small angle neutron scattering data reveal that synPDDA materials always display a different scattering profile from the other materials [25]. This further supports the argument that synPDDA has a significantly different structure compared to the other materials. Before calcination, synPDDA has a different profile at low-q values, indicating that the packing densities of polymer and clay are quite different from the rest. After calcination, the profile is different at high-q values, and is closest to a natural clay at these smaller length scales.
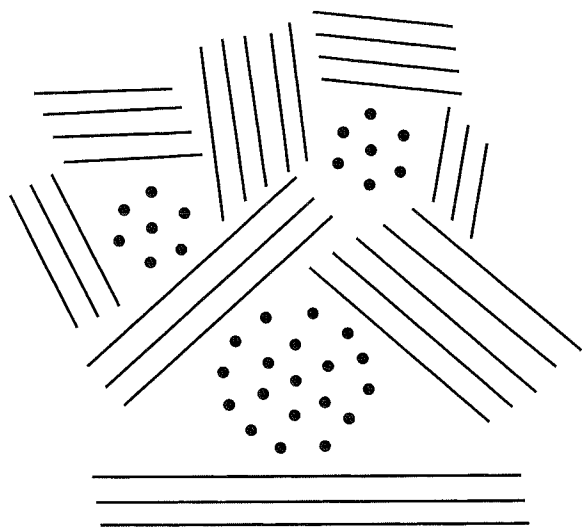
Fig. 5. Proposed polymer bundles that create the pore size distribution seen in Fig. 4(d) for synPDDA SOCC, as viewed directly down the axis of the 'fibers'.

3.2. HDS results

Table 2 provides HDS results from a model heavy oil feed (1 wt% S as dibenzothiophene in hexadecane). Reactivity at three different temperatures was measured: 400°C, 350°C, and 300°C. The total percentage conversion is presented and followed in parentheses by the biphenyl selectivity. Results for Co–Mo catalysts derived from SOCCs are compared to two commercial catalysts: Crosfield's 465 (Co–Mo–alumina) and 504 (Ni–Mo–alumina).

Table 2
HDS of a model oil feed[a]. Values are %conversion (biphenyl selectivity[b])

Catalyst	400°C	350°C	300°C
Crosfield 465 (Co/Mo)	82 (80)	56 (91)	20 (85)
Crosfield 504 (Ni/Mo)	98 (44)	58 (46)	27 (76)
Co/Mo synTEA	66 (80)	45 (47)	nd
Co/Mo synPDDA	35 (66)	26 (65)	15 (60)
Co/Mo synHPMC	26 (89)	20 (60)	12 (41)
Co/Mo synLi	21 (61)	17 (58)	nd

[a] The model feed is 1 wt% S as dibenzothiophene in hexadecane.
[b] Biphenyl selectivity = (%biphenyl yield/%total conversion) × 100.
nd = not determined.

The reactivities for the synLi- and synHPMC-supported catalysts are almost the same, and are lower than the others. Not coincidentally, these materials are composed of much narrower pores (Figs. 3 and 4) that become blocked by carbonaceous by-products from the HDS reaction. This is evidenced by the sharp decrease in pore volume after HDS (see Table 3). In fact, all of the materials lost pore volume during the sulfiding and HDS processes. Fig. 6 displays a strong correlation between mesopore volume remaining after HDS and the HDS conversions at various temperatures. The synTEA-supported material retains the most mesopore volume among the SOCC-derived materials, and possesses a HDS activity commensurate with the commercial alumina-supported materials. Almost all of the pore volume lost during HDS is recouped following calcination (Table 3), suggesting that this loss is due to coke formation.

3.3. TPR results

TPR has been proven as an effective tool for studying the structure of sulfided, supported transition metals [26]. Provided a high hydrogen partial pressure and a high reaction temperature are used, a complete picture of all sulfidable species can be obtained. In fact, four different sulfur species occur: (1) stoichiometric sulfur species in agreement with bulk thermodynamics; (2) non-stoichiometric sulfur species, S_x; (3) S–H groups; and (4) adsorbed H_2S. A correlation has been found between thiophene HDS activity and the S_x reduction temperature [$T_{red}(S_{surf})$] when many different transition metals are compared [26]. Co–Mo– and Ni–Mo–alumina catalysts display by far the best behavior in this respect [26]—the T_{red} of S_x is only 127°C and the thiophene HDS reaction rate constant is very high at 91×10^{-3} m^3/kg s. In this work we have ranked relative percentage conversions of DBT with respect to the $T_{red}(S_{surf})$ of various supported Co–Mo HDS catalysts. Fig. 7 displays the TPR data for the Co–Mo–synTEA catalyst as an example, which has a $T_{red}(S_{surf})$ of 150°C. Fig. 8 shows the $T_{red}(S_{surf})$ and %DBT conversion data for all the catalysts studied, which displays a clear correla-

Table 3
Effect of HDS on pore volumes (cc/g) of catalysts

Catalyst	After calcination		After Co–Mo loading and calcination		After HDS		% Mesopores remaining after HDS	After HDS and re-calcination	
	Meso	Macro	Meso	Macro	Meso	Macro		Meso	Macro
Crosfield 465	—	—	0.52	0.38	0.41	0.35	79	0.50	0.33
synTEA	0.35	0.24	0.19	0.18	0.12	0.10	63	0.20	0.16
synPDDA	0.27	0.50	0.15	0.42	0.06	0.18	40	0.18	0.26
synHPMC	0.18	0.11	0.18	0.07	0.05	0.05	28	0.13	0.06
synLi	0.28	0.02	0.20	0.05	0.02	0.10	10	0.16	0.05

