Full Paper

Effect of the Drying Rate on the Performance of Pt-Sn-K/γ-Al₂O₃ Catalyst for Propane Dehydrogenation

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ABSTRACT

The dehydrogenation of propane to propylene over Pt-Sn-K/γ-Al₂O₃ catalysts prepared by sequential impregnation was studied. Three drying rates of 5, 10 and 15 °C/min were applied after the incipient wetness impregnation of the support (1.6-1.8 mm in diameter) with KNO₃. The obtained catalysts were characterized by N₂ physisorption, SEM-EDAX analysis and XRF for textural and chemical properties. Catalytic performance tests were performed in a fixed-bed quartz reactor under kinetically controlled conditions for the proper catalyst screening. The EDAX measurement results illustrated that the potassium concentration profile changed with the drying rate and the catalyst prepared by the lower drying rate exhibited the highest K concentration at the center and the highest propylene yield. These were attributed to the retraction of the impregnation solution during drying at slow rates which results in a lower concentration of acidic sites in the catalyst center, thereby reducing the contact time of the propylene product with strong acid sites during the reaction.

1. Introduction

Propylene is an important building block in chemical industries for producing polypropylene, acrylic acid, cumene and clean automotive fuels. Traditionally, it has been produced as a co-product of ethylene in fluid catalytic cracking (FCC) and steam cracker plants and as a byproduct of petroleum refineries [1]. However, to meet the ever-increasing demand, purposely processes such as the catalytic dehydrogenation of propane to propylene (Eq. 1) has received attention [2]:

$$C_3H_8 \rightarrow C_3H_6 + H_2 \qquad \Delta H^0_{298} = 124 \text{ kJ/mol} \qquad (1)$$

Propane dehydrogenation (PDH) is a highly endothermic reaction and is limited by

thermodynamic equilibrium [3]. Therefore for achieving a high yield of propylene, high reaction temperatures and low pressures, which simultaneously increase side reactions and the catalyst deactivation by coke deposition, are required [4]. Supported chromia (Cr_2O_3) and Pt catalysts are used at high temperatures (550-650 °C) and near atmospheric pressures in commercial PDH technologies [5].

Platinum exhibits high catalytic activities in the dehydrogenation of alkanes. Essentially, all platinum atoms can catalyze the dehydrogenation reaction, while side reactions (hydrogenolysis, coke formation) are structure-sensitive and require large ensembles of Pt surface atoms [6]. On the Pt surface, only low-coordinated Pt sites (kinks, edges) can catalyze the C-C bond cleavage and thus the hydrogenolysis reaction, while nearly all Pt sites are capable of activating the C-H bond [7].

Platinum on high surface area supports is used commercially for the dehydrogenation of light alkanes, however, the selectivity is poor for unpromoted catalysts [8]. Consequently, tin and alkali metal promoters are ordinarily used in Pt-based dehydrogenation catalysts [9]. The promotion of Sn in Pt-based catalysts has been described in both terms of electronic and geometric factors. The electronic effect has been proposed to be due to donating the electronic charge from Sn to Pt which decreases the heat of adsorption of propylene and the barrier for the chemisorption of alkane (often considered to be the rate-determining step). The geometric effect is due to diluting Pt ensembles which increases the selectivity while reducing coke formation [10].

Alkali metal promoters block the acidic sites of the support which are responsible for side reactions such as cracking, isomerization and polymerization [11]. Furthermore, they can modify metal dispersion, promote hydrogen spill-over and increase the bare Pt-surface [12].

Tasbihi et al. [13] found that the addition of Li and K to Pt-Sn/γ-Al_2O_3 catalysts significantly promoted the catalytic performance in the dehydrogenation of isobutane with order of selectivity of Pt-Sn-K>Pt-Sn-Li. Nagaraja et al. [14] reported that the addition of K (0.4-1.45 wt %) to the bimetallic Pt-Sn/γ-Al_2O_3 catalyst improved the n-$C_4^=$ yield in the dehydrogenation of n-butane with the highest yield (39.8 %) obtained for 0.95 wt % K at 550 °C. Siri et al. [15] also studied the effect of the addition of alkali metals (Li, Na and K) and reported that K improved the stability of the catalyst in the isobutane dehydrogenation reaction.

Never-the-less, the stability of Pt-based catalysts is still not satisfactory and further developments are necessary. Some processes use steam or hydrogen in feed as diluents or to decrease the coke formation rate [16]. Moreover, the continuous or cyclic regeneration of the deactivated catalyst by coke burning is an integral part of commercial dehydrogenation technologies.

