Carbon Monoxide Conversion Using Functionalized Clay Material with Pt^{n+} , H^+ and $(\text{Pt}^{n+}/\text{H}^+)$ Cations

AHMED BELHAKEM^{1,*}, SAMIA A. GHOMARI² and FAWZI TALEB¹

¹Laboratoire Synthèse Elaboration et Applications des Matériaux Minéraux, F.S.E&I/U, Mostaganem, B.P 1001, 27000 Mostaganem, Algeria

²Laboratoire M.B.A.F.S/F.S.N.V/U. Mostaganem, B.P 1001, 27000 Mostaganem, Algeria

*Corresponding author: E-mail: ahmedbel39@hotmail.com; abelhakem65@yahoo.fr

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Sodium acetate intercalated halloysites, functionalized with Pt^{n+} , H^+ and $(\text{Pt}^{n+}/\text{H}^+)$ cations, were used as catalysts in the carbon monoxide conversion reaction. Experiments were carried out at 3.5×10^3 torr, 523 K and H_2/CO ratio (about 2) or $\text{H}_2/\text{CO} = 67\%/33\%$ v/v). Platinum ionic species, their distribution and average size particle were determined by X-Ray absorption near edge structure (XANES) and titration of adsorbed H_2 by O_2 techniques, respectively. The obtained results showed that CO conversions were higher with $(\text{Pt}^{n+}/\text{H}^+)$ than with H^+ or Pt^{n+} cations used as catalysts. These results were in accordance with the fact that H^+ and Pt^{n+} combination generates a higher level of acidity. The activation/deactivation process showed that catalysts could be easily regenerated after each reaction by heating at 250 °C for 5 h. For the present study, a higher selectivity toward light hydrocarbons ($\text{C}_1\text{-C}_4$) was noticed. The catalysts nature, structure and texture played a major role on the quality and quantity of the final products.

Keywords: Halloysite structure and texture, Platinum oxidation states, CO hydrogenation.

INTRODUCTION

The carbon monoxide conversion is an advantageous process to obtain clean products and to respect environmental restrictions^{1,2}. The quality and quantity of the final products is related to the judicious selection of catalysts type and the reaction conditions. The application of low cost and easily available materials (perlite³, chitosan⁴, mesoporous aluminas⁵, soils⁶, sludge⁷, illite⁸, kaolinites⁹⁻¹¹, vermiculite¹²) in environmental treatments was widely investigated. However the use of modified clays as alternative adsorbents and catalysts received a special attention.

The modification could be achieved, inter alia, by intercalation of organic/inorganic molecules and the modified clay is functionalized with cations in order to increase acidity and consequently to achieve higher catalytic performances. According to the literature, the intercalation products primarily served for nanocomposites preparation¹³⁻¹⁵. The nature of the final products is inherent to the structure/texture and type of the involved catalysts used for functionalization.

This paper reports the application of the Algerian clay material in the catalytic reaction of carbon monoxide conversion. Intercalated and functionalized halloysite clays were used in the carbon monoxide conversion and we obtained remarkable results compared to the literature¹⁶⁻¹⁸. The appro-

priate combination of both acidity and solids topologies makes these materials more active and selective. The presence of different ions and particularly the combination platinum/ammonium confers good performances to catalysts and allows the formation of light products which are converted by the acidic-materials phase¹⁹⁻²⁴.

EXPERIMENTAL

Preparation of catalysts: Halloysite clay from Djebel Debbagh, Guelma (eastern region of Algeria) was ground, ultrasonically dispersed in deionized water, filtrated and dried. Materials intercalation occurred *via* a process described elsewhere²⁵. In order to achieve functionalization, solids were exchanged with an NH_4OH solution. H-forms were obtained by heating materials at 623 K for 8h for NH_3 evacuating. Pt-forms were obtained by impregnating solids with a $(\text{PtCl}_4, 5\text{H}_2\text{O})$ solution. Combined $(\text{Pt}^{n+}/\text{H}^+)$ -solids were obtained by exchange with NH_4OH firstly and then followed by impregnation with the $(\text{PtCl}_4, 5\text{H}_2\text{O})$ solution. Characteristics of the used materials in this reaction type were reported on Table-1 which give different levels of functionalization which are 95 % for ammonium and 40 % for platinum ions.