Mesopores $= 10$ Å $< x < 100$ Å radii.
Macropores $= x > 100$ Å radius.
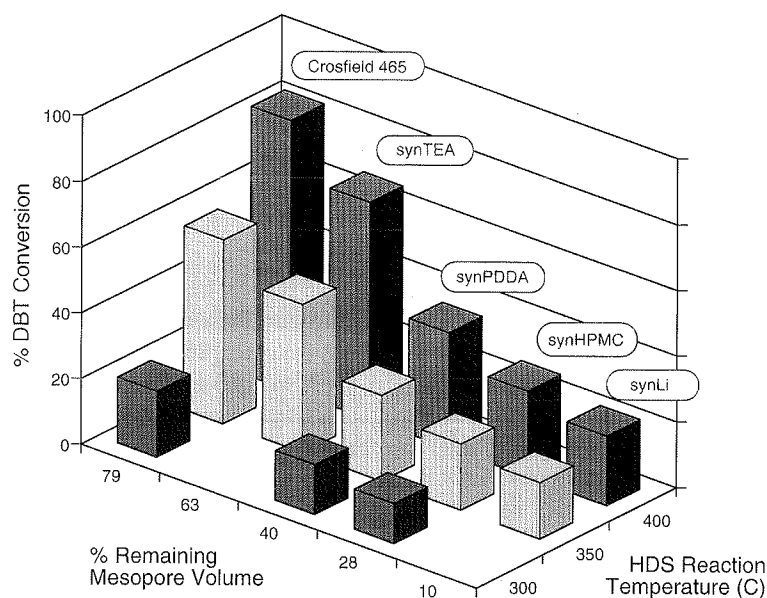
Fig. 6. Correlation between percentage HDS DBT conversion as a function of reaction temperature in degrees Celsius and the percentage mesopore volume remaining after HDS for the various Co–Mo loaded supports.

tion between HDS activity and stability of the surface sulfur species.

4. Conclusions

A new class of potential supports for Co–Mo HDS catalysts has been prepared from synthetic organo-clay complexes, specifically from hectorite clays. When the pores are too large (approaching macropores) the activity goes down. It is the mesoporous range which is of most interest for increasingly dominant heavy oils, however. The choice of 1 wt% S as DBT in hexadecane (rather than a smaller, more typical solvent) was intentionally made to reflect this interest in heavier oils. The most promising size range occurs for the catalyst derived from synTEA with an average pore radius of about 30 Å. In general, a lower activity and selectivity to biphenyl is observed for the SOCCs than for commercial catalysts, although it is encouraging that synTEA is close. Keeping in
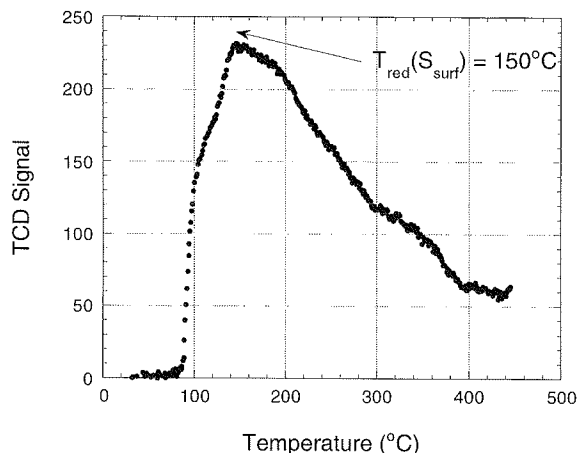
Fig. 7. Temperature programmed reduction data of the non-stoichiometric sulfur surface species on a Co–Mo catalyst derived from synTEA after use in HDS of a model oil feed.
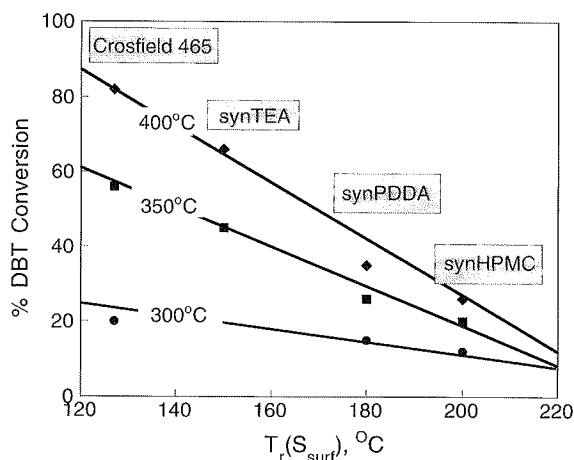

Fig. 8. Plot of %DBT conversion vs. reduction temperature of the surface sulfide species showing that the ease of reduction of the sulfide controls catalyst activity. Data is plotted for SOCC-derived samples in a column—a single $T_{red}(S_{surf})$ applies for all three reaction temperatures.

mind that this system is not yet tuned, future work is warranted. Some cracking activity is observed, which is not surprising considering that a calcined clay is being used. The fact that the cracking activity is low is consistent with the relatively low surface acidity of the hectorite precursors. In future, it would be desirable to tune the pore size of the catalyst resulting from a particular SOCC through synthetic control (polymer type, concen-

tration, etc.). Of most interest in this respect are the cationic polymers, including molecular modeling and small angle neutron scattering of their solution structures. Future work will also involve a thorough evaluation of the contribution of surface acidity to catalyst performance; one important variable to examine in this respect is the amount of Li in the catalyst. The HDS catalytic application of these mesoporous materials is currently being evaluated with an actual crude oil with its inherently more complex mixture of heavier components.

Acknowledgement

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