The dispersion and distribution of Pt and/or promoters has a strong influence on the catalytic performance in the dehydrogenation of alkanes. They are largely determined by impregnation conditions (e.g., by using competitive adsorbates [17]) and are essentially fixed by calcination [18, 19].

However, when the metal precursor-support interactions are weak, the intermediary drying step may change the distribution of the metal in the final catalyst. The drying step is very important to crystallize the salt on the pore surface of the support. This step can result in irregular and uneven concentration

distributions if not performed properly [20]. Despite its importance, to the best of our knowledge, there is little research about the effect of the drying step on the performance of dehydrogenation catalysts.

In this work, the effect of the drying rate following the incipient wetness impregnation of potassium precursor during the preparation of Pt-Sn-K/γ-Al$_2$O$_3$ catalysts on their characteristics and catalytic performance in propane dehydrogenation is studied.

2. Experimental
2.1. Catalyst preparation
The commercial spherical γ–Al$_2$O$_3$ (1.6–1.8 mm in diameter) was used as the support. The trimetallic Pt-Sn-K/γ-Al$_2$O$_3$ catalyst samples were synthesized by the sequential impregnation of the support with the HCl-acidified aqueous solutions of SnCl$_2$.2H$_2$O, H$_2$PtCl$_6$.6H$_2$O and KNO$_3$ to achieve the desired nominal loadings of Pt (0.5 wt %), Sn (0.7 wt %) and K (0.64 wt %) in the final catalysts. Pt and Sn were impregnated by the wet impregnation method followed by drying overnight at 120 °C and calcination at 530 °C for 2 h. Potassium was incorporated by incipient wetness impregnation followed by heating up to 120 ºC at different rates (5, 10, 15 ºC/min for samples A, B and C, respectively) and drying at the same temperature overnight, and then calcination.

2.2. Catalyst characterization
The N$_2$ adsorption/desorption isotherms of the samples were determined at 77.4 K on the NOVA2000 Quanta-Chrome USA instrument. The specific surface area of the samples was calculated using the Brunauer-Emmett-Teller (BET) method in the P/P$_0$ range of 0.05 to 0.25. The mesopore size distribution was obtained from the desorption branch of the isotherm using the Barrett-Joyner-Halenda (BJH) model. The total pore volume was calculated from the saturation of mesopores around P/P$_0$ = 0.99. The platinum, tin, potassium and chlorine contents of the samples were measured by X-ray fluorescence (XRF) measurements on a Philips PW2404 XRF. Scanning electron microscope (SEM) experiments were performed with a VEGA-TESCAN, equipped with energy dispersive X-ray analysis (EDAX).

2.3. Performance tests
Catalytic performance tests were performed in a fixed-bed tubular quartz reactor (ID = 15 mm) under kinetically controlled reaction conditions (T = 620 °C, P = 1 bar, weight-hourly space velocity (WHSV) = 2 h^{-1} and H$_2$/HC = 0.8 mol/mol). In each run, 2 g of the catalyst diluted with the same amount of SiC was loaded. The reaction products were analyzed for C$_1$-C$_3$ hydrocarbons with an online gas chromatograph (Agilent 6890N), equipped with thermal conductivity detector (TCD) and flame ionization detector (FID). Reaction data were taken at different times on stream after the steady state condition was reached.

To interpret the reaction data, a model based on the first-order surface reaction and first-order independent deactivation kinetics was used which gave [10]:

$$\ln\left(\frac{1-X_A}{X_A}\right) = k_d t + \ln\left(\frac{1-X_{A0}}{X_{A0}}\right) \tag{2}$$

where X_{A0} and X_A are the fractional conversions of propane at the beginning (that is, time-zero conversion) and at any time on stream of t respectively, and k_d is the deactivation rate constant. The plot of the left-hand-side of Eq. 2 versus time should result in

a straight line with a slope of k_d while the intercept giving the time-zero conversion. Higher X_{A0} values are the indicative of the higher activity of the catalysts whereas the higher k_d corresponds to a lower stability of the catalyst. Alternatively, $1/k_d$ values represent the measure of the lifetime of the catalyst.