Characterization of catalysts: Starting and modified halloysite materials were characterized by X-ray powder diffraction (Philips PW 1830 diffractometer with CuK_α

TABLE-1
 ELEMENTAL ANALYSIS AND ACIDITY OF DIFFERENT CATALYSTS (HALD30)

Solids	TO ₂	Acidity (I)					
		Brønsted			Lewis		
		423 K	523 K	623 K	423 K	523 K	623 K
Na ⁺ -HalD30	Na ⁺ _{0.086} (Al _{0.086} Si _{0.90})O ₂	15	9	7	51	37	29
Pt ^{nt} (40)- HalD30	Pt ^{nt} _{0.034} Na ⁺ _{0.052} (Al _{0.086} Si _{0.90})O ₂	21	12	10	59	41	34
H(95)- HalD30	H _{0.082} Na _{0.004} (Al _{0.086} Si _{0.13})O ₂	20	11	8	56	39	31
(Pt ^{nt} , H)- HalD30	(Pt ^{nt} /H) _{0.083} Na ⁺ _{0.003} (Al _{0.086} Si _{0.130})O ₂	23	13	11	61	42	35

(I): Acidity determined by pyridine adsorption⁵³

radiation). The surface areas were estimated according to BET method using the Micromeritics ASAP 2010 analyzer. Elementary analyses were obtained by ICP argon plasma (Jobin Yvon JY24) and flame absorption (Pye-Unicam SP9). The titration of adsorbed H₂ by O₂ method was used to determine a platinum metallic dispersion and its average particle size²⁶⁻²⁸. Selective chemisorption of H₂ on reduced Pt surfaces or selective titration by H₂ on O-recovered Pt surfaces is the classical method used by catalytic scientists to measure the concentration of Pt surface sites on supported Pt catalysts. The reactions representing H₂ chemisorption and H₂ titration are shown in eqns. (1) and (2), respectively.

The numbers of moles of H₂ consumed in the above surface reactions are directly related to the number of surface Pt atoms (sites). The stoichiometry of H₂ adsorbed per surface Pt in reaction (1) is 0.5 H₂ per Pt site and for reaction (2), it is 0.5 H₂ per Pt site; titration of O-precovered Pt sites give an enhancement of three times in sensitivity for determination of the number of Pt sites. It is noteworthy that the chemisorption directly measures the number of Pt surface sites and does not require prior knowledge of Pt particle geometries or size distributions, since the amount of H₂ consumed is independent of all assumptions. Thus, chemisorption should give the most reliable and accurate data concerning true concentrations of Pt surface sites. Sample weights typically used for chemisorption analysis are between 0.1 and 1 g, thus a statistically relevant quantity of sample is always analyzed. X-ray absorption near edge structure (XANES) technique, with the Pt LIII-edge mode, allowed the identification of platinum oxidation and/or reduction states^{29,30}. Each spectrum was recorded, at 25 °C under 1 bar of N₂ pressure and with a step of 2 eV (from 11450 to 12450 eV). The energy/angle calibration was performed using various model compounds (representative of the coordination chemistry of the investigated Pt) as references: metallic Pt foil (thickness 7.5 mm), Na₂Pt(OH)₄ and Na₂Pt(OH)₆.

Hydrogenation reaction: Reaction tests were performed in a continuous-flow system with a fixed-bed stainless steel reactor with 645 mm long, vertically mounted and an internal/external diameter were 21.8 mm/ 27 mm. At the beginning, 3 g of catalysts were extruded in crystallites of 1mm, then placed between two layers of inert quartz in 1:1:1 proportion. Catalysts were heated, *in situ*, under air flow (20 mL min⁻¹) at 523 K for 6 h. Then the temperature was raised to 773 K for 10 h. The reduction was performed at 4 bar pressure, with 10 mL/min flow increase, under H₂ flow for 2h at 300 °C with an

intermediate stage of 1 h at 150 °C. The catalysts were reduced in a flow of hydrogen at 673 K for 5 h with temperature ramping rate at 3 K/min. The cell containing catalysts was cooled and purged at 25 °C under N₂ flow. Hydrogenation reactions were performed at 523 K, 3.5 103 torr, 1:1 CO/H₂ ratio at space velocity 0.6 L g_{cat}⁻¹ h⁻¹ and with various gas stream time. Formed products were analyzed with gas chromatograph phase, Carlo-Erba HRGC 5300 provided with a thermal conductivity detector and a programmed heating. The chromatographic column (length 3 m, diameter 4 mm) filled with WCOT Al₂O₃/KCl and fused silica was connected on line with the reactor. As given in literature³¹⁻³⁴, hydrocarbon distributions were presented as C_n/C₃ ratios and selectivity was determined as follow:

Carbon converted to products

Total carbon converted

RESULTS AND DISCUSSION

XRD patterns of intercalated halloysite and their different characteristics were given on Fig. 1 and Table-2, respectively. It is noteworthy to mention that the best crystallized catalyst was the one treated during 30 days. H₂/O₂ titration measurements revealed a homogenous distribution of the metallic platinum. The average diameter, calculated with Van Hardeveld and Hartog relations³⁵ for regular truncated cubooctahedron geometry, was 0.3 nm with covered metallic surface area neighbouring 109 m²/g_{catalyst}. X-ray absorption near edge structure (XANES) study showed that Pt L_{III}-XANES spectra were similar to those observed for model compounds with Na₂Pt(OH)₄ and Na₂Pt(OH)₆ references. Moreover, Pt L_{III}-absorptions edges were intense and centred around 11569.5 eV. A low shift of this value, observed around 11567.2 (ΔE = 2.1 eV), suggested an increase of electrons number and consequently a decrease of valence. This was due to Pt⁴⁺ to Pt²⁺ platinum reduction. Consequently, platinum was principally in tetravalent and bivalent forms. It was reported by some studies^{36,37} that a slight amount of metallic Pt form was detected during the simultaneous

 TABLE-2
 CHARACTERISTICS OF HALLOYSITE

Samples	d-spacing (Å)	Intercalated fraction (%)	Surface area (m ² /g)
Halloysite	7,6	0	58(64*)
D7j	10,1	28	474
D15j	10	53	612
D30j	10,1	91	884

*Determined by BET

Fig. 1. XRD patterns of halloysite: unmodified halloysite; D7J: halloysite- CH_3COONa (7 days); D15J: halloysite- CH_3COONa (15 days); D30J: halloysite- CH_3COONa (30 days). hh: hydrated halloysite; h: halloysite; hi 00l: higher order basal reflections of intercalated halloysite; hi: non-basal reflections of intercalated halloysite; hk: (0 0 1) reflection of halloysite; hac.: free acetates; c: calcite; q: quartz

reduction with H_2 . The transformation into metallic platinum seems to be difficult.

CO hydrogenation: Bifunctionalized $(\text{Pt}^{n+}/\text{H}^+)$ -halloysite showed 35 % increase in catalytic activity compared to those exchanged with H^+ or Pt^{n+} -catalysts used separately. Comparatively to findings showed elsewhere³⁸, results obtained in the present work are interesting. It appears that high catalytic performances could be attributed to the bifunctionalization with ionic platinum combined with hydronium ions. The latter was at the origin of a good acidity level and a uniform distribution of acid sites within the catalysts. In Fig. 2, C_n/C_3 vs. carbon number was represented. The effects of bifunctionalization and surface area offered by HalD30 catalyst was emphasized by obtaining a higher overall conversion degree towards light products. CO dissociation reaction produced carbide and oxide compounds. Due to the high surface coverage of hydrogen ($\theta_{\text{H}_2} > 0.95$) in comparison with that of the CO, the oxide is removed by reaction with H_2 to yield H_2O . The total hydrogenation of the surface and the presence of carbide produced methane. These carbon-hydrogen species might then participate in chain growth mechanisms. It is noteworthy to mention that carbon monoxide conversion remarkably increased. Moreover, the distribution of alkanes was affected. The Pt^{n+}

Fig. 2. Hydrocarbon distribution for CO hydrogenation on different functionalized catalysts

and H^+ ions addition improved the conversion and promoted the hydrogenation of alkenes to alkanes. The hydrogenation of alkenes to the corresponding alkanes is an important factor determining hydrocarbons synthesis. The intermediate ethylene was easily hydrogenated in order to suppress the carbon chain growth. Therefore, the selectivity of C_2 and C_4 decreased while the selectivity of C_4^+ and isoalkanes increased.

Results showed on Fig. 3 corroborate previous observations. We emphasized on the relationship between intercalated and functionalized catalysts on one hand and on the good selectivity towards C_1 and C_3 alkenes intermediates, the main alkanes formation precursors, on the other hand. Electronic evolution of platinum might have induced variations of the intrinsic solids properties. Consequently it might have influenced their catalytic behaviours. On the other hand, the hydrogen, adsorbing in the vicinity of metal particles, contributed to an "extension" of the reactive domain. Indeed, the OH group densities as well as the hydrogen surface diffusivity, probably played a predominant role in the evolution of carbon monoxide conversion and were the basis of the observed differences in catalysts behaviour. Some studies suggested the use of isotopic exchange experiments designed for H mobility measurements in order to highlight the exact role of surface diffusion³⁹⁻⁴¹. Following the noticed differences in conversion rate, some authors suggested the occurrence of secondary reactions like oligomerisation and/or cracking phenomena⁴²⁻⁴⁵.