3. Results and discussion

Figure 1 shows the N_2 adsorption/desorption isotherms and pore size distribution (PSD) of the alumina support. The isotherm is of type IV which is typical of mesoporous materials with an H1 hysteresis loop according to IUPAC classification (Fig. 1a) showing a narrow distribution of relatively uniform (cylindrical) pores [21]. The BET surface area was determined as 215 m^2/g. The PSD curve found by the Barrett-Joyner-Halenda (BJH) model showed three peaks, with the largest one centered around 4.5 nm (Fig. 1b).
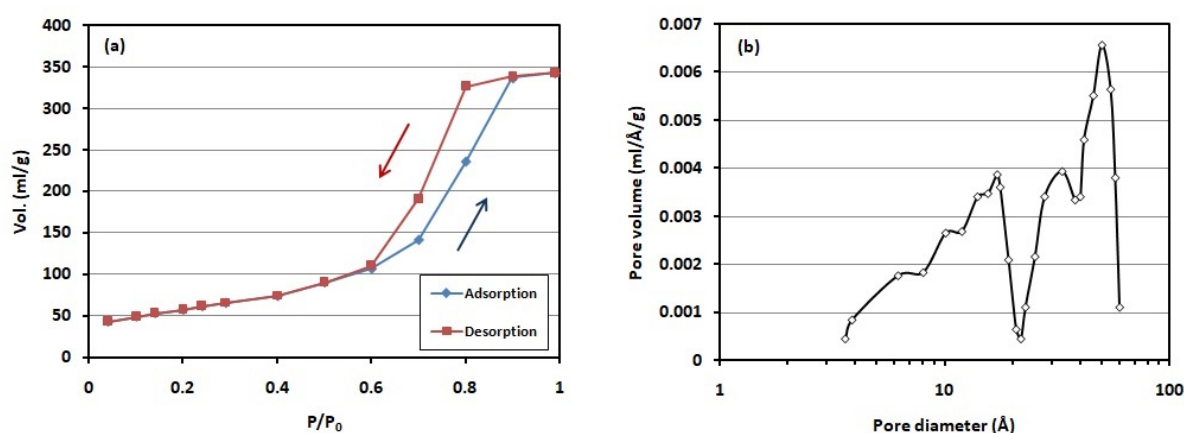

Figure 1. Nitrogen physisorption results of the support: (a) adsorption/desorption isotherms and (b) pore size distribution.

Table 1 summarizes the composition of catalyst samples measured by the XRF analysis. All samples showed metal loadings close to the corresponding nominal values. The chlorine contents (originated from Pt and Sn precursor solutions) were also similar and were within the desirable range ($\leq$ 1 wt %) for commercial catalysts. Chlorine is necessary for the re-dispersion of the sintered Pt(-Sn)

particles by the oxychlorination treatment following coke burning in the continuous catalyst regeneration (CCR) unit of the UOP Oleflex process [5]. However, a higher chlorine content is not desirable because it increases the acidity of the catalyst and promotes acid-catalyzed side reactions which increase coke formation and thereby reduce the lifetime of the catalyst [22].

Table 1

XRF results for the PtSnK/γ-Al_2O_3 catalysts prepared with different drying rates.

Sample drying rate (°C/min)	Component (wt %)				
	Al_2O_3	Pt	Sn	K_2O	Cl
5	97.2	0.46	0.7	0.8	0.8
10	97.1	0.47	0.8	0.7	0.8
15	97.2	0.45	0.6	0.7	0.7

Unlike Pt and Sn precursors, the potassium precursor has little interaction with the carrier surface [17]; therefore, it is susceptible to re-distribution during drying. Table 2 shows the EDAX results for potassium concentration over the cross section of the catalysts dried at different rates. It illustrates that upon increasing the drying rate from 5 to 15 °C/min, the potassium concentration profile shifts from an egg-yolk-like to uniform and then to an egg-shell-like.

Table 2

EDAX results for the PtSnK/γ-Al$_2$O$_3$ catalysts prepared with different drying rates.

Sample drying rate (°C/min)	K (%)		
	Surface of catalyst pellet	400 μ from center	Center of catalyst pellet
5	0.7	0.8	0.9
10	0.9	0.9	0.9
15	0.8	0.7	0.7

The different radial concentration profiles of potassium can be accounted for by the weak KNO$_3$-alumina interaction which allows the mobility of K during drying. If the drying rate is too low, evaporation occurs at the meniscus, which retracts the retained solution down the pore causing some deposition of the salt on pore walls but concentration of the solute deeper in the pore. On the contrary, in the case of fast drying, the rate of the evaporation of water and the steam generation is greater than the rate of capillary flux within the pores [23]. It causes temperature gradients that force the solution toward the outer parts of the particles where most of the salt deposition occurs, giving an egg-shell distribution of the solute in the catalyst pellet (Fig. 2).
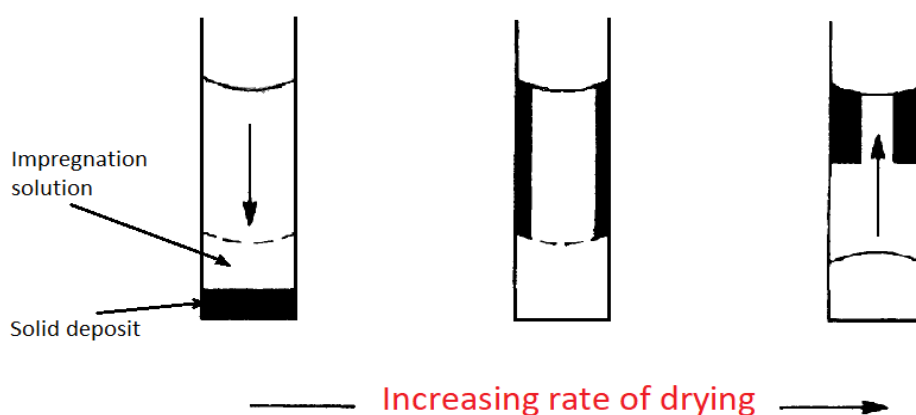

Figure 2. Schematic representation of the pore profile after drying at different rates.

Figure 3 illustrates the effect of the drying rates on the propane conversion and propylene selectivity of the catalysts. The catalysts showed significantly different performances in terms of the propane conversion and the propylene selectivity. This difference could not be due to the composition of the catalyst as the samples showed similar compositions (Table 1).

The highest propane conversion was

observed on the sample with the lowest drying rate (Fig. 3a). The sample also showed the highest propylene selectivity (Fig. 3b). In this sample, K is concentrated at the center of catalyst pellets where the highest concentration of the product (propylene) is expected to exist. Propylene is much more reactive than propane and can undergo consecutive reactions in the presence of acidic sites thereby decreasing the propylene selectivity. Therefore, the highest selectivity is expected when the highest propylene concentration in the pores is in the vicinity of the lowest concentration of acidic sites (or the highest concentration of the neutralizing alkali promoter), which is found for the catalyst with the lowest drying rate. The opposite result were obtained for the catalysts with the highest drying rate as shown in Table 2.
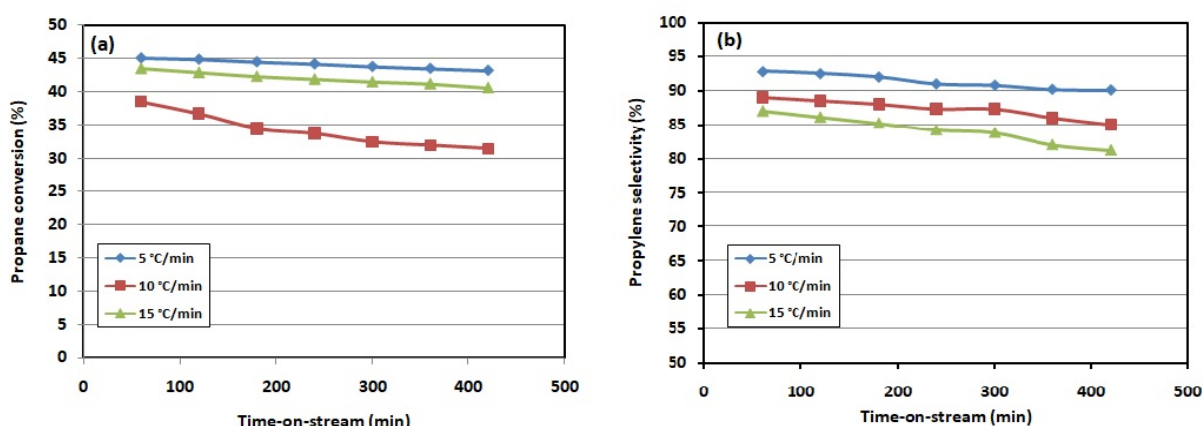

Figure 3. The effect of the rate of the drying of catalysts on (a) the propane conversion and (b) the propylene selectivity (T = 620 °C, P = 1 bar, $H_2/C_3H_8 = 0.8$ mol/mol, WHSV = 2 h^{-1}).