Fig. 3. Alkenes/alkanes ratios of the C_2 and C_3 fractions for CO hydrogenation on different functionalized catalysts

The physical interactions effects generated by the introduction of CO and Pt-CO species were detected by FTIR at 2070 cm^{-1} . This involves the activation of C-H bonds between materials and present ions, by induced polarization phenomena. Due to this effect, H-HalD30 catalysts showed an important formation of methane, a notable increase of C_3 fraction and a low ethylene/ethane ratio.

Generally, differences observed in activity and selectivity for clay materials could be related to differences in ions type inserted within these materials, to platinum oxidation states and particularly to acidities generated. Furthermore, as reported elsewhere⁴⁶⁻⁴⁸, halloysite acidity investigated *via* FTIR technique showed the presence of three bands at 1450 , 1548 and 3609 cm^{-1} , which correspond to Lewis, weak and strong Brønsted acidity, respectively.

Effect of ion exchange: Fig. 4 showed the conversion rates were around 50, 40 and 30 % for $(\text{Pt}^{\text{n+}}/\text{H})$, $\text{Pt}^{\text{n+}}$ and H -HalD30, respectively. This was due to the catalysts structure/texture and the reaction conditions^{49,50}. However, the carburization phenomenon of catalysts during the pre-treatment operation was incomplete. Therefore the initial increase of activity was due to a continuation of ions transformation. The subsequent deactivation observed, after 50 min of reaction, was probably due to the deposition of coke and high-molecular weight hydrocarbons which affect enormously catalytic performances and inhibit activities towards the conversion of carbon monoxide.

Fig. 4. Effect of exchanged catalysts on CO conversion vs. time reaction

In this reaction type, heats transfer occurring between adsorbates and catalytic active surface of solids was exothermic. These thermal exchanges, probably due to electrostatic fields generated by the simultaneous presence of different ions and especially platinum with its valence states, were more marked in the case of catalysts exchanged with $(\text{Pt}^{\text{n+}}/\text{NH}_4^+)$ and $\text{Pt}^{\text{n+}}$ ions. Reactions tests performed with $\alpha\text{-Al}_2\text{O}_3$ ⁵¹, functionalized zeolites and carbides^{52,53}, under similar reaction conditions, showed lower CO conversions than those obtained in the present study. As far as differences between exchanged catalysts in CO conversion are concerned, we could assume that reactions taking place on different acid sites created into catalysts, generate differences in thermal and electronic balance adsorbates-adsorbates and adsorbates-adsorbents and this phenomenon affect enormously materials catalytic behaviours by inhibiting the active sites.

Simultaneously presence of ammonium and platinum ions, with different valence states, revealed good activities in CO conversion and consequently towards final products. Then and as shown in Fig. 5, reactions realized with $(\text{Pt}^{\text{n+}}/\text{NH}_4^+)$ -catalysts were higher than those observed for catalysts exchanged with only platinum or ammonium. This was due to the electronic environment generated within the surface of the functionalized material. Indeed, the functionalization with combined ions $(\text{Pt}^{\text{n+}}/\text{H}^+)$, allowed a formation of higher concentrations of water and hydrocarbons triggered by a higher acidity rate generated by inserted ions.

Unlike exchanges observed for platinum or combination ions, the H-catalysts exhibited a lower carbon monoxide conversion (less than 20 % of the results shown previously). These results could be explained by the low participation of this ions type. Therefore; it triggered a low acidity comparatively to $\text{Pt}^{\text{n+}}$ - and $(\text{Pt}^{\text{n+}}/\text{H})$ -catalysts. Exchange with only hydronium ions might alter energies of adsorbates-adsorbents formed bonds

Fig. 5. Effect of exchanged catalysts on distribution of $\text{C}_1\text{-C}_7$

within the active surface and consequently the adsorption ability of the reactive molecules. It seems that exchanged H^+ ions did not cover the entire surface and consequently prevented the reaction conversion to occur completely. Thereby, clay material surfaces were relatively low covered, leading then to a low hydrocarbon distributions and a low rate of CO conversion.

Due to their structure and texture, natural halloysites favour the formation of linear products. Nevertheless, intercalated and functionalized halloysites bias towards a high iso-alkenes/*n*-alkanes ratio. It is well known that alkenes reactivity on acid catalysts is proportional to the carbon number and varies with catalysts nature.