Figure 4 shows the plots of Eq. 2 for different catalyst samples using the experimental conversion-time data. Favorable fits are observed illustrating the applicability of the kinetic expressions used for the main reaction and the catalyst deactivation. The applicability of an independent decay law for catalysts implies that both reactant and product could act as coke precursors [24].
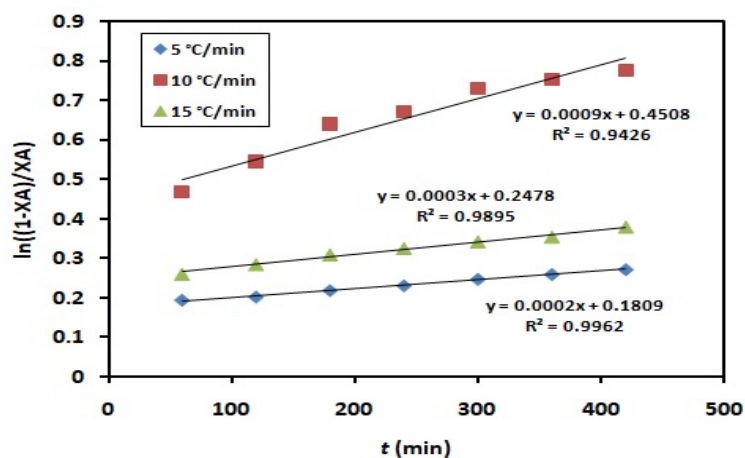

Figure 4. Plots of Eq. 2 for the catalyst samples prepared with different heating rates (T = 620 °C, P = 1 bar, $H_2/C_3H_8 = 0.8$ mol/mol, WHSV = 2 h^{-1}).

Table 3 shows the time-zero conversions and stability of the catalyst as calculated from Figure 4. Sample A showed both the highest activity and stability as implied from X_{A0} and $1/k_d$ values, respectively (Table 3). The order of stability was A > C > B. Catalyst A also showed the highest selectivity (Fig. 3b).

Therefore, the heating rate of 5 °C/min appears to be an optimum one.

It is noteworthy that the order of the stability of the catalyst was the same as that of the activity of the catalyst. In other words, the higher the activity of the catalyst; the higher is its stability (Table 3).

Table 3
Kinetic parameters for the catalyst samples with different drying rates.

Sample	X_{A0}	k_d (min^{-1})	$1/k_d$ (min)
A (5 °C/min)	0.455	0.00022	4500
B (10 °C/min)	0.389	0.00085	1200
C (15 °C/min)	0.438	0.00032	3200

Table 4 compares the textural properties of the support with those of the fresh and used catalyst A. The textural properties of the support and prepared catalyst are very close with a small decrease in the surface area and pore volume of the prepared catalyst which can be attributed to the low metal loadings and relatively mild preparation condition which did not cause significant phase changes or sintering of the support. Similarly, the textural properties of the fresh and used catalysts are

similar which is due to the low coke formation during the test run (400 min). This implies that the observed deactivation of catalyst during this time span was predominantly due to the active site blockage (fouling) by carbonaceous materials rather than by the pore blockage. The latter occurs when the reactant(s) is(are) the coke precursor and reaction is strongly diffusion limited [25]. These are, however, not the case for the PDH reaction over mesoporous catalysts [26].

Table 4
Textural properties of the support, fresh and used samples.

Sample	Specific surface area (m^2/g)	Pore volume (ml/g)	Average pore diameter (nm)
Support	214	0.56	8.70
A (fresh)	206	0.55	8.70
A (used)	203	0.51	8.65

4. Conclusions

The application of different drying rates after the incipient wetness-impregnation of the high-surface alumina support with the potassium precursor affects the performance of the resulting Pt-Sn-K/γ-Al$_2$O$_3$ dehydrogenation catalysts. The differences can be attributed to the different distribution of the

alkali metal promoter which, in turn, affects the distribution of the acid sites of the support. The catalyst prepared at the lowest rate of drying (5 °C/min) produces the highest propylene yield and exhibits the highest stability, which can be attributed to the "egg-yolk" distribution and high concentration of the alkali metal at the center of the catalyst.

The decay kinetics and the characterization of the spent catalysts revealed that deactivation was due to the active sites blockage by carbonaceous deposits rather than the pore blockage. This could be due to the mesporous nature of the used γ-Al_2O_3 support, which provides the catalysts with the capability to accommodate the coke formed during the reaction.

Acknowledgement

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