Effects of time reaction: According to the time reaction, the rate and the selectivity of the final products varied for $(\text{Pt}^{\text{n+}}/\text{H}^+)$ -HalD30 catalysts. The variation of $\text{C}_1\text{-C}_7$ hydrocarbon distribution as function of the final products at two time reaction (15 and 80 min) is shown (Fig. 6). An increase of light hydrocarbons was observed for the first time reaction. This phenomenon was probably due to the net difference of the acidity of functionalized clays. After 80 min of time reaction, a rate of final products was diminished. This decrease can be explained by the rapid deactivation due to the coke deposit which blocked active catalytic surface. As mentioned on Fig. 7a and 7b, it was observed that iso-/*n*-alkanes ratios corresponding to C_4 and C_5 fractions were higher for catalysts exchanged $(\text{Pt}^{\text{n+}}$ and $\text{H}^+)$ than for the other catalysts. These results suggest that alkenes are formed during secondary reactions such as: oligomerization, cracking or skeletal isomerization. The presence of different ions types and combinations, different platinum states valences and different acid sites distributions shifted the balance towards a maximum hydrocarbons production. Indeed the higher density of acid sites and their

Fig. 6. Hydrocarbon distribution for CO conversion on functionalized catalysts vs. time of reaction (15 and 80 min)

Fig. 7. (a) Iso/normal for C_5 and C_4 alkanes and alkenes for CO hydrogenation after 15 min of time reaction

Fig. 7. (b) Iso/normal for C_5 and C_4 alkanes and alkenes for CO hydrogenation after 80 min of time reaction

distribution are responsible for the hydrogen transfer process occurring on reactive surfaces thus affecting directly this reaction type.

Due to their structure and texture, halloysite clay materials were deactivated easily and rapidly, mainly during the first 20 min of time of the gas stream treatment. By increasing the time factor and the $\text{C}_1\text{-C}_7$ distribution, alkenes/alkanes and iso/*n*-hydrocarbons ratios approached those obtained elsewhere with Fischer-Tropsch zeolites reactions⁵⁴⁻⁵⁶.

Hydrocarbons selectivity: During this reaction, carbon dioxide was also obtained. The calculation of its quantity may explain some aspects of this reaction type. The selectivity of free CO_2 was determined according to the formula cited above. Values corresponding to these selectivities varied between 30 and 40 %, as indicated on Fig. 8, depending on the conversion process^{57,58}.

Fig. 8. Obtained free CO_2 with different exchange catalysts

As mentioned (Fig. 8), for three kinds of catalysts, the obtained CO_2 rate was high, for C_1 and C_3 light products. Selectivities corresponding to linear hydrocarbons were higher for $(\text{Pt}^{n+}/\text{H}^+)\text{-HalD30}$ catalysts. These findings were reported in literature^{59,60}. The intermediates alkenes formed played an important role in the chain growth and adsorption phenomena as indicates elsewhere⁶¹⁻⁶³. A presence of oxygenates products (alcohols and carbonyl compounds), formed from alkenes *via* hydroformylation reactions, confirmed by ^{13}C infrared analysis, with values around 170 ppm and 205 ppm at 3400 and 1730 cm^{-1} , respectively. As observed in literature⁶⁴⁻⁶⁷, in the case of functionalized halloysite, branched hydrocarbons, were also detected. To conclude it is noteworthy to emphasize that ions types and dispersion manners inside catalysts and the catalysts structure/texture play the major role in the quantity and quality of the final outcome.

Conclusion

The activity of H-based catalysts was low in comparison to Pt^{n+} -catalysts or $(\text{Pt}^{n+}/\text{H})$ -catalysts. Catalytic behaviours depend on ions-solids forms. Materials exchanged with platinum or combination ions showed obvious acidic properties. The latter favour interception and conversion of alkenes produced in this reaction type. Cn/C_3 ratio could be associated with higher ionic proportion. Differences in products distribution observed for different catalysts could be a consequence of different alkenes selectivity, solids acidities and their structure/texture.

Ions combinations within catalysts remarkably affect products distribution. Analysis of the lighter hydrocarbon fraction revealed that deactivation of acid sites *vs.* the time reaction occurred strongly with platinum or Pt^{n+}/H -catalysts than with H-catalysts. However, the relative proportion of lighter hydrocarbons remained higher for all catalysts. Exchange of solids with different ions and their combination seems to participate in carbon monoxide conversion, with a higher selectivity towards light products.

Selectivity seems to be dependent on many factors *i.e.*, the structure of support, the elements (Pt^{n+} and/or H^+) introduced within catalysts, the acidity strength and the distribution of acidic sites inside the catalysts.

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